9.17
Metal Complexes for Hydrometallurgy and Extraction

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9.17.1 INTRODUCTION

Extractive metallurgy covers a huge range of mechanical and chemical processes, some of which date back several thousand years.\(^1,2\) In terms of recovery from primary sources (metal ores) these processes are often broken down into the unit operations: concentration, separation,
reduction, and, when a high-purity product is required, additionally refining.\textsuperscript{1–3} The wide range of technologies applied is partly a consequence of the different challenges presented by the concentrating operations which need to address precious metals which are often present at $<10^{-3}\%$ in natural deposits and the more abundant metals such as Al and Fe, which can approach 50\% metal content. Base metals fall between these extremes; production of 1 ton of electrical grade copper typically requires movement of 800 tons of rock (Figure 1).

In the broadest sense, coordination chemistry is involved in the majority of steps prior to the isolation of a pure metal because the physical properties and relative stabilities of metal compounds relate to the nature and disposition of ligands in the metal coordination spheres. This applies both to pyrometallurgy, which “produces metals or intermediate products directly from the ore by use of high-temperature oxidative or reductive processes” and to hydrometallurgy, which “involves the processing of an ore by the dissolution, separation, purification, and precipitation of the dissolved metal by the use of aqueous solutions.”\textsuperscript{4}

This review will focus on processes which depend on the selection or design of ligands to enhance the effectiveness of the four unit operations listed above. In general, the application of such ligands relates to equilibria involving distribution of a metal between two phases.

Liquid–liquid distributions form the basis of solvent extraction and related processes, and smelting processes.

Liquid–solid distributions are involved in ion-exchange and other adsorption-based separation processes, separation processes based on crystallization or precipitation, flotation processes for ore dressing, and smelting processes.

Examples of the formation of volatile metal compounds or complexes leading to separations based on gas–liquid and gas–solid distribution are much rarer.

Since the last review in Comprehensive Coordination Chemistry (CCC, 1987),\textsuperscript{4} R & D activity on the recovery of metals from secondary sources has increased significantly, reflecting economic and environmental requirements to recycle materials and to remove them from process streams prior to discharge of effluents. Integrating recycling processes with those for the generation and use of materials is favored in the “Industrial Ecology” approach, which requires an audit of the materials and energy consumption in a total system.\textsuperscript{5–8} A systems engineering approach can then be used to minimize the impact of the total system. The relative ease of tracking metal-containing materials in such systems, in contrast to organic compounds, has resulted in these being favored in industrial ecology case studies.\textsuperscript{9}

Another factor which has increased the applications of coordination chemistry to extractive metallurgy since the mid-1980s is the emergence of hydrometallurgy as an alternative to pyrometallurgy in the recovery of base metals. The proven robustness of the hydrometallurgical process involving solvent extraction in the nuclear industries\textsuperscript{10} and the commercial success of heap leaching/solvent extraction/electrowinning processes for copper\textsuperscript{11–14} (Section 9.17.5.1) have stimulated the development of new leaching and separation technologies for a wide range of metals. The use of hydrometallurgy to replace or complement pyrometallurgical operations is summarized in Figure 2.

One of the most important roles of coordination chemistry in hydrometallurgical processes is to effect the separation and concentration of the target metal. The design of metal complexing agents with the appropriate “strength” and selectivity to meet the requirements of the front-end of the flowsheet, leaching, and the back-end, reduction to generate pure metal (Figure 3), presents challenging targets for the coordination chemist.
In the sections which follow processes based on metal complex formation are described in the order they occur in the flowsheets in Figures 2 and 3, i.e.,

mineral processing,
leaching,
separation and concentration, and
reduction.

The application of these methods is described in some detail for recovery of base metals and platinum group metals in Sections 9.17.5–9.17.6 focusing mainly on solution-based hydrometallurgical operations, largely those involving solvent extraction, because the nature of the metal complexes formed is usually best understood in such systems. NB. Extraction of lanthanides and actinides is not included as this subject is treated separately in Chapters 3.2 and 3.3.
9.17.2 MINERAL PROCESSING

Natural mineral deposits are usually heterogeneous mixtures of solid materials that require crushing and grinding to liberate the minerals containing the metal values. Such operations often represent a sizeable fraction of the total capital and energy costs of metal recovery. One of the potential advantages of hydrometallurgical routes for metal recovery is that it is sometimes possible to carry out heap leaching on ores which have not had to be milled, for example in the recovery of copper from oxidic or transition ores (see Section 9.17.5.1).

Separation of milled solid materials is usually based on differences in their physical properties. Of the various techniques to obtain ore “concentrates,” those of froth flotation and agglomeration exploit differences in surface activities, which in many cases appear to involve the formation of complexes at the surface of the mineral particles. Separation by froth flotation (Figure 4) depends upon conversion of water-wetted (hydrophilic) solids to nonwetted (hydrophobic) ones which are transported in an oil-based froth leaving the undesired materials (gangue) in an aqueous slurry which is drawn off from the bottom of the separator. The selective conversion of the ore particles to hydrophobic materials involves the adsorption of compounds which are usually referred to as “collectors.”

Some of the more commonly used types of collector are listed in Table 1. Many of these contain sulfur atoms in their polar “head groups” and are used in the recovery of base metals from their

![Figure 4 Schematic representation of a froth flotation separator.](image-url)
sulfidic ores. They are effective under oxidizing conditions and it is proposed that chemisorption is involved in bonding with the formation of metal–sulfur and/or sulfur–sulfur bonds. The modes of chemisorption depend on the redox properties of the collector, and mechanisms resulting in the liberation of elemental sulfur from the surface of sulfidic ores are proposed.

\[ \text{MS}_\text{s} + 2\text{RX}^- = (\text{RX})_2\text{M} + \text{S}_\text{s} + 2e^- \]

Details of the structures of complexes formed at the surface of the ore particles are difficult to obtain, but it is noteworthy that the majority of the collectors used have ligating head groups which are capable of forming polynuclear complexes. Bidentate groups that would form five- or six-membered chelate rings are more rarely used. The stability of such complexes is likely to favor removal of metal atoms from the surface, transferring them to the liquid phase rather than surface ligation, which is needed to generate hydrophobic particles.

Several reviews on ore processing by flotation are available. In addition to providing details of the chemistry of collectors they describe the use of activators and depressants. The former usually convert the surfaces of an ore particle which does not bind strongly to conventional collectors to one that does. The addition of Cu\(^{2+}\) ions to enhance the flotability of minerals such as sphalerite, a zinc sulfide, has been exploited for some time. Formation of a surface layer of CuS has been assumed to account for this, but the mechanisms and selectivities of such processes continue to be investigated.

Depressants are used to make materials less floatable, and again have been used for some time. A recent example is the use of phosphoric acid to depress the flotation of a sedimentary phosphate ore, enhancing the selectivity of recovery of calcite and silica. Natural and synthetic polymers have also been used as depressants.

Several of the ligating functions in the collectors shown in Table 1 are also present in compounds which are used in metal-surface engineering, e.g., the dialkyldithiophosphates are anti-wear agents in lubricants. This emphasizes the need for a better understanding of ligand design features to achieve strong and selective binding to surfaces of lightly oxidized metals or to minerals if a more rational approach is to be used to the development of new “actives” for mineral processing and surface engineering.

9.17.3 LEACHING

Leaching is the primary process in hydrometallurgy whereby the metal values of a solid metal-bearing material are transferred into an aqueous solution by the action of a lixiviant. Typically, leaching is applied to ores, spent catalysts, pyrometallurgically derived intermediates, metal scraps, and by-products from metal refining. Processes generally fall into two categories, those in which the formal oxidation state of the metal remains unchanged and those where dissolution is accompanied by a redox process.

In addition to water molecules the coordination chemistry of leaching generally involves simple inorganic anionic ligands, ammonia, or acetonitrile. Many of the well-established processes (see Table 2) were considered in CCC (1987), and are also described in a recent comprehensive text on hydrometallurgy.

Bioleaching, particularly of sulfidic ores, has received much attention since the early 1980s. The conditions needed and mechanisms for such processes have been reviewed. Microbial processes involve complete oxidation of sulfide to sulfate, e.g.,

\[ \text{MS}_\text{s} + 2\text{O}_2 = \text{MSO}_4 \]

This is often accompanied by oxidation of metals, particularly iron,

\[ \text{Fe}^{2+} = \text{Fe}^{3+} + e^- \]

which is important (see below) because the ferric ion is very effective in oxidative leaching of both simple and complex sulfides:

\[ \text{MS}_\text{s} + 2\text{Fe}^{3+} = \text{M}^{2+} + 2\text{Fe}^{2+} + \text{S}_\text{s} \]
There are some examples of commercially successful bioleaching operations for copper, uranium, and gold, but the full potential of microbial processes is likely only to be realized by better understanding and integration of the reactions involved and the engineering needed. The regeneration of Fe$^{3+}$ salts as above is important in heap leaching operations; see, for example, Section 9.17.3.3. Microbial leaching of metals from sulfidic minerals has been practiced for many years without the realization that microorganisms are involved. In both bio- and “inorganic”-leaching processes, metal complex formation at the surface of mineral particles being leached is often accompanied by catalytic redox reactions which labilize the metal ions, leading to complicated reaction sequences. An understanding of these is important for the design and operation of processes which minimize the formation of toxic by-products, are selective and achieve a high recovery of the desired metal, operate at a reasonable rate and produce pregnant leach solutions suitable for downstream processing. In the sections which follow the chemistry of leaching processes is described where the efficacy of the process is dependent on strong, selective, and rapid complex formation and where a knowledge of the composition of streams is important for understanding the downstream “separation and concentration” steps which involve coordination chemistry (Sections 9.17.5–9.17.6).

### 9.17.3.1 Leaching of Gold and Silver into Basic Media

It has been more than a hundred years since MacArthur and Forrest developed a process for the leaching of gold based upon the use of an alkaline cyanide solution. Despite the toxicity of cyanide solutions this is still the most widely used process for both Ag and Au, and has been extensively reviewed. The dissolution of gold in its native form by cyanidation involves oxidation to Au$^1$, 

$$\text{Au}_{(s)} + 2\text{CN}^- = [\text{Au(CN)}]_2^- + e^-$$

coupled to the reduction of dioxygen, 

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-$$

and depends on the formation of very stable aurocyanide complexes. The formation of these complexes is a complicated process; 35 equilibria have been proposed in a model system to account for their generation at a rotating gold electrode. 

Species, including cyanide, that bind strongly to the surfaces of gold-bearing materials result in passivation and, when high-purity cyanide solutions are used, gold dissolution is negligible, consistent with a two-step mechanism. AuCN$_{(s)}$ is formed rapidly at the gold surface, and a subsequent rate-determining step involves the addition of a second ligand, followed by the dissolution of Au(CN)$_2^-$

$$\text{Au}_{(s)} + \text{CN}^- = \text{AuCN}_{(s)} + e^-$$

$$\text{AuCN}_{(s)} + \text{CN}^- = [\text{Au(CN)}]_2^-$$

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ligand</th>
<th>Metal</th>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>OH$^-$, Cl$^-$</td>
<td>Zr, Nb, Mo, Hf, Ta, W</td>
<td>Cl$^-$, OH$^-$</td>
</tr>
<tr>
<td>Ti</td>
<td>Cl$^-$</td>
<td>Ru, Rh, Pd, Os, Ir, Pt</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>Cr</td>
<td>SO$_4^{2-}$, Cl$^-$</td>
<td>Ag</td>
<td>NH$_3$, CN$^-$, CH$_3$CN, Cl$^-$</td>
</tr>
<tr>
<td>Mn</td>
<td>SO$_4^{2-}$</td>
<td>Au</td>
<td>CN$^-$, (NH$_2$)CS, SO$_3^{2-}$, SCN$^-$, Cl$^-$</td>
</tr>
<tr>
<td>Fe</td>
<td>SO$_4^{2-}$, Cl$^-$</td>
<td>Sn</td>
<td>OH$^-$, Cl$^-$</td>
</tr>
<tr>
<td>Co</td>
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<td>Sb</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>Ni</td>
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<td>Pb</td>
<td>OH$^-$, Cl$^-$, CH$_3$CO$_2^-$</td>
</tr>
<tr>
<td>Cu</td>
<td>SO$_4^{2-}$, Cl$^-$, NH$_3$, CH$_3$CN</td>
<td>Lanthanides</td>
<td>SO$_4^{2-}$, CO$_3^{2-}$</td>
</tr>
<tr>
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<td>SO$_4^{2-}$</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Se, Te</td>
<td>Cl$^-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: 2, 4

Table 2 Metals recovered by leaching and types of ligands employed.
The low solubility of AuCN(s) is thought to be a consequence of a polymeric structure based on linear chains, \(-\text{Au-CN-Au-CN}\), which lie parallel to one another with a close-packed arrangement of gold atoms in which each is in contact with six nearest neighbors. The addition of cyanide and dissolution of \([\text{Au(CN)}_2]^-\) is believed to take place at the chain ends. This process is enhanced by the presence of \(\text{Ag}^{2+}\) or other ions such as \(\text{Pb}^{2+}\) (see below) normally present in the gold-bearing ores.

Sulfide is a well-known passivating species, and recently Jeffrey et al., using a rotating electrochemical quartz micro-balance, suggested that \(\text{Au}_2\text{S}_3\) is formed at surfaces. This passivity has led to a preference for recovering gold from oxidic matrices rather than refractory ores which have sulfidic matrices, but since the majority of gold deposits available for exploitation in the twenty-first century are refractory ores, methods are needed to improve leaching. Lead acetate has traditionally been used to enhance gold leaching, but the origins of this are not fully understood. In the absence of sulfide the addition of as little as a few ppb of \(\text{Pb}^{2+}\) results in a large increase in the rate of dissolution of pure gold into high-purity cyanide solution. This is believed to result from cementation of Pb on the gold surface, providing cyanide ions better access to AuCN(s) “chain ends” (see above). The binding of hydroxyl ions to the ends of AuCN chains accounts for the decrease in rates of cyanidation when the process is carried out at a pH >12.

The toxicity of cyanide has led to the development of alternative lixiviants for gold and silver; see also Sections 9.17.3.2 and 9.17.3.3. Thiosulfate is potentially a cheaper reagent for use in alkaline or near-neutral solutions in the presence of a mild oxidant such as dioxygen.

\[
4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} = 4[\text{Au(S}_2\text{O}_3)_2]^{3-} + 4\text{OH}^-
\]

Alkaline conditions must be used to prevent the decomposition of thiosulfate. The resulting pregnant leach solutions also contain the monothiosulfato complex, \([\text{Au(S}_2\text{O}_3)_3]^-\).

