

METAL COMPLEXES IN HYDROMETALLURGY AND EXTRACTION

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Abstract

The modes of action of the commercial solvent extractants used in extractive hydrometallurgy are classified according to whether the recovery process involves the transport of metal cations, Mn^+ , metalate anions, MX_n^- , or metal salts, MX_x into a water-immiscible solvent. Well-established principles of coordination chemistry provide an explanation for the remarkable strengths and selectivities shown by most of these extractants. Reagents which achieve high selectivity when transporting metal cations or metal salts into a water-immiscible solvent usually operate in the inner coordination sphere of the metal and provide donor atom types or dispositions which favour the formation of particularly stable neutral complexes that have high solubility in the hydrocarbons commonly used in recovery processes. In the extraction of metalates, the structures of the neutral assemblies formed in the water-immiscible phase are usually not well defined and the cationic reagents can be assumed to operate in the outer coordination spheres. The formation of secondary bonds in the outer sphere using, for example, electrostatic or H-bonding interactions are favoured by the low polarity of the water-immiscible solvents.

Keywords: Metal complexes, hydrometallurgy, extraction



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Introduction

Although the techniques for the recovery of metals have advanced steadily since the bronze and iron ages,^{1,2} it can be argued that the need to accelerate the pace of development of new technologies for extractive metallurgy has never been greater if we are to respond to the rapidly increasing demand for metals, the diminishing supplies of high grade ores, and the pressures to recycle.^{3,4} Governments worldwide are proposing policies to ensure that new technologies are developed in order to maintain supplies of critical metals, in particular those, such as the rare earth elements, that are becoming essential for communications and greener energy production.^{5–8}

This review article describes the coordination chemistry of commercial solvent extraction processes that are used to achieve the separation and concentration of the metals of value in

extractive hydrometallurgy. Hydrometallurgy, which is underpinned by coordination chemistry, is often favoured over traditional pyrometallurgy by industry as it can lead to excellent materials and energy balances because reagents are recycled. Also, hydrometallurgical plants are smaller than those for pyrometallurgical processing so can be located close to the mining operations, and are often environmentally favoured due to lack of SO₂ emission that is frequently associated with pyrometallurgy. The technology is well suited to metal recovery from low grade, mixed metal, ores and can be adapted to the recovery of metals from secondary sources, for example catalytic converters and electrical goods.³ Even with these advantages, the embodied energy associated with the production of metals is not necessarily higher for metals obtained via smelting or blast furnaces.⁹ As such, the choice between technologies is not always clear cut and in some cases, for example in the extraction of precious metals, a combination of pyro- and hydrometallurgical processes is preferred.

A hydrometallurgical flow sheet usually involves the operations shown in Fig. 1. After dissolution of the ore into an aqueous medium (leaching), the metal to be recovered can be separated and concentrated using solvent extraction and the resulting, high purity, aqueous solution is reduced to generate the metal.¹⁰

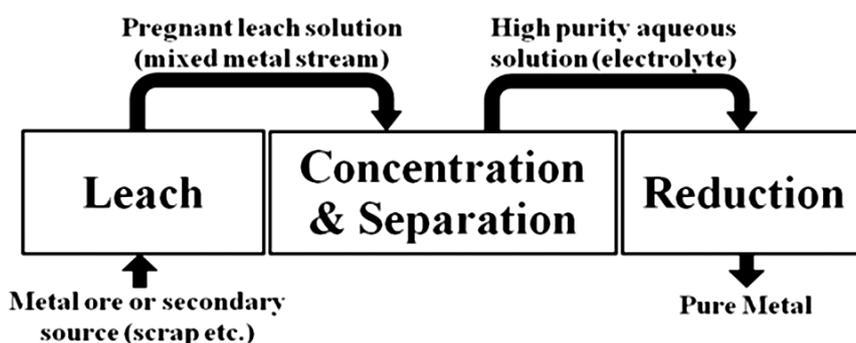


Fig. 1 The key operations in a hydrometallurgical process to recover metals from minerals or from secondary sources.

Most metals are obtained from oxidic or sulfidic ores and leaching processes can involve a wide range of conditions.¹¹ A lot of development work has been undertaken recently on pressure and oxidative leaching of base metal sulfides to generate elemental sulfur as the major by-product and sulfate solutions for downstream processing. Chloride media are

favoured for the recovery of precious metals, whilst nitrate, chloride and sulfate streams are involved in the extraction and purification of f-block elements.¹² While a number of methods can be used to achieve the concentration and separation operations shown in Fig. 1, this review will only consider solvent extraction. This technology, first developed for large scale operations for uranium production in the Manhattan Project,¹⁰ has proven robust and can be used in continuous, rather than batch processes.

An idealised representation of a flow sheet using solvent extraction to achieve the concentration and separation of a desired metal is shown in Fig. 2. At the front end of such a system, the aqueous solution from leaching (the “pregnant leach solution”) is contacted with the solvent extractant in a mixer-settler (Fig. 3) which selectively transfers the desired metal to a water-immiscible phase. After phase separation, the aqueous solution (the raffinate) is recycled back to leaching and the water-immiscible phase (the “organic”) is moved to another mixer-settler where it is contacted with an aqueous ‘stripping’ solution to create a concentrated, pure aqueous solution of the metal for reduction. The stripped water-immiscible phase (the “organic”) is reused and the aqueous solution from electrolysis, the “spent electrolyte” is reused in stripping.

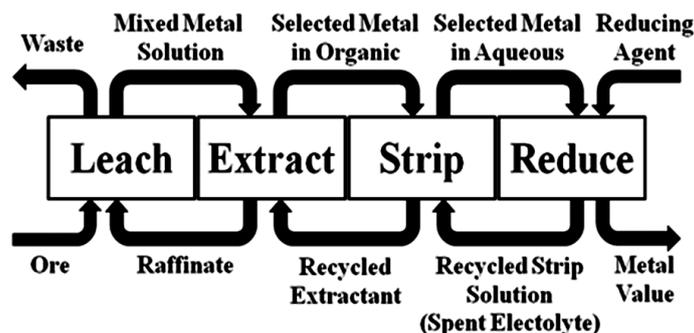


Fig. 2 The incorporation of solvent extraction to achieve metal separation and concentration in a hydrometallurgical circuit which involves recycling of all reagents.

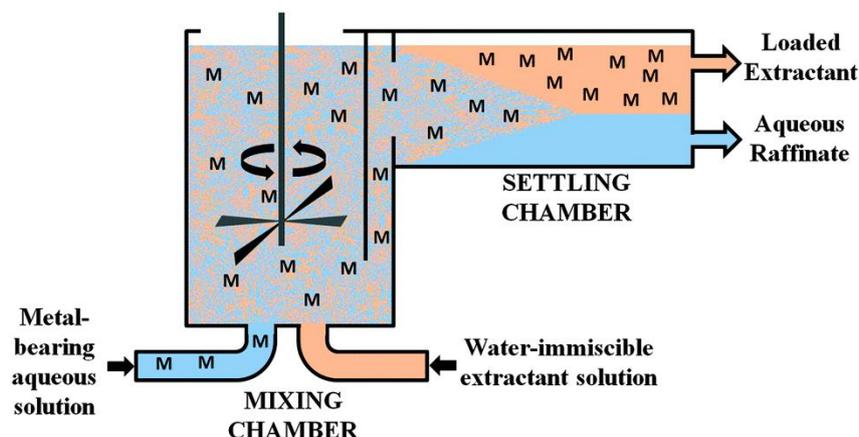
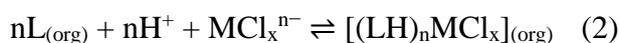


Fig. 3 Schematic representation of a mixer-settler for continuous operation of solvent extraction.

