1. INTRODUCTION

1. 1. Precious Metals: Significance and Resources

Platinum, palladium, rhodium, iridium, osmium and ruthenium constitute the platinum group metals (PGM). They are rare elements, platinum is the most common with an abundance of about 10^{-6} %, whereas the others have abundances of the order of 10^{-7} % of the earth's crust. In all ores the "values" of PGM are in grams per ton. They occur in nature as metals, often as alloys such as osmiridium, and in arsenide, sulphide and other ores. PGM are commonly associated with major base metals as well as gold and silver. PGM together with gold and silver form the family of precious metals (1).

In the past few decades, precious metals have found new applications outside the jewellery and decorative industries due to its excellent physical and chemical properties. In this sense, precious metals have become widely used in many technological fields such as: automotive catalytic converters, catalysis in the chemical and petroleum refining industries, electronics, glass industry, medical sciences, etc. Therefore, at present there are available important sources of precious metals based on scrap materials, named secondary sources, besides natural ores which constitute primary sources. In particular, obsolete electronic scraps and spent automotive converters constitute a significant portion of precious metals secondary sources (2). Specifically, the use of platinum, palladium and rhodium in the catalytic converters of automobiles in order to ensure a significant reduction in the level of hydrocarbons emitted by automotive exhausts, is a very important supply of precious metals stem from scrapped vehicles where the PGM concentrations in these catalysts are in general, higher than those of the richest ore bodies (3). In 1994 a substantial share of world demand for Pt(35%), Pd(15%) and Rh(91%) was used for the autocatalyst production, and by the year 2000 the total quantity of catalyst substrate available for recycling is estimated in Europe at 3500-40000 tones per year (4).

Despite the increasing significance of precious metals secondary sources, the bulk of the production still originates from primary sources. The most important precious metals producing areas are placed in South Africa, Russia and Canada, and it is noteworthy that in all these cases the metals occur along with copper-nickel sulphides. What distinguishes each

deposit is its geological origin and its richness in terms of quantity and relative abundance of the various base and noble metals. South Africa is the only country among the major producers that mines PGM-bearing ores primarily for the recovery of these metals. In Russia and Canada, PGM are derived mainly as a by-product of the processing high grade copper/nickel ores, being the metals recovered from copper anode slimes (5). Copper anode slimes are obtained when copper anodes are dissolved in an electrolytic solution and the precious metals that these anodes contain as impurities, remain undissolved and form the so-called anode slimes.

The scarcity and growing demand of precious metals to be used in advanced technological applications makes imperative the development of procedures for their recovery from primary and secondary materials. Moreover, because the market values of precious metals is in many cases very high, their full recoveries to be re-used are justified from the economical view point.

Procedures for metal recovery may be broadly divided in pyrometallurgical and hydrometallurgical processes. Pyrometallurgical alternatives are usually applied to concentrated process steams and are based on operations involving high temperatures, such as roasting, smelting and converting. However, hydrometallurgical schemes deal with less concentrated process streams and consist of a combination of chemical unit processes such as, leaching, solvent extraction, precipitation and electrowining. Recently, due to depletion of high grade ore resources and environmental legislation, increasingly significant proportions of metals are obtained through hydrometallurgy (6). Nevertheless, in many cases both hydrometallurgy and pyrometallurgy, are employed and combined in the concentration and separation of precious metals. Precious metals recovery may be generally broken down into several main stages strongly dependent on the metal source such as, ore concentration by physicochemical techniques like flotation, smelting to produce a rich fraction in precious metals, leaching and final refining. Secondary precious metals production is complex in the sense that precious metals scraps and reverts come in an extremely wide range of tonnages, chemical compositions, physical forms and contained values, consequently smelting and refining facilities have to be particularly well equipped to handle this full and varied range of revert materials (5).

The present work concentrates in the final precious metals refining to produce the individual metals of the overall process.

1. 2. Precious Metals Recovery: Conventional and Alternative Routes

The conventional routes for the separation and recovery of precious metals consist of a series of very tedious selective dissolution-conditioning and precipitation steps, generally insufficient in terms of degree of separation because of the similarity in properties of these metals, leading to such phenomena as coprecipitation. Moreover, the multiples precipitation and redissolution steps to provide the desired product purity, with the consequent wash streams, involve increased recycle and retreatment. Owing to the long time needed to complete the whole process, considerable amounts of precious metals in the plant are "lock up", which in turn, places an economic constraint on the process (7).

To overcome these problems and replace the traditional routes, intensive research and development to meet new challenges has been done. Among the modern separation technologies which emerged, solvent extraction has been proved to be one of the most powerful separation method for metal recovery and in recent years was incorporated in the flowsheets of the major refining companies. In hydrometallurgy, solvent extraction is a separation and recovery technique where the metal of interest is extracted from an aqueous solution into an immiscible organic phase, by means of an extracting reagent. To understand precious metals solvent extraction schemes, it is firstly necessary to outline some of the fundamental chemistry of the precious metals as well as the extraction mechanisms of the extracting reagents.

1. 3. Fundamental Chemistry of Precious Metals

Precious metals are noble metals and, as such, can be dissolved only with great difficulty. It is possible to attempt the total dissolution of the precious metals by the most powerful oxidants. Strong oxidizing conditions in the industry for solubilization of PGM feedstocks consists of *aqua-regia* treatment. *Aqua-regia* leaching is slowly being phased out in preference for the more efficient wet chlorination technique in which the leaching agent is hydrochloric acid, with the addition of chlorine to increase the solution oxidation potential.

The HCl/H$_2$O$_2$ lixiviant combination is a common variant (8). Therefore, we need to consider separation schemes in chloride media.

Precious metals exhibit a wide variety of oxidation states and coordination complexes as shown in Table 1 (9-11).

The precious metals complexes formed vary considerably with the oxidation state. Whereas the majority of precious metals form full chlorocomplexes, the trivalent metals form mixtures of chloroaquo species in equilibrium with each other very dependent on the total chloride concentration. In addition to this, the basic chemistry of some of these elements has not been fully investigated under the conditions in the leach solutions.

Chlorospecies of precious metals, in general terms, have slow kinetics compared with base metals but there is a still a wide variation between the different precious metals and oxidation states. The metal extraction rates depend on various factors such as electronic configuration, stereochemistry and stability of the oxidation state among others; several general rules to predict qualitative extraction rates have been established (12, 13). Cox (7) determined that the rates of substitution of precious metal ions follow the order: Au(I), Ag(I) >>Pd(II) >Au(III) >Pt(II) >Ru(III) >>Rh(III) >Ir(III) >Os(III) >>Ir(IV), Pt(IV), with the states from Rh(III) being termed inert. On the other hand, Grant (11) determined semi-quantitative values of relative substitution kinetics of the precious metals which are summarized in Table 1, and in general terms are in good agreement with the data contributed by Cox.

Silver is stable in the univalent state, gold is stable both in the uni- and trivalent state, and the redox equilibria among them is simpler than PGM. On the other hand, PGM may exist in the divalent to octavalent state and the change in the oxidation state is complicated. The redox behavior of the precious metals is exposed in Table 2, where it can be seen that the stability of the higher oxidation states tends to decrease as one moves across the Periodic Table from left to right, whereas they increase in going from the second to the third row (11).