Dissolution is depressed by the build-up of sulfur-containing coatings on the ore particles. The presence of ammonia and \(\text{Cu}^{2+}\) ions in the leach solution appears to overcome this problem and greatly enhances dissolution. The coordination chemistry of such an ammonia–thiosulfate–copper–gold system is complicated. Its interpretation must take into account the influence of ligands on the \(\text{Cu}^{2+}/\text{Cu}^{+}\) and \(\text{Au}^{+}/\text{Au}\) redox couples and the occurrence of oxidative decomposition reactions of thiosulfate involving the formation of tetrathionate and other compounds. Extensive thermodynamic calculations and \(E^\circ–\text{pH}\) diagrams under typical leaching conditions have been used to clarify which species predominate and mechanistic studies have provided a greater understanding of reaction pathways.

It is believed that copper acts as the oxidant in these systems, effecting the dissolution of gold as an ammine complex,

\[
\text{Au(s)} + [\text{Cu(NH}_3)_4]^{2+} = [\text{Au(NH}_3)_2]^+ + [\text{Cu(NH}_3)_2]^{2+}
\]

which then transfers the \(\text{Au}^{1}\) ion to thiosulfato ligands.

The ammonia stabilizes \(\text{Cu}^{II}\) relative to \(\text{Cu}^{I}\) allowing it to be regenerated in the presence of air, and although the reduction of \(\text{Cu}^{II}\) by thiosulfate is normally rapid in a pure aqueous solution, in the presence of ammonia in these systems it proceeds much more slowly.

\[
2[\text{Cu(NH}_3)_4]^{2+} + 8\text{S}_2\text{O}_3^{2-} = 2[\text{Cu(S}_2\text{O}_3)_3]^{5-} + \text{S}_4\text{O}_6^{2-} + 8\text{NH}_3
\]

Reagent losses of this type need to be minimized if the technology is to achieve wide application.

### 9.17.3.2 Leaching of Gold and Silver into Acidic Media

Sulfidic matrices often require an oxidative pre-treatment prior to leaching the gold (see above). Bio-oxidative processes to achieve this usually generate acidic aqueous phases which must be neutralized prior to cyanidation. To avoid this neutralization step, lixiviants such as thiourea have been considered, which can be used in acidic media. The thiourea-based processes have a
much lower environmental impact than conventional cyanidation and are claimed to show greater selectivity and faster kinetics of gold dissolution.

Stable cationic complexes of Au(I) are formed with thiourea in acidic solutions in the presence of oxidants such as Fe(III) or hydrogen peroxide,

\[
2Au(s) + 4CS(NH_2)_2 + 2Fe^{3+} = 2[Au(CS(NH_2)_2)_2]^{1+} + 2Fe^{2+}
\]

Lacoste-Bouchet et al.\textsuperscript{66} have shown that acidic thiourea is a more selective leachant for gold over copper than alkaline cyanide solutions.

Oxidation of thiourea occurs fairly rapidly with H_2O_2 but more slowly with Fe(III),

\[
2SC(NH_2)_2 = NH_2(NH)CSSC(NH)NH_2 + 2H^+ + 2e^-
\]

The resulting formamidine disulphide acts as a gold oxidant,\textsuperscript{60}

\[
2Au(s) + 2SC(NH_2)_2 + NH_2(NH)CSSC(NH)NH_2 + 2H^+ = 2[Au(CS(NH_2)_2)_2]^{1+}
\]

regenerating thiourea, but is not stable in acidic solutions and decomposes irreversibly, producing elemental sulfur and cyanamide:

\[
NH_2(NH)CSSC(NH)NH_2 = CS(NH_2)_2 + CN(NH_2) + S(s)
\]

Thiourea can also be lost from the system by the formation of stable iron sulfate complexes,\textsuperscript{63,66}

\[
Fe^{3+} + SO_4^{2-} + SC(NH_2)_2 = [FeSO_4(CS(NH_2)_2)]^{1+}
\]

Such reagent losses need to be minimized to ensure that thiourea leaching finds widespread use. Leaching with chlorine in acidic media proceeds via a Au(I) intermediate;

\[
Au(s) + Cl^- + 1/2Cl_2 = [AuCl_2]^{-}
\]

\[
AuCl_2^- + Cl_2 = AuCl_4^-
\]

faster than traditional cyanidation.\textsuperscript{70–74} The Cl_2 can be generated \textit{in situ} from the reaction of chloride and hypochlorite salts, and can be operated as part of the oxidative treatment of the ores.\textsuperscript{70}

9.17.3.3 Leaching of Base Metals

A review of processes for leaching of base metals from their ores has appeared recently.\textsuperscript{2} Recent developments involving the generation and composition of sulfate-, chloride-, or ammonia-based streams which are used to feed solvent extraction processes are considered briefly below.

9.17.3.3.1 Leaching of base metals into sulfate media

Sulfate process streams are commonly used in metal recovery because they are readily derived by leaching with sulfuric acid or by oxidation of sulfidic ores. Metal recovery from such streams rarely involves the formation of metal sulfate complexes because the sulfate ion is a weak ligand for base metal cations and consequently acidic ion exchange extractants are commonly employed (see Section 9.17.5), which generate sulfuric acid which can be returned to the leaching stage,

\[
MSO_4 + 2LH_{2(org)} = ML_{2(org)} + H_2SO_4
\]

Following the success of the Moa Bay plant in Cuba where commercial acid pressure leaching of limonitic ores has been practiced since the 1950s,\textsuperscript{75–80} there has been a large amount of work undertaken on high-pressure acid leaching of lateritic ores\textsuperscript{81–88} which represents nearly 70% of the
world’s Ni reserves and also represents a major resource for cobalt. Until recently, these oxidic ores have remained largely unexploited due to the absence of appropriate technology, but as they are located close to the surface they can be mined at a significantly lower cost than sulfidic ores from which the majority of nickel is presently extracted. The investment in the pressure leaching of lateritic nickel ores has been based on the increased confidence gained by the growing number of successful pressure oxidation plants brought on stream for gold and zinc recovery. Apart from bringing pressure technology into the mainstream, these plants have produced a pool of engineering and equipment designing expertise, which can be applied to laterites projects. More than 90% of the Ni and Co in laterite ores (1.0–1.6% nickel) can be leached by sulfuric acid at \( \geq 240 \, ^\circ C \) and 0.2–1.1 MPa, typically producing relatively dilute leach solutions containing 3–6 g L\(^{-1}\) of nickel and around 40 g L\(^{-1}\) H\(_2\)SO\(_4\). The processes are relatively selective for nickel and cobalt over iron and the content of the latter can be further reduced by precipitation as Fe\(^{III}\) oxy-hydroxides on raising the pH.

Oxidative pressure acid leaching is also applied to copper–nickel mattes. Nickel recoveries of >99% are obtained when leaching is carried out at 135–160 °C at oxygen partial pressures of 140–350 kPa,

\[
\text{Ni}_3\text{S}_2(s) + \text{H}_2\text{SO}_4 + 1/2\text{O}_2 = \text{NiSO}_4 + 2\text{NiS}(s) + \text{H}_2\text{O}
\]

\[
2\text{NiS}(s) + 4\text{O}_2 = 2\text{NiSO}_4
\]

\[
\text{NiS}(s) + \text{CuSO}_4 = \text{NiSO}_4 + \text{CuS}(s)
\]

giving a solution depleted in both iron and copper with respect to the matte. Further purification can be achieved by addition of Ni metal and ammonium sulfate, which leads to precipitation of CuS and jarosite,

\[
\text{CuSO}_4 + \text{Ni}(s) = \text{NiSO}_4 + \text{CuS}(s)
\]

\[
3\text{Fe}_2(\text{SO}_4)_3 + (\text{NH}_4)_2\text{SO}_4 + 12\text{H}_2\text{O} = 2\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6(s) + 6\text{H}_2\text{SO}_4
\]

Heap leaching of copper oxides and transition ores and acid/neutral leaching of zinc calcine are well-established processes to generate the feed solutions for the hydrometallurgical recovery of these metals.  

### 9.17.3.3.2 Leaching of base metals into chloride media

Different approaches are needed for the dissolution of oxides, silicates, and sulfides. Generally, the processes dealing with sulfides require oxidizing conditions, and much work has been described aimed at generating sulfur as a by-product using reactions such as

\[
\text{ZnS}(s) + 2\text{FeCl}_3 = \text{ZnCl}_2 + 2\text{FeCl}_2 + \text{S}(s)
\]

\[
\text{Cu}_2\text{S}(s) + 4\text{FeCl}_3 = 2\text{CuCl}_2 + 4\text{FeCl}_2 + \text{S}(s)
\]

The resulting mixed-metal feeds can be processed using solvent extractants and the processes—see, for example, Figure 6 (Section 9.17.5.1.2)—often involve electrowinning of the metals from chloride solutions, providing chlorine for regeneration of the ferric chloride leachant,

\[
2\text{FeCl}_2 + \text{Cl}_2 = 2\text{FeCl}_3
\]

In the Falconbridge process, copper-containing nickel mattes produced by preliminary pyrometallurgical processing of ore concentrates (see Figure 2) are oxidized by chlorine in reactions in which Cu\(^{II}\) is responsible for electron transfer to the metal.

\[
\text{Ni}_3\text{S}_2(s) + 2\text{CuCl}_2 = 2\text{NiS}(s) + \text{NiCl}_2 + 2\text{CuCl}
\]
NiS\(_{(s)}\) + 2CuCl\(_2\) = NiCl\(_2\) + 2CuCl + S\(_{(s)}\)  
2CuCl + Cl\(_2\) = 2CuCl\(_2\)

The sulfur liberated is involved in a complicated sequence of reactions which lead to almost complete removal of copper from the matte as very insoluble CuS\(_{(s)}\).\(^{101–103}\)

\[
\begin{align*}
\text{Ni}_3\text{S}_2\text{(s)} + S\text{(s)} + 6\text{CuCl} &= 3\text{NiCl}_2 + 3\text{Cu}_2\text{S}\text{(s)} \\
\text{Ni} + S\text{(s)} + 2\text{CuCl} &= \text{NiCl}_2 + \text{Cu}_2\text{S}\text{(s)} \\
\text{Cu}_2\text{S}\text{(s)} + S\text{(s)} &= 2\text{CuS}\text{(s)} \\
S + 2\text{CuCl} &= \text{CuS} + \text{CuCl}_2
\end{align*}
\]

Société Le Nickel (SLN) employ similar chemistry at their operations to treat mattes obtained from the pyrometallurgical treatment of Ni-bearing oxidic laterite ores.\(^{104}\) It has demonstrated at laboratory scale that Ni-containing lateritic ores may be directly leached into HCl acid solution without pyrometallurgical pre-concentration at atmospheric pressure and relatively low temperature (ca. 70°C).\(^{105}\)

### 9.17.3.3 Leaching of base metals into ammoniacal media

Ammoniacal leaching is typically applied to oxidic nickel-bearing materials that have been subjected to a “reductive roast,” which converts the cobalt and nickel present to their metallic form (or as ferro-alloys) and most of the iron to Fe\(^{II}\). \(^{106,107}\)

\[
\text{NiO}\text{(s)} + \text{H}_2 = \text{Ni}\text{(s)} + \text{H}_2\text{O}
\]

The resulting calcine is leached with an ammonia/ammonium carbonate solution,

\[
\text{FeNi}\text{(s)} + \text{O}_2 + 8\text{NH}_3 + 3\text{CO}_2 + \text{H}_2\text{O} = [\text{Ni(NH}_3)_6]^{2+} + \text{Fe}^{2+} + 2\text{NH}_4^+ + 3\text{CO}_3^{2-}
\]

Good separation from iron is achieved by formation of solutions of stable Ni\(^{II}\) and Co\(^{II}\) ammine complexes, whilst any Fe\(^{II}\) leached is oxidized and precipitates as Fe\(^{III}\) oxyhydroxides.

Ammoniacal leaching of chalcocite ores\(^{108–110}\) generates two Cu streams, an enriched ore—covellite—which can be treated in a conventional smelter, and a fairly concentrated aqueous solution (ca. 5 M, pH 8.5–10) containing ammine complexes,

\[
\text{Cu}_2\text{S}\text{(s)} + 2\text{NH}_3 + 2[\text{NH}_4^+] + 1/2\text{O}_2 \rightarrow \text{CuS}\text{(s)} + [\text{Cu(NH}_3)_4]^{2+} + \text{H}_2\text{O}
\]

which can be conveniently treated by solvent extraction (see Section 9.17.5.1.3).

### 9.17.4 SEPARATION AND CONCENTRATION

Some of the types of equilibria involved in the unit operations separation and concentration are listed in the introduction, Section 9.17.1. Those which depend most on coordination chemistry, and for which details of metal complex formation are best understood, are associated with hydrometallurgy. Once the metal values have been transferred to an aqueous solution, the separation from other metals and concentration can be achieved by one of the following processes.\(^3\)

(i) Selective crystallization, e.g., removal of PbCl\(_2\) from the chlorometallate complexes of other base metals (see Section 9.17.3.3.2).

(ii) Selective precipitation, e.g., the sequential separation of CuS and ZnS, followed by co-precipitation of CoS and NiS is achieved in the Outokumpu process by the generation of H\(_2\)S \textit{in situ} resulting from addition of pyrite to an acidic solution of the mixed metal chlorides.
Selective reduction, e.g., cementation of copper by addition of scrap iron to aqueous solutions of Cu\(\text{II}\) salts, Cu\(^{2+}\) + Fe\((s)\) = Cu\((s)\) + Fe\(^{2+}\).

Selective adsorption of ions or complexes onto solid materials, e.g., cyanogold(I) complexes onto activated carbon (see Section 9.17.6.1) or the uptake of lanthanides on ion exchange resins.

Selective transfer of ions or complexes into water-immiscible phases, e.g., the solvent extraction of uranyl nitrate into tri-butyl phosphate.

The choice between the use of solid-state supported extractants and solvent extraction is often made on the basis of the concentration of the desired metal in the aqueous feed. Solvent extraction is usually not effective for treating very dilute feeds because an impractically large volume of the aqueous phase must be contacted with an organic extractant to achieve concentration of the materials across the circuit. However, solvent extraction is preferred for treating moderately concentrated feeds because most ion-exchange resins and related materials have relatively low metal capacities and very large quantities of resin are required. In this review we will focus on reagents used in solvent extraction because, in the main, the nature of the complexes formed are better understood.