The nature of the counter anion present in the pregnant leach solution has a major influence on the selection of the metal-extracting reagent used in downstream processing. As chloride is a good inner-sphere ligand it is possible to generate extractable, charge-neutral, complexes $[MCl_x(L)_n]$ by using a neutral reagent L which effectively “solvates” the metal salt, MCl_x , as in eqn (1) (“Metal Salt Extractants” section below). Such solvating reagents may be present in the inner or outer coordination sphere, or both.



At high chloride concentrations, chloridometalates MCl_x^{n-} are more likely to be present in the aqueous solution. These can be transferred to the water-immiscible solvent by formation of outer sphere assemblies or ion pairs, $[(LH)_nMCl_x]$, with cationic extractants, LH^+ , for example as in eqn (2) (see “Metalate Extractants” below).



A different strategy is needed for metal removal from sulfate streams because sulfate is a weak inner sphere ligand,¹¹ and the most effective approach is to generate a charge-neutral complex in the organic phase, $[M(L)_n]$, by combining anionic ligands L^- with the metal cation M^{n+} as in eqn (3).



Good materials balances within the flow chart outlined in Fig. 2 rely on the retention of reagents within the three closed loops. Consequently, it's important that a solvent extractant

and its metal complexes have a really low solubility in water and a high solubility within the water-immiscible phase, usually a high boiling hydrocarbon on the grounds of safety and value. The low polarity of such kerosene diluents favours the formation of H-bonds and other sorts of secondary bonding between extractant molecules. These interactions within the outer coordination sphere of a complexed metal ion can contribute significantly to the strength and selectivity of an extractant and may be employed in conjunction with more conventional aspects of ligand design which influence the soundness of the inner coordination sphere, to develop reagents which meet the wants of a specific circuit.¹²

In addition to showing the acceptable strength and selectivity of extraction any new reagent should:

- Facilitate fast metal transfer between the 2 liquid phases in both loading and stripping and rapid phase disengagement, otherwise the throughput of metal within the overall process are going to be low;
- Show high chemical stability under the conditions of operation to cut back make-up costs and minimise the transfer of degradation products to other parts of the circuit or to the environment.

Commercial extractants

Only a tiny low percentage of the solvent extractants described within the literature has been extensively tested or utilized in commercial operations.¹³ Most often, the reagents employed in commercial operations are formulations which contain the extractant blended with modifiers that enhance solubility, phase disengagement properties, and metal transfer. These formulations are frequently denoted by trade numbers which frequently make it difficult for a non-expert to spot the active components. Also, reports on the performance of the foremost commercially viable reagents have often been written by metallurgists and engineers and consequently relatively little attention has been paid to the elemental chemistry involved within the processes, particularly the structures of the assemblies formed within the water-immiscible phase.

This article reviews the coordination chemistry that underpins the employment of various classes of business solvent extractants. We specialize in examples where this chemistry is well understood and where the structures of the assemblies formed within the water-

immiscible phase are best defined. An understanding of the coordination chemistry, which regularly involves interactions within the outer- similarly as within the inner-coordination spheres can usually account for the strength and selectivity of metal transfer to the organic phase and may aid the planning of recent reagents and processes.

Metal cation extraction

These reagents transfer metal cations, Mn^{+} , from the aqueous phase by an exchange process during which the metal cation usually substitutes ionisable protons on the extractant, as shown in eqn (3).

As the equilibrium in eqn (3) is pH dependent, the “strengths” of the extractants may be compared by recording the pH values at which they're 50%-loaded with metal (the “pH_{1/2} values”), see for instance Fig. 4. Strong extractants for metal cations have low pH_{1/2} values, indicating that they're capable of recovering metals from highly acidic feed solutions. Conversely, a weak extractant for metal cations is just capable of recovering metals at high pH. The pH-dependence of the equilibrium shown in eqn (3) makes it possible to regulate the loading and stripping of the metal within the organic phase by varying the pH of the aqueous phase with which it's in-tuned.

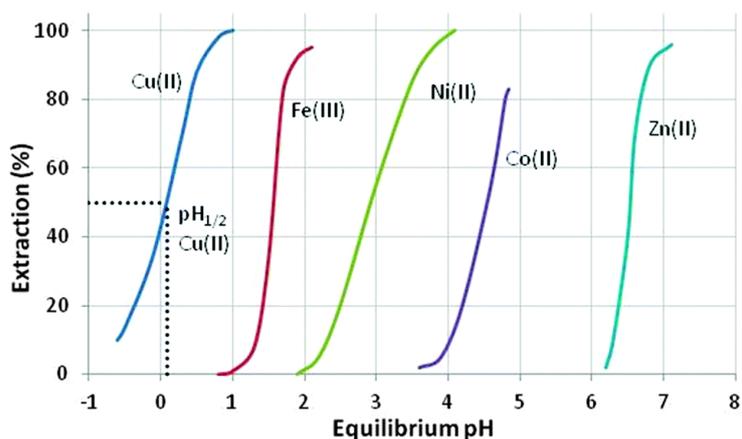


Fig. 4 The pH dependence of metal cation loading by AcorgaP50.‡

In some cases weak extractants have to be first converted to their alkali metal or ammonium salts to ensure that loading of the desired metal cation is successful. The cation exchange process in eqn (4) is facilitated by the sodium ion having a higher hydration energy than the

Mn⁺ cation, favouring its transfer to the aqueous phase, and by the [M(L)_n] complex being more thermodynamically stable than the sodium salt.



Oxime extractants

Phenolic oximes of the types shown in Table 1,§ are used extensively in copper recovery,11 accounting for ca. 25% of world production.14 The sequence of reactions outlined in Scheme 1 ensures that the leachant, the extractant and the stripping solution are recycled and leads to an excellent materials balance.

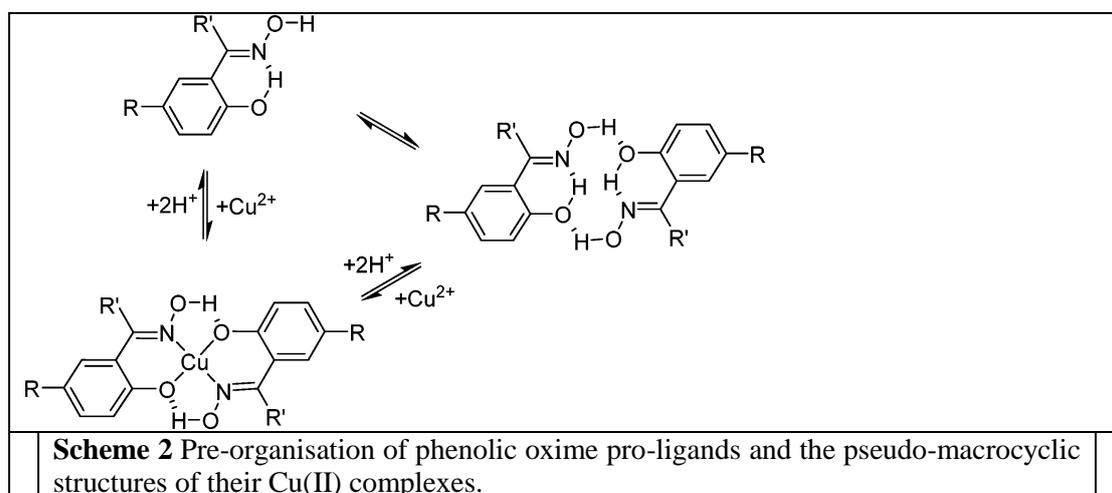
Table 1 The structures and common commercial names of some hydroxy-oxime extractants§ ¹¹