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TABLE 1. Precious metal oxidation states and chlorocomplexes

(Data exposed in this Table is from Ref. 9 except: *Complexes Formed*, Refs. 10 and 11, and *Relative Substitution Kinetics*, Ref. 11)

Metal	Electronic Config.	Co-ord. Number	Ionic Structure	Complexes Formed low ⟵ [Cl⁻] ⟶ high			Relative Subst. Kinetics (*)
Au(III)	d^8	4	Sq. Pl.	$AuCl_4^-$		$AuCl_4^-$	10^1-10^{-1}
Ag(I)	d^{10}	2	Linear	$AgCl_2^-$		$AgCl_4^{-3}$	10^4-10^6
Ru(III)	d^5	6	Oct.	$RuCl_3(H_2O)_3$		$RuCl_6^{-3}$	10^{-3}-10^{-4}
Ru(IV)	d^4	6	Oct.	$Ru_2OCl_8(H_2O)_2^{-2}$		$RuCl_6^{-2}$	10^{-5}-10^{-6}
Rh(III)	d^6	6	Oct.	$RhCl_4(H_2O)_2^-$	$RhCl_5(H_2O)^{-2}$	$RhCl_6^{-3}$	10^{-3}-10^{-4}
Pd(II)	d^8	4	Sq. Pl.	$PdCl_4^{-2}$		$PdCl_4^{-2}$	1
Pd(IV)	d^6	8	Oct.	$PdCl_6^{-2}$		$PdCl_6^{-2}$	-
Os(III)	d^5	6	Oct.	$OsCl_4(H_2O)_2^-$	$OsCl_5(H_2O)^{-2}$	$OsCl_6^{-3}$	10^{-7}-10^{-9}
Os(IV)	d^4	6	Oct.	$OsCl_6^{-2}$		$OsCl_6^{-2}$	10^{-10}-10^{-12}
Ir(III)	d^6	6	Oct.	$IrCl_4(H_2O)_2^-$	$IrCl_5(H_2O)^{-2}$	$IrCl_6^{-3}$	10^{-4}-10^{-6}
Ir(IV)	d^5	6	Oct.	$IrCl_6^{-2}$		$IrCl_6^{-2}$	10^{-8}-10^{-10}
Pt(II)	d^8	4	Sq. Pl.	$PtCl_4^{-2}$		$PtCl_4^{-2}$	10^{-3}-10^{-5}
Pt(IV)	d^6	8	Oct.	$PtCl_6^{-2}$		$PtCl_6^{-2}$	10^{-10}-10^{-12}

It should be noted that both Os and Ru can exist in the +8 oxidation state
ABBREVIATIONS. **Sq. Pl.** Square Planar and **Oct.** Octahedral
(*) Relative substitution kinetics data considering a value of 1 for Pd

TABLE 2. Redox behaviour of precious metals in acidic chloride media (11)

Elements situation as in the Periodic Table. Standard reduction potentials are given in V

Ru(VIII)/Ru(IV)/Ru(III)	Rh(IV)/Rh(III)	Pd(IV)/Pd(II)	Ag
$E°>1.4$ $E°=0.83$	$E°>1.4$	$E°=1.29$	-
Os(VIII)/Os(IV)/Os(III)	Ir(IV)/Ir(III)	Pt(IV)/Pt(II)	Au(III)/Au(I)
$E°=1.0$ $E°=0.42$	$E°=0.96$	$E°=0.74$	$E°=0.93$

Generally, in precious metals extraction kinetic factors tend to be very important, and reactions that should be possible from thermodynamic considerations are less successful as a result. Solvent extraction processes for precious metals recovery must cope with a wide range of complexes in different oxidation states, which vary, often in a poorly known manner, both kinetic and thermodynamic stability (7).

1. 4. Solvent Extraction Mechanisms

Nowadays, there are available a great number of commercial extractants for solvent extraction and related technologies and also there is an important deal of effort to produce new reagents. The extractant role in metal extraction is to form metallic lipophile complexes which can be transferred from the aqueous feed to the organic phase through a chemical interaction.

Several extraction mechanisms can be enumerated.

- Anion Exchange

Basic extractants (B) are organic reagents that can easily form a salt in the organic phase while in contact with an aqueous acid solution (HX):

$$B_{org} + HX_{aq} \Leftrightarrow BH^+X^-_{org} \tag{1}$$

where the subindexes "org" and "aq" denote the organic phase and the aqueous phase respectively. Then, contacting the organic phase with an aqueous solution containing anionic metal species, $MX_n^{-(n-m)}$ (n>m), anion exchange occur as follows:

$$(n-m)\,BH^+X^-_{org} + MX_n^{-(n-m)}{}_{aq} \Leftrightarrow (BH^+_{(n-m)}MX_n^{-(n-m)})_{org} + (n-m)X^-_{aq} \tag{2}$$
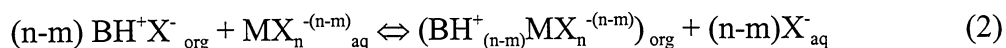
Thus, the amine salt should be considered as being the extracting reagent and not the free amine.

High-molecular weight amines and quaternary ammonium halides are basic extractants currently used in commercial solvent extraction processing.

- Cation Exchange

Organic acids (HL) can extract metallic cations (M^{+m}) according to the reaction:

$$mHL_{org} + M^{+m}_{aq} \Leftrightarrow ML_{m\ org} + mH^+_{aq} \qquad (3)$$
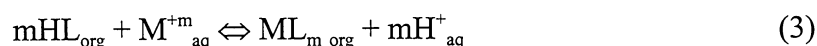
The above equation describes a cation exchange reaction wherein hydrogen ions are exchanged for the metal cation. Extractants which have been found useful extracting metals by this mechanism are, organic derivatives of phosphorous acids, monocarboxylic acids and sulphonic acids among others.

- Chelation

This mechanism is performed by acidic extractants that possess donor groups capable of forming bidentate complexes with metal ions. The equilibrium chemical reaction describing the metal extraction is the same as that reported for cation exchange systems. Examples of chelating reagents are hydroxyoximes, derivatives of 8-hydroxyquinoleine and β-diketones.

- Solvatation

Solvating or neutral extractants (S) possess only donor groups that do not contain dissociating protons, and because no anionic or cationic groups are available in the molecule, the metal species are extracted from the aqueous phase as neutral complexes and the neutralizing ion is a water soluble negatively charged ligand (X^-). The extraction reaction can be written as:

$$yS_{org} + M^{+m}_{aq} + mX^-_{aq} \Leftrightarrow MX_mS_{y\ org} \qquad (4)$$
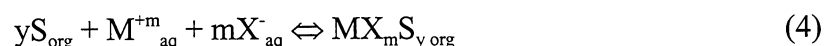
As solvating extractants can be mentioned organic reagents containing oxygen bonded to carbon, such as ethers, esters, alcohols and ketones and those containing oxygen or sulphur bonded to phosphorous as phosphoric esters, phosphine oxides and phosphine sulphides.

1. 5. Modern Refining of Precious Metals involving Solvent Extraction

The introduction of solvent extraction has led to the development of new processes for the recovery of precious metals.

Nowadays, three major refineries: International Nickel (INCO) and Matthey-Rustenburg Refiners (MRR) in the United Kingdom and Lonrho in South Africa, are operating with flowsheets based in extensive usage of solvent extraction to achieve precious metals separation. However, it should be point out that for obvious reasons these industrial processes are not known in full detail and in some occasions there is not agreement among the authors. Taking into account several flowsheets published and in spite of the complexity of the mentioned three commercial flowsheets, not shown here, a number of common features between them can be found (7, 10, 11, 14).

Because gold and silver can be easily separated from the remaining precious metals, they tend to be removed at an early stage. All procedures use chloride leaching that leaves silver in the residue which is the first metal removed. Gold can be separated by a solvating reagent, though in the Lonrho refining flowsheet gold is recovered via reductive precipitation with SO_2. Palladium and platinum are recovered by means of solvent extraction in all cases. Palladium is selectively extracted before platinum by using extractants containing sulphur or hydroxyoximes, and then tributyilphosphate (TBP) or an amine is employed to recover platinum. In the past, both palladium and platinum were co-extracted in the Lornho process, but at present these elements are no longer co-extracted.

Ruthenium and osmium have a very complex aqueous chemistry and are removed usually by distillation of the tetroxides MO_4, however there is one procedure for ruthenium recovery by means of solvent extraction which is employed in the Lonrho process.

Iridium and rhodium are left in the aqueous raffinate after platinum and palladium extraction. Whereas iridium can be extracted in the +IV oxidation state by amines or TBP, rhodium is recovered through ion exchange. In the case of the INCO process, iridium and rhodium are both recovered by means of precipitation.