9.17.4.1 Solvent Extraction Processes

This technology lends itself to continuous, rather than batch, processing and has been proven robust since first applied for the extraction of uranium in the early 1940s.\(^{10}\) The types of extractant used can be classified according to the types of reactions involved in phase transfer.\(^{111}\)

(i) **Extraction by cation exchange** is characterized by the formation of an electrically neutral metal complex in which the extracted metal cation has displaced another cation (most commonly a proton) from the complexing agents. When the extraction involves the release of a proton, as with copper recovery by the phenolic oximes (I), the equilibrium is dependent on the pH of the aqueous phase, and the pH associated with 50% loading of the extractant (the pH\(_{1/2}\)) is often used to indicate the “strength” of an extractant at a stated concentration, and for a defined composition of aqueous feed.

\[
\begin{align*}
\text{(I)} & & \\
\text{[2R-OH]_2 = Cu}^{2+} & & \text{[2R-OH]_2 + 2H}^+ \\
\end{align*}
\]

(ii) **Extraction by anion exchange** involves the transfer of an anionic metal complex from the aqueous phase, displacing an ion from the organic solvent. Such reactions are commonly used for transport of chlorometallate complexes, e.g.,

\[
[\text{FeCl}_4]^- + [\text{R}_4\text{N}]\text{Cl}_{(\text{org})} = [\text{R}_4\text{N}]\text{[FeCl}_4]_{(\text{org})} + \text{Cl}^-
\]

Often, the cationic component of the ion pair is generated by the protonation of an organic base, e.g.,

\[
[\text{FeCl}_4]^- + \text{HCl} + \text{R}_3\text{N}_{(\text{org})} = [\text{R}_3\text{NH}]\text{[FeCl}_4]_{(\text{org})} + \text{Cl}^-
\]

(iii) **Extraction by solvation** is characterized by the displacement of some or all of the water molecules in the coordination sphere of a metal cation or its complexes by neutral organic donors, typically ethers, ketones, or neutral phosphorus(V) molecules containing P=O units, e.g., the extraction of uranium(VI) from nitrate solutions by tri-\(n\)-butyl phosphate (TBP).

\[
\text{UO}_2\text{(NO}_3)_2 + 2\text{TBP}_{(\text{org})} = [\text{UO}_2\text{(NO}_3)_2\text{(TBP)}_2]_{(\text{org})}
\]
Extraction by physical distribution involves the transfer of a discrete molecular entity from the aqueous phase to an inert solvent. Such a situation arises only for solutes which are only weakly solvated and very few examples exist in extractive metallurgy.\(^4\)

Whilst this classification is useful in giving an indication of the types of chemical changes which occur at the metal centers, it oversimplifies the situation in many cases. For example, changes in the solvation spheres of anionic species in both (ii) and (iii) are also very important in defining the free energies of extraction.\(^\text{112}\) Frequently, acidic ligands used as cation exchangers are also present in the second coordination sphere in an undissociated form, acting as solvating extractants in species such as \([ML_2\cdot 2LH]\), etc. (see below).

Recently, reagents have been used which operate as both cation and anion exchangers, providing binding sites in organic solvents for both components of a metal salt, either by mixing extractants (binary systems)\(^\text{113}\) or by using ditopic ligands.\(^\text{114,115}\)

The sections below review the coordination chemistry of the most important classes of extractants used commercially. Particular attention is paid to the importance of secondary bonding between extractant components. This facilitates the assembly of ligating packages which match the coordination requirements of particular metal cations or their complexes and enhances both the selectivity and “strength” of extraction. Hydrogen bonding between ligands—e.g., esters of phosphorus(V) acids (see Section 9.17.4.3)—is particularly prevalent in the hydrocarbon solvents commonly used in industrial processes.

### 9.17.4.2 Hydroxy-oxime Extractants

The history and chemistry of the hydroxy-oxime extractants which were originally developed for Cu recovery has been extensively reviewed.\(^\text{11,13,14}\) Szymanowski’s book\(^\text{14}\) provides comprehensive cover of the literature prior to 1993 and assigns chemical structures to reagents which in most metallurgy texts are referred to only by codes provided by reagent suppliers. An updated version of this information is provided in Table 3.

All commercial activity is currently based on the phenolic-oximes. A convenient Mg-catalyzed process for the manufacture of parent salicylaldehydes has been developed.\(^\text{116}\)

Extraction equilibria based on the “pH-swing” process

\[
2LH_{\text{org}} + M^{2+} = ML_{2-\text{org}} + 2H^+
\]

have been extensively investigated.\(^\text{14}\) Reagents can be selected or combined to meet the “extractant strength” requirements of different Cu-recovery circuits—see Section 9.17.5.1. Ketoximes are slightly weaker extractants than aldoximes and operate efficiently when the leach liquor is relatively warm and the pH is ca. 1.8 or above.\(^\text{13}\) The aldoximes are stronger and thus are used in modified formulations for recovery at low temperatures and pH.\(^\text{13}\) The extent to which interligand H-bonding influences the stability of complexes in the organic phase, and hence the selectivity and efficiency of extraction, provides a good example of how supramolecular chemistry can be exploited in hydrometallurgy, allowing quite simple, inexpensive reagents to provide organized donor sets in nonpolar solvents. Such effects are also of great importance in selecting the appropriate carboxylic acid or organophosphorus acid extractants—see below.

In the solid state, H-bonding between the oxime OH groups and phenolate oxygen atoms within a complex unit is almost invariably observed,\(^\text{117}\) leading to pseudo-macrocyclic complexes (as in (2)) with VO\(^{2+}\), CoNO\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), or Pd\(^{2+}\). In the complexes which have planar donor sets, i.e., those of Ni\(^{11}\), Cu\(^{11}\), and Pd\(^{11}\), the “goodness-of-fit” of the metal is dependent on the size of the cavity prescribed by the pseudo-macrocycle.\(^\text{117}\) The pseudo-macrocyclic structure is also present in the solid state forms of some free ligands (e.g., (3))\(^\text{117}\) and is retained in solution.\(^\text{118,119}\) Although the dimeric forms of the free ligands are not planar\(^\text{117}\) and have a step conformation to reduce repulsion between the central phenolic protons, they are partially preorganized for complex formation and the dimers should be considered in modeling extraction equilibria,\(^\text{118,120}\)

\[
(LH)_{2-\text{org}} + M^{2+} = ML_{2-\text{org}} + 2H^+
\]
Table 3 The commercial\textsuperscript{a} names and structures\textsuperscript{b} of commonly used reagents containing hydroxy-oximes.

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>$R^3$</th>
<th>Reagents containing phenolic oximes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>C$<em>3$H$</em>{19}$</td>
<td>H</td>
<td>P1, P50, P5100, P5200, P5300, P5050, M5615, M5397, M5640 (Acorga)</td>
</tr>
<tr>
<td>C$_6$H$_3$CH$_2$</td>
<td>C$<em>3$H$</em>{19}$</td>
<td>H</td>
<td>P17 (Acorga)</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>C$<em>3$H$</em>{19}$</td>
<td>H</td>
<td>SME529 (Shell), LIX84 LIX84-1 LIX84-R (Cognis), LIX984 (Cognis as 1:1 mixtures with LIX860)</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>C$<em>{12}$H$</em>{25}$</td>
<td>H</td>
<td>LIX64 (Cognis)</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>C$<em>3$H$</em>{19}$</td>
<td>H</td>
<td>HS-LIX 65N (Cognis), LIX 65N (General Mills), HS-LIX64N (Cognis in 44:1 mixture with LIX63), LIX 64N (General Mills in 44:1 mixture with LIX63)</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>C$<em>3$H$</em>{19}$</td>
<td>Cl</td>
<td>LIX70, LIX71 (in mixture with LIX 65N), LIX73 (in mixture with LIX 64N) (General Mills)</td>
</tr>
<tr>
<td>H</td>
<td>C$<em>{12}$H$</em>{25}$</td>
<td>H</td>
<td>LIX860, LIX622, LIX6022, LIX864 (as mixture with LIX 64N), LIX865 (as mixture with LIX65N)(Cognis)</td>
</tr>
</tbody>
</table>

Reagents containing $\alpha$-hydroxyoximes

2-Ethyl-pentyl 2-ethyl-pentyl LIX63 (Cognis), LIX 64N (General Mills in 1:44 mixture with LIX 65N), HS-LIX 64N (Cognis in 1:44 mixture with LIX 65N)

Source:\textsuperscript{14}

\textsuperscript{a} Details of some of the modifiers and other additives in these formulated reagents are available in references 14 and 118.  
\textsuperscript{b} The $R^2$ substituents on the phenolic oximes are usually multiply branched alkyl groups containing mixtures of isomers.
Interactions of the monomeric, dimeric, or other forms of the extractant with a modifier (Y) are also important in interpreting extraction equilibria, e.g.,

\[
(LH)_2^{\text{(org)}} + 2Y^{\text{(org)}} = 2LHY^{\text{(org)}} \text{ or }
\]

\[
LH^{\text{(org)}} + Y^{\text{(org)}} = LHY^{\text{(org)}}
\]

where the modifier competes with metal cations for the donor functionalities. Work in this area has been reviewed and the importance of the preorganized dimer, particularly in saturated hydrocarbon solutions, in the recovery of copper has been established. The head-to-tail pseudo-macroyclic structure is preserved in cis-octahedral Ni\textsuperscript{II} complexes formed in the presence of \(\alpha,\omega\)-diamines.

The bite angle defined by such eight-membered pseudo-chelate rings favors tetrahedral coordination geometry and consequently selectivity for first transition series metal dication does not follow the Irving–Williams order. Zn\textsuperscript{II} is more strongly extracted by D2EHPA than other first transition series M\textsuperscript{2+} ions (see also Section 9.17.5.2), and Co\textsuperscript{II} can be selectively extracted from solutions containing Ni\textsuperscript{II} salts by the sulfur-donor extractants Cyanex 301 and Cyanex 302 (see Section 9.17.3).

For divalent metals which readily form tetrahedral complexes and for trivalent metals which show a preference for octahedral donor sets, neutral D2EHPA complexes are formed with 4:1 and 6:1 ligand:metal stoichiometries respectively,

\[
4LH^{\text{(org)}} + M^{2+} = [ML_2(LH)_2]^{\text{(org)}} + 2H^+
\]

\[
6LH^{\text{(org)}} + M^{3+} = [ML_3(LH)_3]^{\text{(org)}} + 3H^+
\]

which allows the eight-membered chelate rings to be preserved. For divalent octahedral metal ions the formation of charge neutral complexes is achieved with an equatorial arrangement of two eight-membered chelate rings and two neutral axial donors, either LH monomers or L\textsubscript{2}H\textsubscript{2} dimers.

Although the lanthanide cations most commonly give complexes with coordination numbers of 8 or 9, the [ML\textsubscript{2}(LH)\textsubscript{3}] species predominate on extraction with phosphorus(V) acids and it has been suggested that the bulk of the L \(\cdots\) LH chelate ring favors a lower coordination number. The phosphorus(V) acids are very effective reagents for the extraction and separation of lanthanides (See chapter 3.2).

9.17.4.4 Carboxylic Acids

Whilst carboxylic acids are readily available and inexpensive, they are relatively weak extractants and have not found much use in the recovery of base metals until recently when Versatic 10 has been piloted for the separation of Ni from Mn and Mg (Section 9.17.5.4). As with the phosphorus(V) acid extractants, the propensity for association leads to substantial levels of solvation of caboxylato
Table 4  The commercial names and structures of phosphorus(V) acid extractants.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$R$</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>CH$_2$CH(C$_2$H$_5$)C$_4$H$_9$</td>
<td>MEHPA, SBX50</td>
</tr>
<tr>
<td>RO–P–OH</td>
<td>C$<em>{18}$H$</em>{37}$iso</td>
<td></td>
</tr>
<tr>
<td>(phosphoric)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>CH$_2$CH(C$_2$H$_5$)C$_4$H$_9$</td>
<td>D2EHPA, DP-8R,</td>
</tr>
<tr>
<td>RO–P–OR</td>
<td>C$<em>{10}$H$</em>{21}$iso</td>
<td>Hostarex PA216 P204</td>
</tr>
<tr>
<td>O</td>
<td>C$<em>{18}$H$</em>{37}$iso</td>
<td>DP10-R</td>
</tr>
<tr>
<td>(phosphoric)</td>
<td></td>
<td>TR-63</td>
</tr>
<tr>
<td>OH</td>
<td>CH$_2$CH(C$_2$H$_5$)C$_4$H$_9$</td>
<td>Hoe F 3787</td>
</tr>
<tr>
<td>RO–P–OR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mono-thio phosphoric)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RO–P–OR</td>
<td>CH$_2$CH(C$_2$H$_5$)C$_4$H$_9$</td>
<td>DEHTPA</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(di-thio phosphoric)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>CH$_2$CH(C$_2$H$_5$)C$_4$H$_9$</td>
<td>PC-88A, SME, YP-AC,</td>
</tr>
<tr>
<td>R–P–OR</td>
<td>4050-MOOP, Ionquest 801</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(phosphonic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>CH$_2$CH(CH$_3$)CH$_2$C$_4$H$_9$</td>
<td>Cyanex 272</td>
</tr>
<tr>
<td>R–P–R</td>
<td>CH$_2$CH(CH$_3$)CH$_2$C$_4$H$_9$</td>
<td>PIA-8</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(phosphinic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R–P–R</td>
<td>CH$_2$CH(CH$_3$)CH$_2$C$_4$H$_9$</td>
<td>Cyanex 302</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mono-thio phosphinic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH</td>
<td>CH$_2$CH(CH$_3$)CH$_2$C$_4$H$_9$</td>
<td>Cyanex 301</td>
</tr>
<tr>
<td>(di-thio phosphinic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R–P–N–P–R</td>
<td>R = aryl or aryloxy</td>
<td>DS 5968, DS 6001</td>
</tr>
<tr>
<td>R'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
complexes by neutral carboxylic acid molecules and to the formation of polynuclear complexes. Extraction can be represented by the general equation:

\[
M^{m+} + p\text{H}_2\text{O} + (n/2 + m/2)(\text{LH})_{2(\text{org})} = 1/x(\text{ML}_n^m\text{mLH}_p\text{H}_2\text{O})_{x(\text{org})} + n\text{H}^+
\]

With copper, for example, monomeric \([\text{CuL}_2], [\text{CuL}_2\cdot\text{LH}], [\text{CuL}_2\cdot2\text{LH}], [\text{CuL}_2\cdot4\text{LH}], \) and dinuclear \([\text{CuL}_2]\_2, [(\text{CuL}_2\cdot\text{LH})_2], [(\text{CuL}_2\cdot2\text{LH})_2] \) species have all been observed.\(^\text{125}\)

9.17.4.5 Amine Salt Extractants

The applications of hydrophobic amine salts (see Table 5) as anion exchange extractants to recover a diverse range of metals in the form of anionic, usually chloro, complexes was reviewed\(^\text{4}\) in \textit{CCC} (1987). The order of preference shown by this class of extractants for simple inorganic anions

\[
[R_3\text{NH}]_2X_{(\text{org})} + Y^- = [R_3\text{NH}]_2Y_{(\text{org})} + X^-
\]

follows the sequence \(\text{ClO}_4^- > \text{NCS}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-\) and represents the readiness by which such anions leave the aqueous phase.\(^\text{126,127}\) Large anions with more diffuse charge are less favorably hydrated and consequently are more readily accommodated in the organic phase as ion-pairs. Similar principles account for the favorable transport of simple chloro metallates from acidic chloride streams

\[
M^{2+} + 2\text{H}^+ + 4\text{Cl}^- + 2R_3\text{N}_{(\text{org})} = [R_3\text{NH}]_2[M\text{Cl}_4]
\]

and are exemplified in processes in \textit{Sections 9.17.5} and \textit{9.17.6}. This type of extraction mechanism is particularly important for substitution-inert metal ions, where replacement of inner-sphere ligands by cation exchange reagents occurs so slowly that impractically long contact times would be required in solvent extraction.