Phenolic oximes			
Substituents			Commercial name(s)
R	R'	R''	
H	C ₉ H ₁₉	H	Acorga P50
H	C ₉ H ₁₉	Me	Acorga K2000, LIX 84-I, SME 529
H	C ₉ H ₁₉	Phenyl	LIX 65N
H	C ₁₂ H ₂₅	Phenyl	LIX 64
Cl	C ₉ H ₁₉	Phenyl	LIX 70
H	C ₁₂ H ₂₅	H	LIX 860, LIX 622

α -Hydroxyoximes		
Substituents		Commercial name(s)
R = R'	n-C ₄ H ₉ (C ₂ H ₅)CHCH ₂	LIX 63

$\text{CuO}_{(s)} + \text{H}_2\text{SO}_4$	$\rightleftharpoons \text{CuSO}_4 + \text{H}_2\text{O}$	(Leaching)
$\text{CuSO}_4 + 2\text{LH}_{(\text{org})}$	$\rightleftharpoons [\text{Cu}(\text{L})_2]_{(\text{org})} + \text{H}_2\text{SO}_4$	(Extraction)
$[\text{Cu}(\text{L})_2]_{(\text{org})} + \text{H}_2\text{SO}_4$	$\rightleftharpoons \text{CuSO}_4 + 2\text{LH}_{(\text{org})}$	(Stripping)
$\text{CuSO}_4 + \text{H}_2\text{O}$	$\rightleftharpoons \text{H}_2\text{SO}_4 + \frac{1}{2} \text{O}_2 + \text{Cu}$	(Electrolysis)
CuO	$\rightleftharpoons \text{Cu} + \frac{1}{2} \text{O}_2$	(OVERALL)
Scheme 1 The sequence of reactions and overall materials balance for copper recovery from oxide ores by the leach/solvent extraction/electrowinning process. ¹²		

The suitability of the phenolic oxime reagents in these operations arises from their coordination chemistry. They are strong enough extractants ($\text{pH}_{1/2} < 1.0$) to load copper from aqueous leach solutions that are sufficiently acidic to ensure that iron(III) remains in the aqueous phase. This strength and the selectivity for Cu^{2+} over other base-metal cations arises in part from the pseudo-macrocyclic structure of the copper complex (Scheme 2). The strong interligand H-bonds between the oxime hydrogen and the phenolic oxygen atoms define a planar donor set and a cavity which is a particularly good fit for $\text{Cu}(\text{II})$.¹²



The selectivity of metal extraction in reactions of the type shown in eqn (3) is revealed by the difference in the $\text{pH}_{1/2}$ values for the various metals. It is clear from the S-curve plots shown in Fig. 4 that Acorga P50 will reject $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ when $\text{Cu}(\text{II})$ is present. The efficacy of extraction of the metals shown in Fig. 4 is roughly that which would be predicted by the Irving–Williams order but with those metals which have a preference for the planar geometry of the pseudo-macrocyclic donor set, $\text{Ni}(\text{II})$, and $\text{Cu}(\text{II})$, being favoured.

Oximic reagents are susceptible to hydrolysis under acidic conditions.¹⁵ However, in two phase systems the imine bond can show remarkable resistance to hydrolysis, depending on the hydrophobicity of the reagent. Ketoximes appear to be more stable than aldoximes and the phenolic oximes are more stable than the aliphatic α -hydroxyoximes such as LIX 63.

Whilst used mainly in Cu recovery, phenolic oximes can be used to separate Pd(II) and Pt(IV). In this case, the former is extracted as a 2 : 1 complex, [Pd(L)_n], at pH \geq 3.0 whilst the kinetic inertness of Pt(IV) ensures that it is only loaded very slowly and so remains in the aqueous phase.¹⁶

Extraction of Mo(VI) and U(VI) by the aliphatic reagent, 5,8-diethyl-7-hydroxydodecan-6-one oxime (LIX 63), has been shown to involve the complexation of the metal cation MO₂₂₊, forming the neutral complex [MO₂(LIX63-H)₂] in which two reagent molecules are deprotonated.¹⁷ Eu(III) and Th(IV) can be recovered using 3,5-di-tert-butyl-2-hydroxybenzaldehyde oxime, which is structurally similar to commercially available salicylaldoximes. The stoichiometry of [EuCl₂(L)] was inferred from plots of log D against the log [L] (where D = distribution coefficient = [M]_{org}/[M]_{aq}), whereas, under the same conditions, Th(IV) forms [ThCl(L)₃] in the water-immiscible phase.¹⁸ The presence of both the extractant anion (L⁻) and an anion from the aqueous feed solution (chloride) indicates that these latter extractions do not proceed by the simple cation exchange process shown in eqn (3), but display characteristics of the metal salt extraction processes.

Stripping of loaded hydroxyoximes is usually achieved by contacting the loaded organic phase with an acidic aqueous solution. Controlling the pH can allow selective stripping of phenolic oximes which have been loaded with more than one metal, e.g. the more weakly bound Ni(II) can be completely transferred from a Cu(II)/Ni(II)-loaded solution of LIX 84 at pH 3, whereas the copper remains in the organic phase until the pH of the aqueous phase is lowered further.¹⁹

Phosphinic, phosphonic and phosphoric acid extractants

Commercial extractants based on phosphinic, phosphonic acids and phosphoric acids are listed in Table 2. These have one ionisable proton, with the exception of the phosphate monoesters, which have two. Their metal donor atoms (X = O or S) can be varied to suit the hard–soft properties of different metals.

Table 2 The structures and common commercial names of metal cationic extractants based on phosphorus (V) acids¹¹

Monoalkylphosphoric acids		
$\begin{array}{c} \text{HO} \quad \text{OH} \\ \diagdown \quad / \\ \text{P} \\ / \quad \backslash \\ \text{RO} \quad \text{O} \end{array}$		
Substituents		Commercial names
R	n-C ₄ H ₉ (C ₂ H ₅)CHCH ₂	MEHPA

Dialkylphosphonic acids		
$\begin{array}{c} \text{R} \quad \text{XH} \\ \diagdown \quad / \\ \text{P} \\ / \quad \backslash \\ \text{RO} \quad \text{O} \end{array}$		
Substituents		Commercial names
R	n-C ₄ H ₉ (C ₂ H ₅)CHCH ₂	PC 88A, P507, Ionquest 801

Dialkylphosphinic acids and derivatives		
$\begin{array}{c} \text{R} \quad \text{XH} \\ \diagdown \quad / \\ \text{P} \\ / \quad \backslash \\ \text{R} \quad \text{X}' \end{array}$		
Substituents		Commercial names
R	t-C ₄ H ₉ CH ₂ (CH ₃)CHCH ₂	Cyanex 272
X = X'	O	
R	t-C ₄ H ₉ CH ₂ (CH ₃)CHCH ₂	Cyanex 302
X	O	
X'	S	
R	t-C ₄ H ₉ CH ₂ (CH ₃)CHCH ₂	Cyanex 301
X = X'	S	

Dialkylphosphoric acids and derivatives		
$\begin{array}{c} \text{RO} \quad \text{XH} \\ \diagdown \quad / \\ \text{P} \\ / \quad \backslash \\ \text{RO} \quad \text{X}' \end{array}$		
Substituents		Commercial names
R	n-C ₄ H ₉ (C ₂ H ₅)CHCH ₂	D2EHPA, DEHPA, P204, Baysolvex DEDP
X = X'	O	
R	n-C ₄ H ₉ (C ₂ H ₅)CHCH ₂	Hoe F 3787
X	O	
X'	S	
R	n-C ₄ H ₉ (C ₂ H ₅)CHCH ₂	DEHTPA
X = X'	S	

