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# Palladium Recovery by Reactive Precipitation using a Cyanex 301-Based Stable Emulsion

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**Abstract:** Cyanex $301^{®}$, di(2,4,4-trimethylpentyl) dithiophosphinic acid, has been combined with gelatin and alginate to prepare a stable emulsion that can be used for the reactive precipitation of palladium (metal reaction with the sulfur functional group of Cyanex 301). The ionotropic gelation of alginate leads to material precipitation. The process has been successfully tested for Pd binding from 0.1–5 M HCl solutions. The maximum binding capacity was found to be close to 350 mg Pd $g^{-1}$ Cyanex 301. A 1:1 stoichiometric relation between Cyanex 301 and Pd has been identified. Extractant dependency plots showed that the ligand in the Pd-Cyanex 301 complex can also have a solvation number higher than one. Palladium uptake is not significantly affected by the presence of competing metals such as Cu, Ni, Zn, or Pt. Quantitative stripping of Pd from the precipitated bio-polymer could not be achieved.

**Keywords:** Palladium, Cyanex 301, alginate, gelatin, emulsion, precipitation

## INTRODUCTION

The increasing demand of the industry for precious metals (such as the so called platinum group metals, PGMs) is related to the development of

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catalytic systems (for oil industry, fine chemistry, automotive catalysts and the like, and the manufacturing of high-tech electronic devices). For some PGMs the demand is not balanced by the offer due to the limited resources available. Additionally, the mineral resources are frequently located in politically or socially unstable areas; this makes the recovery of these strategic metals from secondary sources a key issue for the development of advanced technologies. For these reasons a series of metallurgical processes have been investigated in the last decades for the recovery of precious and strategic metals from low grade ores and more specifically from industrial wastes (spent catalysts, electronic devices and the like) (1). Special attention has been paid to pyro- and hydro-metallurgical processes after grinding waste material. Preliminary physical separations, such as gravimetric and magnetic, allow to increase the relative proportion of these valuable metals, thus justifying the treatment of these second sources by conventional processes (2, 3). In hydrometallurgical processes the ground material is generally subjected to strong acid leaching (using for example chloride solutions, aqua regia etc.), resulting in acidic mixtures containing a wide variety of metals including PGMs but also base metals (BMs) (2, 4–9). Solvent extraction is a powerful technique for the recovery and the separation of metals from complex matrices, but its efficiency decreases in the treatment of very dilute solutions, such as those containing PGMs (9–15). Sorbents, including ion exchange resins (16–18), and chelating resins (19, 20), can represent an alternative to solvent extraction processes. Solvent-impregnated resins have also been investigated for palladium and platinum recovery, since they combine the advantages of the selectivity of solvent extraction reagents with the simplicity of column operation, which eliminates the need for efficient mixing of the phases, minimizes losses of extractant to the aqueous phase, and prevents solvent entrainment (16, 21). A wide range of materials have been investigated for the recovery of PGMs from dilute solutions using biosorbents (22–24), or synthetic materials (25, 26). Recently, a number of studies have been dedicated to the immobilization of solvent extraction reagents using biopolymers for the manufacturing of a new class of impregnated resins (27–30). Exploitation of biopolymers allows reducing the use of toxic materials and takes advantage of renewable resources compatible with sustainable growth. There is an increasing demand for the development of green chemistry processes to minimize the impact of the processes on the environment.

A series of Cyanex® extractants (tri(2,4,4-trimethylpentyl)phosphine oxide or Cyanex 921, tri(isobutyl)phosphine sulfide or Cyanex 471X, di(2,4,4-trimethylpentyl) monothiophosphinic acid or Cyanex 302, and di(2,4,4-trimethylpentyl) dithiophosphinic acid or Cyanex 301) have been tested for the recovery of platinum or palladium (9, 14, 15, 28–35). The use of these reagents in the two typical configurations of solvent extraction and solvent impregnated resins presents the usual drawbacks associated with these techniques. The former requires a strict control of phase separation and extractant and solvent losses; with the latter, metal uptake may be slow being generally controlled by diffusion processes in the pores of the solid matrix.