The flowsheet of these processes were compared by Flett (14) in 1982. An updated comparison between them is presented in Table 3.

Other recovery schemes have been reported or patented. Dhara (12) proposed a total refining scheme for PGM based on the use of amines. Warshawsky has also reported an integrated ion exchange and liquid-liquid extraction process for precious metals using PGM-selective polyisothiourea (PITU) resins and liquid-liquid extraction with tertiary amines (10).

TABLE 3. Updated comparison between Lonrho, MRR and INCO processes

	Lonrho	MRR	INCO
Au	PP	SX (MIBK)	SX (DBC)
Ag	PP	PP	PP
Pd	SX (DHS)	SX (Om)	SX (DOS)
Pt	SX (TBP or Am)	SX (Am)	SX (TBP)
Rh	IX	IX	PP
Ir	SX (TBP)	SX (Am)	PP
Os	Dt	Dt	Dt
Ru	SX (TBP or Am)	Dt	Dt

NOMENCLATURE. Separation Techniques: **Dt** distillation, **IX** ion exchange, **PP** precipitation, **SX** solvent extraction. Extractants: **Am** Amine, **DBC** dibutylcarbitol, **DOS** di-n-octyl sulphide, **DHS** dihexyl sulphide, **MIBK** methylisobutylketone, **Om** hydroxyoxime and **TBP** tributyl phosphate.

From the analysis of the flowsheets discussed, there is no doubt that solvent extraction and in less extent, ion exchange, at present are well established in the refining of precious metals. It is easily anticipated that development of improved extractants and resins may be readily adopted by the refineries (10).

1. 6. Metal Separation Techniques

In this section, separation methods for metal recovery more or less related to solvent extraction science: liquid-liquid extraction, solid-liquid extraction, liquid membranes and two-phase aqueous-aqueous extraction are described, giving special attention to the methodologies used in this work. Some of these techniques have industrial application and other are considered as emerging technologies. Although separation methodologies will be reviewed from the hydrometallurgical point of view, it is important to emphasize that most of them may found application in a great variety of areas such as, preconcentration and separation of

chemical species in analytical chemistry, processing related to nuclear energy, production of organic and inorganic compounds, fuel industry, petrochemistry, biotechnology, pharmaceutical and food industries, along with environmental needs deriving from these industries.

1. 6. 1. Solvent Extraction

Solvent extraction, also named liquid-liquid extraction, involves the distribution of different components between two immiscible phases, aqueous and organic, usually with chemical reaction. The organic phase is a solution containing a lipophilic extractant which forms complexes with the metal ions existing in the aqueous solution. Solvent extraction owes its origins to analytical chemistry in which dilute aqueous solutions may be concentrated using an extractant reagent (15). The industrial application of solvent extraction was pioneered in the 1940s by the nuclear field, specially for the recovery of uranium and plutonium from spent nuclear fuel (16). Nowadays, industrial applications of liquid-liquid extraction are extensive. In hydrometallurgy, solvent extraction is a widely used and well-established process for the recovery of metals such as transition elements, actinides and precious metals (17).

In the extraction step of a solvent extraction process, the metal ions are transferred to the organic phase by complex formation with the extractant. The reaction is reversible, therefore by chanching the chemical conditions the metal transfer from the organic phase to the aqueous phase can be attained, constituting the stripping step.

Concerning industrial solvent extraction units there are many types of extractors available. Liquid-liquid extraction operations can include both batch and continuous operating approaches. For batch processing the equipment is just a stirred tank, whereas devices such as mixer-settlers, columns and centrifugal contactors are utilized for continuous operation (18).

One of the most significant advantages of solvent extraction is that the specific complexation between the extractant and different metal ions, provides the difference in extractability which permits the selective separation of the metals. Nevertheless, in spite of the positive aspects, there are still some inherent drawbacks in solvent extraction systems: lower ability for enrichment, generally the volume ratio between an organic phase and an aqueous

phase can not be very large in order to prevent solvent loss, and difficulty in phase separation (19).

1. 6. 2. Liquid Membranes

Liquid membranes permeation simultaneously combines both extraction and stripping steps in a single process, constituting a potential alternative to conventional liquid-liquid extraction.

The principle of a liquid membrane process is that the organic phase is reduced to a film separating the two aqueous phases which correspond to the feed and strip solutions in the extraction process. The coupling of the extraction and stripping steps results in the continuous transport of the metal ions through the membrane. In a liquid membrane, metal transport is governed by kinetics parameters rather than chemical equilibrium between the phases.

Two kinds of liquid membranes are commonly used: liquid surfactant membranes (LSM) and supported liquid membranes (SLM). Each contains and extraction reagent incorporated into the organic phase to act as the carrier for the metal ions (6, 20).

- Liquid Surfactant Membranes (LSM)

LSM is a three-phase process. It consists in the creation of an organic membrane film by making a stabilized water-in-oil emulsion with the strip liquor and organic phase and then suspending this stabilized emulsion in the feed solution. Metal complexes are formed at the organic-feed interface and due to the thinness of the membrane, they permeate very rapidly to the interface organic-strip where decompose causing metal enrichment in the stripping phase. There are some inconveniences in the application of this technology, for example the need for intermittent breakdown and reforming of the membrane to recover the stripping phase once is fully loaded, and the differences in ionic strength between the feed and strip solutions on either side of the membrane can lead to swelling due to osmotic diffusion of water.

Although the unsuitability of LSM, in Austria this technology was used to recover valuable metals from industrial waste waters (21).

- Supported Liquid Membranes (SLM)

SLM offer a more convenient configuration consisting of a thin layer microporous polymer film in which the organic phase is adsorbed. This membrane separates the feed from the strip solution. As the carrier is immobilized, solutions can be continuously fed and withdrawn. SLM are generally thicker than LSM resulting in lower metal fluxes, and with flat sheets the size of the feed and strip interfaces are the same. However, generally it is easier to control the ionic strength of the aqueous phases in SLM thereby reducing water transport and, unlike LSM, breakdown of the membrane is less likely to occur. Furthermore the SLM configuration allows easy scale-up as performance is directly related to the membrane area. Similarly to LSM, the mechanism of the mass transfer consists in the formation of a solute carrier complex in the aqueous-membrane interface which diffuses across the membrane to the other side where it decomposes to form the solute and regenerate the carrier.

In the laboratory, SLM experiments are usually carried out in a two-compartment membrane cell provided of agitation where a flat-sheet membrane is sandwiched between the two compartments. For industrial purposes, a planar geometry is not very effective since the ratio of surface area to volume is too low. Hollow fiber modules may be used to supply high surface area. A set of few hundred hollow fibers are used in a standard module and the organic carrier solution is held within the pores of the membrane cell. The source and receiving phases are in and outside the hollow fibers, respectively or vice versa (22, 23).

SLM are receiving a lot of attention in the past years, even more than LSM, and despite of still there are not industrial applications of SLM, the importance of this technique is demonstrate by the fact that pilot plant studies in the hydrometallurgical field are going-on.

The advantages of SLM over other separation techniques are listed as follows: 1) combination of the processes of extraction, stripping and regeneration into a single stage with the possibility of achieve high enrichment and separation factors, 2) small amount of organic phase is necessary, hence the usage of solvent and extractant is considerably reduced, it is outstanding from the environmental point of view since many chemicals used in metal recovery are toxic, moreover very expensive reagents can be employed and 3) low capital and operating cost as well as energy consumption.

Concerning the handicaps in the use of SLM we can enumerate: 1) absence of a scrubbing section and difficulties in multistaging processes, 2) loss of extractant by solubility in the adjacent aqueous solutions which may be magnified because of the small inventory of organic phase in the system, 3) progressive wettability of the support pores and 4) the production of deposits of reaction products could reduce flux by blinding the membrane.

1. 6. 3. Solid-Liquid Extraction

Solid-liquid and liquid-liquid extraction involve similar chemical principles but differ in technological aspects. In solid-liquid extraction te solid or resin phase plays the role as the organic phase in solvent extraction processes.

