

CHAPTER THREE

3.1 EXTRACTION AND REFINING OF METALS

The extraction and refining of metals which are used in nuclear power reactors is a highly specialised field of chemistry involving complicated chemical treatments. One of the most complex problem is the separation of individual metals in a high state of purity because physical properties of these metals are markedly affected by minute quantities of impurities. There has thus been a continuous research to have the improved quality of the refined products. Over the years new techniques have been developed in the search for higher yields and greater purity. The conventional separation methods such as fractional distillation, ion-exchange, chromatography, precipitation etc., are not always satisfactorily selective for the metals which are used in a nuclear reactor technology either as a fuel or for other purposes and it is often difficult to obtain these metals in high purity [72]. The commercial refining of these metals is therefore, often tedious and time-consuming.

Continuous research is being carried out to have more effective methods for the separation and purification of these metals. Liquid-liquid extraction procedures seems to be more promising for isolating these metals as well as for other metallurgical processing and much effort has been put in for their development [73-79]. The expansion in this technique, however, came after World War-II, in connection with the problems

of nuclear technology. This technique soon attained a prime position among the separation techniques because of its ease, simplicity, selectivity, versatility, rapidity, low contamination, economical and could easily lend themselves to multistage operations [80-82]. Utilizing apparatus no more complicated than separatory funnel, requiring several minutes at the most to perform, applicable both to trace and macro levels of metals and results in cleaner separation. The resolving power is unusually greater for such a simple process [83]. The conventional separation methods always have a limitations for tenable metals, this is mostly because of co-precipitation. In solvent extraction procedures, co-extraction analogous to co-precipitation does not occur. Therefore, very high purity could be achieved when liquid-liquid extraction is adopted for separation and purification of these metals. The applicability of the extraction technique is broad since separation of most of the inorganic as well as organic material can be achieved.

3.2 THE LIQUID-LIQUID EXTRACTION

Solvent extraction is a process in which one substance is transferred from one liquid phase into another liquid phase when normally two immiscible liquid phases come into contact with each other. Generally, one liquid phase is an aqueous solution and the second phase is an organic solvent i.e., a substance in the liquid state which is immiscible with aqueous solution and can dissolved the distribuend to a certain degree [84]. An extractant can be defined as a substance with solvent properties used in

solution in a suitable diluent. The diluent is used to dissolve the extractant and improve its physical properties [85]. The extractant reacts with distribuend either by solvation, chelation or ion-pairing process etc., to extract it from the second phase.

At equilibrium the concentration of distribuends and other components of the system in each phase have values independent of initial presence of distribuends in one or the other phase. At equilibrium the distribution between two liquid phases is governed by Gibb's phase rule.

$$P + V = C + 2$$

where, P is the number of phases, V the variance or degrees of freedom and C is the number of components of the system. When phase rule is applied to the system dealing with a solute distributed between two immiscible solvents at constant temperature and pressure, it gives only one degree of freedom [86]. The most commonly used terms for expressing the effectiveness of extraction in a liquid-liquid extraction system are described below:

i) Distribution Law (K_D)

In an extraction system, the distribution of a substance between two immiscible solvents at a particular temperature occurs according to the classical Nernst distribution law [87] which states as, " a solute will distribute itself between two essentially immiscible solvents so that at equilibrium the ratio of the concentrations of the solute in the two phases at a

particular temperature will be constant, provided the solute is not involved in chemical interactions". Mathematically it can be expressed as,

$$K_d = \frac{[\Lambda]_o}{[\Lambda]_w} = D$$

where D and K_d are used for distribution ratio and distribution coefficient respectively.

$$D = \frac{\text{Total conc. of a substance in organic phase}}{\text{Total conc. of a substance in aqueous phase}}$$

The term K_d is a constant, independent of the total solute concentration. Such an expression of the distribution law is valid only for an ideal system. In practice, the distribution coefficients vary appreciably, because they are determined from the total concentration of the solute in each phase rather than from the concentration of a single molecular species. Therefore, any tendency for the solute to be distributed abnormally in either phase will show deviation from the normal distribution coefficient. This variation occurs due to the fact that the same molecular species is not present in both phases, because of the tendency of solute to change its form via association, ionization or polymerization etc., in phases. It is more ideal when applied to very dilute solutions where the ratio of the activities approaches unity. It is not applicable where the distributing species undergoes dissociation or association in either phase.