A characteristic of the phosphorus(V) acid extractants is that they form stable dimeric structures in non-polar solvents, almost like those of carboxylic acids (see below). When the extractant is present in excess, formation of metal complexes involves the retention of 1 of the hydrogen bonds within the dimer, whilst the opposite is broken to release a proton which is replaced by the metal cation; this ends up in the formation of an 8-membered pseudo-chelate. Extraction of M^{2+} cations of the bottom metals by the commercial reagent Cyanex 272 and related phosphoric, phosphonic and phosphinic acids, usually gives complexes with 4 : 1 ligand : metal stoichiometry, $[M(L)_2(LH)_2]$. The 8-membered, hydrogen-bonded rings in these complexes are able to subtend O–M–O angles greater than 90° and will contribute to those reagents showing selectivity for base metals which adopt tetrahedral coordination geometries. The convenience of extraction of M^{2+} cations of the primary transition series reflects this, and follows the sequence $Zn > Cu > Mn > Co > Ni$ which isn't the Irving–Williams order of stability. The high affinity for zinc by the orthophosphoric acid D2EHPA is that the basis for its application in an exceedingly recently commissioned plant for the recovery of zinc on a 150 000 tonne p.a. scale.²⁰

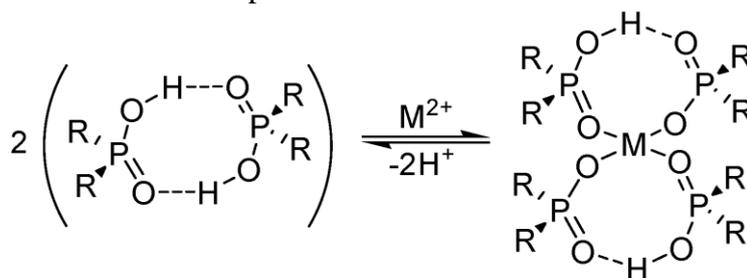


Fig. 5 Complex formation equilibrium involving phosphonic acids.

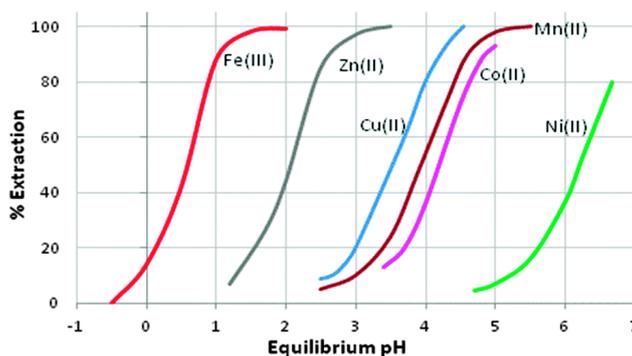


Fig. 6 The pH-dependence of metal cation loading by Cyanex 272; data are adapted from [ref. 22](#).

The 8-membered pseudo-chelate motif has been identified in X-ray crystal structure determinations, e.g. within the complex $[Ni(Ph_2PO_2)_2(Ph_2PO_2H)_2(DMF)_2]$ during which diphenylphosphinic acid is employed as a model for Cyanex 272 (Fig. 7).²¹

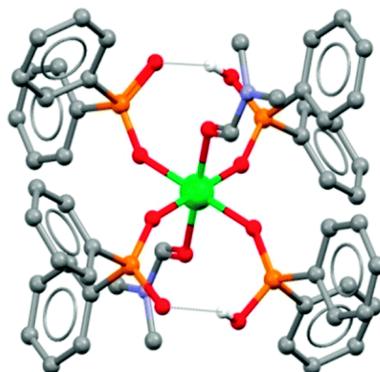


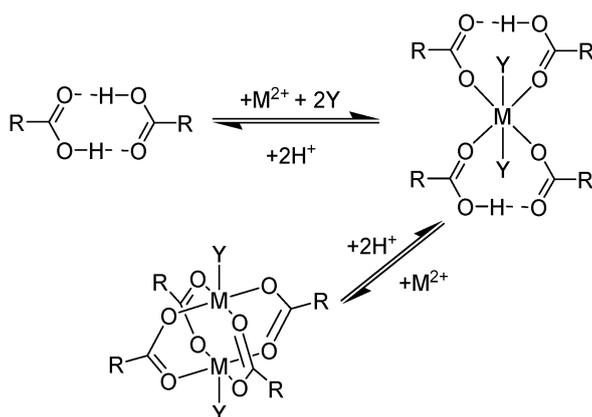
Fig. 7 The structure of $[\text{Ni}(\text{Ph}_2\text{PO}_2)_2(\text{Ph}_2\text{PO}_2\text{H})_2(\text{DMF})_2]$ from single crystal X-ray diffraction.²¹

Phosphorus (V) acids are shown to be effective within the recovery of a good range of metals, particularly d- and f-block elements, the latter often in synergistic mixtures (see below). D2EHPA extracts MoO_2^{2+} during a 4 : 1 L : M ratio, possibly forming a fancy just like that in Fig. 5 with the Mo(VI) atom retaining two cis-oxo groups in a very six coordinate structure. Cyanex 600, a variant of Cyanex 272 (Table 2) has been shown to extract Mo from acidic solutions that contain Cu, Fe and Al cations.²³

Carboxylic and other organic acids

Carboxylic acids, just like the phosphorus(V) acids have a propensity to associate in low polarity solvents but during this case this results in more complicated speciation than would be inferred from the equilibrium shown in eqn (3). The acid dimer, $[\text{RCO}_2\text{H}]_2$, shown in Scheme 3, is especially stable in hydrocarbon solvents. One or both of the protons may be replaced by metal cations to come up with mono- or dinuclear complexes and remaining coordination sites can then accommodate neutral acid or water molecules.¹¹ Consequently, an outsized number of species of the formula $[\text{M}(\text{RCO}_2)_n(\text{RCO}_2\text{H})_m(\text{H}_2\text{O})_p]_x$ can coexist within the water-immiscible phase, with the charge on the extracted action, Mn^+ , being counterbalanced by an appropriate number of carboxylate anions.²⁴ These variations of speciation contribute to the carboxylic acids showing poor selectivity as metal extractants and that they are much weaker pH swing extractants than the phosphorus(V) acids. Just like the hydroxamic acids (Table 3), they can't be accustomed process aqueous feed solutions of base metals without first precipitating all of the iron(III) because they form very stable complexes

of this cation. Hydrophobic, straight-chain carboxylic acids are good surfactants and their propensity to make soaps ends up in problems in phase disengagement in solvent extraction processes. Reagents which are employed in metal recovery, e.g. Versatic acid (Table 3,§) have branched alkyl chains to beat this problem.



Scheme 3 Some of the neutral complexes formed on extraction of M^{2+} cations by hydrophobic carboxylic acids ($Y = H_2O$ or RCO_2H).

Table 3 The structures and common commercial names of other metal cation extractants§ ¹¹

Substituents		Commercial name(s)
	R	Branched aliphatic groups (C_9H_{19}) Versatic acid 10
	R	Branched aliphatic groups LIX 1104
	R	$i-C_{11}H_{23}$ Kelex 100 ^g

a Gravimetric reagents containing 8-hydroxyquinoline are often referred to as oxines. These should not be confused with oximes which contain a $C=N-OH$ unit.