Various types of resins can be distinguished for solid-liquid techniques.

- Ion-Exchange and Chelating Resins

Processes based on ion-exchange resins consist in the exchange of metal ions present in an aqueous solution with the counter-ions of insoluble polymers containing fixed anionic or cationic groups. Ion exchange resins allow the use of simple equipment, easy phase separation and they not suffer problems of reagent losses and phase disengagement compared with solvent extraction. However, ion exchange technology shows lower mass transfer rates, needs large size equipment and longer process time. Moreover, conventional ion-exchange resins containing groups such as sulphonic or carboxylic acids, have limited potential for use in the recovery of metals because of their low selectivity (6).

Chelating resins are polymers with covalently bound chains containing groups that are able to form complexes with specific metal ions, and may overcome the problem of low selectivity associated to conventional ion-exchange resins and consequently encourage the application of ion-exchange to a broader range of process solutions (24). Despite the high selectivity of these resins, their very complicated methods of synthesis as well as their high cost have limited its application in separation processes on a technological scale (25).

- Impregnated Resins

Taking into account the limitations exposed in the previous section and the recent advances in the synthesis of new organic reagents for solvent extraction, the development of impregnated resins as a link between solvent extraction and ion-exchange processes has been an important field of development in separation science. Impregnated resins have been proved suitable for many technological fields, nevertheless industrial applications are only found in the nuclear industry (25).

The introduction of impregnated resins into extraction and recovery processes dates back to the work done in the 1970s by Warshawsky (26), Grinstead (27) and Kroebel and Meyer (28). Impregnated resins are based on the idea of adsorbing an organic solvent extraction reagent onto a polymeric support. There are two kinds of impregnated resins depending upon the methods of preparation: extractant-impregnated resins and Levextrel resins. The first approach is based on physical adsorption of an extractant onto a high-surface macro-porous polymer bead by soaking the polymeric resin in a diluent containing the extractant. The second approach employs in-situ incorporation of the extractant during the resin copolymerization process and the extractant is retained in the resin structure rather than by chemical bonding. Although numerous extractants are available for the preparation of impregnated resins, only some reagents such as liquid phosphoric esters, aliphatic amines, and aliphatic and aromatic oximes have appropriate characteristics to be used in Levextrel resin synthesis, and at the present Levextrel resins are limited to phosphoryl compounds (25).

The are several preparation methods for producing efficient extractant-impregnated resins, from now referred just as impregnated resins. One of the most simple method is the dry impregnation method, in which the extractant is adsorbed directly to the macroporous support after contacting a solution of the extractant with the polymer and subsequent evaporation of the organic solvent. The immobilization or impregnation of the reagent on the hydrophobic internal surface of macroporous nonionic resins seems to be due to a mechanism of adsorption involving Van der Waals forces between alkyl chains and/or aromatic rings of most ligands and those of the resin backbone, thus the extractant keeps its solvent extraction properties after the impregnation process.

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Impregnated resins maintain the advantages of ion-exchange technology, but they may have associate problems such as reagent losses, having a negative effect on the lifetime of the the resin and slow rate process.

- Impregnated Resins combined with Fluidized Bed

The application of impregnated resins in industrial processes and commercial scale can present some difficulties in solids handling, continuous operation, process control and number of required units. Hence, it seems suitable to combine this type of metal extraction with fluidized bed technology. Is then possible to carry out the required operations such as solvent-extractant mixing, metal extraction and metal stripping in a single unit. Furthermore it allows continuous work and good control of the system. The combination of impregnated resins and fluidization can improve the extraction of metals with respect to present technologies such as fixed bed and fluidized beds of ion-exchange resins, microfiltration with membranes, electrolysis and liquid-liquid extraction systems. This is attributed to different facts: 1) better selectivity of impregnated resins than with ion-exchange resins, 2) impregnated resins have not unstability problems, often found in membranes, and fluidization technology can work with flow-rates higher than those found in microfiltration processes, 3) energy contribution is lower than that required in electrolysis and saturation of the electrodes is avoided in this system, and finally 4) there are no extractant losses, neither difficulties in the phase separation and volumes are much lower than those used in liquid-liquid extraction (29). Some disadvantages of these systems should be mentioned: particles can be drag by the liquid and consequently a recovery system may be needed, and due to the continuous movement inside the bed and the collisions among the resin particles, some of them may experience erosion and breaking phenomena.

1. 6. 4. Two-Phase Aqueous-Aqueous Extraction

Cloud point extraction is a water based separation method which utilizes coacervation characteristics of some class of nonionic surfactants. Since cloud point involves two aqueous phases, may be classified as a two-phase aqueous-aqueous extraction procedure. Cloud point extraction has been found to be applicable for separating numerous organic compounds (30,

31, 32), however the research related to cloud point extraction in metal separation is rather limited (33, 34).

Aqueous solutions of nonionic surfactants become cloudy at well-defined temperature; this temperature is referred as the cloud point (CP). If the solution is heated above its CP, the solution may separate into two phases: a phase containing the surfactant in high concentration, which is also named coacervate phase or surfactant rich-phase, and a dilute phase with a low concentration of surfactant which can be very low but generally is above the critical micelle concentration (cmc). Since the CP is a critical point, the difference in concentration in the coacervate and dilute phases increases as the solution temperature increases above the CP, i.e., exactly at the cloud point, the two phases have identical compositions (30).

CP extraction utilizes the two phases as a separation field in a similar manner to solvent extraction: when a nonionic surfactant is added into an aqueous solution containing a solute and the resulting solution is subject to phase-separation by heating, the solute is partitioned between the two phases according its affinity to the surfactant (34). After equilibration, the two phases may be separated in a phase splitter completing the separation. If the dilute phase contains solute and surfactant in low enough concentrations, it can be recycled to the process or emitted to the environment. The solute can be recovered from the coacervate phase. If multiple contacting units are necessary, the process can be run continuously as with traditional liquid-liquid extraction (30).

It is considered that advantages of CP extaction are: 1) no organic solvents are required, 2) the surfactants employed are nontoxic and nonvolatile, 3) cost saving from requiring a relatively small amount of surfactant and 4) high ability to concentrate a variety of solutes.

As negative point can be mentioned the fact that because the driving force for the phase separation depends on the solution temperature, in the case of working over ambient temperature the process might become not economically viable due to energy consumption.

1.7. Extractants employed in this Work

1.7.1. Amines

High molecular weight organic amines have been widely used, since the second world war, as liquid ion-exchangers in analytical chemistry, in hydrometallurgy, in the nuclear industry, etc. Nevertheless, amines are still attracting interest (35).

The main aspect of metal extraction by amines lies in their selectivity towards anionic metal complexes rather than towards simple anions. Thus, the extractability of the anionic species depends upon the aqueous phase conditions more than on the differences in the specific affinities of anions for the bulky alkyl cation. As far as this factor is concerned, the extractions by all these reagents are similar in general aspects, and closely parallel to the aqueous conditions affecting the sorption of anionic complexes on anion exchange resins.

In the case of primary, secondary and tertiary amines, the extraction is considered to take place by the formation of an ammonium salt which may undergo, under proper experimental conditions, an anion exchange reaction with metal anionic complexes. In contrast, quaternary amines do not require protonation before they can react.

The interaction of amine salts and quaternary ammonium ions with metal anionic complexes is mainly electrostatic; thus, as the degree of extraction is due to the extent of ion-pair formation, selectivity will depend on charge, ion size, and extent of complex formation in the aqueous phase. Selectivity is generally achieved by varying the ligand concentration in the aqueous phase. Numerous studies on the extractability of metal chlorides from hydrochloric acid indicate a similar order of metal extraction irrespective of the amine class. However, quaternary amines are usually better extractants of metal chlorides than are tertiary amines, and these are better than secondary and primary amines. A notable exception to this rule is perhaps the extraction by bulky amines, where steric factors play a predominating role. Steric factors generally affect the basicity of amines, which in turn affects the stability and polarity of their salts. Another important factor influencing the extraction of metals by amines is the aggregation of the amine in the organic phase, which depend on the properties of the diluent and the nature of the ammonium cation and anion (36, 37).