ii) Distribution Ratio (D)

The distribution of a solute between two immiscible solvents can be described by the distribution ratio, D, which can be expressed as,

$$D = \frac{\text{Amount of a substance in a known volume of the organic phase}}{\text{Amount of a substance in a known volume of the aqueous phase}}$$

or

$$D = \frac{[A]_o}{[A]_{aq}}$$

where, [A] represents the concentration of a substance 'A' and the subscripts 'o' and 'aq' refer to the two solvents organic and aqueous respectively. It is a mathematical ratio when extracting species of a substance or metal in an organic as well as in an aqueous phase is same. In case when the extracting specie is different in both phases i.e., due to association or dissociation which occurs in the organic phase then distribution ratio will be different.

iii) Percent Extraction (%E)

Practically, the term, percent extraction is important than distribution ratio which can be correlated with 'D' by the following equation:

$$\%E = \frac{100 D}{D + V_a/V_o}$$

where, V_a and V_o are the volumes of the aqueous and organic phases. When $V_a = V_o$ then equation would be reduced to,

$$\%E = \frac{100 D}{D+1}$$

The percent extraction may vary with the volume ratio of the two phases as well as with distribution ratio 'D' i.e., at extreme values of D, % extraction becomes less sensitive to change in D. For example at a phase volume ratio of unity, for any value of D below 0.001 the solute may be considered to be quantitatively retained in the aqueous phase. Similarly, at large D values, the change in the value of percent extraction '% E' is negligible. Thus, % extraction is an important relationship in extraction process.

iv) Separation Coefficient or Factor (B)

Since solvent extraction is used as a method of separation, therefore, effectiveness of separation of two solutes is important. The term separation coefficient or factor 'B' is related to the individual distribution coefficients as given below,

$$\beta = \frac{K_{d1}}{K_{d2}}$$

where K_{d1} and K_{d2} represent the distribution coefficients of the two extractable species. This indicates that two species can only be separated with one extraction when the values of K_{d1} and K_{d2} are grossly different. When in a system, one of the distribution ratio is very small and other relatively large, then complete separation can easily and quickly be achieved. On the other hand

if the separation factor is large but the smaller distribution ratio is of sufficient magnitude, then various techniques such as addition of masking and demasking and oxidizing and reducing agents are necessarily applied to suppress the extraction of the undesired component.

3.2.1 Process of Solvent Extraction

The nature and interactions of one extraction system may differ from an other one but in general, it involves three essential aspects common to every metal extraction process. These are described below.

a) Chemical Interaction in the Aqueous Phase

These interactions are responsible for the reaction of metals in the aqueous phase leading to the formation of an extractable species. In solvent extraction process, metal could be extracted into organic phase as an anionic, cationic or neutral compound or species. The extraction is achieved by forming organic-soluble neutral complexes in the aqueous phase by direct reaction between ionic species of interest and an appropriate organic compound. Complex formation may be accomplished by coordination, including chelation as well as simple coordination or by ion association etc. [88].

b) Distribution of Extractable Species

In solutions where specific chemical forces are not active,

the classical principle of "like dissolves like" is of great help in predicting the solubility and distribution of a solute. However, in the systems where hydrogen-bonding exist, it is not possible to predict the solubility of a given solute [89]. Collander has been observed low K_D values in system involving hydrogen bonding [90]. According to Pasquinelli mutual solubilities of a pair of liquids are related with electric and magnetic properties of the pure components [91]. Solubility of metal salts in aqueous media are mainly due to the high dielectric constant and basic character of water which results in the dissociation and solvation of ionic species. It has been observed that low affinity of a solute to the aqueous and high affinity to the organic phase cause the distribution to favour the organic phase [92]. By affinity is meant the total interaction energy, which include solvation, electrostatic, dipole, hole-formation energies and entropy factors etc. In a qualitative manner, the factors which causes low affinity of a species for the aqueous phase are zero or low charge, large size, non-polar in nature, absence of electronegative atoms at the surface, low water activity, and highly ordered water structure. Thus, solvents of higher or moderate dielectric constants will favour distribuends capable of ionic dissociation over those that are not and solvents of high ordered hydrogen-bonded structure will favour small distribuends, which require a low hole-formation energy over large ones. Many ion-association extractions are aided by the use of salting-out agents, high concentration of electrolytes to produce a mass action effect.

c) Chemical Interactions in the Organic Phase

Chemical interactions of the extracted species in the organic phase would naturally lower its concentration in this phase and hence, improve extractability e.g., in carboxylic acid extraction, distribution ratio increases due to dimerization of acid in organic solvent. Ion-association complexes tend to form higher aggregates in organic solvents at higher concentration because of their polar nature. Similarly in polymerization reactions, the value of 'D' will be found to vary with the concentration of the extracted material.