An understanding of the interactions in ion-pairs, e.g., a combination of electrostatic and hydrogen bonding in species such as \([R_3\text{NH}]_2[M\text{Cl}_4],\) is needed for a more rational design of anion exchange extractants, and is timely considering the recent extension of supramolecular chemistry to the design of anion receptors.\(^\text{128–130}\) The trialkylguanidinium salts, LIX 79,\(^\text{131–133}\) (see Table 5) represent an example of a class of extractant which is likely to recognize the outer coordination sphere of an anionic metal complex (see also \textit{Section 9.17.6.1}).

### Table 5 Commercially available anion exchange extractants.

<table>
<thead>
<tr>
<th>Class</th>
<th>Commercial name</th>
<th>Substituents(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>Primene 81R</td>
<td>(t)-C(<em>{12})–C(</em>{14})</td>
</tr>
<tr>
<td></td>
<td>Primene JMT</td>
<td>C(<em>{12})–C(</em>{14})</td>
</tr>
<tr>
<td>Secondary</td>
<td>Adogen 283, Adogen 283D</td>
<td>di-(-)octyl</td>
</tr>
<tr>
<td></td>
<td>ditridecylamine, HOE 2652</td>
<td>di-tridecyl</td>
</tr>
<tr>
<td></td>
<td>Amberlite LA-1</td>
<td>Undefined</td>
</tr>
<tr>
<td></td>
<td>Amberlite LA-2</td>
<td>Undefined</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Alamine 336, Adogen 364</td>
<td>tri-C(<em>6)–C(</em>{10})</td>
</tr>
<tr>
<td></td>
<td>Adogen 381, Alamine 330, TIOA</td>
<td>tri-(-)octyl</td>
</tr>
<tr>
<td>Quarternary</td>
<td>Adogen 364, Aliquat 336</td>
<td>methyl, tri-C(<em>6)–C(</em>{10})</td>
</tr>
<tr>
<td>Other(guanidine)</td>
<td>LIX 79</td>
<td>Undefined</td>
</tr>
</tbody>
</table>

\(^a\) Commercial anion exchange extractants are often complex, poorly defined mixtures. Information is given where available from Chemical Abstracts.
### 9.17.4.6 Solvating Extractants

A diverse range of neutral organic molecules has been used to stabilize or to enhance the solubilities of neutral metal-containing entities in an organic phase. Some examples of commercial significance are listed in Table 6. When used alone they efficiently transport metal salts across a circuit. An example is the use of tributyl phosphate (TBP) in recovery of uranyl nitrate,

$$\text{UO}_2(\text{NO}_3)_2 + 2\text{TBP}_{(\text{org})} = [\text{UO}_2(\text{NO}_3)_2(\text{TBP})]_{(\text{org})}$$

<table>
<thead>
<tr>
<th>Structure</th>
<th>$R$</th>
<th>$R'$</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>8\text{H}</em>{17}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{13}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{12}\text{H}</em>{23}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
<td></td>
<td></td>
<td></td>
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<td>$\text{C}_2\text{H}_9^a$</td>
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<td></td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>8\text{H}</em>{13}^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>8\text{H}</em>{17}^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{13}^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_5^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>10\text{H}</em>{21}^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{13}\text{H}</em>{27}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
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<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
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<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
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<td></td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Cyanex 923 contains a mixture of n-octyl and n-hexyl groups and Cyanex 925 a mixture of normal and branched octyl groups.
They are also used in combination with other cation exchange reagents as synergistic extractants, often stabilizing the resulting complex by completing the metal coordination sphere. An example is the addition of TBP to thienoyltrifluoroacetone, HTTA, which enhances the extraction of AmIII or lanthanide ions by formation of neutral complexes of general formula \([M(tta)_3(TBP)]_n\).\(^{134,135}\)

9.17.5 BASE METALS

9.17.5.1 Copper

The application of solvent extraction to copper recovery has been a major growth area since the last review of this series.\(^{11,13}\) Almost 30% of world production in 2000 involved the use of sulfuric acid heap leaching, solvent extraction, and electrowinning, far exceeding earlier predictions.\(^{136}\)

9.17.5.1.1 Extraction of \(\text{Cu}^{II}\) from sulfate solutions

The commercial success of this technology is based on the very good materials balance which applies when processing oxidic ores, using the phenolic oxime “pH-swing” extractants (Section 9.17.3) in conjunction with a conventional electrolysis process. The reactions involved in the flowsheet are listed in Figure 5. The relatively “strong” phenolic oxime reagents ensure that high recovery is possible from pregnant leach solutions which can have pH values as low as 1.5.\(^{13}\) Acid released on extraction is re-used in leaching and the acid needed for stripping is generated by the electrolysis process. The “strength” of a formulated reagent can be tuned to meet the requirements of a particular feed solution, e.g., it can be reduced by selecting a ketoxime over an aldoxime or by the addition of modifiers, see Section 9.17.4.2.

The reagent suppliers provide loading and stripping isotherm data, which allow metallurgists to select appropriate reagents and to design circuits with the appropriate numbers and configurations of extraction and stripping stages.\(^{137}\)

The key separation achieved by the phenolic oxime reagents is copper from iron, which is often present in comparable or higher concentrations in pregnant leach solutions. The intrinsic selectivity for Cu over Fe shown by both the aldoxime and ketoxime extractants is high,\(^{14}\) and in practice in formulated reagents depends markedly\(^{138,139}\) on the nature of the modifiers used (see Section 9.17.4.2). Entrainment of droplets of the aqueous feed solutions into the kerosene solution of the extractant\(^{140}\) often represents the main route for transfer of iron across the flowsheet into the electrowinning tankhouse. Keeping the Fe concentration in the electrolyte down to a level which ensures good current efficiencies is usually achieved by taking a bleed from the tankhouse and returning this to the leachant.\(^{139}\) An alternative approach is to purify the electrolyte, “polishing” to remove Fe to a very low level using the “Diphonix” resin which shows a remarkably high selectivity for FeIII over CuII.\(^{141}\) This avoids the loss of acid and beneficial additives from the tankhouse. The iron

![Figure 5](image-url)
can be released from the resin by reductive stripping with sulfurous acid because Fe\textsuperscript{II} binds much more weakly to the bisphosphonic acid chelating units in the resin, LH\textsubscript{3(s)}\textsuperscript{−}.

\[
\text{Loading \ LH}_{3(s)}^- + \text{Fe}^{3+} = \text{FeL}_{(s)}^- + 3\text{H}^+ \\
\text{Stripping \ 2FeL}_{(s)}^- + 4\text{H}^+ + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} = 2\text{LH}_{3(s)}^- + 2\text{Fe}^{2+} + \text{H}_2\text{SO}_4
\]

Co-extraction of Mo and Cu is potentially a problem with certain feed solutions, and again selectivities are very dependent on the nature of modifiers present in formulated reagents. The Mo species extracted have not been fully characterized, but may include a neutral dioxo complex, [MoO\textsubscript{2}L\textsubscript{2}], which can be assumed to have an N\textsubscript{2}O\textsubscript{2}\textsuperscript{2−} donor set similar to that in the Cu\textsuperscript{II} complex, and molybdate complexes solvated by neutral phenolic oxime ligands such as [Mo\textsubscript{O}\textsubscript{4}H\textsubscript{2−}LH]. Formation of solvated forms of molybdic acid is supported by evidence that extraction is favorable at very low pH values and that the complexes are readily stripped by aqueous ammonia to produce ammonium molybdate.

\[
[\text{MoO}_4\text{H}_2\cdot\text{LH}]_{(org)} + 2\text{NH}_4\text{OH} = \text{LH}_{(org)} + [\text{NH}_4]^2[\text{MoO}_4] + 2\text{H}_2\text{O}
\]

Formation of polynuclear complexes by phenolic oximes is also possible with such oxo–metal species in high oxidation states, e.g., [(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}N][Mo\textsubscript{2}O\textsubscript{5}(sal-2H)], which has both a μ\textsubscript{2}–oxo-bridge between the two metal centers and two Mo–N–O–Mo oximinato bridges formed by the doubly deprotonated salicylaldoxime ligands, sal-2H. Commissioning new oxime extraction plants has been driven by major developments in leaching technologies—Section 9.17.3—which allow mixed oxide/sulfidic and sulfidic ores to be processed. When such leach processes do not consume sulfuric acid there is potentially a problem of acid build-up in the front end of this circuit because 1.54 g of H\textsubscript{2}SO\textsubscript{4} is generated per g of copper extracted. This release of acid is also a problem with very high tenor feeds because the extraction equilibrium shown in Figure 5 is depressed. In practice it has been shown that the extraction isotherms are not as adversely effected as might be expected, presumably due to the buffering effects of very high concentrations of sulfate which reduce the activity of proton.

\[
\text{H}^+ + \text{SO}_4^{2−} = \text{HSO}_4^−
\]

A creative approach has been proposed to deal with the acid generated from copper extraction from high tenor feeds by using it for heap leaching of another ore which has a high content of basic materials. This is planned for the acidic raffinate from Cu extraction from the 65 g L\textsuperscript{−1} pregnant leach solution from HPAL of the Konkola Deeps sulfide deposit, using it to leach the Chingola refractory ore and thus generate a conventional low tenor feed (5 g L\textsuperscript{−1} Cu) for a separate solvent extraction process. The electrolytes from both SX processes are to be combined for electrowinning.

An alternative strategy to treat feed solutions from leaching processes which do not consume acid is to use extractants which transport metal salts rather than metal ions. The ditopic ligands based on functionalized salicylaldimines described in Section 9.17.4.1 are strong extractants forming well-characterized 1:1:1 complexes, LCuSO\textsubscript{4}. The copper-binding site has to be “detuned,” e.g., by introduction of a 2,2’-biphenylene bridge as in (6), which disfavors formation of a planar N\textsubscript{2}O\textsubscript{2}\textsuperscript{2−} donor set, to allow the copper to be acid-stripped.
9.17.5.1.2 Extraction of CuII from chloride solutions

Oxidative leaching of sulfidic ores with ferric chloride generates elemental sulfur, avoiding the liberation of SO2 and produces (Section 9.17.3.3.2) pregnant leach solutions with high concentrations of FeCl2, FeCl3, CuCl2, and other metal chlorides. In the CUPREX process extraction with a neutral ligand L such as CLX50, (7), transports CuCl2 across a circuit with a good materials balance (see Figure 6).

The extraction equilibrium in the CUPREX process is dependent on the activity of Cl− in the feed solutions which in turn is dependent on the stability of chlorometallate complexes [MClx]2−x and [MClx]3−x for the di- and tri-valent metals present, rather than the simple stoichiometry represented by the equation shown in Figure 6.

Figure 6 A simplified flowsheet and materials balance for the recovery of copper from sulfidic ores by chloride leaching, solvent extraction and electrowinning, using for example reagents such as 7.
Systematic studies\textsuperscript{150,153} with CLX50, (7), decyl esters of pyridine monocarboxylic acids (8)–(10), and dipentyl esters of pyridine dicarboxylic acids (11)–(15) showed that extraction of Cu\textsuperscript{II} is strongly dependent on the activity of water and the total concentration of ionic and molecular species in the aqueous phase. For the monoesters, copper distribution is dependent on
\[
Cu^{2+} + 2Cl^- + 2L_{\text{org}} = CuL_2Cl_2(\text{org})
\]
and
\[
Cu^{2+} + iCl^- = [CuCl_i]^{2-i}
\]
but more complicated behavior is observed for CLX50 in kerosene. The monoester model ligands (8)–(10) form neutral complexes, [CuL_2Cl_2]\text{(org)}\text{\textsuperscript{149}} which appear to be too stable to strip effectively with hot water. The diesters (11)–(15) are weaker extractants and readily water-stripped. There are marked differences in the strengths of these extractants and the dependence of Cu extraction on chloride concentration which are not easily accounted for in terms of steric factors associated with the location of the carboxylate groups. ESR spectra suggest that similar complexes are formed, with the exception of the 2,6-dicarboxlate (14), which exhibits a hyperfine splitting not found in complexes of the other ligands.\textsuperscript{153}

As Cu\textsuperscript{II} is substitution-labile,\textsuperscript{154} the rates of mass transfer are dependent on interfacial processes, which have been shown\textsuperscript{155} to be fast for both loading and stripping in conventional contactors, but possibly too slow in stripping for the industrial application of columns. The low activity of water in these feed solutions ensures that activity of proton is high in acidic solutions. In addition to the problem this creates with regard to the corrosiveness, there is a tendency for even the very weakly basic pyridine nitrogen in CLX50 (7) to become protonated by aqueous feeds with high acidity allowing extraction of Fe\textsuperscript{III} by an ion-pairing mechanism,
\[
L_{\text{org}} + H^+ + FeCl_4^- = [LH][FeCl_4]_{\text{org}}
\]
which reduces the otherwise very high Cu/Fe selectivity.

The phenolic oxime reagents (Section 9.17.4.2) have also been used to recover copper from chloride leach solutions,\textsuperscript{156}
\[
2L'H_{\text{org}} + CuCl_2 = CuL'_2(\text{org}) + 2HCl
\]
but the high proton activity in these feeds limits the efficiency of these processes and steps have to be taken to adjust and control pH.\textsuperscript{148,157} A creative solution to this problem is to use a mixture of a “pH-swing” extractant (Equation (1)) and either a solvating or an ion-pairing (Section 9.17.4.6) extractant. The approach has been reviewed recently.\textsuperscript{157,158} On contacting the aqueous feed the majority of the copper extracted is transferred to the organic phase by the solvating or the ion-pairing reagents by reactions such as,
\[
\begin{align*}
Cu^{2+} + 2Cl^- + 2L_{\text{org}} &= CuL_2Cl_2(\text{org}) \\
Cu^{2+} + 2Cl^- + 2[R_4N]Cl_{\text{org}} &= [R_4N]_2[CuCl_4]_{\text{org}} \\
Cu^{2+} + 2Cl^- + 2[R_3NH]Cl_{\text{org}} &= [R_3NH]_2[CuCl_4]_{\text{org}}
\end{align*}
\]
Scrubbing the loaded organic phase with water or ammonia removes HCl, transferring the copper to the “pH-swing” extractant, e.g., as in,
\[
\begin{align*}
[R_3NH]_2[CuCl_4]_{\text{org}} + 2L'H_{\text{org}} + 4NH_3 &= [CuL'_2]_{\text{org}} + 2[R_3NH][Cl]_{\text{org}} + 2HCl \\
[R_3NH]_2[CuCl_4]_{\text{org}} + 2L'H_{\text{org}} + 4NH_3 &= [CuL'_2]_{\text{org}} + 2R_3N_{\text{org}} + 4[NH_4]Cl
\end{align*}
\]
which then can be stripped with sulfuric acid to give a sulfate electrolyte for conventional electrowinning.\textsuperscript{159} Examples of this approach include combinations of Alamine336 and LIX 54.
(18) for extraction and separation of Cu and Zn,\textsuperscript{160–163} CLX50 and LIX 54 for recovery of Cu from >2 M chloride solutions,\textsuperscript{157} (16) and (17) for recovery of Cu from dilute chloride solutions phase,\textsuperscript{164} or (16) and (18).\textsuperscript{157}

There has been much development of processes to electrowin Cu from chloride media,\textsuperscript{165} but to date no major plants using the solvent extraction coupled with electrowinning from chloride media have been commissioned.