An alternative method is described in the present paper: biopolymers (alginate and gelatin) have been used for stabilizing a Cyanex 301 emulsion, which was tested for the reactive precipitation of palladium. According to this method, a Cyanex 301 emulsion is formulated as a slightly viscous solution that precipitates when mixed with the metal solution (metal ions react with the extractant), thus isolating the metal in the coagulated phase. This approach can be compared to other biphasic systems developed over the last decades, including PEG (polyethylene glycol) biphasic aqueous systems (36, 37), aqueous phase micellar extraction (coupled with ultrafiltration) (38–40), or surfactant liquid membrane systems (41–43). The main advantage of these three systems is that they use virtually nontoxic, nonflammable, and inexpensive components. In the case of the present system, the stabilization of the emulsion allows the extractant to be confined in a less volatile and less flammable and therefore less environmentally hazardous environment. Compared to other techniques involving encapsulated materials, the incorporation of the extractant in the biopolymer gel enhances the availability and accessibility of the binding sites and improves the binding kinetics.

## EXPERIMENTAL

### Preparation of Cyanex 301 Stabilized Emulsion

Ten grams of extractant (Cyanex 301, from Cytec, Canada, used as supplied) were mixed with 10 g of a gelatin (VWR Prolabo, France) solution (20% w/w in water). The gelatin solution was prepared by dissolving solid gelatin in boiling water. The dropwise addition of the extractant to the gelatin solution after adding 5 g of concentrated sodium hydroxide (10 M) produced a white viscous gel. Three hundred and eighty grams of alginate (ACROS, Switzerland) solution (1.5% w/w in water) were added to the extractant-gelatin mixture under agitation. A very clear and slightly yellowish stable emulsion was obtained. The concentration of Cyanex 301 in the emulsion was 2.5%. Other emulsions were prepared using lower concentrations of Cyanex 301 in the extractant-biopolymers mixture, i.e., 1.5, 0.5, and 0.25%.

The stable stock emulsion was generally diluted ten times with demineralized water immediately before use. The actual concentration of Cyanex 301 in the dilute emulsion (in the typical preparation) was thus 2.5 g $L^{-1}$, and, taking into account the other components, the dry weight content of the emulsion was 4.42 g $L^{-1}$.

### Metal Uptake Procedure

A 10 g Pd $L^{-1}$ in 1.1 M HCl stock solution was prepared by dissolving the metal salt ($PdCl_2$) under heating. Test solutions were prepared by dilution of the Pd stock solution using appropriate acidic solutions (HCl solutions at the nominal concentration required for the experiments). The HCl and chloride concentrations were calculated taking into account the HCl concentration in the mother solution, the HCl concentration used in the dilution, and the chloride ions from the palladium salt.

Standard conditions for binding experiments consisted in contacting for a minimum of 36 h under agitation 30 mL of the Pd solution (at metal concentrations in the 20–200 mg $L^{-1}$ range) with 1, 2, or 3 mL of the diluted stock emulsion. Concentrations were corrected to take into account the dilution due to the addition of given volumes of emulsion. The stock emulsion was diluted 10 times just before the experiment. The amount of Cyanex 301 was 2.5, 5, and 7.5 mg, respectively. The Pd and emulsion mixtures were contained in flasks kept under constant agitation using a reciprocal shaker. It is important to note that to obtain a good dispersion of the emulsion in the palladium solution, the mixture was initially subjected to a strong agitation (at the nominal speed of 500 rpm for 5 minutes). After 36 h of agitation the solution was filtered using a Whatman GF-C filter membrane (pore size: 1.2–1.4 μm) and the filtrate was analyzed for the residual metal concentration using inductively coupled plasma atomic emission spectrometry, ICP-AES (Jobin-Yvon 2000, Longjumeau, France). Mass balance was used for the determination of binding capacities, reported as a function of the Cyanex 301 content in the emulsion. In the calculation of the binding capacities, it was assumed that the acidic medium of the palladium solution causes complete precipitation of the alginate material (including Cyanex 301). The binding capacity was reported as a function of the dry weight of the emulsion introduced in the solution and supposed completely precipitated.