Amine type extractants have been used in a great variety of solvent extraction applications, for example in the nuclear field (38), for Ni and Co recovery (39), extraction of

Zr anf Hf (40), recovery of Zn from galvanizing zinc ashes (41) and in the flowsheets for precious metals recovery previously discussed. Processes based on the usage of amines and solvent extraction for the extraction of precious metals have been proposed (10, 12) and recently amines have also been used to prepare impregnated resins (42) and as carriers in supported liquid membranes (43) focused on precious metals recovery.

One of the extractants used in this work is Alamine 336 which is an organic reagent with a great commercial acceptance for metal recovery schemes. Alamine 336 is a mixture of saturated and straight chain trialkylamines with carbon chains C_8 and C_{10}, in which the proportion of the carbon chain C_8 is about 2 to 1.

1.7.2. 8-Hydroxyquinoline Derivatives

8-Hydroxyquinoline also called oxine has the particular ability to form stable complexes with several metallic ions. The reactivity of oxines with a large number of metals is due to the formation of stable five-membered chelates through the replacement of the hydrogen from the acidic phenolic group and coordination to the nitrogen. This reaction is not selective but the reagent may become more selective by introduction of some groups in specific positions (36). Nevertheless recently, the unique property of 8-hydroxyquinoline derivatives to act as chelating agents and as anion exchange agents, when in protonated form, has been the key factor for the success of this extractants in solvent extraction systems (44).

Several hydroxyquinoline derivatives have been synthesized and used for metal extraction. Kelex 100 is the best known member of this family of extractants and is employed in this study. The main active component of Kelex 100 is 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline and its structure is shown in Figure 1 (45).
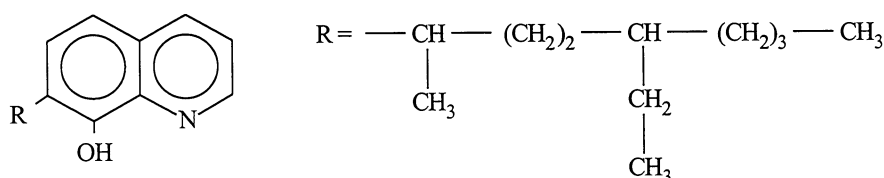

FIGURE 1. Detailed structure of Kelex 100

Initially, Kelex 100 had been developed specifically to compete with the hydroxyoxime group of extractants for Cu extraction (46), however commercial application of this extractant for this purpose was never materialized. Kelex 100 can extract a large number of metals: separation of Zn and Cd (47) and Co extraction (48) have been reported in the literature. Recently, research has been conducted in the area of solvent extraction of precious metals using 8-hydroxyquinoline derivatives (49-52). Supported liquid membranes containing Kelex 100 have also been developed for Rh separation (53).

1.7.3. Organothiophosphorous Acids

Prior to introduce organothiophosphorous extractants it is necessary to consider some features of acidic organophosphorous compounds. Organophosphorous acids group includes organic esters of phosphoric acids, phosphonic acids and phosphinic acids. Of these, the alkylphosphoric derivatives, especially di-2-ethylhexyl phosphoric acid (DEHPA), have proven to be the most versatile to date. One of the advantages of DEHPA is its versatility for the extraction of many metals, for example: Zn, U, V, Co, Ni and rare earths (54).

Whereas organophosphorous acid compounds have been extensively investigated, less in known about their analogues, where one or more oxygen atoms have been replaced by sulphur atoms. The dialkyl dithiophosphoric acids have also been found to be useful solvent extraction reagents and appear to occupy a position intermediate between the two types of reagents with respect to certain properties, and their study is of interest since although sulphur and oxygen atoms bear a small resemblance to each other, their tendencies for complex formation differ greatly. The presence of sulphur atoms is attractive because of the chemical properties they are expected to give the molecules, properties which can be predicted by Pearson's Hard and Soft Acids and Bases (HSAB) principle. In fact, soft metals are efficiently extracted by thiophosphorous extractants (55-57). Solvent extraction of Pd with didodecyl monothiophosphoric acid (58) as well as of Pt and Pd with bis(2,4,4-trimethylpentyl) phosphinodithioic acid (59) have been reported. Selective Pd recovery from industrial wastewater was achieved using liquid surfactant membranes prepared with di-(2-ethylhexyl) monothiophosphoric acid (MSP-8) (60). Although have not been applied to precious metals,

solvent impregnated resins containing dialkyldithiophosphoric acid on Amberlite XAD2 were successfully prepared and employed for Cu extraction (61).

In this work, di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) has been selected for palladium recovery.

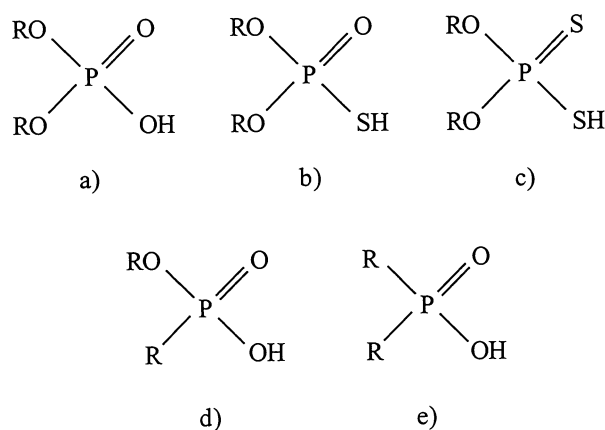In Figure 2, the structures of acidic organophosphorous and organothiophosphorous compounds are depicted.

FIGURE 2. Organophosphorous and organothiophosphorous compounds

a) alkyl phosphoric acid, b) alkyl thiophosphoric acid, c) alkyl dithiophosphoric acid, d) alkyl phosphonic acid and e) alkyl phosphinic acid. (R represents alkyl chains)

1.7.4. Neutral Polyethers

Neutral polyethers are carbon-bonded oxygen-donor extractants which can extract metals by solvatation. Crown-ethers are known to extract various metals, specially alkalines and alkaline earths (62, 63). In a similar manner as crown ethers, nonionic surfactants containing noncyclic polyoxyethylene chains may form metal complexes. With noncyclic polyethylene glycol and its derivatives, a number of studies have been made on the solvent extraction of alkaline and alkaline earth metals (64, 65), different divalent heavy metals (66) and Au (67).

The overall degree of water or oil solubility of nonionic surfactants may be varied by chanching the ratio of the hydrophilic and the hydrophobic portions of the molecule. The high

water solubility of the polyethylene oxide chain is due to hydrogen bonding between the solvent and the oxygen atoms in the chain. Since hydrogen bonding is a temperature-sensitive phenomenon, for each nonionic emulsifier molecule exists a temperature, the cloud point (CP), at which the degree of hydration of the hydrophilic portion is just insufficient to solubilize the remaining hydrocarbon fragment. Consequently, the emulsifier separates from the solution. Usually, for a given hydrophobic unit, a molecule with a large polyethylene oxide tail can exist in solution at higher temperature owing to a greater amount of hydrogen bonding than can a molecule with a shorter polyethylene oxide tail (68).