The hydroxamic acid LIX 1104 (Table 3) has been accustomed extract Fe, Co, Ni, Cu, Zn and Cd, loading at pH 3–7; 25 Cu(II) is stripped with ca. 1 M acid, whilst Fe(III) requires 4

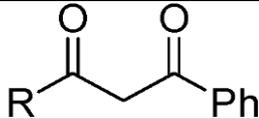
M acid. Deprotonation to administer the hydroxamate generates an O₂⁻ chelating donor set which is thought to make extremely stable Fe(III) complexes kind of like the highly stable, iron-chelating siderophores found in nature.

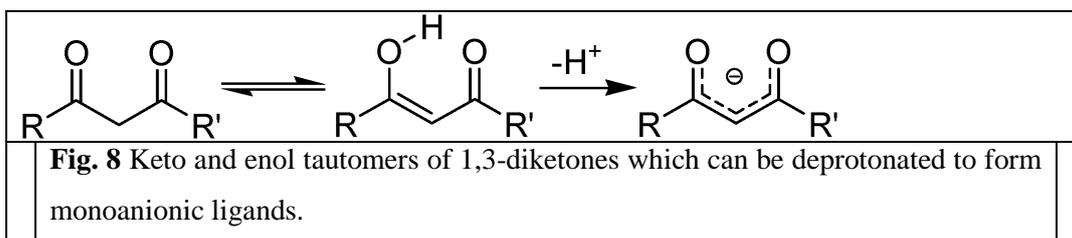
8-Hydroxyquinolines (LH) have a longstanding record of use in gravimetric and quantitative chemical analysis, yielding stable neutral complexes [M(L)_n] with metal di-, tri-, and tetracations when solutions are buffered to favour the deprotonation of the radical. The hydrocarbon-soluble reagent Kelex 100 (Table 3) will be accustomed recover gallium from spent Bayer liquor during which it's present in concentrations of 100–300 mg L⁻¹.26. The extraction is undertaken on the alkaline liquor after alumina has been precipitated and involves the reaction shown in eqn (5). A major amount of aluminium and sodium are co-extracted, but these are selectively stripped by contacting with 6 M HCl leaving only gallium within the organic phase as [(LH₂)GaCl₄], a neutral assembly of tetrachloridogallium(III) and monoprotonated Kelex 100. Reagents specifically designed to extract metalate anions are discussed below.



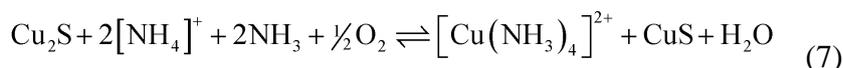
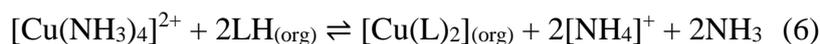
β-Diketones (Table 4,§) are weak extractants which operate under basic conditions that promote the formation of the bidentate monoanionic ligands as in Fig. 8.^{27,28}

Table 4 The structures and commercial names of some common β-diketone metal cation extractants§ ¹¹

β-Diketones		
		
Substituents	Commercial name(s)	
R	i-C ₇ H ₁₅	LIX 54
R	C(CH ₃)(C ₂ H ₅)C ₃ H ₇	XI-N54
R	CH(C ₂ H ₅)C ₃ H ₇	XI-55
R	C(CH ₃) ₂ C ₆ H ₁₃	XI-57



LIX 54 was introduced as an advert reagent for the recovery of copper from ammoniacal solutions.²⁹ the two : 1 complex within the extraction process shown in eqn (6) is assumed to possess a planar structure analogous to it of the acetylacetonate complex shown in Fig. 9.³⁰ The aqueous raffinate contains a combination of ammonium ions and ammonia which is recycled back to the leaching of chalcocite, Cu₂S (eqn (7)) to get the ammine complex and enriched covellite (CuS) that's further processed in a very conventional smelter.



LIX 54 has the advantage over the phenolic oximic reagents described earlier for Cu extraction in this its low viscosity allows high ligand concentrations to be used and it's more easily stripped. Unfortunately, it's subject to chemical degradation in ammoniacal conditions, converting it to the ketimine and other products over time.²⁸

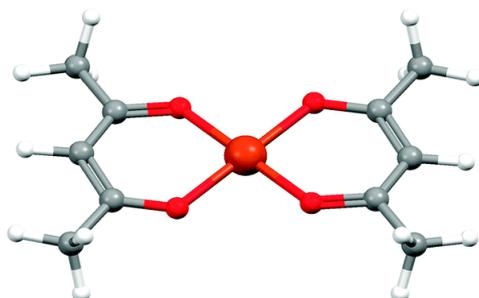


Fig. 9 The structure of bis(acetylacetonato)copper(II) from single crystal X-ray diffraction.³⁰

Metalate anion extraction

A number of leaching processes generate solutions within which the metals are present as metalate anions, MX_xn⁻. this can be particularly the case for the chloridometalates of the platinum group metals that oxidative leaching in acidic chloride media is that the most practicable approach to dissolution.²² Also, the efficiency of recently developed chloride-

leaching processes for base metals¹² makes it practicable to recover these metals from acidic chloride streams, despite these being more corrosive than the more common sulfate-based streams.

The use of solvent extraction to concentrate and separate the metal values which are present as metalate anions requires the formation of neutral assemblies (often named as “ion pairs”) within the water immiscible phase. This may be achieved in two ways. Mixing an answer of a neutral extractant with an acidic solution can cause protonation of the extractant and therefore the “pH-swing” process shown in eqn (2) within which loading is favoured by lowering the pH of the aqueous phase and stripping by raising pH.¹² Amines, ketones and phosphine oxides (Table 5,§) are used commercially during this way. Alternatively, an extractant that carries a permanent electric charge may be employed in an anion exchange process, eqn (8). All through in this case, loading and stripping are influenced by variation of the concentration of the counteranion Y⁻ in an “anion-swing” process.¹²

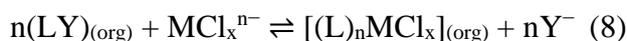


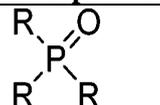
Table 5 The structures and common commercial names of some anion extractants§ ¹¹

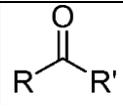
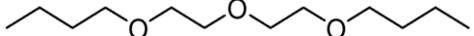
Primary amines (H₂NR)	
Substituent(s), R	Commercial name(s)
C ₁₆₋₂₂ H ₃₄₋₄₆ (mixture of isomers)	Primene JM-T
C ₁₂₋₁₄ H ₂₆₋₃₀ (mixture of isomers)	Primene 81-R

Secondary amines (HNRR')		
R = R'	C ₁₃ H ₂₇	Ditridecylamine, HOE 2652
R	C ₁₂ H ₂₅	Amberlite LA-2
R'	C ₁₂₋₁₄ H ₂₅₋₂₉	
R = R'	C ₈ H ₁₇ (mixture of isomers)	Adogen 283

Tertiary amines (NR₃)	
C ₈ H ₁₇	TOA, Alamine 300
C ₈ H ₁₇ and C ₁₀ H ₂₁ (2 : 1)	Alamine 336
C ₈ H ₁₇ (mixture of isomers)	Alamine 308
C ₈ H ₁₇ (2-ethylhexyl)	TEHA
C ₁₀ H ₂₁ (mixture of isomers)	Alamine 310
C ₁₂ H ₂₅	Alamine 304

Quaternary amines (NR ₃ R'X)		
R	C ₈ H ₁₇ and C ₁₀ H ₂₁ (2 : 1)	Aliquat 336
R'	CH ₃	
X	Counter-ion	Cl ⁻

Phosphoric acid esters and phosphine oxides			
	R	O-n-C ₄ H ₉	TBP
	R	C ₈ H ₁₇	TOPO