In addition to binding isotherms, complementary experiments were carried out to measure the effect on binding capacities of HCl concentration (in the 0.1–5 M range) and NaCl addition (in the 0.1–5 M added chloride concentration range). In these experiments the metal concentration was determined, after filtration, as described above.

## RESULTS AND DISCUSSION

### Binding Isotherm for Pd in 1 M HCl Solutions

Figure 1 shows the Pd binding isotherm obtained in 1 M HCl solutions under different experimental conditions (i.e., varying the amount of emulsion added to metal solution: 1, 2, or 3 mL, corresponding to Cyanex concentrations of 81, 156, and 227 mg $L^{-1}$, respectively). The amount of emulsion added to metal solution did not affect the binding capacity as shown in the figure. The perfect superimposition of the 3 sets of data allowed analyzing the results on the basis of a large number of experimental points (i.e., 30 points).

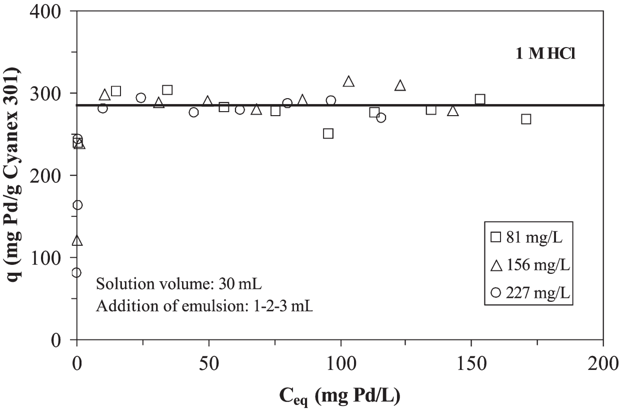


***Figure 1.*** Influence of the amount of emulsion added to palladium solution on the binding isotherm of Pd in 1 M HCl.

Figure 1 can be discussed on the basis of sorption isotherms, assuming that the whole mass of the emulsion was precipitated after being added into the metal solution. The initial slope of the isotherm is very steep, indicating a high efficiency of the emulsion material for Pd sequestration. Additionally, after a strong (and almost vertical) initial increase the uptake curve is followed by a plateau, reached for residual concentrations of Pd as low as 10 to 15 mg $L^{-1}$. The isotherm can be considered very favorable and quasi irreversible. This is important for the design of the process since it allows saturation of the biosorbent material at very low target metal concentrations.

The maximum binding capacity ranged between 316 and 350 mg Pd $g^{-1}$ Cyanex 301, which means a binding capacity close to 3 mmol Pd $g^{-1}$ Cyanex 301. Taking into account the molar mass of Cyanex 301 (i.e., 322 g $mol^{-1}$); this corresponds approximately to a 1:1 molar ratio of Pd to Cyanex 301.

Taking into account the presence of the other components in the emulsion (10 g Cyanex 301 for a total mass of 17.7 g extractant + biopolymers, on a dry weight basis) the maximum binding capacity can be converted to about 183 mg Pd $g^{-1}$ total dry mass. This is slightly better than the level reached in the sorption process using the same emulsion preparation for the immobilization of Cyanex 301 into alginate capsules (28). In the latter case, the maximum sorption capacity did not exceed 150 mg Pd $g^{-1}$ (dry material). Cyanex 301, therefore, is used more efficiently in the emulsion form than in the encapsulated form, very likely due to a better accessibility of its reactive functional group.

## Influence of HCl Concentration

A key parameter for designing a process for industrial leachates is the effect of the acid concentration. The recovery of Pd (from a 100 mg Pd $L^{-1}$ solution) was tested for HCl concentrations between 0.1 and 5 M. The amount of emulsion added to the palladium solution did not change significantly the binding capacity of Pd. The mean value of the binding capacity, taking into account all experimental data, was 343 ($\pm$18) mg Pd $g^{-1}$ Cyanex 301.