3.2.2 The Types of Extraction Processes

Complexing of metal ions or other species leading to the formation of uncharged species are of many types. In general, the extraction process may be classified on the basis of mechanism of the extraction reactions. However, reaction mechanism is known only in few cases. The classification based on reaction mechanism is therefore, mainly conventional. Some of these are briefly described below.

a) Simple Physical Distribution:

This type of distribution generally occurs in inert systems such as distribution of argon between nitromethane and water or of benzene between cyclohexane and water etc.

b) **Distribution involving solvation:**

This type of distribution is found in various systems such as in the case of mercuric bromide ' HgBr_2 ' between cyclohexane and water or between toluene and water. In these processes coordinative solvation occurs in one or both phases.

c) **Distribution of ion-associates:**

This type of distribution involves ionic dissociation at least in aqueous phase. These systems are simplest when the distribuend is mainly in molecular form in the organic solvent and dissociated in the aqueous phase. Metal chelates are often of this type.

d) **Distribution Involving Reaction with excess of Ligand:**

Such distributions were observed in the extraction process of mercuric halides from aqueous halide solutions or of iodine from iodine solutions etc.

e) **Distribution Involving Aggregation:**

Distribution of benzoic acid between benzene and highly acidic aqueous solution involves dimerization in the organic phase and a simple undissociated molecular species in the aqueous phase.

f) **Ion-exchange Reactions:**

In these reactions either a cation is exchanged, usually for an hydrogen ion as in the extraction of iron(III) with dinonylnaphthalene sulphonic acid, or an anion is exchanged, as in the extraction of pertechnetate ions with a quaternary ammonium

nitrate. These are the cases where the distribution ratio is governed by one predominant reaction. In most cases more than one reaction occurs thus, the equilibrium becomes more complicated.

It is more convenient to classify the extraction systems according to the nature of extractant or solvent types used. These can be classified on the basis of polarity, basicity and dielectric constant etc. Various extractants are briefly described in the following lines.

i) **Innert Solvents**

Innert solvents extract only non-polar species. These are graded according to polarity, polarizability, hydrogen-bonding ability etc. These are also used as diluents e.g., cyclohexane, benzene, chloroform, toluene xylene etc.

ii) **Basic Solvents**

Basic solvents extract mainly by solvating through hydrogen ions when they extract acids or anionic metal complexes e.g., the extraction of plutonium (IV) from hydrochloric acid by trioctylamine in xylene or metal ions as in the extraction of uranyl nitrate with tri-n-butyl phosphate [93]. These solvents are graded according to their basicity i.e., from long chain tertiary amines through phosphine oxide, phosphates, ketones to ethers.

iii) **Acidic Extractants**

These extractants usually extract the metal ion or other species by the cation-exchange reaction i.e., exchanging hydrogen

ions for the extracted cations. These are graded according to their acidity i.e., from dialkyl phosphates to carboxylic acids etc. The carboxylic acids are relatively weak extractants and are fairly soluble in aqueous phase whereas sulfonic acids are much stronger extractants.

iv) Chelating Extractants

Chelating reagents constitutes the more important class of the extractants. They form reasonably strong coordination with the metal ions and may be more basic such as 8-hydroxyquinoline or more acidic like 'HTTA'. These complexing agents may also exist as neutral or charged of various denticity and containing zero, one or several displaceable hydrogen ions.