9.17.5.1.3 Extraction of Cu\textsuperscript{II} from ammoniacal solutions

Ammoniacal leaching of chalcocite ores\textsuperscript{108,109,166,167} generates two Cu streams, an enriched ore, covellite, which can be treated in a conventional smelter, and a fairly concentrated aqueous solution (ca. 5 M, pH 8.5–10) containing ammine complexes,

\[
\text{Cu}_2\text{S}_{(s)} + 2\text{NH}_3 + 2[\text{NH}_4^+] + 1/2\text{O}_2 \rightarrow \text{CuS}_{(s)} + [\text{Cu}(\text{NH}_3)_4]^{2+} + \text{H}_2\text{O}
\]

Solvent extraction with a weakly acidic reagent,

\[
[\text{Cu}(\text{NH}_3)_4]^{2+} + 2\text{LH}_{(org)} \rightarrow [\text{CuL}_2]_{(org)} + 2[\text{NH}_4^+] + 2\text{NH}_3_{(aq)}
\]

regenerates the leachant. Stripping with sulfuric acid and conventional electrowinning of the copper regenerates the extractant without consumption of acid,

\[
[\text{CuL}_2]_{(org)} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2\text{LH}_{(org)}
\]

\[
\text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu}_{(s)} + \text{H}_2\text{SO}_4 + 1/2\text{O}_2_{(g)}
\]

giving the materials balance;

\[
\text{Cu}_2\text{S} \rightarrow \text{Cu} + \text{CuS}
\]

The pH of the lixiviant and the leach conditions are such that very little of the iron present in the ores and only small quantities of other transition metals are transferred to the pregnant leach solution, which typically has a composition of ca. 280 g L\textsuperscript{–1} Cu, 440 mg L\textsuperscript{–1} Zn, <1 mg L\textsuperscript{–1} Fe, Mn, and <1 mg L\textsuperscript{–1} Ni.\textsuperscript{108} Consequently, the Cu extractant is not required to show very high selectivity over iron or high “strength” because the extraction equilibrium is effectively buffered by [NH\textsubscript{4}\textsuperscript{+}]/NH\textsubscript{3}. The diketone extractant LIX 54, (19), with a mixture of isomeric forms of the heptyl group, provides appropriate “strength” and selectivity, performing well in a small continuous SX-plant,\textsuperscript{109} but is prone to chemical degradation, forming the ketimine (20) exclusively at the octanoyl carbon atom in the presence of high levels of NH\textsubscript{3} at 45 °C.\textsuperscript{168,169} Reagents with sterically hindered acyl groups as in XI-N54 and XI-57 (21,22) or the n-heptyl analog (23) show much greater resistance to chemical degradation and better strip kinetics than LIX 54.\textsuperscript{168,170} Acylpyrazolones (24) also form neutral β-diketonate-type complexes suitable for extraction of a range of metals into organic solvents and have been considered\textsuperscript{171} as alternatives to LIX 54 for use in ammoniacal leach circuits. Although they are stronger extractants than LIX 54,\textsuperscript{4,172} the low solubility of their metal complexes has limited their usefulness in Cu recovery.\textsuperscript{171} The structurally related diazopyrazolones (25) have pH\textsubscript{1/2} values, ca. 3.7, and their chemical stability on contact with ammoniacal feeds meets the requirements of the flowsheet outlined above, but their very intense colors may restrict their use as commercial extractants.\textsuperscript{173,174} The bulk of the arylozo
group in these ligands leads to significant deviations from planarity of the \( \text{N}_2\text{O}_2^{2-} \) donor sets, accounting for their weakness in comparison with the phenolic oximes (Section 9.17.4.2).\(^{174}\)

Ni and Cu in ammoniacal feeds can be effectively separated by quantitative co-extraction with the phenolic oxime LIX 84 (Section 9.17.4.2) followed by selectively stripping of the more weakly bound Ni with dilute sulfuric acid.\(^{169,175}\)

**9.17.5.1.4 Recovery of Cu\(II\) from secondary sources**

The diverse range of applications of copper in different alloys and products presents challenging problems for recycling.\(^9,176\) Many of the recycling processes to recover copper from mixtures with other metals are based on hydrometallurgy using sulfate, chloride, or ammoniacal streams. Copper can be selectively extracted using phenolic oximes\(^{169,176–180}\) or diketones,\(^{169,176,179}\) even when the aqueous feed contains Cu-complexing agents which have been used in etching processes to generate the waste stream. Where the small volumes of copper recovered by solvent extraction in such plants do not justify the capital investment of an electrowinning plant the strip solution can be evaporated to generate a copper salt.

**9.17.5.2 Zinc**

Approximately 80% of Zn production involves hydrometallurgy, in which roasted sulfide concentrates are dissolved in sulfuric acid.\(^{181}\) Currently, the major separation steps involve the precipitation of other metals from the sulfate stream (Figure 7).\(^{181,182}\) The precipitation of iron is achieved by raising the pH with calcine, the mixture of zinc/iron oxides from roasting, producing large volumes of iron oxy-hydroxide materials, the disposal of which presents major challenges.\(^{183–185}\)

Roast:

\[
2\text{ZnS} + 3\text{O}_2 = 2\text{SO}_2 + 2\text{ZnO}
\]

and

\[
4\text{FeS} + 7\text{O}_2 = 4\text{SO}_2 + 2\text{Fe}_2\text{O}_3
\]

Acid production:

\[
2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4
\]
Acid leach:

\[
ZnO + H_2SO_4 = ZnSO_4 + H_2O
\]

and

\[
Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O
\]

Neutral leach/iron precipitation:

\[
Fe_2(SO_4)_3 + H_2O + 3ZnO = 3ZnSO_4 + 2FeO(OH)
\]

Electrowinning:

\[
2ZnSO_4 + 2H_2O = 2Zn + 2H_2SO_4 + O_2
\]

Zinc electrowinning requires high electrolyte purity.\(^{186}\) Cementation with powdered zinc to remove heavy metals such as Cd, Hg, and Pb, and other precipitation techniques are most commonly employed. In some plants germanium is recovered from the electrolyte with 8-hydroxyquinoline reagents such as Kelex 100 (26).\(^{184,187–189}\)

\[
Zn + Cd^{2+} = Zn + Cd^{2+}
\]

**9.17.5.2.1 Extraction of Zn\(^{II}\) from sulfate media**

The use of D2EHPA to purify and concentrate ZnSO\(_4\) electrolytes from which the majority of the iron has been removed by precipitation has received much attention, forming the basis of the ZINCEX processes.\(^{165,190}\) These processes have been developed to treat a range of primary and...
secondary materials,\textsuperscript{190–193} including sulfides via pressure leaching. D2EHPA shows a good selectivity for Zn over the most common impurities in these sulfate streams, Mn, Co, Ni, Cu, Mg, and Cd, see Section 9.17.4.3.

Anglo America’s Skorpion project\textsuperscript{195} which uses the ZINCEX process will be the first major application of solvent extraction for Zn recovery from primary sources, involving a capital investment of $454 million in southern Namibia. The use of the pH-swing extractant D2EHPA coupled with the scrubbing of Zn-loaded organic solutions ensures that chloride and fluoride ions originating from minerals associated with the zinc silicate ore are not carried forward to the Zn electrolyte. Any iron which has not precipitated following neutralization of the pregnant leach solution is strongly extracted by D2EHPA and the resulting Fe\textsuperscript{III} complexes are not stripped under the conditions used to generate the Zn electrolyte. To ensure that the recycled extractant is not eventually poisoned a bleed is treated with 6M HCl, regenerating D2EHPA and producing FeCl\textsubscript{3} as a waste stream.

As a consequence of D2EHPA’s high affinity for Fe\textsuperscript{III} the commercial success of the ZINCEX-based processes for Zn recovery depends on removal of almost all the iron from feed solutions prior to solvent extraction of the zinc. An alternative strategy is to develop a pH-swing extractant with a high Zn\textsuperscript{II}/Fe\textsuperscript{III} selectivity which would be used in a circuit analogous to the well-proven commercial operations for copper (Section 9.17.5.1.1) to treat oxidic ores by sulfuric acid leaching, solvent extraction, and electrowinning. The DS5869 reagent (27) (Table 4), which contains a tetra-substituted bisdithiophosphoramide, shows a remarkable discrimination for Zn\textsuperscript{II} over most of the other metal ions in the first transition series.\textsuperscript{196} The bulky substituents at the phosphorus atoms disfavor formation of a planar arrangement of the S\textsubscript{4}2− donors or formation of neutral 3:1 complexes such as [FeL\textsubscript{3}]\textsubscript{org} with transition metals.

\textsuperscript{196} The soft S\textsubscript{2}− donor sets presented by these bidentate ligands lead to very strong binding of heavy metals (Table 7) which are not stripped by sulfuric acid, ensuring that these deleterious elements do not transfer to the Zn electrolyte.\textsuperscript{196} However, co-extraction of copper is accompanied by reduction to Cu\textsuperscript{I} which has proved very difficult to strip to regenerate the reagent and will lead to poisoning of the extractant unless all traces of copper are removed from the feed solution.

\textbf{Table 7} Metal loading\textsuperscript{a} (mg L\textsuperscript{-1}) of a 0.3 M solution of DS5869\textsuperscript{b}

<table>
<thead>
<tr>
<th>Metals extracted</th>
<th>Zn</th>
<th>Cd</th>
<th>Cu</th>
<th>Hg</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>6400</td>
<td>110</td>
<td>105</td>
<td>100</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metals rejected</th>
<th>Fe</th>
<th>Ge</th>
<th>Sn</th>
<th>As</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>4</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>Mg</td>
<td>Mn</td>
<td>Co</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
</tr>
</tbody>
</table>

Source:\textsuperscript{196}  
\textsuperscript{a} After contacting with an equal volume of an aqueous solution (pH 2.0) containing 10.7 g L\textsuperscript{-1} Zn, 4.1 g L\textsuperscript{-1} Fe\textsuperscript{III}, and ca. 100 mg L\textsuperscript{-1} of the other metals.  
\textsuperscript{b} See Table 4 for structure.

9.17.5.2.2 Extraction of Zn\textsuperscript{II} from chloride media

Selective extraction of zinc from chloride solutions is required for recovery from primary sources via new sulfide ore leaching technology (Section 9.17.3.3.2) and from secondary sources...
which arise from the production and use of galvanized steel such as pickle liquors. The potential advantages of Zn recovery directly from chloride leaching of sulfidic ores are similar to those described in Section 9.17.5.1 for Cu recovery. The use of phosphate triesters to transfer Zn in the form of neutral \([\text{ZnCl}_2\text{L}_2]\) complexes has not proved successful because they show poor selectivity over Fe\(^{III}\). The bis-benzimidazole reagent ZNX50 (Table 6) was developed to show high Zn\(^{II}/\)Fe\(^{III}\) selectivity. The very weakly basic nitrogen atoms ensure that the reagent is not easily protonated, limiting transfer of iron by a competing ion-pairing mechanism

\[
L_{(\text{org})} + H^+ + [\text{FeCl}_4]^- = [\text{LH}]\text{[FeCl}_4\text{]}L_{(\text{org})}
\]

even in relatively acidic feed solutions, see Table 8. A study of the concentration dependence of Zn extraction by ZNX50 suggests that a dinuclear complex, \([\text{Zn}_2\text{Cl}_4\text{L}_2]\), is formed in the organic phase. The high activity of proton in concentrated chloride solutions limits the efficiency of acidic, pH-swing, extractants (see also Section 9.17.5.1.2),

\[
2L'H_{(\text{org})} + \text{ZnCl}_2 = \text{ZnL'}_{2(\text{org})} + 2\text{HCl}
\]

The use of a combination of a pH-swing extractant, \(L'H\), and a solvating extractant, \(L\), in flowsheets similar to that outlined in Figure 8 has been proposed by several groups to transport zinc from chloride to sulfate media. An advantage of this approach is that stripping the zinc into a sulfate medium allows conventional electrowinning processes to be used. The zinc is transferred from the aqueous feed mainly by the solvating (or ion pairing) extractants,

\[
\text{Zn}^{2+} + 2\text{Cl}^- + L_{(\text{org})} = \text{ZnLCl}_2_{(\text{org})}
\]

Scrubbing this loaded organic solution with aqueous ammonia triggers the transfer of the zinc to the acidic extractant \(L'H\),

\[
\text{ZnLCl}_2_{(\text{org})} + 2L'H_{(\text{org})} + 2\text{NH}_3 = \text{ZnL'}_{2(\text{org})} + 2[\text{NH}_4\text{]}\text{Cl}
\]

from which it can be stripped with sulfuric acid,

\[
\text{H}_2\text{SO}_4 + \text{ZnL'}_{2(\text{org})} = \text{ZnSO}_4 + 2L'H_{(\text{org})}
\]

**Table 8** Selectivity of loading\(^a\) of ZNX50.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Zn</th>
<th>Fe</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous feed</td>
<td>50 g L(^{-1})</td>
<td>110 g L(^{-1})</td>
<td>25 mg L(^{-1})</td>
<td>1.5 g L(^{-1})</td>
<td>25 mg L(^{-1})</td>
<td>25 mg L(^{-1})</td>
</tr>
<tr>
<td>Loaded organic</td>
<td>15 g L(^{-1})</td>
<td>6 mg L(^{-1})</td>
<td>15 mg L(^{-1})</td>
<td>&lt;5 mg L(^{-1})</td>
<td>&lt;5 mg L(^{-1})</td>
<td>&lt;5 mg L(^{-1})</td>
</tr>
</tbody>
</table>

Source: \(^{197}\)

\(^a\) Of a 0.3 M solution in Escaid after contact with an equal volume of a simulated chloride pregnant leach solution.