The distribution coefficients ($K_d = q/C_{eq}$) were determined for the various Cyanex 301 amounts and are shown as log-log plots in Fig. 2 as a function of HCl concentration. Table 1 summarizes the mean values of the distribution coefficients for the different amounts of emulsion. An increase in the amount of Cyanex 301 in the system (proportional to the amount of emulsion) increases the value of $K_d$. The variation of the distribution coefficient with the emulsion amount (EA) follows the equation:

$$\log K_d = 1.23 \log(\text{EA, mmol L}^{-1}) + 0.29 \quad (R^2 : 0.961) \tag{1}$$

where the slope value of ~1 agrees with the 1:1 Pd to Cyanex 301 stoichiometric relationship discussed earlier.

The data in Fig. 2 are consistent with the results obtained for Cyanex 301 encapsulated in composite alginate/gelatin beads, a system for which Guibal and Vincent showed a weak effect of HCl concentration on the Pd binding(28). In the case of Pd uptake by Cyanex 302 encapsulated in biopolymer (alginate), Mimura et al. observed that the distribution coefficient strongly decreased with increasing $HNO_3$ concentration (30). The authors reported that the log-log plots of $K_d$ versus [$HNO_3$] had a slope close to $-2$ indicating that 2 $H^+$ were exchanged for each Pd bound to the Cyanex 302-encapsulated beads. In the case of Pd(II) extraction by tri-*n*-octylamine-impregnated resins in HCl solutions, Akita et al. also observed that the log-log plots of the

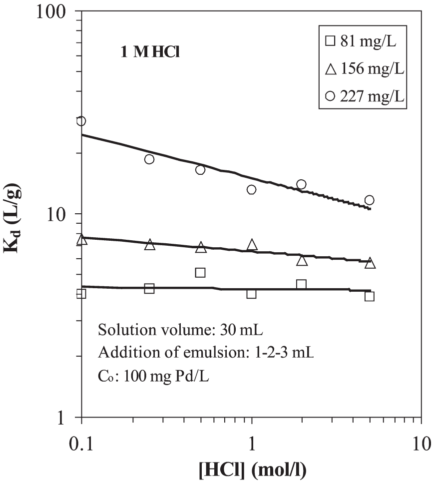


***Figure 2.*** Influence of HCl concentration and emulsion amount on Pd distribution coefficient.

***Table 1.*** Influence of HCl concentration and emulsion amount on Pd distribution coefficient

| Emulsion amount (mg $L^{-1}$) | $\log K_d$ (L $g^{-1}$)[a] | Concentration range |
|---|---|---|
| 81 | 0.63 (±0.042) | 0.1–5 M |
| 156 | 0.82 (±0.047) | 0.1–5 M |
| 227 | 1.19 (±0.069) | 0.25–2 M |

[a] Numbers in brackets indicate standard deviation.

distribution coefficient versus the activity of HCl had a slope of −2 (44). They concluded that the extraction reaction involved first the binding of HCl onto the extractant followed by the exchange of two chloride ions with one $PdCl_4^{2-}$.

Overall, the system investigated in the present work seems to be much less dependent on the acidity of the solution. For a low emulsion amount (81 mg $L^{-1}$), the distribution coefficient is constant in the whole range of HCl concentrations investigated, while for higher emulsion amounts (156 and 227 mg $L^{-1}$) the distribution coefficients decrease slightly with increasing solution acidity.

The lack of any significant effect of the HCl concentration on the Pd uptake indicates that Cyanex 301 acts as a solvating extractant and not as a cation exchanger. At the high acidities used in this work, the weak acidic group of Cyanex 301 (-SH with a $pK_a$ of 2.84) (45) is undissociated and the metal is extracted through interaction with the thiophosphoryl group ($P = S$). The slight decline of $K_d$ values with increasing acidities can probably be ascribed to the competition of HCl for the $P = S$ group.

## Influence of Chloride Ion Concentration

Similar experiments were performed with 0.1 M HCl solutions by adding increasing concentrations of NaCl. Also in this case, the addition of increasing amounts of NaCl hardly influenced the Pd binding capacity. The mean value for the Pd binding capacity (under most experimental conditions) was 350 (±19) mg Pd $g^{-1}$ Cyanex 301. This value is very close to those obtained with HCl solutions of increasing concentrations, indicating that the effect of chloride ions is independent of the acidity of the solution and the form of chloride ion addition, i.e., salt versus acid.