v) Anion Exchangers

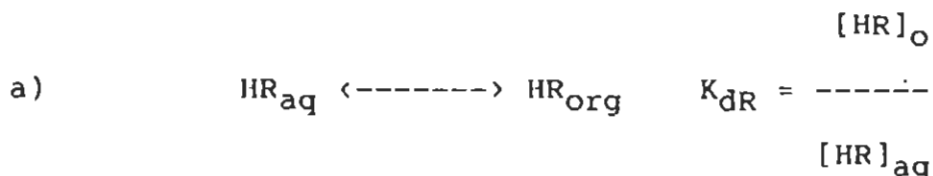
The anion exchangers in solvent extraction process are generally protonated forms of various high molecular weight amines and quaternary compounds. The extraction of metal complexes can proceed either by an anion exchange reaction or an addition reaction. The interaction of amine salts and quaternary ammonium ions with metal anionic complexes is mainly electrostatic thus, extraction depends upon the extent of ion-pair formation. Selectivity of this system depends on the charge, ion size and extent of complex formation in the aqueous phase. Generally, extraction increases with increasing the concentration of ligand. The relative order of metal complex extraction from chloride solution is primary, secondary and tertiary amines. The reverse order is true for sulphate

complexes. Third phase formation, or the splitting of the organic phase into two parts is common in these systems. This problem is eliminated by the addition of diluent modifiers such as long-chain aliphatic alcohols etc.

There are several classifications of extracting agents available however, on the basis of the nature of the extractants and their extraction behaviour i.e., what they do or what they are, involving various mechanisms such as chelation, ion-association and solvation processes are dealt within three sections under the headings given in Table 3.1.

3.3 EXTRACTION EQUILIBRIUM IN CHELATE EXTRACTION SYSTEM

The equation describing the extraction of metal chelates may be derived by considering the reactions occurring between an aqueous and an organic phase containing metal ions as well as chelate extractant respectively. The chelating agent distributes between the two phases. Symbol HR is used as general formula for the reagent.



The reagent will dissociate in the aqueous phase,

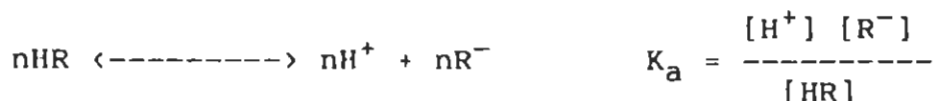
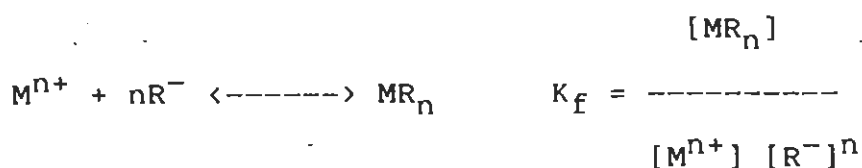


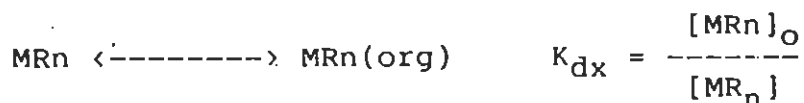
Table 3.1 Classification of Extracting Reagents -

Extractant	Type of Extraction	Nature of Extractant
Organic acids such as carboxylic, sulfonic, phosphoric, phosphonic, phosphinic acids and acidic chelating agents.	Extraction by compound formation	Cation Extractants
Polyphenylmetalloid type, polyalkylsulfonium type, polyalkylammonium type, and salts of high-molecular weight aliphatic amines.	Extraction by ion-pair formation.	Anion exchangers
Carbon-, sulfur-, or phosphorus-bonded oxygen-bearing extractants, alkylsulfides and Organic sulfoxides.	Extraction by solvation.	Solvating agents

b) Formation of extractable chelate.



which, in turn, distributes between the phases.



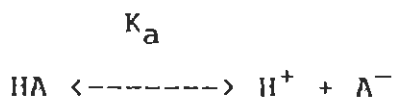
The distribution ratio can be evaluated if the metal chelate MR_n may be assumed to be the only metal containing species in the organic phase and the metal ion, M^{n+} , essentially the only metal-containing species in the aqueous phase. Thus,

$$D = \frac{[M]_o}{[M]_{aq}} = \frac{[MR_n]_o}{[M^{n+}]} = \frac{K_f K_a^n K_{dx}}{K_{dR}^n} \frac{[HR]_o^n}{[H^+]^n}$$

The validity of this equation, has been verified and extended for many chelate extraction systems [94-95].

Factors Influencing the Chelation Process

The important factors which effect the chelation process are basicity of the chelating agent and it is directly related with pK_a value i.e., higher is the pK_a value more basic is the chelating agent. Anion concentration and electronegativity of the donor atom will also determine the extent of chelate formation, this may be conveniently visualized as follows.