Ketones and ethers			
	R	Me	MIBK
	R'	i-C ₄ H ₉	
	R = R'	i-C ₄ H ₉	DIKB
			DBC

Designing organic reagents to relinquish high selectivity of extraction of metalate anions is challenging because the extractants don't enter the inner coordination sphere and consequently it's unimaginable to use a metal's preference for a selected coordination geometry or donor atom type. As transfer of a metalate anion into a non-polar, water-immiscible, solvent requires removal of most or whole hydration sphere, it's generally tougher to extract small, highly charged, anions. This phenomenon is well documented and has been spoken because the Hofmeister bias because it's associated with the Hofmeister Series that was established in 1888 to rank the efficacy of inorganic anions within the coagulation of proteins.³¹

Solvent extraction processes to separate metalate anions on the premise of their charge are easier to implement in practice when the metals are kinetically inert because they are doing not lose coordinated anions to get lower charged, more readily extractable species during the contact time in a very mixer settler. An example is that the use of tri-n-butylphosphate (TBP, Table 5) to recover Pt(IV) selectively as its dianion PtCl₆²⁻ from acidic chloride streams which contain Ir(III) and Rh(III) as their trianions IrCl₆³⁻ and RhCl₆³⁻. In these processes, it's important to take care of the oxidation potential of the feed solution²² to confirm that the Ir(III) isn't converted to the more readily extracted Ir(IV) complex, IrCl₆²⁻. Hydrophobic amines (Table 5) are very efficient extractants for PGM chloridometalates, but their high

basicity makes it tougher to strip the loaded solution; this latter process is in the midst of the irreversible formation of inner sphere complexes as in eqn (9).

Formation of such inner sphere complexes is a smaller amount of an issue when tertiary amines of the Alamine type (Table 5) are used as extractants, presumably as a consequence of steric hindrance.²² rather more weakly basic alkyl amides are used for the extraction of Pt(IV) from acidic chloride streams and have the advantage of being way more readily stripped. Tertiary amines within the Alamine® series, particularly Alamine 336, are shown to be useful within the separation and extraction of uranium as $(R_3NH)_4UO_2(SO_4)_3$ from sulfate leach solutions.^{20,32} This provides an alternate to standard uranium extraction from nitrate streams by tributyl phosphate (TBP) within the PUREX process, which is best described as neutral metal-salt extraction.



The Hofmeister bias underpins the efficient recovery of gold as its monoanion, $AuCl_4^-$, from mixed-metal chloride streams and several other of the reagents listed in Table 5 are utilized in gold recovery, including the triether dibutylcarbitol (DBC) which has been exploited by variety of Platinum Group Metal (PGM) refiners. Whilst this provides good separation from most of the valuable metals, it's not very selective over a number of the metalloid elements (see Fig. 10), particularly at high HCl concentrations, presumably because under these conditions other monoanionic chloridometalates are present.²² DBC and methylisobutyl ketone (MIBK, Table 5), which is employed extensively in gold recovery from chloride solutions, are fairly soluble in aqueous HCl solutions presenting problems of loss of reagent in continuous operations.

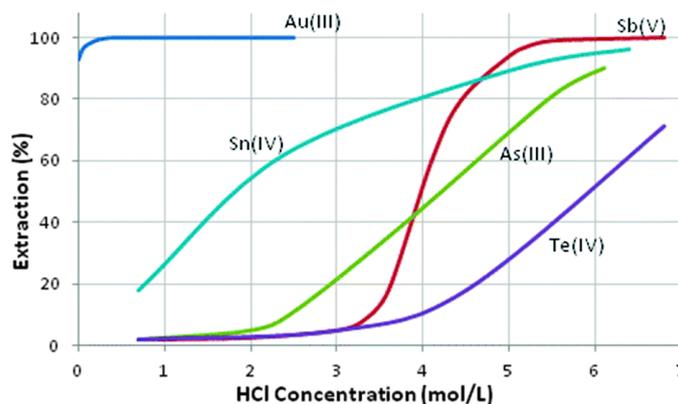
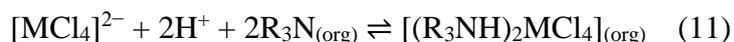


Fig. 10- Selectivity of gold extraction with dibutylcarbitol.²²

Because metalate extraction involves the transfer of preformed complexes from the aqueous phase, conventional (inner sphere) coordination chemistry doesn't play a component determining the selectivity of binding of the metalate anions to the organic cations within the assemblies (ion pairs) that form within the organic phase. However, the relative stability of the metalates formed initially within the aqueous phase does contribute to the distribution coefficients for extraction. This is often exploited to great effect within the separation of Co(II) from Ni(II) within the Outokumpu process.³³ Dissolution of a Co/Ni matte in chloride solutions generates CoCl_4^{2-} which is significantly more stable than its nickel analogue, NiCl_4^{2-} , and consequently a transparent separation may be effected using Alamine reagents because the process represented by eqn (10) and (11) is more favourable when $M = \text{Co}$.



In general, the structures of assemblies formed in commercial metalate extraction processes don't seem to be well understood. They involve electrostatic, hydrogen bonding, and other supramolecular interactions.¹² New kinds of metalate extractants are developed to use the concepts of anion recognition and might overcome the Hofmeister bias, providing the chance of opening up new flow sheets for metal recovery.¹² For instance, tris-2-ethylhexylamine (TEHA) could be a model for the trialkylamine reagents Alamine 330 etc., and shows the expected selectivity for FeCl_4^- over ZnCl_4^{2-} (Fig. 11). In contrast, the monoamido derivative L1 in Fig. 11 may be a much stronger extractant for Zn(II), requiring a lower concentration of chloride to effect 100% recovery of Zn(II) compared to Fe(III). Such a

reagent will allow the selective recovery of zinc from the oxidative chloride leaching of sulfidic ores or from pickling liquors from galvanising processes, both of which involve aqueous solutions with an far more than iron.

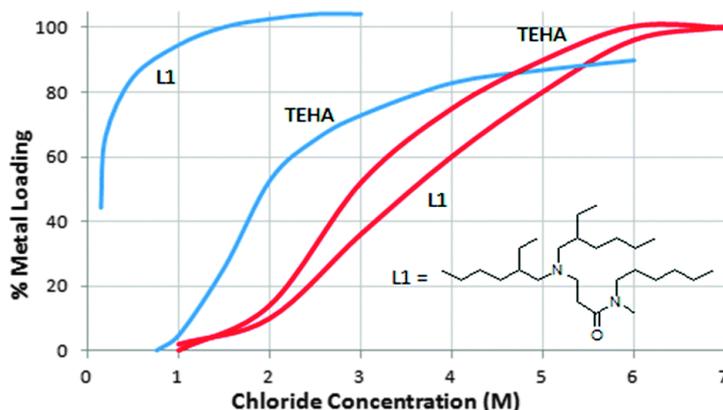


Fig. 11 Loadings of $[ZnCl_4]^{2-}$ (blue lines) and $[FeCl_4]^{2-}$ (red lines) by TEHA and a closely related monoamido derivative (L1) as a function of chloride concentration in the aqueous feed.

An alternative approach to the recovery of base metals from oxidative chloride leaching of sulfidic ores is to transfer the chloride salt to the water-immiscible phase, and is discussed within the following section.