The distribution coefficients were also calculated and are shown in Fig. 3 as log-log plots of $K_d$ vs. $[Cl^-]$ for various amounts of emulsion added. Table 2 reports the mean values of the distribution coefficients (with the standard deviation) for the given experimental conditions. As in the case of the effect of HCl concentration, an increase in the amount of Cyanex 301 in

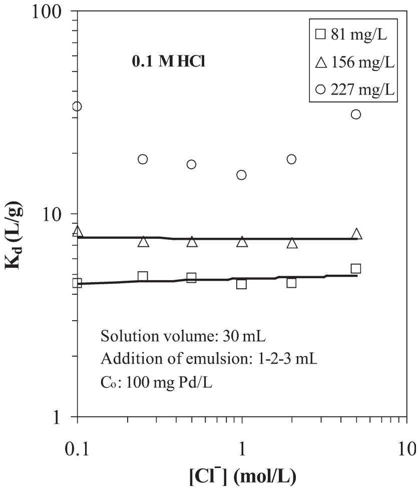


***Figure 3.*** Influence of total chloride concentration and emulsion dosage on Pd distribution coefficient.

the system increases the value of $K_d$. The variation of the distribution coefficient with emulsion amount (EA) follows the equation:

$$\log K_d = 1.23 \log(\mathrm{EA}) + 0.34 \quad (R^2:0.968) \tag{2}$$

The coefficients in this equation are very close to those obtained by varying the HCl concentration, confirming that the effect of the chloride ions is independent of the solution acidity, and the 1:1 stoichiometric ratio of the ligand to the metal.

The data in Fig. 3 show that the $K_d$ values are almost independent of the NaCl concentration for 81 and 156 mg $L^{-1}$ emulsion, while at higher emulsion amount (227 mg $L^{-1}$) the $K_d$ values exhibit a minimum in the 0.25–2 M $Cl^-$ concentration range.

The concentration of chloride ions in large excess may have several effects on the binding mechanism:

***Table 2.*** Influence of total $Cl^-$ concentration and emulsion amount on Pd distribution coefficient (HCl: 0.1 M)

| Emulsion amount (mg $L^{-1}$) | $\log K_d$ (L $g^{-1}$)[a] | Concentration range |
|---|---|---|
| 81 | 0.68 (±0.029) | 0.1–5 M |
| 156 | 0.88 (±0.025) | 0.1–5 M |
| 227 | 1.24 (±0.037) | 0.25–2 M |

[a] Numbers in brackets indicate standard deviation.

a. competition of chloride anions for binding to the reactive groups;
b. competition of chloride ions with the reactive group for interaction with Pd ions (metal speciation);
c. changes in the activity coefficients of all ionic species present in the system; and
d. salting out and/or electrolyte invasion of the polymeric matrix at very high salt concentrations. The latter effects are likely responsible for the increased $K_d$ values observed in Fig. 3 at the highest NaCl concentrations for 227 mg $L^{-1}$ emulsion amount. In the present study, however, the overall effect of the chloride ions on metal uptake is much smaller than in typical solvent extraction systems. For example, Côté and Demopoulos observed the exchange of two protons and four $Cl^-$ ions for the extraction of one tetrachloropalladate ion by two molecules of hydroxyquinoline derivatives, as shown by logarithmic slope analysis of distribution coefficients vs. concentrations of HCl, NaCl and extractant (11).

## Influence of Cyanex 301 Concentration on Pd Uptake

To obtain more information on the stoichiometry of the reaction between Cyanex 301 and Pd, a series of experiments were performed using increasing amounts of Cyanex 301 in the stabilized emulsion (i.e., 0.25, 0.5, 1.5, and 2.5%; emulsion volume: 1 mL in 30 mL of palladium solution). Fig. 4 shows the binding isotherm obtained with this series corresponding to Cyanex 301 concentrations of 8, 16, 48, and 81 mg $L^{-1}$, respectively. The series of data obtained with increasing volumes of emulsion (2 mL and 3 mL at 2.5% Cyanex 301 content in the stock emulsion) are also included in the figure. Increasing the Cyanex 301 content in the stabilized emulsion increases the maximum binding capacity. For Cyanex 302 encapsulated