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[A^-] = \frac{K_a[HA]}{[H^+]}$$

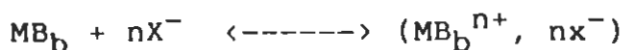
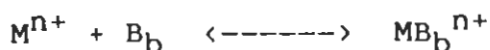
Where HA is used as a general symbol for the chelating reagent. Other factor such as lower electronegativity of the donor atom tends to form stronger bonds [88]. Resonance, entropy and ring size etc., also play an important role in chelation process i.e., more possible the resonating structures as well as less strained ring would give more stable chelate.

3.4 ION ASSOCIATION COMPLEXES

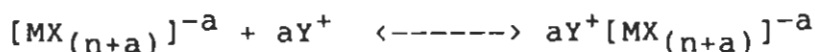
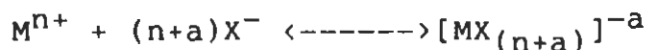
Ion-association complexes are uncharged species formed by the association of ions due to electrostatic forces of attraction [90]. The extent of such association forces increase with decreasing dielectric constant of the solvent below 40 to 50 [96]. Two categories of such complexes are important. The first include those ion-pairs which results from a reagent having a large organic ion such as tetraphenylarsonium ion. The second type of ion-pair is essentially like that of the first with the exception that solvent molecules are directly involved in its formation. In extraction of uranyl nitrate with isobutyl alcohol, the extractable complex is probably $UO_2(BuOH)_6(NO_3)_2$ in which the coordinated solvent molecules contribute both to the size of the cation and the resemblance of the complex to the solvent [97].

3.4.1 Extraction Equilibrium in Ion-association process.

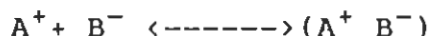
Metal ion may be incorporated in either cation or anion of the extractable ion-pair. This may be illustrated in the following equilibrium reactions.



or



Where B is a neutral mono or polydentate ligand, X^- is an anion, Y^+ is a polycation needed to form the ion pair. The ion-association of two ions A^+ and B^- can be expressed as:



$$K = \frac{[A^+ B^-]}{[A^+][B^-]}$$

The existence and behavior of such complexes was predicted by N. Bjerrum and confirmed by Fuoss and Kraus [98-99]. The ion pair formation constant 'K' is related to the dielectric constant of the solvent, temperature and the size of the ion involved.

Thus:
$$K = \frac{4\pi N e^2}{1000 KT} Q (b)$$

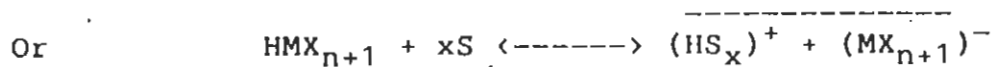
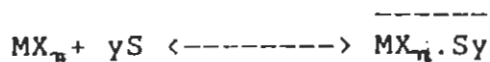
$$b = \frac{e^2}{\epsilon KT}$$

Where, N is avogadro's number, e is the unit of charge, K is the Boltzman constant, $Q(b)$ is a function, and E is the distance between charge centre of the ion pair when in contact.

3.5 EXTRACTION BY SOLVATION PROCESS

According to the classification of extracting reagents given in Table-3.1, all oxygen-bearing organic solvents extract neutral inorganic species by virtue of solvation [100]. It requires the transfer of a formally neutral species from the aqueous to the organic phase by solvation of the hydrogen ion in case of acid extraction or the hydrogen ion of a complex metal acid species or by solvation of the metal ion of a neutral salt species. The solvating power depends strongly on the basicity of the reagent. It is reported that oxygen-containing solvents are very weakly basic and do not form oxonium salts [92]. In the carbon-bonded oxygen donors such as ethers and ketones, water usually forms hydrogen-bonded bridge between the solvating agent and the solute. However, in case of organophosphorus donors, water is often eliminated from the organic phase.