Several works have been conducted on the cloud point extraction of organic compounds (31-32), membrane proteins (69) and Zn (33) as well as Au (34), in which isooctylphenoxy polyethoxyethanol (Triton X Series) and polyoxyethylene nonyl phenyl ether (PONPE) were used as nonionic surfactants. In this work PONPE surfactants with different average chain lengths, are used for cloud point extraction of Au. The chemical structure of PONPE is presented in Figure 3. Since such nonionic surfactants have a number of electron-donating oxygen atoms in their molecules, high affinity to Au can be expected. Indeed, the strong affinity of PONPE to Au has been proved in solvent extraction (67), cloud point extraction (34) and micellar-enhanced ultrafiltration (70).
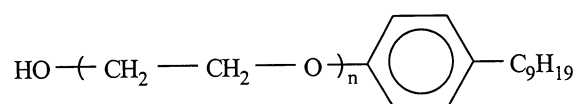
$$HO \text{---} (CH_2 \text{---} CH_2 \text{---} O)_n \text{---} \bigcirc \text{---} C_9H_{19}$$

FIGURE 3. Polyoxyethylene nonyl phenyl ether with "n" oxyethylene units (PONPEn)

2. THE SCOPE OF THIS WORK

This study is focused on the recovery of precious metals from hydrochloric acid solutions through emergent or well established metal recovery techniques based or on the principles of solvent extraction technology. This subject is of a great importance due to the

high value and scarcity of precious metals, consequently the need of developing and consolidating new separation and concentration processes is necessary.

The metals, extractants and extraction techniques object of this study have been selected considering practical application and/or fundamental research contributions on the basis of the precious metals research planning at the Department of Chemical Engineering, Universitat Politècnica de Catalunya, as well as other cooperating groups.

The work presented in this thesis is organized in the following manner:

- Paper 1

The role played by sulphur-containing extracting reagents is of prime importance in the separation, purification and concentration of precious metals. Di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) is a promising selective extractant for Pd(II). The liquid-liquid extraction of Pd(II) with DEHTPA is studied in Paper 1.

- Paper 2

In Paper 2, the transport of Pd(II) through a supported liquid membrane containing DEHTPA as a mobile carrier is reported.

- Paper 3

Intensive work has been conducted in the separation/refining of Rh(III) using an alkylated 8-hydroxyquinoline, Kelex 100, by liquid-liquid extraction (51, 52) as well as supported liquid membranes (53). In Paper 3, Kelex 100 is employed in the study of the permeation of Ir(IV) as well as metal common impurities, through a supported liquid membrane designed for Rh(III) separation.

- Papers 4 and 5

DEHTPA is used to prepare impregnated resins for selective Pd(II) extraction. Paper 4 deals about the preparation and physico-chemical characterization of the resins containing DEHTPA whereas in Paper 5, Pd(II) recovery is described.

- Papers 6 and 7

The importance of amines in metal recovery has been previously discussed. Alamine 336 is a long chain teriary amine used in Paper 6 to prepare impregnated resins. These resins are characterized and applied to Pd(II) extraction. In Paper 7, Alamine 336 impregnated resins are employed for Pd(II)-Pt(IV)-Rh(III) separation.

- Paper 8

Studies concerning technologies oriented towards practical application of impregnated resins for industrial and commercial metal recovery processes are needed for the consolidation and definitive establishment of impregnated resins. In this paper, scale-up of Pd(II) recovery by means of resins impregnated with Alamine 336 is performed in a fluidized bed column.

- Papers 9, 10 and 11

Despite of the attractive ability of cloud point extraction to separate and concentrate metals, cloud point extraction for metal recovery has not been studied extensively. In these papers, cloud point extraction of Au(III) using nonionic surfactants with different number of oxyethylene units, PONPEn, is treated. Paper 9 emphasizes in the study of liquid-liquid separation characteristics of PONPE solutions. Paper 10 is mainly devoted to the basic study of cloud point extraction of Au(III) by PONPE; the results obtained are subsequently applied in Paper 11 in which a flowsheet for the recovery of gold from printed substrate based on the usage of cloud point extraction is reported.

3. EXPERIMENTAL PROCEDURES

3.1. Liquid-Liquid Extraction

The distribution studies of DEHTPA between the aqueous phase and the organic phase were carried out by shaking mechanically equal volumes of aqueous and organic solutions at room temperature until equilibrium was attained. After phase separation the equilibrium pH

was measured and the ligand in the aqueous phase was analyzed by ICP, being calculated the extractant concentration in the organic phase by means of a mass balance.

In a similar manner, the solvent extraction tests were carried out in batch experiments, and after the phase separation the metal extraction was determined by measuring the metal concentration by ICP in the aqueous phase and calculating the concentration in the organic phase from the mass balance.

Metal stripping tests were performed by contacting metal loaded organic phase with the stripping agent and then analyzing the metal in the aqueous phase.

3.2 Supported Liquid Membranes

The metal transport through supported liquid membranes (SLM) has been studied using two-compartment cells provided of proper agitation. The SLM were prepared by soaking overnight the polymeric support into the solution containing the carrier. In Paper II the experimental set-up illustrated in Figure 4 was employed and the metal concentration in the feed phase was measured at definite time intervals by removing small solution volumes. In Paper III, the cell depicted in Figure 5 was used, the duration of the experiments was two hours and the metal concentration in the feed and stripping solutions at the end of the test were masured. In all the permeation experiments the metal concentrations were analyzed by atomic absorption spectroscopy, except in case of tests with metal mixtures in which ICP was used.

3.3. Impregnated Resins

Impregnated resins were prepared by using a dry impregnation method, mixing an appropriate amount of extractant dissolved in an organic solvent with dry Amberlite XAD2 until total evaporation of the diluent was reached. Characterization of the impregnated resins was performed by determining the extractant concentration on the resin and measuring the free specific surface of the resins applying the Brunauer, Emmet and Teller (BET) equation.

The distribution of the organic ligand between the aqueous phase and XAD2 as well as metal extraction were studied by performing batch experiments as described for liquid-liquid experiences, in which given amounts of resin were stirred with aqueous solutions of adequate

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content until equilibrium was achieved. Similarly, metal stripping tests were carried out by contacting metal loaded resins with a stripping solution and finally determining the metal concentration in the aqueous phase.
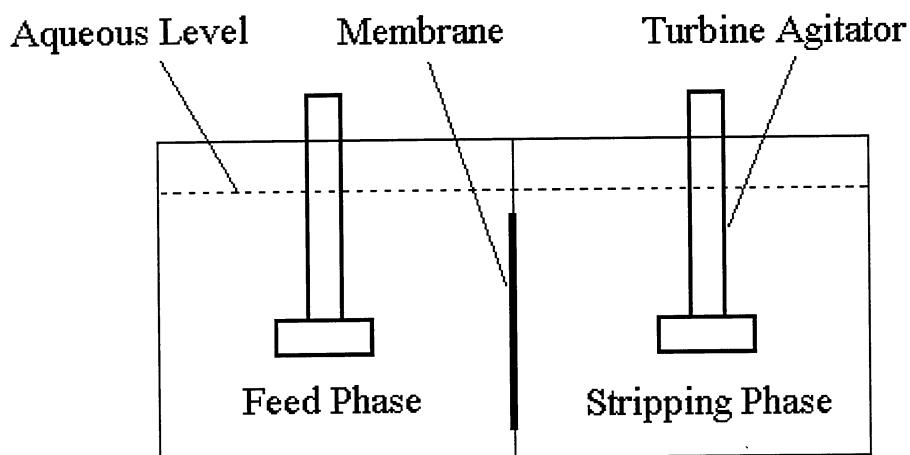

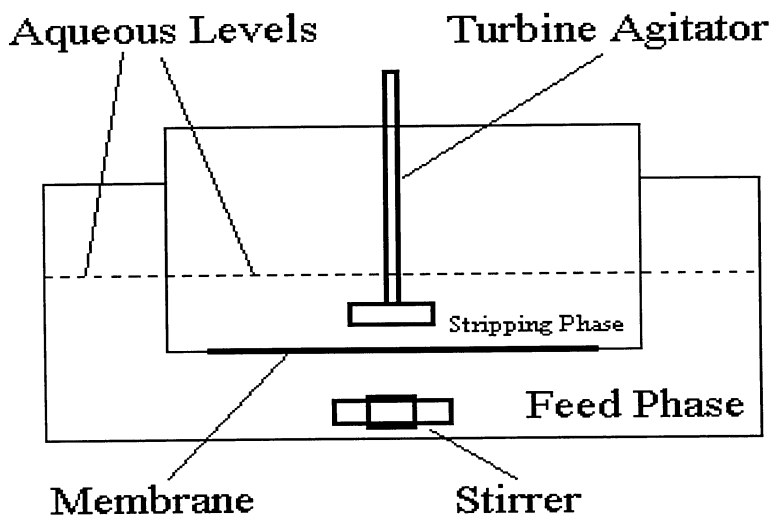**FIGURE 4.** Experimental set-up employed in Paper II

FIGURE 5. Experimental set-up employed in Paper III

3.4. Impregnated Resins Combined with a Fluidized Bed Column

Metal extraction with impregnated resins was also conducted in a fluidized bed column made in polymethylmethacrylate. A peristaltic pump was used to circulate the solution from a well-mixed tank through the fluidized bed column. The solution leaving the column was continuously recirculated to the mixed tank. Samples from the stirred tank were taken at different elapsed times and finally analyzed by atomic absorption spectroscopy.