![Figure 8](image) An outline flowsheet to transport zinc from chloride to sulfate media using a mixture of an acidic (pH-swing) extractant \(L'H\) and a solvating extractant \(L\).
and electrowon in the conventional manner,

\[ \text{ZnSO}_4 + H_2O = \text{Zn} + \text{H}_2\text{SO}_4 + 1/2\text{O}_2 \]

The ammonia scrubbing of loaded anion exchange extractants, e.g., \([\text{R}_3\text{NH}]_2\text{[ZnCl}_4\text{]}_{\text{org}}\), proceeds similarly (see also Section 9.17.5.1.2), and thus in each case the mixed extractant system achieves the overall process,

\[ \text{ZnCl}_2 + 2\text{NH}_3 + H_2O = \text{Zn} + 1/2\text{O}_2 + 2[\text{NH}_4\text{]}\text{Cl} \]

In the systems reported, the \(\beta\)-diketone reagent LIX54 has been used as the acidic extractant with either ZNX50 as a solvating extractant\(^\text{199}\) or Alamine 336 as an anion exchange extractant.\(^\text{187}\) Aliquat 336 has been used alone to extract Zn\(\text{II}\) and Cd\(\text{II}\) from chloride streams.\(^\text{200}\) The Zn/Cd selectivity depends on whether the chloride or thiocyanate form of the extractant [R\(_4\)N]X is used, which is rationalized on the basis of the different types of thiocyanate complexes formed by zinc and cadmium.

### 9.17.5.2.3 Zn/Fe recovery from secondary sources

The increased use of galvanized steel has required the development of technology to separate and recycle zinc and iron.\(^\text{195}\) Electric arc furnace (EAF) dusts contain significant quantities of zinc, together with heavy metals, most commonly lead and cadmium, and halides which make them difficult to process in both pyro- and hydro-metallurgical primary zinc recovery plants.\(^\text{195,202,203}\) Variations of the ZINCEX process using D2EHPA as a Zn extractant have been tested in a number of locations.\(^\text{190}\) Other reagents proven in primary metal recovery have also been evaluated, e.g., Cyanex 301 for recovery from spent batteries\(^\text{195}\) and ZNX50 from EAF dusts.\(^\text{195}\) Despite the need for new technology to effect the Zn/Fe separation and the recycling of zinc, the relatively low value of the two metals places great pressure on keeping the costs of processes down and commissioning of large new plants has been slow.

The use or safe disposal of the iron residues from zinc production (see Figure 7) presents a major technical problem.\(^\text{204}\) The use of chelating aminomethylene phosphonic acid extractants such as (28) and (29) to recover iron from these residues has been proposed.\(^\text{205}\) These give much higher Fe\(\text{III}\)/Zn\(\text{II}\) selectivity than D2EHPA but are more difficult to strip. A reductive-stripping process is proposed.\(^\text{187,205}\)

As in primary recovery the slow introduction of new technology to recover zinc, which nearly always requires a separation from iron, appears to be related to the relatively low market value of this metal.\(^\text{187}\)

\[ (\text{28}) \quad (\text{29}) \]

### 9.17.5.3 Nickel and Cobalt

The decade 1990–2000 has seen a large volume of research on the application of solvent extraction of nickel,\(^\text{175,206–226}\) responding to the development of protocols for the high-pressure acid leaching (HPAL) in horizontal agitated autoclaves of nickel and cobalt into solution from lateritic ores\(^\text{81–88}\) which have followed the success of the Moa Bay plant in Cuba where commercial acid pressure leaching of limonitic ores has been practiced since the 1950s.\(^\text{75–78,80,227}\) Nearly 70% of the world’s Ni reserves are in the form of nickeliferous lateritic ores, which also represent a major resource for cobalt. Until recently these oxidic ores have remained largely unexploited due to the absence of appropriate technology, but as they are located close to the surface they can be mined at a significantly lower cost than sulfidic ores from which the majority of nickel is presently extracted. The investment in the pressure leaching of lateritic nickel ores has been based on the...
increased confidence gained by the growing number of successful pressure oxidation plants brought on stream for gold and zinc recovery.

Apart from bringing pressure technology into the mainstream, these plants have produced a pool of engineering and equipment designing expertise, which can be applied to laterites projects.

More than 90% of the nickel and cobalt in laterite ores (1.0–1.6% nickel) can readily be leached by sulfuric acid at ≥240°C, typically producing large volumes of relatively dilute leach solution containing 3–6 g L⁻¹ of nickel and around 40 g L⁻¹ H₂SO₄. In addition to nickel and cobalt these leach solutions contain Al, Cr, Ca, Cu, Fe, Mg, Mn, Na, Si, and Zn. The design of reagents and protocols for the separation and concentration of metal values in these streams has depended heavily on differences in the coordination chemistry of the components.

9.17.5.3.1 Co/Ni separation in sulfate solutions

The most extensively investigated reagents for the recovery of nickel and cobalt from acidic media have been the organophosphorus acids. The commercial and systematic names and the structures of the ligands used have been collected in the table presented earlier (Table 4).

The use of di(2-ethylhexyl)phosphoric acid (D2EHPA) to separate Co from Ni and other metals has been the subject of many fundamental investigations and was reviewed in CCC (1987). Important features for Ni/Co recovery are that D2EHPA exists in organic solvents of low polarity, such as kerosene, in the form of cyclic hydrogen-bonded dimers, and that in the presence of excess extractant these cyclic structures persist upon complexation with different degrees of protonation. The ease of extraction of the divalent metals of the first transition series follows the sequence Zn > Cr > Mn > Cu > Fe > Co > Ni ≈ V. This sequence largely reflects the ease with which the respective metal ions adopt the tetrahedral geometry favored by the bulky dimerized D2EHPA ligands.

D2EHPA is thus a poor extractant for nickel as this shows a preference for a pseudo-octahedral structure in which two axial ligands are either fully protonated extractant molecules, fully protonated extractant dimers, or water molecules depending on extractant concentration, and four equatorial sites are occupied by deprotonated isolated D2EHPA molecules.

For cobalt it is proposed that both tetrahedral and octahedral forms exist in equilibrium. The entropy contribution arising from the dissociation of the octahedral cobalt complex to give the tetrahedral form has been exploited industrially to enhance the separation of cobalt from nickel by performing the separation at elevated temperatures. At high metal loading when the metal-to-extractant ratio approaches the limiting 1:2 stoichiometry it has been proposed that polymeric complexes form in which the PO₂⁻ units act as a bridging ligand. The stepwise change in viscosity observed upon high metal loading in working systems employing D2EHPA (and other phosphorus acid reagents) has often been attributed to the formation of such polymeric complexes.

More recently, reagents containing phosphonic acid, phosphinic acid, and thio-phosphinic acids have been the subjects of considerable attention. These exhibit a greater selectivity for cobalt over nickel than D2EHPA. In a manner analogous to that of D2EHPA, they are believed to exist in the hydrogen-bonded dimerized form in low-polarity solvents. The first of this new generation of ligands to be developed and exploited for Co/Ni recovery was 2-ethylhexyl phosphonic acid (referred to here as PC-88A but also marketed as Ionquest 801). The enhanced selectivity of PC-88A for cobalt has been attributed to the destabilization of the octahedral nickel complex resulting from the greater steric bulk of the ligand caused by having an alkyl group attached directly to the phosphorus atom.

The phosphonic acid reagent Cyanex 272 exhibits even greater selectivity for cobalt. It is currently used in several commercial operations and has been the subject of much fundamental research. The further destabilization of the octahedral nickel complex has been ascribed to steric crowding arising from replacing all alkoxy groups with alkyl groups at the phosphorus atom. Cyanex 272 and di(1,3,3-trimethylbutyl)phosphonic acid (Figure 9) have selectivity factors Kₓ₉ (Co/Ni) of 3.8 × 10² and 3.7, respectively. The steric bulk of the alkoxy groups on the phosphorus atom in the latter is presumed to be similar to that of the alkyl group in Cyanex 272 because although the oxygen atom carries no hydrogen substituents, the P–O bond length (on average 162 pm) is significantly shorter than the P–C bond (on average 185 pm). These observations led Zhu to investigate the steric and electronic effects arising from variation in substituents in the commercial reagents D2EHPA, PC-88A, and Cyanex 272 (Table 9) using molecular mechanics and molecular orbital calculations. The predominant structural parameter
defining the preference for formation of tetrahedral over octahedral complexes was the angle between the alkyl/alkoxy substituents, R and \( R' \), and the phosphorus atom.

Replacing alkoxy with alkyl groups results in an increase in the R–P–R\(^0\) bond angle. This larger bond angle in the phosphinic acid (Cyanex 272) will lead to greater steric hindrance between the equatorial and axial ligands in an octahedral complex, but is assumed to have less effect upon a tetrahedral complex and is thus consistent with the observed increased selectivity for cobalt over nickel along the sequence D2EHPA, PC-88A, Cyanex 272.

The electron density of the oxygen atoms of the reagents also plays a role in determining their strength/selectivity (Table 10). The calculated point charges on the oxygen donor atoms follows the order D2EHPA < PC-88A < Cyanex 272, consistent with the increasing \( pK_a \) along the series and decreased extraction constants for both metals. This decrease is greater for nickel, leading to a larger Co/Ni separation factor along the sequence D2EHPA, PC-88A, Cyanex 272. This same order is expected as a result of the increasing repulsion between the oxygen donor atoms which will lead to a preference for the formation of species of lower coordination number (i.e., tetrahedral vs. octahedral) to minimize electronic repulsion.

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### Table 9
Calculated R–P–R' angles and dihedral angles between the RPR' and OPO' planes in D2EHPA, PC-88A, and Cyanex 272.

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Substituent</th>
<th>R–P–R' (degree)</th>
<th>Dihedral angle (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2EHPA</td>
<td>oxy-2-ethylhexyl oxy-2-ethylhexyl</td>
<td>104.7</td>
<td>90.2</td>
</tr>
<tr>
<td>PC-88A</td>
<td>oxy-2-ethylhexyl 2-ethylhexyl</td>
<td>115.7</td>
<td>91.2</td>
</tr>
<tr>
<td>Cyanex 272</td>
<td>2,4,4-trimethylpentyl 2,4,4-trimethylpentyl</td>
<td>120.1</td>
<td>89.5</td>
</tr>
</tbody>
</table>

### Table 10
Values of \( pK_a \)'s, extraction constants, separation factors, and calculated point charges in D2EHPA, PC-88A, and Cyanex 272.

<table>
<thead>
<tr>
<th>Extractant</th>
<th>( pK_a )</th>
<th>( K_{ex} (\text{Co}) )</th>
<th>( K_{ex} (\text{Ni}) )</th>
<th>( K_{ex} (\text{Co/Ni}) )</th>
<th>Point Charge ( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2EHPA</td>
<td>3.57</td>
<td>5.50 \times 10^{-6}</td>
<td>1.10 \times 10^{-6}</td>
<td>5</td>
<td>0.161</td>
</tr>
<tr>
<td>PC-88A</td>
<td>4.10</td>
<td>1.07 \times 10^{-6}</td>
<td>1.51 \times 10^{-8}</td>
<td>71</td>
<td>0.028</td>
</tr>
<tr>
<td>Cyanex 272</td>
<td>5.05</td>
<td>1.66 \times 10^{-7}</td>
<td>2.00 \times 10^{-10}</td>
<td>830</td>
<td>0.092</td>
</tr>
</tbody>
</table>

Source:122

Phosphorus acids containing P–S bonds in which the sulfur atom acts as the metal ligating atom also received much attention.243,252,255–261 The commercially available reagents bis(2,4,4-trimethylpentyl)phosphinothioic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl)dithiophosphinic
acid (Cyanex 301) are analogs of Cyanex 272 in which one or both oxygen atoms, respectively, have been replaced by sulfur Table 4.

```
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<tbody>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>SH</td>
<td>CH₂</td>
<td>CH₂</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td>SH</td>
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<td>CH₂</td>
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<td>CH₃</td>
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<td>CH₃</td>
<td>CH₃</td>
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</tr>
</tbody>
</table>
```

Like Cyanex 272 they exhibit a preference for Co⁺² over Ni⁺², but are much “stronger” reagents, extracting cobalt at a pH of 1–2, in comparison to the P–O-containing phosphoric, phosphonic, and phosphinic acids, which typically extract in the pH range of 4.5–6. This enhanced strength can be ascribed to the presence of the softer sulfur donors which are preferred by tetrahedral forms of the metals. One of the major disadvantages of the thio-phosphinic acids is their tendency to form organo-phosphorus disulfides in the presence of oxidizing species such as Fe⁺³, Co⁺³, or O₂. In the commercial processes using Cyanex 301 for Co/Ni separation this problem is overcome by the incorporation of an extractant recovery stage in which partially oxidized reagent is regenerated via reduction with H₂ formed from the reaction of metallic zinc with H₂SO₄.

Because the organophosphorus reagents DE2HPA, PC-88A, and Cyanex 272 are selective for Ca⁺² and Mg⁺² over Ni⁺², this precludes their use for nickel recovery from laterite HPAL solutions where these metals are often present at close to saturation levels. The tertiary carboxylic acids represent a source of potential extractants that are inexpensive, readily soluble in kerosene, and chemically stable. However, they have rarely been applied in commercial applications because they show appreciable solubility in aqueous media and poor selectivity. Recently, the reagent Versatic 10 (predominately C₁₀ mono-carboxylic acids, see Section 9.17.4.4) has been extensively tested as it shows selectivity for Ni⁺² over Ca⁺² and Mg⁺² at low pH. It is not selective for Co⁺² over Ni⁺², the difference between pH₁/₂ values being <0.2 pH units. Consequently, it can only be used when cobalt has been removed from the process stream or when a mixed Co/Ni salt is the desired product.

The stoichiometry of Versatic 10 Ni extraction has been the subject of much investigation. Distribution data for the extraction of nickel from aqueous solution is consistent with the generalized equilibrium:

\[
\text{Ni}^{2+} + p\text{H}_2\text{O} + (1+m/2)(\text{HA})_{2\text{org}} = 1/x(\text{NiA}_2\cdot m\text{HA}\cdot p\text{H}_2\text{O})_{x\text{org}} + 2\text{H}^+ \tag{2}
\]

At low Ni-loading the monomeric species NiA₂·4HA predominates, whereas at higher nickel loadings the dimeric complex [NiA₂·2HA]₂ is the major species. The amount of water extracted at first increases with Ni loading to give a ratio of H₂O:nickel of about 2 with Ni < 9 g L⁻¹, and at higher loadings this ratio decreases to 1. The significant water solubility of Versatic 10 at the moderately high pH values required for efficient nickel extraction poses significant difficulties in commercial use. In continuous trials it was found that 50% of the total Versatic 10 inventory was lost in 75 hours, necessitating the incorporation of an additional step in the circuit to recover the reagent from raffinates.

The H₂SO₄ liberated on Ni extraction must be neutralized in order to maintain an efficient equilibrium position in Equation (2). "Pre-neutralizing" Versatic 10 by contacting with a solution of aqueous ammonia prior to Ni extraction much enhances recovery. Pre-neutralization, or saponification, also eliminates the need for pH control in the mixer. Partial (ca. 50%) pre-neutralization of an iso-octane solution of Versatic 10 with saturated aqueous ammonia results in the formation of a single-phase system. Loading of the pre-neutralized extractant proceeds very quickly as the rate of exchange between the amphiphilic aggregates of the microemulsion and the bulk water is extremely fast and at high nickel loadings the system reverts to two phases in which the organic solution is loaded with nickel, free of ammonia and contains little water.