Beside the organophosphorus compounds other oxygen containing neutral extractants such as amine and sulfoxides have received attention recently. Much of this work has been carried out in the Russia and a good description of the chemistry of these compounds as extractants has been given by Mikhailov [101]. Extraction-solvation process can be represented by the equation,



In the extraction process of metal complexes, the solvating agent will replace primary or secondary waters of hydration, thus rendering the complex soluble in the organic phase. The degree of extraction of a metal by a solvating extractant should depend on the number of factors, including the nature and concentration of the anionic coordinating ligand, mineral acid concentration, strength, size and hydration of the anions. According to Marcus and Kertes, strongly electropositive metals can be satisfied by the strongly polar reagents which results their extraction in an unhydrated form [92].

It was observed that extraction occurs by replacement of secondary hydrated water by extractant molecules. In conclusion, the extraction decreases with increasing diluent polarity. Chemical stability of the reagent and purification of organic phases are thus important in these systems.

3.6 TYPES OF EXTRACTION TECHNIQUES

Three different techniques of liquid-liquid extraction are generally used for separation purposes. These are, batch, continuous and countercurrent extractions. These techniques are briefly described below.

Batch Extraction

Batch extraction is the simplest and the most used technique. It involves only a single equilibration of solute and solvents. The only equipment required is the simple separatory funnel i.e., the solution to be extracted is placed in the separatory funnel alongwith the extracting solvent. After the solutions have been thoroughly mixed (until equilibrium is attained) and the two phases have separated, the denser phase is drained through the stopcock and collected in another vessel. This method of extraction provides rapid, simple, and clean separation and is used to most advantage when the distribution ratio of the solute of interest is large and only few extractions will effect quantitative separation.

Continuous or Multiple Extraction

Continuous extractions are particularly applicable when the distribution ratio is relatively small [102]. Thus a large number of batch extractions would normally be necessary to effect quantitative separation. Most continuous extraction devices operate on the same general principle which consists of distilling the extracting solvent from a boiler flask and condensing it and passing it continuously through the solution being extracted. Many different types of apparatus are used in continuous extraction process. The significant fact about this technique is that it can be completed using only small separatory funnels. However, this technique is not encountered too frequently in analytical work.

Countercurrent Extraction

In a countercurrent extraction process, two immiscible solvents are contacted as they flow through each other in opposite directions. The extraction of this type is very efficient because fresh extractant is brought in contact with the solute-depleted aqueous phase and then the solute-enriched extractants contacted with the fresh aqueous phase till the equilibrium state is attained by the system. The countercurrent extraction technique have been applied with great success to the fractionation of organic compound particularly where the distribution ratios are of same order of magnitude. This technique is not common in inorganic compounds because of different distribution ratios of the materials to be separated thus, batch and continuous extraction techniques could be easily employed. There are however, a number of inorganic materials such as rare earth etc., which require fractional methods because of the similarity of distribution ratios. A series of separatory funnels may be used however, when a large numbers of transfers are required for the separation of complicated mixtures, a glass countercurrent distribution apparatus designed by Craig is used [103].

3.7 FACTORS OF PRIME IMPORTANCE IN SOLVENT EXTRACTION TO METALLURGICAL PROCESSING

Solvent extraction is a well-established process within the inorganic, organic and biochemistry as well as in hydrometallurgical industries. The general process of solvent extraction as

applied to metallurgical processing is given in Figure 3.1. The solvent or organic phase is usually a mixture of components including diluents etc., to confer appropriate flow properties of the solvent. Other components may be added such as modifiers to alter physical characteristics, synergists to increase extraction or catalysts to increase the extraction rate. Considering only the unit process of solvent extraction, there are several important factors however, some of these are briefly described below.

Choice of Solvent

For the choice of optimum solvent, a large number of factors both chemical and physical, technical and economical are important. These include commercial availability of solvent, purity, price, solvent strength, selectivity, loading, ease of stripping, rates of extraction and stripping, chemical stability, aqueous-phase solubility of solvent components, organic phase density and viscosity, interfacial properties of the solvent-aqueous systems, volatility and flammability of the solvent, toxicity of the solvent within the working area and the outside environment as well as regeneration of solvent etc. The choice of solvent components favouring any of the above mentioned properties will frequently effect its performance. These properties are briefly discussed below:

a) The Commercial Availability and the Selectivity of Solvent

The first thing encountered in choosing a solvent for extraction purposes is its commercial availability and price. The