3.5. Cloud Point Extraction

The cloud point (CP) of surfactant solutions were recorded by heating slowly these solutions in a thermostatted water bath until the solution became turbid; the temperature at this phenomena was observed was noted as the CP of the solution. The solution was kept at a described settling temperature (ST) overnight in an incubator for achieving the phase-separation. Then the concentration of surfactant in the aqueous phase was determined by UV spectrophotometry. In the case of metal cloud point extraction, the experiments were carried out following similar steps and after reaching the equilibrium, the metal concentration in the aqueous bulk phase was determined by ICP. The surfactant and metal concentrations in the surfactant-rich phase, were calculated on the basis of a mass balance.

Phase-separation history of nonionic surfactant solutions, was studied by measuring the height of the surfactant-rich phase using a travelling microscope from the bottom of the tube against the elapsed time.

4. RESULTS AND DISCUSSION

4.1. Preparation and Characterization of Impregnated Resins

DEHTPA and Alamine 336 were successfully used in the preparation of impregnated resins. In the case of Alamine 336 the impregnation efficiency in terms of extractant retention in the organic support was close to 100%, whereas for DEHTPA around 50% of efficiency was obtained. It can be justified for the major presence of hydrocarbon chains in Alamine 336, compared to DEHTPA, which plays a determinant role in the adsorption of the extractant.

On the basis of surface area measurements it can be concluded that for both extractants, DEHTPA and Alamine 336, during the impregnation process the extractant molecules fill the pore space gradually from the smallest pores of the resin up to the pores with large diameters. In addition to this, the measurement of free surface areas can be used as analytical method for the determination of ligand content on the resin.

4.2. Extractant Distribution between the Organic and the Aqueous Phase

From the liquid-liquid and solid-liquid distribution studies of DEHTPA from the organic phase into the aqueous phase, it was found that the equilibrium distribution of the extractant is displaced towards the organic phase. Moreover, this equilibrium is more shifted to the resin phase, and it seems that the interaction of DEHTPA with the resin phase acts to drive further the displacement of DEHTPA molecules from solution towards the macroporous polymer. The tendency of DEHTPA to form dimers in the organic phase is rather limited in the case of the liquid-liquid system. However, in the case of impregnated resins the aggregation phenomena in the organic phase seems to be significant. The pKa of DEHTPA was also calculated and an average value of 3.68 was found.

4.3. Metal Extraction Kinetics

The extraction kinetic behavior of the extractants was quite different when used in solvent extraction or impregnated resins. Liquid-liquid extraction exhibited very fast extraction rates compared to impregnated resins. In Figure 6, it can be seen that even using less quantity of DEHTPA, liquid-liquid extraction allows faster Pd(II) extraction than impregnated resins. Furthermore, the extraction rates of impregnated resins are strongly dependent on the extractant content in the support. The slow metal extraction performed by impregnated resins is probably due to slow metal diffusion in the resin pores.

Obviously, the role of the metals to be extracted also affected the extraction kinetics. For example Pd(II) was very fast extracted compared to Pt(IV) by DEHTPA in both liquid-liquid extraction and impregnated resins systems. The very large difference on extraction rates between Pd(II) and Pt(IV) allow metal separation. With regard to XAD2/Alamine 336 kinetic features, Pd(II), Pt(IV) and Rh(III) exhibited similar extraction rates
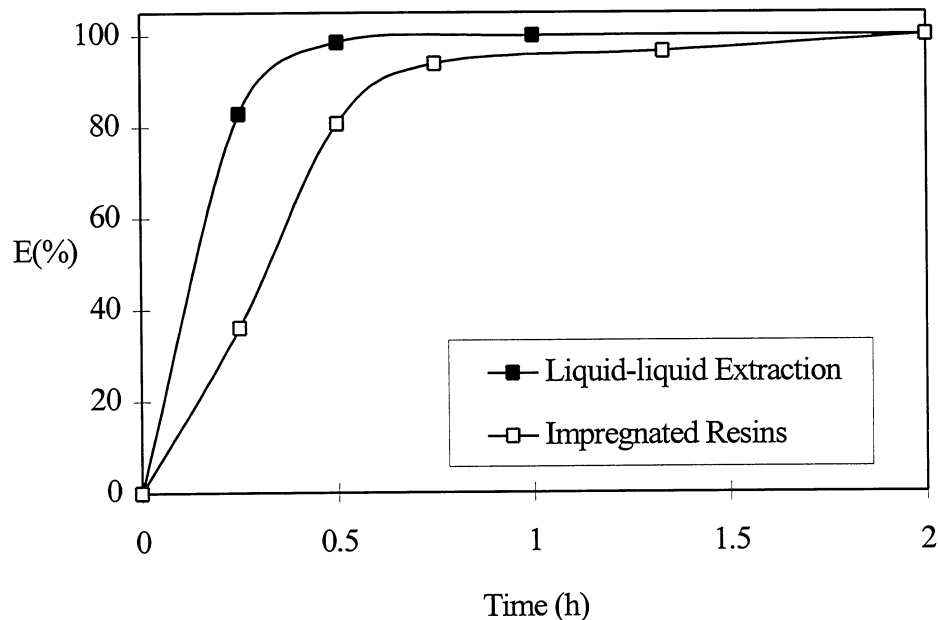
FIGURE 6. Percent extraction of Pd(II) against contact time using liquid-liquid extraction and impregnated resins

Experimental conditions. Liquid-liquid (L-L): 10 ml of 1.88×10^{-4} M Pd(II) in 0.5 M HCl contacted with 10 ml of 0.0025 M DEHTPA in kerosene. Impregnated resins (IR): 20 ml of 9.40×10^{-5} M Pd(II) in 0.5 M HCl contacted with 0.1 g of 1.01 mol DEHTPA/kg dry XAD2 resin. Total amount of DEHTPA: 2.5×10^{-5} moles (L-L) and 7.5×10^{-5} moles (IR). Total amount of Pd(II): 1.88×10^{-6} moles.
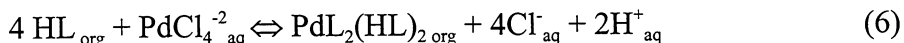
4.4. Metal Extraction Thermodynamics

The percentage extraction and the distribution coefficients for the extraction of different metal ions by solvent extraction and impregnated resins, with the extractants used in this study, diminish with raising HCl concentration and increase when the ligand concentration is increased. The extraction data were analyzed numerically with the program LETAGROP-DISTR (71) by treating each ionic strength separately in order to found the chemical reactions and the stoichiometric equilibrium constants which gave the best fit to the experimental results. The results obtained are summarized as follows:
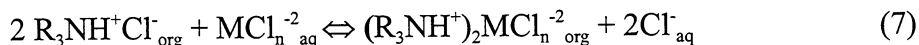
- Pd(II) extraction by DEHTPA dissolved in kerosene

$$2 \, HL_{org} + PdCl_4^{-2}{}_{aq} \Leftrightarrow PdL_{2 \, org} + 4Cl^-{}_{aq} + 2H^+{}_{aq} \tag{5}$$
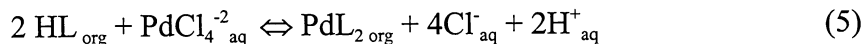
- Pd(II) extraction by XAD2/DEHTPA resins

$$4 \, HL_{org} + PdCl_4^{-2}{}_{aq} \Leftrightarrow PdL_2(HL)_{2 \, org} + 4Cl^-{}_{aq} + 2H^+{}_{aq} \tag{6}$$

- Pd(II) and Pt(IV) extraction by XAD2/Alamine 336 resins

$$2 \, R_3NH^+Cl^-{}_{org} + MCl_n^{-2}{}_{aq} \Leftrightarrow (R_3NH^+)_2MCl_n^{-2}{}_{org} + 2Cl^-{}_{aq} \tag{7}$$

where M represents the metal, being n=4 for Pd(II) and n=6 for Pt(IV).