### 9.17.5.3.2 Co/Ni separation in chloride and ammoniacal solutions

Effective protocols have also been developed for the extraction of nickel and cobalt from chloride and ammoniacal process streams derived from leaching sulfidic ores or mattes. The greater thermodynamic stability of the Co⁺³ chloroanionic complexes such as [CoCl₄]²⁻ over analogous Ni⁺² species has been exploited to effect the separation of nickel and cobalt via an
anion exchange mechanism from acidic solutions of high chloride activity (Co extraction occurs when \([\text{Cl}^-] > 3.0 \text{ M}\)) \(^{103,279}\)

\[
[\text{CoCl}_4]^{2-} + 2[R][\text{Cl}]_{\text{org}} = [R]_2[\text{CoCl}_4]_{\text{org}} + 2\text{Cl}^-
\]  

(3)

The anionic exchange reagents commonly employed in these processes are tri-alkyl ammonium cations, generally dissolved in an aromatic diluent such as xylene. Tris-isooctylamine has been used at Falconbridge Nikkelverk in Kristiansand, Norway for the purification of solutions derived from HCl leaching of Ni–Cu matte for over 30 years. \(^{103}\)

It is essential in processes which employ such reagents to effect Co/Ni separation that metals such as Fe\(^{III}\), Cu\(^{II}\), and Zn\(^{II}\) that also form stable chloro-metallate complexes are removed prior to Co extraction. \(^{103,280}\)

Hydrochloric acid is a very effective lixiviant for nickel/cobalt laterites. \(^{243,256,281}\) Unlike H\(_2\)SO\(_4\), almost complete Ni recovery is achievable without the application of high pressure and temperatures \(^{243}\) and has a significant advantage in terms of energy consumption. However, unlike the solutions obtained from the HCl leaching of Co/Ni intermediates described previously, these solutions contain substantial amounts of magnesium. Thus, while it is possible to use anion exchange reagents to recover the cobalt from such solutions (e.g., as in Equation (3), other types of reagents are needed to separate the nickel from magnesium. Studies using Cyanex 301, Cyanex 302, and Versatic 10 have shown that the carboxylic acid Versatic 10 is most effective. \(^{243,256}\) Cyanex 301 exhibits good selectivity of Ni/Mg extraction from chloride media, but the kinetics of Ni loading are poor and stripping of Ni-loaded solutions requires HCl of concentrations approaching 10 mol L\(^{-1}\). Stripping from Ni-loaded Cyanex 301 and related alkylphosphorodithioic acids can be somewhat improved by addition of octan-1-ol to the organic phase. \(^{243}\) Cyanex 302, a weaker Ni extractant from chloride, shows better kinetic characteristics of loading and stripping, but unfortunately it lacks the specificity to achieve Ni/Mg separation. \(^{243}\)

Ammoniacal leaching has been used for some time to process nickel- and cobalt-containing materials from a wide range of sources under oxidative conditions. \(^{106,175,212,219,224,274,282,283}\) Generating solutions containing Co\(^{III}\)-ammine complexes. The inert nature of \([\text{Co(NH}_3]_6^{3+}\) forms the basis for the separation of nickel and cobalt, using conventional contact times. Phenolic oximes of the type shown in Table 3 extract very little Co\(^{III}\). \(^{175,271,276,277}\) The pH dependence of Ni loading has a characteristic bell shape with maximum uptake in the pH range ca. 5–9. \(^{224,272,273,277}\) At high pH the formation of stable ammine complexes in the aqueous phase reduces Ni loading of the oxime reagent. Investigations of the stoichiometry of loading suggest that the predominant species is the diamagnetic planar bis-oxime complex [NiL\(_2\)], but there is also a possibility that this co-exists with the high-spin, pseudo-octahedral species [NiL\(_2\)(NH\(_3\)_2] at higher pH values (Equation (6)).

\[
\text{Ni}^{2+} + 2\text{LH}_{\text{org}} = [\text{NiL}_2]_{\text{org}} + 2\text{H}^+
\]  

(4)

\[
[\text{NiL}_2]_{\text{org}} + 4\text{NH}_3 + 2\text{NH}_4^+ = [\text{Ni(NH}_3)_6]^{2+} + 2\text{LH}_{\text{org}}
\]  

(5)

\[
[\text{NiL}_2]_{\text{org}} + 2\text{NH}_3 = [\text{NiL}_2(\text{NH}_3)_2]_{\text{org}}
\]  

(6)

\[
[\text{NiL}_2(\text{NH}_3)_2]_{\text{org}} + \text{H}_2\text{SO}_4 = [\text{NiL}_2]_{\text{org}} + 2[\text{NH}_4]_2\text{SO}_4
\]  

(7)

\[
[\text{NiL}_2]_{\text{org}} + \text{H}_2\text{SO}_4 = 2\text{LH}_{\text{org}} + \text{NiSO}_4
\]  

(8)

This use of phenolic oximes to achieve the separation of Ni\(^{II}\) from Co\(^{III}\) also results in the complete rejection of Zn\(^{II}\), Cd\(^{II}\), and Mg\(^{II}\), a distinct advantage over the organo-phosphorus reagents discussed above. Any copper present in the feed will be co-extracted with the nickel but it is possible to acid strip the nickel selectively at moderately high pH and then recover the copper at much lower pH. The equilibration times for Ni loading or stripping are significantly longer than those for copper, often involving contact times of up to 10 minutes. Whilst this order is consistent with the relative labilities of the hydrated divalent metal cations, both are sufficiently labile that it implies that rates are determined by interfacial or organic phase reactions.

A problem encountered with the use of the phenolic oximes in Ni recovery from ammoniacal solution is the co-extraction of ammonia that must be removed prior to generating the electrolyte for
reduction to the metal. Scrubbing of ammonia may be achieved by contacting the ammonia-loaded reagent with a dilute acid solution (Equation (7)). Conditions must be controlled carefully to avoid Ni loss into the wash stream by the standard acid strip reaction (Equation (8)). It has been shown that the hydrocarbon solutions of metal-free phenolic oximes also load ammonia. Adducts of salicylaldoximes with α,ω-diamines with 2:1 stoichiometries have been characterized in the solid state.

The β-diketone LIX-54 (30) shows a similar dependence of Ni-loading on pH to the phenolic oximes with Ni-uptake decreasing at pH > 9, attributable to the formation of nickel ammine complexes in the aqueous phase. The stoichiometry of the extraction reaction can be represented by the general equilibrium shown in Equation (4).

Equilibrium is reached in both stripping and extraction within 10 minutes. Extraction of nickel by LIX-54 has been found to be slightly exothermic ($\Delta H^\circ = -44.8$ kJ mol$^{-1}$) and stripping very slightly endothermic ($\Delta H^\circ = 10.9$ kJ mol$^{-1}$). The advantage of β-diketones as Ni extractants from ammoniacal media is that neither the reagent nor its nickel complex transfer ammonia into the organic phase. The absence of NH$_3$ bound to nickel in such complexes has been confirmed via IR spectroscopy.

Very good extraction of Co$^{II}$ from Ni$^{II}$ can be achieved using the amido-bis-thiophosphoryl extractant DS6001 (see Table 4). After the removal of Zn$^{II}$ or Cu$^{II}$ from the feed solution, Co$^{II}$ can be selectively extracted at pH 3–4 and then Ni$^{II}$ at pH 4–6 in the presence of a range of metal cations commonly obtained in HPAL solutions from laterites. The affinity of this reagent for the divalent cations, Zn$^{II}$ > Co$^{II}$ > Ni$^{II}$, accords with its ability to present a soft S$_4^{2-}$ tetrahedral donor set (see also Section 9.17.4.3).

### 9.17.6 PRECIOUS METALS

The greatly increased use of the precious metals (Pt, Pd, Rh, Ir, Ru, Os), Ag, and Au in applications from jewellery to electronic devices, exhaust control catalysts to dental materials has stimulated considerable research into their recovery. A typical flowsheet for the solvent extraction of the PGMs (Figure 10) involves pressure or heap leaching in chloride media under conditions which generate a pregnant leach solution devoid of base metals, but containing a myriad of chloro complexes. The volatile osmium and ruthenium species OsO$_4$ and RuO$_4$ are removed by distillation and the remaining PGMs are subjected to various solvent-extraction steps until only rhodium is present, which is then separated by precipitation. Many extractants have been tested and some have been put into commercial operations to recover Au, Pd, Pt, and Ir in flowsheets of the type shown in Figure 10. Most modern hydrometallurgical installations rely heavily on solvent-extraction technologies, especially in refining high-grade metals. The design of new extractants (Section 9.17.4) must pay particular attention to the type of aqueous media used, usually chloride, bromide, or thiocyanate. Soft-base donor ligands such as the organo-sulfur compounds have been much studied, and some researchers have addressed problems of the kinetic inertness of many of these metals by lowering oxidation states—see Section 9.17.6.3.

The commercial extractants currently used fall into the following categories: α-hydroxy-ketoximes, phenolic-oximes, dialkylsulfoxides, esters of pyridine mono and di-carboxylic acids, alkyl derivatives of 8-hydroxyquinoline, trialkylamines, alkyl derivatives of aniline, aliphatic ethers, and ketones. Many of the reagents developed initially for the recovery of base or radioactive metals have also been investigated as potential PGM extractants, e.g., phosphine oxides, dialkylsulfoxides, dialkyl- and diphenyl-thioureas, thiopicolinamides, thiobenzanilide, phosphate diesters, tetra-thioethers, dialkylthietanes, amino acids such as dialkylglycine, dialkylsuccinamic acid,
and most recently, calixarenes. Several extractants have been designed for special applications, such as fluorinated amides for use in CO$_2$. A review by Yordanov and Roundhill deals with PGM-recovery by chelate and macrocyclic ligands, and Wisniewski and Szymanowski have surveyed the use of existing commercial extractants in the flowsheets for the INCO, Matthey, and Lonhro PGM-recovery processes. The following sections consider the recovery of individual precious metals.

9.17.6.1 Au$^+$, Au$^{III}$

Gold is conventionally recovered by leaching ores or recycled materials with alkaline cyanide solutions in the presence of oxygen. The gold, as [Au(CN)$_2$]$^-$ or [Au(CN)$_4$]$^{3-}$, in the pls is concentrated by zinc cementation (Merill–Crowe), carbon absorption (carbon-in-pulp or CIP), or via ion exchangers and then electrowon. Advances in hydrometallurgy and the imposition of increasingly stringent environmental controls have prompted research into solvent extraction as an alternative technology for concentration and separation.

Quaternary ammonium salts were first used as extractants from alkaline solutions. Aliquat 336, Adogen 481, and Adogen 483 (Table 5) have been tested in plant feasibility studies conducted by Riveros. The advantages of these reagents (good selectivity, fast kinetics, high loading capacity, low water solubility, and good phase separation) were outweighed by the proposed stripping protocols which involved acidic solutions of thiourea, which generate hydrogen cyanide, or via incineration of the gold-loaded extractant.

$$[R_4N][Au(CN)_2]_{(org)} + 2HX + 2CS(NH_2)_2 = [R_4N][X]_{(org)} + [Au(CS(NH_2)_2)]_2[X] + 2HCN$$

The affinity of [Au(CN)$_2$]$^-$ for primary, secondary, and tertiary amines is very low at pH values typical for cyanide feed solutions, but in 1983 Mooiman et al. showed that the addition of solvating phosphorus(V) oxides enhanced extraction at higher pH. During the course of this work it was discovered that TBP and DBBP (see Table 6) could themselves extract gold. This led to subsequent investigations on phosphates and phosphorus oxides.

Caravaca et al. evaluated the primary amines Primene 81R, Primene JMT (Table 5), and tridecylamine and concluded that for Primene 81R and tridecylamine the extraction occurs via,

$$4RNH_2_{(org)} + H^+ + [Au(CN)]_2^- = [(RNH)_3](Au(CN)_2)3RNH_2]_{(org)}$$

i.e., by a combination of anion exchange and solvation effects. The stoichiometry of the assembly is different for Primene JMT,

$$4RNH_2_{(org)} + 2H^+ + 2Au(CN)_2^- = [(RNH)_3]_2(Au(CN)_2)_{2}2RNH_2]_{(org)}$$

Figure 10 A typical solvent extraction flowsheet for PGM refining.
Selectivity over other metallacyano species was poor, decreasing in the order tridecylamine > Primene 81R > Primene JMT. The best extraction conditions proved to involve neutral or slightly elevated pH. The addition of Cyanex 921, Cyanex 923, or TBP (Table 6) allowed extractions to be performed under more alkaline conditions and improved the selectivity over other metals.

In the late 1980s Henkel Corporation developed a series of dialkylguanidine derivatives (31) for the recovery of Au and Ag from low-grade cyanide liquors. The dialkylguanidinium cation $[RH]^+$ functions as an anion exchange extractant whose concentration is controlled by the pH swing:

$$R_{(org)} + H^+ = [RH]^+_{(org)}$$

At pH $\leq 10.5$ the guanidine is protonated and phase transport of $[Au(CN)_2]^{-}$ is favored,

$$[RH]^+_{(org)} + Au(CN)_2^- = [RH][Au(CN)_2]_{(org)}$$

Increasing the pH to $\geq 13.5$ favors deprotonation of the guanidinium reagent and $Au(CN)_2^-$ is released,

$$[RH][Au(CN)_2]_{(org)} + OH^- = R_{(org)} + [Au(CN)_2]^- + H_2O$$

Early tests using N,N'-bis(2-ethylhexyl)guanidine resulted in excellent selectivity for gold, but it was found that longer-chain alkyl groups were needed to prevent losses of the reagent to the aqueous phase. Another problem encountered was the transport of hydroxide during Au stripping,

$$[RH][Au(CN)_2]_{(org)} + OH^- = [RH][OH]_{(org)} + [Au(CN)_2]^-$

which is then released into the aqueous feed solution when the reagent is recycled,

$$[RH][OH]_{(org)} + [Au(CN)_2]^- = [(RH)(Au(CN)_2)]_{(org)} + OH^-$$

The consequent increase in pH of the feed solution significantly reduces the efficiency of Au extraction.

$$\text{HN} - \text{R}$$
$$\text{HN} = \text{R}$$

(31)

Hydroxide transfer was reduced to undetectable levels by varying the composition of the organic phase, and the LIX 79 reagents, trialkylguanidines of unspecified composition (Table 5), have been subsequently commercialized. Working trials at two gold mines revealed the selectivity of LIX 79 to be $Au > Zn > Ag > Ni > Cu > Fe$. Addition of 50 g L$^{-1}$ of tridecanol was needed to prevent formation of a third phase. Reduced metal loading of LIX 79 when cyanide concentrations in the feed solution are increased has been ascribed to ligand competition and formation of more highly charged cyano complexes in the aqueous phase. Extraction of gold has been undertaken using LIX 79 in liquid membranes and robust hollow-fiber membranes as alternatives to solvent extraction for recovery from dilute feeds. A similar study, for recovery from acidic chloride media, has used Cyanex 923 as the carrier in liquid membranes.