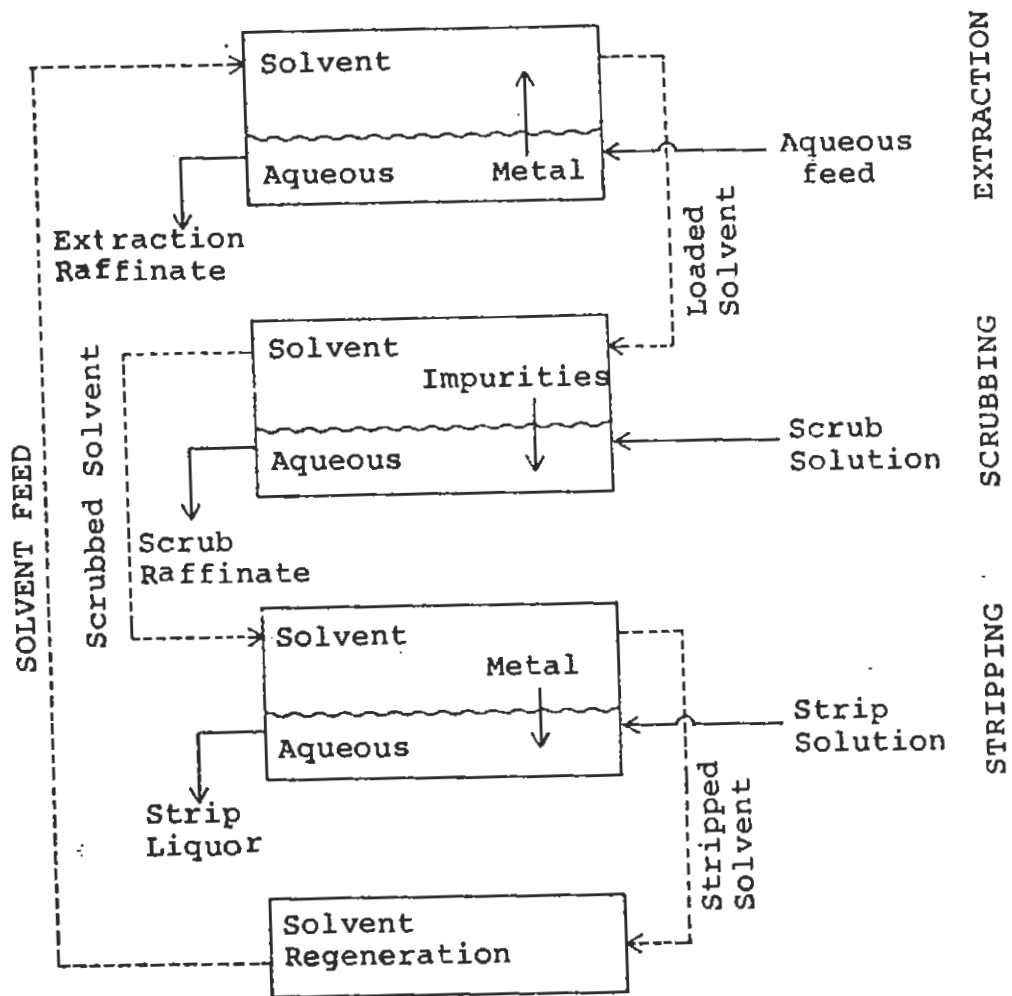


Fig. 3.1 The general process of solvent extraction as applied to metallurgical processing.

cost of solvent can form high proportion of the capital cost of a plant thus, the price of the solvent components are important role in solvent choice. In general, prices of reagents decrease in the following order: acid chelating extractants > basic extractants > acid extractants and modifiers > diluents etc. The selectivity is the ability of a solvent to extract one component of a solution in the presence of another. Therefore, the choice of a solvent selection may be made on the basis of either experience or semiempirical consideration i.e., like substances are miscible or polar solvents are used for the extraction of polar substances from non-polar media and vice versa. The distribution coefficient of the solute must be high if it is going to be readily extracted from one phase. Thus, solvent must be selective in its action which is only possible when distribution coefficient of the various solutes must be distinctly different.

b) Solvent Density

A density difference between organic phase (solvent) and aqueous phase of at least 0.1 g/cm^3 is necessary for rapid phase separation i.e., greater the difference in the solvent densities, the faster will be the rate at which the immiscible layers separate. Generally, solvents are less dense than the aqueous phase and the density of the most of the diluents is around 0.8 g/cm^3 .