In the case of Pd(II) extraction with XAD2/DEHTPA resins, when an important mass, 0.2 g or more, of concentrated impregnated resin was used, several hours after the metal extraction test a greasy precipitate was observed in the aqueous solution. This precipitate was analyzed by infrared spectroscopy and ICP, and its composition was found to be Pd complexed with the extractant. For this reason DEHTPA was not used for column operation. Nevertheless, with the experimental conditions employed in the batch experiments reported in this work, the precipitate formation was almost not detected.

4.5. Metal Stripping

Thiourea dissolved in HCl was proved to be an excellent strippant agent, and was used for the back-extraction of Pd(II) bonded to DEHTPA in kerosene as well as in the case of XAD2/DEHTPA impregnated resins, and in the stripping of Pd(II) and Pt(IV) loaded on XAD2/Alamine 336 resins. Other stripping reagents were also tested with satisfactory results: thiocyanate in HCl to strip Pd(II) loaded with DEHTPA in kerosene, and $HClO_4$ as well as HCl for the stripping of Pd(II) and Pt(IV) loaded with XAD2/Alamine 336 resins; however the extent of Pt(IV) back-extraction in the case of using HCl was less than 50%.

4.6. Permeation of Pd(II) through Supported Liquid Membranes

The experimental data corresponding to Pd(II) extraction by Supported Liquid Membranes (SLM) containing DEHTPA were described by a physicochemical model which consists of: diffusion process through the feed aqueous diffusion layer, fast interfacial chemical reaction and diffusion through the membrane.

During the transport experiments, different rate-controlling processes took place depending on the composition of the system. At the beginning of the experiment, the metal was practically all bound to the extractant and the rate of metal transfer was controlled by the diffusion in the membrane. Then, as long as the metal aqueous feed concentration decreased, the permeation process was controlled by Pd(II) diffusion through the aqueous boundary film.

4.7. Cloud Point Extraction of Au(III)

The cloud point (CP) temperature of PONPE solutions was found to decrease as the HCl concentration diminished and was lowered by adding NaCl or using more hydrophobic surfactants. Phase separation of surfactant solutions was attained by allowing these solutions to settle at a temperature above the CP. The surfactant concentrations in both aqueous and surfactant-rich phases are only function of the temperature difference between the settling temperature (ST) and CP, not depending of the concentrations of HCl and NaCl. The adequate difference temperature between ST and CP in order to obtain a stable surfactant-rich phase formation was found to be 10-30°C.

PONPE7.5 solutions gave much lower CP than PONPE10 solutions, allowing phase-separation at ambient temperature. Moreover PONPE7.5 system provided very high distribution ratio of Au(III), which was higher than that obtained when PONPE10 was used. With increasing surfactant concentration, the extraction efficiency also increased; nevertheless if an excess of surfactant was employed a lowering of the distribution ratio was observed due to an increased volume of the surfactant-rich phase.

4.8. Selectivity of Metal Recovery Systems

In general terms, the metal selectivity exhibited for the systems investigated in this work were strongly dependent on the extractant characteristics.

DEHTPA was selective for Pd(II) over Cu(II), Fe(III), Pt(IV), Rh(III) and Zn(II) at high HCl concentrations.

Separation of Pd(II) and Pt(IV) from solutions containing Rh(III) with XAD2/Alamine 336 impregnated resins was achieved, since these resins co-extracted Pd(II) and Pt(IV) by means of Reaction 7 whereas for Rh(III) the extent of metal sorption was very low.

Separation of Au(III) from some heavy metals: Pt(IV), Pd(II), Zn(II), Cu(II) and Fe(III) was achieved through CP extraction with PONPE7.5. CP extraction exhibited higher concentration and inferior separation compared with solvent extraction.

Studies on Ir(IV) extraction by Kelex 100, using liquid-liquid extraction and SLM demonstrate that Ir(IV) and Rh(III) have similar behaviour, thus a procedure for separating both metals using Kelex 100 is not feasible. Moreover, SLM/Kelex 100 system was found to have very serious limitations for selective Rh(III) extraction, since an important number of potential hydrometallurgical impurities permeate through the membrane to the stripping solution: Zn(II), Pb(II), Cd(II), Bi(III), Te(IV), Ir(IV) or were responsible for the blockage of the membrane: Pt(IV), Pd(II), Ag(I), Pb(II), Bi(III). On the other hand Ni(II), Co(II), As(V), Se(IV), Cu(II) were the metals which do not permeate through the membrane and hence did not perturbate the system.

4.9. Applications

- Pd(II) Recovery in a Fluidized Bed Column

Scale-up of Pd(II) extraction by XAD2/Alamine 336 resins from HCl solutions was successfully performed using fluidized bed technology. The Pd(II) mass transfer coefficient exhibited a maximum when optimum flow rate was used and increased when initial palladium concentration was reduced.

- Recovery of Gold from Printed Substrate via Cloud Point Extraction

Gold was successfully recovered from a printed substrate also containing Cu, Ni and Zn by means of CP extraction with PONPE7.5. A flowsheet for this process based on the usage of CP extraction was established. After the leaching step, CP was applied for separating Au(III) from the other metals. Au(III) was then recovered from the surfactant-rich phase by extracting the surfactant with chloroform and leaving the metals in the aqueous solution.

5. CONCLUSIONS

Metal recovery techniques and extractants studied in this work exhibit good performance for precious metals extraction from HCl solutions.

Liquid-liquid extraction allow fast Pd(II) extraction and stripping when DEHTPA dissolved in kerosene is used as organic phase. Pd(II) can be selectively extracted by DEHTPA over Cu(II), Fe(III), Pt(IV), Rh(III) and Zn(II).

DEHTPA and Alamine 336 are appropriate extractants for preparation of impregnated resins suitable for selective extraction of Pd(II) over metal impurities and co-extraction of Pd(II) and Pt(IV) against Rh(III) respectively. Impregnated resins maintain the advantages of ion-exchange technology, for example easy phase separation, and also keep the selectivity characteristics of the extractants. However, the extraction and stripping kinetics of impregnated resins are slow compared to solvent extraction. Moreover, impregnated resins combined with fluidized bed technology can improve the recovery of metals with respect to other technologies; nevertheless when combining impregnated resins and fluidized bed technology special attention must be taken in order to prevent flotation of the resins.

Supported liquid membranes (SLM) are very attractive since they combine the processes of extraction and stripping in a single stage. SLM/DEHTPA system permits selective Pd(II) transport. The experimental data for the metal permeation can be fully explained by equilibrium considerations and a model based on a diffusion controlled process. On the other hand, an extensive study concerning the permeation of common metal impurities through a SLM of Kelex 100 designed for Rh(III) separation demonstrates that several metals might contaminate the receiving phase, and at the same time an important number of other metals are extracted by Kelex 100 but no well stripped; thus these metals may cause blockage of the membrane.

Selective cloud point (CP) extraction of Au(III) using the surfactant PONPE7.5 is achieved at ambient temperature in a similar manner as in solvent extraction not requiring the use of organic solvents. The phase-separation characteristics of PONPE solutions are governed by the difference between the settling temperature (ST) and the CP. The application

of CP extraction is demonstrated for the recovery of Au from a printed substrate, although the usage of an organic solvent, chloroform, is necessary in the stripping step.

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