The development of more benign alternatives to cyanide for gold-leaching (see Section 9.17.3.1) such as thiourea, thioocyanate, or thiosulfate, which form stable complexes in water has prompted research to identify suitable solvent extractants from these media. Cyanex 301, 302, 272, Ionquest 801, LIX 26, MEHPA, DEHPA, Alamine 300 (Table 5) have been evaluated as extractants for gold or silver from acidic thiourea solutions. Whilst the efficacy of Cyanex 301 and 302 was unaffected by the presence of thiourea in the aqueous feed, the loading of the other extractants is severely depressed. Formation of solvated complexes of gold and of an inner-sphere complex of silver has been proposed.

Oxidative leaching with ammonium thiosulfate (Section 9.17.3.1) generates solutions containing a mixture of the mono- and di-thiosulfato complexes, $[Au(S_2O_3)^-]$ and $[Au(S_2O_3)_2]^{3-}$. Gold can
be recovered selectively from such solutions using mixtures of an amine extractant with a solvating extractant such as TBP or a trialkyl amine oxide.\textsuperscript{348–351}

There has been a renewed interest in recovery of gold from chloride media containing both Au\textsuperscript{I} and Au\textsuperscript{III} chloro-complexes. Vest \textit{et al.}\textsuperscript{352} and Salvadó \textit{et al.}\textsuperscript{353} independently evaluated various substituted benzoylthioureas (\textbf{32}) as Au\textsuperscript{III} extractants.\textsuperscript{352,353} Good kinetic selectivity is reported for Au\textsuperscript{III} and Pd\textsuperscript{II} over the other PGMs, based on the higher lability of their chloro complexes.\textsuperscript{352}

Chloroform solutions of calixarenes (\textbf{33–38})\textsuperscript{293,354} show high affinity for Au\textsuperscript{III} and good selectivity over Fe\textsuperscript{III} in some cases.\textsuperscript{293} Spectroscopic data indicate that complex formation with thioethoxy calix[4]arenes involves formation of inner-sphere complexes with Au–S bonds.\textsuperscript{354}

Extraction of gold from acidic chloride media by S-decyldithizone (\textbf{39}) is associated with oxidation of the extractant to the 2H-tetrazolium cation. Reductive stripping results in the regeneration of the extractant and precipitation of Au\textsuperscript{0} as a black powder.\textsuperscript{355}

Relatively little has been reported on solvating extractants for recovery from chloride media\textsuperscript{356} since BUTEX (see Table 6) was used by INCO in the 1970s,\textsuperscript{357} and subsequently MIBK by Johnson Matthey and Anglo.\textsuperscript{358} Recently, 2-ethylhexanol has been shown to have a higher Au capacity, a higher selectivity over other metals, and to be more easily stripped than other alcohols tested previously.\textsuperscript{356} The Minataur\textsuperscript{TM} process\textsuperscript{359} uses a solvating extractant of undisclosed composition to effect a very efficient separation from other metals present in the cathode sludge obtained from conventional CIP/electrowinning.\textsuperscript{360,361}

9.17.6.2 Ag\textsuperscript{I}

The extractive metallurgy of silver involves a wide range of processes reflecting the diverse sources of this element. It is recovered in significant quantities from sulfidic ores or as a high-value by-product from zinc/lead, copper, nickel, tin, and gold production, mainly by pyrometallurgy.\textsuperscript{182} The coordination chemistry involved in hydrometallurgical recovery is generally based on
leachants similar to those for gold (see above), but there has not been widespread use of selective complexing agents in separation, concentration, and refinement operations. Solvent-extraction processes have received more attention in recovery from secondary sources such as photographic fixing solutions. The working system chosen by the majority of investigators usually comprises a nitrate feed and a chloroform organic phase which is attractive for the experimentalist, as investigation of complex formation and extraction by NMR is straightforward. Two comprehensive reviews have recently been published providing a survey of the literature up to 2000. Since then more than 50 further papers have been published, many involving the use of extractants in membranes or on solid supports. The extractants reported are predominantly based on macroring ligands, examples include calixarenes with pendent sulfur or nitrogen donors and crown ethers. Sulfur-containing macrocycles show remarkably high selectivity for Ag⁺ over base metal cations.

Both the mono- and tri-nucleating ligands (40) and (41) transport Ag⁺ exclusively from a feed solution containing Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Pb²⁺, and Cd²⁺. The relative ease of separation of silver from base metals by traditional processes, and its decreasing value relative to the PGMs make it likely that extractants based on expensive ligands are unlikely to be commercialized in the near future. The much simpler solvating extractants tri-n-butyl- and tri-n-octyl-phosphine sulfide have been shown to give high recoveries of Ag⁺ from concentrated chloride media after stripping with thiosulfate. Selectivities are lower than for tri-iso-butyl-phosphine sulfide, the active ingredient of Cyanex 471X. Analysis of the concentration dependencies of extraction equilibria indicate that the less-hindered n-alkyl derivatives form a dinuclear Ag⁺ complex in the organic phase,

\[ 2[AgCl_3]^{2-} + 2L_{(org)} = [Ag_2L_2Cl_2]_{(org)} + 4Cl^- \]

although the Cyanex 471X ligand has been claimed to give a mononuclear complex, [AgL₂Cl].

9.17.6.3 Pt⁴⁺, Pt²⁺

The refining of platinum is technically more challenging than gold or silver due to the lack of easily implemented electrorefining steps. The separation from other PGMs is most commonly approached by dissolution of concentrates into HCl solutions (Figure 10). Options for extraction are limited by the very slow rates of ligand exchange shown by the chlorometallates, only Pd⁴⁺ being sufficiently labile for the recovery by processes based on inner-sphere complex formation to be of practical use. The nature of the solvating or ion-pairing extractants currently in use in commercial operations is shrouded in secrecy, but a wide range of reagent types have been tested, and Wisniowski and Szymanowski give a useful summary of extractants used prior to 1996. The 8-hydroxyquinoline reagents (Kelex100), (26), on contact with acidic solutions containing [PtCl₆]²⁻ are readily protonated and transfer platinum to an organic solution as a solvated ion pair,

\[ H^+ + RH_{(org)} = RH_2^+_{(org)} \]

\[ [PtCl_6]^{2-} + 2RH_2^+_{(org)} + 2RH_{(org)} = [RH_2]_{2/2}[PtCl_6 \cdot 2RH]_{(org)} \]
Inner sphere complexes are formal with Pd\textsuperscript{II},
\[
\left[\text{PdCl}_4\right]^{2-} + 2\text{RH}_{\text{org}} = \left[\text{R}_2\text{Pd}\right]_{\text{org}} + 2\text{H}^+ + 4\text{Cl}^-
\]
and, at low concentrations of HCl the extraction of Pd\textsuperscript{II} is favored. Pt\textsuperscript{IV} can be selectively stripped into water at pH 1.5–2.0, and then the Pd\textsuperscript{II} recovered with 6–8 M HCl or by reduction with hydrogen.\textsuperscript{297}

Quantitative extraction of Pt\textsuperscript{IV} by n-octylaniline affords a method of separation from Fe\textsuperscript{III}, Co\textsuperscript{II}, Ni\textsuperscript{II}, and Cu\textsuperscript{II} in hydrochloric acid.\textsuperscript{306} A similar ion-pairing mechanism accounts for extraction by TOPO\textsuperscript{305,310} and Alamine 304\textsuperscript{304} (see Tables 5 and 6 for reagent structures):

\[
\left[\text{PtCl}_6\right]^{2-} + 2\text{R}_3\text{N}_{\text{org}} + 2\text{HCl} = \left[\text{R}_3\text{NH}_2\right]_{\text{org}} \left[\text{PtCl}_6\right]_{\text{org}} + 2\text{Cl}^-
\]

It has been shown that upper-rim substitution of some dithiocarbamoyl-derivatized calix[4]arenes affects selectivity of Pt\textsuperscript{IV} extraction.\textsuperscript{327,329} Some selectivity over Pb\textsuperscript{II}, Hg\textsuperscript{II}, and Pt\textsuperscript{II} has been achieved by the introduction of 2-pyridyl-N-oxide groups on the lower rim, but Sn\textsuperscript{II}, Ag\textsuperscript{I}, Pd\textsuperscript{II}, and Au\textsuperscript{III} were still extracted to a greater extent.\textsuperscript{328}

An inner-sphere complex (42) is formed when toluene solutions of 3,3-diethylthietane are contacted with solutions of Pt\textsuperscript{IV} in hydrochloric acid, but extraction is slow:\textsuperscript{322}

\[
\left[\text{PtCl}_6\right]^{2-} + 2\text{L}_{\text{org}} = \left[\text{PtCl}_4\text{L}_2\right]_{\text{org}} + 2\text{Cl}^-
\]

The kinetic inertness of $[\text{PtCl}_6]$\textsuperscript{2–} in solvent extraction reactions can be dramatically altered by the addition of SnCl\textsubscript{2}.\textsuperscript{79,285} After a 10-minute contact time, negligible quantities of Pt\textsuperscript{IV} are extracted from 0.1 to 12 M HCl solutions by thiobenzanilide in chloroform, whereas almost quantitative recovery is recorded after the addition of a slight excess of SnCl\textsubscript{2}.\textsuperscript{319} Reduction of Pt\textsuperscript{IV} to Pt\textsuperscript{II} and formation of mixed Pt/Sn complexes are thought to be responsible. Extraction of Pt\textsuperscript{II} from chloride solutions by the macrocyclic tetrathioethers (43)–(45) is very slow, but is considerably enhanced by the addition of thiourea.\textsuperscript{321}

König, Schuster, and others have demonstrated that by controlling the pH of the aqueous phase, N-benzoyl-N’,N’-dialkylthioureas can be used to separate Pt\textsuperscript{II}, Pd\textsuperscript{II}, Ru\textsuperscript{III}, Rh\textsuperscript{III}, Os\textsuperscript{III}, and Ir\textsuperscript{III} from base-metal chlorides.\textsuperscript{382–385} Extraction of Pt\textsuperscript{IV} by N-acyl-N’-alkylthiourea and N-acyl-N’,N’-dialkylthiourea reagents is substantially accelerated by addition of SnCl\textsubscript{2} and is accompanied by reduction to Pt\textsuperscript{II}.\textsuperscript{296} Ring opening of the OS\textsuperscript{−} chelate rings and cis/trans-isomerization of the resulting dichloroPt\textsuperscript{II} complexes has been shown to depend on HCl concentration by \textsuperscript{1}H and \textsuperscript{195}Pt NMR spectroscopy.\textsuperscript{317,366} The coordination chemistry of this class of reagent and formation of other types of isomer based on E/Z arrangements of the N’N’dialkyl groups and cis/trans-arrangements (Figure 11) of the bis-chelates has been reviewed.\textsuperscript{387}
9.17.6.4 PdII

The development of new technology for extraction and recycling of palladium has been stimulated by its increasing use in automobile catalysts, which now consume ca. 55% of world production. A range of options for extraction from acidic media and for separation from other PGMs is possible because PdII is relatively substitution-labile. This allows cationic exchange, e.g.,

$$\frac{1}{2}PdCl_4^{2-} + 2L_{(org)} = PdL_2_{(org)} + 2H^+ + 4Cl^-$$

or solvating reagents

$$\frac{1}{2}PdCl_4^{2-} + 2L_{(org)} = PdL_2Cl_2_{(org)} + 2Cl^-$$

to be used to effect separation from platinum. The thermodynamic stability of chloropalladate(II) complexes also allows recovery using anion exchange reagents, e.g.,

$$[PdCl_4]^{2-} + 2[R_3NH]Cl_{(org)} = [R_3NH]_2[PdCl_4]_{(org)} + 2Cl^-$$

but achieving good selectivity of extraction by the anion exchange route is a challenging problem. The lower charge density of the PtIV complex [PtCl_6]^{2-} leads to this being preferentially extracted with reagents having lower charge density on the cation, e.g., quaternary alkyl ammonium or phosphonium salts. This Pt/Pd selectivity is reduced when there are substantial quantities of the dinuclear complex [Pd_2Cl_6]^{2-} in the feed solution.

Alkylammonium reagents have also been shown to act as phase transfer catalysts when used in conjunction with cation exchange reagents such as Kelex 100 or solvating extractants such as di-octylsulfide. It has been suggested that formation of the inner-sphere complexes occurs in the bulk organic phase following transport of chloropalladate complexes across the interface in ion pairs with [R_4N]^+. A similar approach has been reported by Belova et al. who have used alkylammonium salts of di(2-ethylhexyl)dithiophosphoric acid (DEHPTA, see Table 4), but in this case the extracted species, [R_4N][PdCl_2L], contain mononanionic PdII complexes with one deprotonated DEHPTA ligand in the inner coordination sphere, except when the reagent is in large excess, when [PdL_2] is formed. Similar results are obtained with D2EHPA.
A number of chelating cation exchangers have been used as extractants. The modes of complex formation by acylthioureas (32) are described in Section 9.17.6.3. Their use has been extended to membrane systems for the recovery of Pd. The use of Kelex 100 and of hydroxyoximes (Table 3) has been reviewed and methods for improving rates of phase transfer have been surveyed by Szymanowski.

The quadridentate ligand (46), LH₂, has been used to extract palladium from solutions containing platinum. Equilibrium studies indicated that a mono-deprotonated form of the ligand is involved, giving [PdCl(LH)].

The dialkyaminomethyl phosphonates, (47) and (48), could function as either a cation exchanger using its phosphonate group or as an anion exchanger using a protonated form of the amino group. Equilibrium studies suggest formation of a mono-chloro complex containing one deprotonated and three neutral solvating ligands.

Whilst many solvating ligands have been studied, the dialkyl sulfide reagents (see Table 6) remain the most important commercially.

9.17.7 CONCLUSIONS

Since the publication of the CCC (1987) the expanding use of hydrometallurgical methods for the recovery of base and precious metals has provided a major stimulus for applying coordination chemistry to leaching, separation, and concentration operations. This large volume of research and development work has not resulted in the commercialization of many new classes of metal extractants, and instead “playing new tricks with old reagents” has been very much a feature. The development of any new extractant by a specialty chemical company is most likely to succeed when there is collaboration with metal producers at the outset to define the design requirements and to ensure the reagent supplier receives reward for the value of improvements in the metal recovery process. Playing “new tricks with old reagents” should include synergistic combinations of extractants resulting from ligand assembly processes that in future should exploit design principles emerging from supramolecular chemistry.

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