c) Viscosity of the Solvent and Emulsion Formation

For successful operation of a liquid-liquid extraction

process, it is essential that the viscosity of the solutions be sufficiently low to permit ready flow of the solutions through the equipments, use of low-power agitators for phase dispersion and ready phase separation etc. Therefore, low viscosity solvents are generally recommended for the extraction processes. Emulsions are easily produced when the densities of two solvents are similar. The emulsion formation produces trouble in the extraction process and certain measures are then be needed to overcome these troubles i.e., introduction of certain electrolytes or other solvents etc.

d) Interfacial Properties and the Solvent Stability

Higher interfacial tension for rapid separation of two phases is necessary for a good solvent system. Interfacial tension is the difference between the surface tensions of two liquids. The interfacial properties influence the extraction rate and the characteristics of the dispersion. In the same way for solvent choice, the chemical stability of the various solvent components is important because of certain reasons i.e., when a solvent reacts with the aqueous phase its degradation may occurs and the problem of analytical control of the solvent composition increased. Moreover, the products of degradation deleterious to the physical or chemical performance of the process. Thus, stability of the solvent is important.

e) Solvent Recoverability

The recoverability of an extractant is almost as important as its selectivity. The recovery of solute from a solvent has

more practical significance. In either case it is necessary to separate extractant and solute after distribution. The frequent formation of azeotropic mixtures prevent a complete resolution. Since the solvent is usually present in much greater quantity than the solute, therefore, it is energetically simple to remove the solute from the solvent. The removal of the solute from the final extract phase is called stripping. Sometimes it is necessary to remove the solute from the organic phase to a more suitable medium. In case of volatile solvent, small amount of water is added to the extract and solvent is evaporated on water bath. On the other hand, when the extracting solvent is non-volatile the solute is stripped by shaking solvent with acids or other reagents under conditions whereby extractable complex is destroyed. Stripping is the simplest and an effective recovery technique available.

f) Salting-out Agents

The addition of optimum concentrations of inorganic salts to the aqueous phase greatly increase the distribution ratio of many metal complexes to the organic phase. Ions of the salts involved in this process cause common ion effect as well as strongly bind the water molecules around them, thereby depleting the water molecules for use as a solvent. In metal extraction systems generally, the salts of nitrate, halide and thiocyanate are used as salting-out agents.

g) Volume of Extracting Solvent

Since the distribution ratio in liquid-liquid extraction is a concentration ratio in both phases, the actual fraction of the total solute extracted will vary with the ratio of the solvent volumes. So for best results, large number of extractions with small volumes of solvent are necessary.

h) Backwashing

The combined organic phases from several extractions of the original aqueous phase contain practically all of the elements desired and possibly some of the impurities that have been extracted to a much smaller extent, depending on their relative distribution ratios. This combined organic phase, when shaken with one or more small portions of fresh aqueous phase containing optimized aqueous composition initially used for extraction will result in a redistribution of the impurities in favour of the aqueous phase. In this process the element of interest will remain in the organic phase, due to its high distribution ratio. Therefore impurities can be removed by backwashing with minimum loss of the element of interest.

i) Modification of Oxidation State and the use of Masking Agents

The selectivity of an extractant can be improved by changing the oxidation state of some ions to prevent the formation of an extractable metal complex. Appropriate oxidizing or reducing agents are used for these achievements. Suitable masking agents are also used for the removal of certain interferences [92].

j) Diluents and Modifiers

As the viscosities of many reagents are much too higher for direct use in solvent extraction equipment therefore, it is common practice to dissolve these reagents in an organic diluent. These are usually hydrocarbons selected on the basis of a flash point above 60°C, to minimize evaporation loss and the risk of fire, and with a specific gravity of about 0.8 to aid phase separation as well as improve the physical properties of the solvent. In general, the diluents used contain a mixture of paraffinic, aromatic and naphthenic hydrocarbons.

Because of the solubility limitations of the metal complex, a phenomenon known as third-phase separation can occur. The organic phase splits into two phases, to overcome this problem, a third component, known as diluent modifier is added to restore these organic phases into a single phase. These are invariably solvating reagents such as tributyl phosphate, isodecanol or phenol etc. The addition of modifiers can also improve the phase separation.

In conclusion, solvent extraction procedures are designed on the basis of research aimed to achieve conditions in a particular system for the quantitative recovery of a pure metal, leaving the extractant in a form ready for recycling.