Metal-salt extractants

These reagents transport the metal cation and its attendant anion(s) from solution as a salt, MX_y , (eqn (1)) and, because they seem to create the salt soluble within the water immiscible phase, they're frequently cited by metallurgists as "solvating extractants".³⁴ This historically useful terminology is misleading because the reagent usually doesn't merely interact with the outer sphere of a neutral metal salt, MX_y , to come up with a hydrophobic species but also functions as an inner-sphere ligand for metal, as within the CUPREX and PUREX processes described below.^{35,36}

Attention also has to be paid to the conditions under which the extractants listed in Tables 6 and 7§ are used. When contacted with highly acidic solutions of metal salts, the oxygen atom within the phosphate esters (e.g. TBP), the ketones (e.g. MIBK) or the phosphine oxides (e.g. Cyanex 923) will be protonated and therefore the resulting cations can form ion-pair

assemblies with metalate anions, transferring them to the water-immiscible phase by the mechanisms discussed above.

Table 6 The structures and common commercial names of some metal salt extractants§

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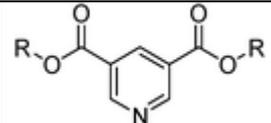
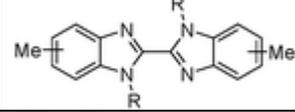
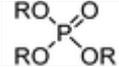
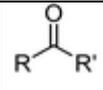
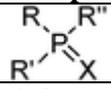
Substituents			Commercial name(s)
	R	C ₁₀ H ₂₁	Acorga CLX50
	R	COOC ₁₃ H ₂₇	Acorga ZNX50
	R	n-C ₄ H ₉	TBP
	R	Me	MIBK
	R'	i-C ₄ H ₉	
	R = R'	i-C ₄ H ₉	DIBK

Table 7. The structures and common commercial names of some phosphine oxide and phosphine sulfide extractants§ 11,37,38

Phosphine		
		
Substituents		Commercial name(s)
R = R' = R''	i-C ₄ H ₉	Cyanex 471
X	S	
R = R' = R''	CH ₃ (CH ₂) ₇	Cyanex 921, TOPO
X	O	
R = R' = R''	i-CH ₃ (CH ₂) ₇	Cyanex 925
X	O	
R = R' = R''	CH ₃ (CH ₂) ₅ and CH ₃ (CH ₂) ₇	Cyanex 923
X	O	

In the PUREX process, first developed for the recovery of plutonium and uranium as a part of the Manhattan Project, 10 two molecules of tri-n-butylphosphate (TBP, Table 6) bind to the uranyl cation within the equilibrium shown in eqn (12). This operates on a “nitrate-swing”

during which the loading and stripping are controlled by variation of the concentration of acid within the aqueous phase. Because it's a coffee viscosity and is fairly immune to radiation damage, TBP are often used because the diluent, (the water-immiscible phase), and consequently TBP molecules are present within the outer/solvation sphere.



The equatorial plane of the uranyl dication is defined by two bidentate nitrate ions and by two P O groups within the X-ray crystal structure shown in Fig. 12 of a model compound that contains the tri-iso-butyl analogue of TBP.³⁹

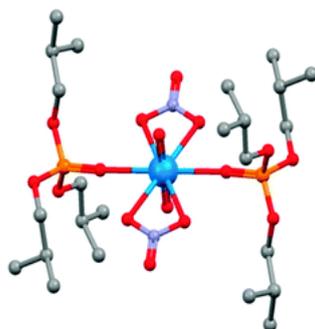
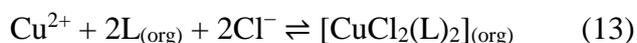


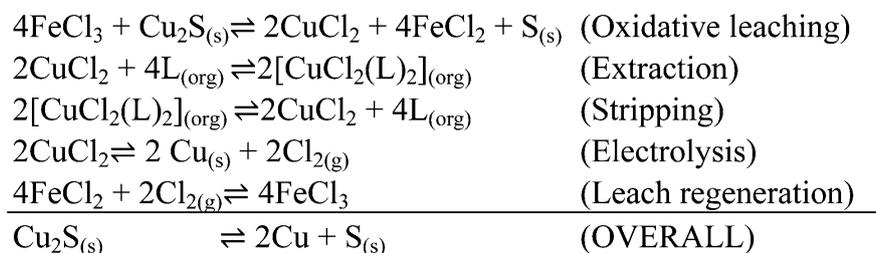
Fig. 12 The structure of $[\text{UO}_2(\text{NO}_3)_2(\text{iso-TBP})_2]$ from single crystal X-ray diffraction.³⁹

The CUPREX process was developed to recover copper from chloride solutions.³⁵ It uses a neutral ligand, didecyl pyridine-3,5-dicarboxylate, CLX50 (Table 6) to come up with the neutral, kerosene-soluble, four-coordinate copper complex $[\text{CuCl}_2(\text{L})_2]$ in line with the reaction in eqn (13). Variation of chloride concentration and temperature are wont to control copper loading and stripping.³⁵



The sequence of reactions shown in Scheme 4 makes it possible to process sulfidic ores by using oxidative chloride leaching that generates elemental sulfur. This avoids the formation of SO_2 and its recovery as vitriol, which are a consequence of smelting sulfide concentrates. The chlorine liberated within the electrolysis at the tip of the method is employed to regenerate the leachant by oxidising ferrous chloride, thus ensuring a wonderful overall materials balance.³⁵ an identical sequence of reactions may be used¹¹ within the recovery of

zinc using ZNX50, the bis-benzimidazole shown in Table 6, but during this case the extraction involves the formation of the dinuclear complex $[Zn_2Cl_4(L)_2]$.



Scheme 4 The equilibria and overall materials balance for the CUPREX process.³⁵

The trialkylphosphine oxide reagent, Cyanex 923 (Table 7), extracts La(III) and Sm(III) from acid solutions. Analysis of the distribution ratio data indicates that two molecules of Cyanex 923 are involved within the extracted species with the charge on the Ln(III) cations satisfied by the coordination of three nitrate anions.³⁸

The best understood metal salt reagents (as within the examples above) operate with reagent molecules being bound within the inner coordination sphere of the metal cation and with the counter anions acting as ligands or contact ion pairs. This mechanism doesn't work well for extraction of sulfate salts because sulfate may be a weak inner sphere ligand and is intrinsically difficult to move from a solution thanks to its high hydration energy. To beat these problems, some ditopic reagents are designed to convey separated ions pairs M^{2+} and SO_4^{2-} with the reagent providing appropriate binding sites for every. The ditopic reagent HNT (Fig. 13) could be a strong nickel sulfate extractant, operating in a very zwitterionic form with a trianionic binding site for Ni^{2+} provided by the three salicylaldiminate units and a tricationic site for the SO_4^{2-} provided by the protonated pendant amine groups. Nickel is stripped almost quantitatively by contacting the loaded organic phase with dilute oil of vitriol giving a 98% recovery during a circuit comprising two extraction and one stripping stage.⁴⁰ Commercial exploitation of this reagent for the recovery of nickel from pressure leaching of lateritic ores failed because the imine linkages are sensitive to hydrolysis under the acidic conditions preferred for stripping. Also, the reagent isn't sufficiently selective for sulfate over chloride to come up with an $NiSO_4$ electrolyte of the purity required to work a traditional sulfate electrowinning plant for nickel.⁴⁰

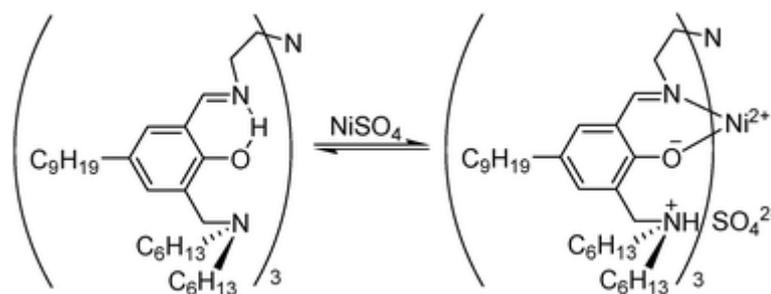


Fig. 13 Uptake of NiSO₄ by HNT to give a neutral complex [Ni(HNT)SO₄] containing a zwitterionic form of the ligand.

Synergistic and other extractants

In the metal-recovery processes discussed above, the modes of action of the extractants and therefore the coordination chemistry involved in forming charge-neutral assemblies are well defined. The processes involve the transport of either a metal cation, M²⁺, a metalate anion, MY_{xn}⁻, or a metal salt, MY_x, into the water-immiscible phase. A number of the extractants, e.g. phosphine oxides and trialkylphosphates in Tables 6 and 7, can perform quite one in every of these roles, transporting metalate anions after they are during a protonated form and metal salts after they are in their neutral form. However, a tactic frequently utilized in extractive hydrometallurgy to realize efficient separation and concentration of metals is to use mixtures of solvent extractants.⁴¹ Most of those synergistic systems rely upon the complementarity of reagents that show different modes of action to boost extraction.

Both the α -hydroxyoxime LIX 63 and therefore the neodecanoic acid, Versatic 10 are weak Ni extractants, requiring several stages of extraction with interstage pH-adjustment to recover Ni effectively from sulfate streams. In contrast, a mix of those reagents is far stronger, recovering Ni at a pH_{1/2} value quite two units below with the individual reagents.⁴² Normally, the origin of the synergism in blends of extractants isn't well defined. Within the case of the LIX63/Versatic 10, early work suggested that it had been the hydroxy-oxime which was deprotonated with the acid functioning as a neutral solvating extractant. More recently, on the idea of the structures of model systems, deprotonation of the Versatic acid to relinquish a push like [Ni(RCOO•LIX63)₂] is believed to be more likely.

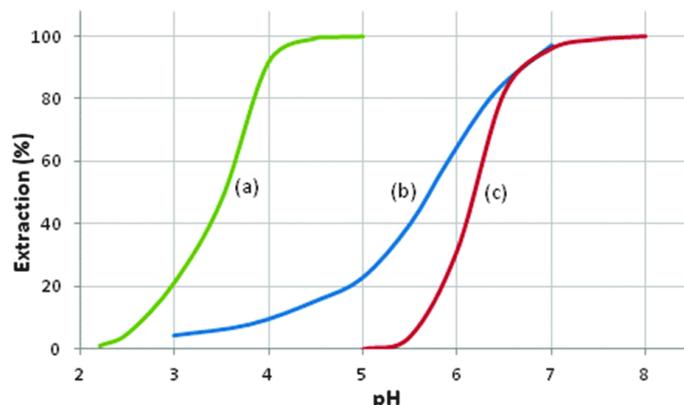


Fig. 14 The pH dependence of Ni-loading from a solution typifying a laterite pregnant leach solution by: (a) a blend of Versatic 10 and LIX 63; (b) Versatic 10; (c) LIX 63.⁴²

X-ray structure determinations of Ni(II) complexes formed by model carboxylic acids and α -hydroxyoximes that have aromatic or shorter aliphatic groups to boost the formation of crystalline forms, support structures during which it's the acid instead of the oxime that's deprotonated to balance the charge on the nickel dication (Fig. 15).⁴³ Inter-ligand chemical bonding generates meridional tridentate [NO₂]⁻ donor sets with 5- and 7-membered chelate rings resulting from the N–OH group of the oxime unit acting because the hydrogen bond donor to the uncoordinated oxygen atom of the carboxylate. The importance of such H-bonding interactions within the outer coordination spheres of metal complexes has been recognised and might be incorporated into ligand design to tune the strength and selectivity of extractants.¹²

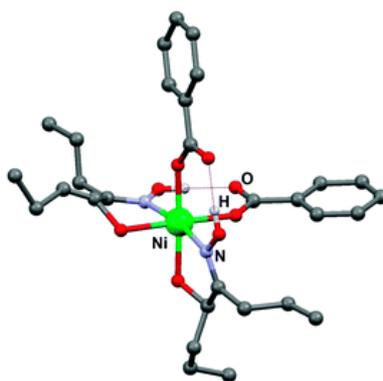


Fig. 15 Molecular structure of a Ni(II) complex containing a di-n-propyl analogue of LIX63 (R = CH₃CH₂CH₂-) and benzoic acid instead of Versatic acid from single crystal X-ray diffraction.⁴³

There are many samples of synergistic systems getting used within the extraction of f-block elements, particularly those involving phosphorus(V) acids.^{44,45} Light lanthanide elements

will be separated using blends of extractants like PC 88A, Cyanex 302 and D2EHPA, and while there's some information on the stoichiometries of the assemblies formed, their structures aren't still defined because the Ni(II) systems described above.⁴⁶

In some cases the principal role of the extractant isn't as a ligand but as a surfactant, stabilising reverse micelles within which the metal is found within the "water pool". Extraction of metalate anions by this mechanism is shown schematically in Fig. 16. Recent work on the extraction of lanthanides by malonamides provides important information on the composition and structures of the reverse micelles formed.⁴⁷ An understanding of the supramolecular chemistry involved in forming such large assemblies is vital to defining the origin of the chemical potential which favours the transfer of the metal-containing species from a regular aqueous phase into the water pool within the reverse micelle.⁴⁸

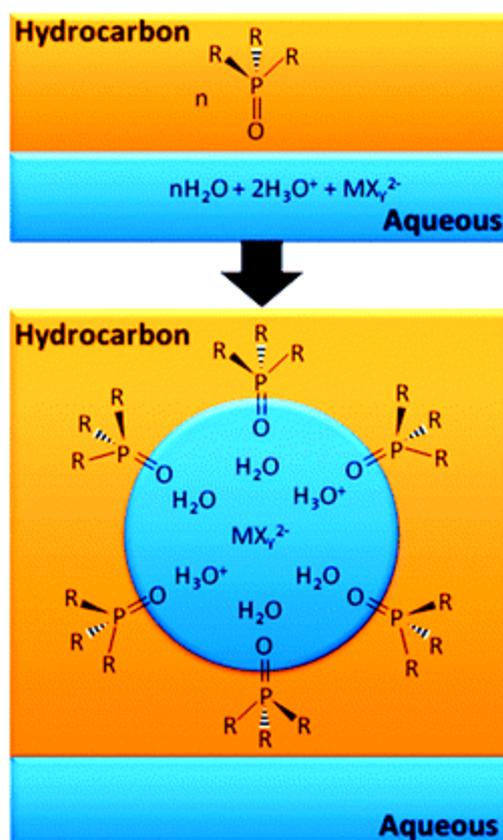


Fig. 16 Reverse micelle formation by protonated and neutral phosphine oxide extractants with a metalate anion in the acidic "water pool".⁴⁹

Conclusions

Solvent extraction of d- and f-block metals provides many examples where ligand design may be wont to great effect to attain the separation and concentration operations in extractive hydrometallurgy. This is often particularly true when the extractants operate within the inner coordination sphere of the metal ion, and high strength and selectivity of complex formation may be controlled by ensuring that the donor atom types and dispositions meet the wants of the targeted metal. It's also been recognised that interactions between ligands within the outer sphere may be accustomed to tune the strength and selectivity of extraction. The importance of those secondary bonding interactions arises because the water-immiscible solvents usually have very low polarities which favour formation of outer-sphere interactions such as hydrogen bonds. Indeed, when the extractants transport metalate anions, $MY_{x_n}^-$, the inner coordination sphere usually remains unchanged and it's only variations within the effectiveness of the secondary bonding which might make to selectivity and strength of recovery.

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