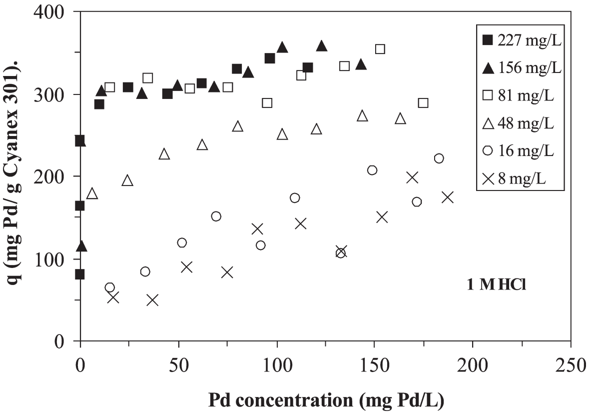


***Figure 4.*** Influence of Cyanex 301 amount on Pd binding isotherm.

beads, Mimura et al. also observed an increase of the maximum sorption capacity with an increase of the amount of extractant immobilized in gel capsules (30).

The initial part of the curves indicates an increase in the affinity of the emulsion for Pd for increasing amounts of Cyanex 301. At the highest extractant concentrations the uptake plateau is reached at very low Pd concentration, while for low extractant concentrations the plateau is reached when the residual Pd concentration exceeds about 100 mg Pd $L^{-1}$. Final Cyanex 301 total concentrations higher than 100 mg $L^{-1}$ (obtained by doubling or tripling the emulsion addition) do not increase the binding capacity at saturation. For high Cyanex 301 additions (i.e. 83–227 mg Cyanex 301/L) the binding isotherms were superimposed with a quasi-irreversible shape (sharp initial curve followed by the equilibrium plateau for a residual concentration close to 10 mg Pd $L^{-1}$). At lower Cyanex 301 doses the "favorability" of the binding isotherm progressively decreased: both the maximum binding capacity and the initial slope of the isotherm (representative of the affinity of the binding reagent for the solute) decreased.

The Pd distribution coefficients are reported in the log-log plots of Fig. 5 as a function of Cyanex 301 concentration for a number of increasing Pd concentration levels. The data are grouped for low (20 to 80) and high (80 to 200) Pd mg/L in panels A and B, respectively.

The data in Fig. 5 clearly show that the process appears more appropriate for the treatment of dilute solutions. The $K_d$ values are much higher at low Pd concentration (lower than 60 mg Pd $L^{-1}$), especially when the Cyanex 301 concentration is high ($>100$ mg $L^{-1}$, i.e., $>0.5$ mmol $L^{-1}$) and added in the presence of substantial amounts of biopolymers (i.e., using larger amounts of 2.5% Cyanex 301 stock emulsion).

In spite of the dispersion of the data, which may be explained by the difficulty in achieving perfectly reproducible conditions for the agitation and mixing of emulsion and solution, an interesting behavior of the uptake data emerges from Fig. 5. For Cyanex 301 concentrations lower than 0.25 mmol/L, the $K_d$ values do not increase with increasing ligand concentrations (and, actually even decrease in the lowest Cyanex 301 concentration range). Only beyond 0.25 mmol/L Cyanex 301, the expected increase of metal $K_d$ with ligand concentration is observed. The slope of the $K_d$ data in the Cyanex 301 concentration range higher than 0.25 mmol/L is between $\sim$1 and $\sim$2 in panel A of Figure 5 (lower Pd concentrations) and about 1 in panel B (higher Pd concentrations).

These extractant dependency values can be compared to those obtained in typical solvent extraction and functionalized polymer systems. For example, Uheida et al. found that Pd(II) is extracted by nonylthiourea in chloroform by forming complexes containing one or two ligand molecules (46). Preston and Du Preez reported extractant dependencies between 2 and 3 for the extraction of Pd(II) from HCl solutions into xylene solutions of various dialkyl sulfoxides (47). Similarly, in a study of Pd(II) uptake by a macromolecular resin

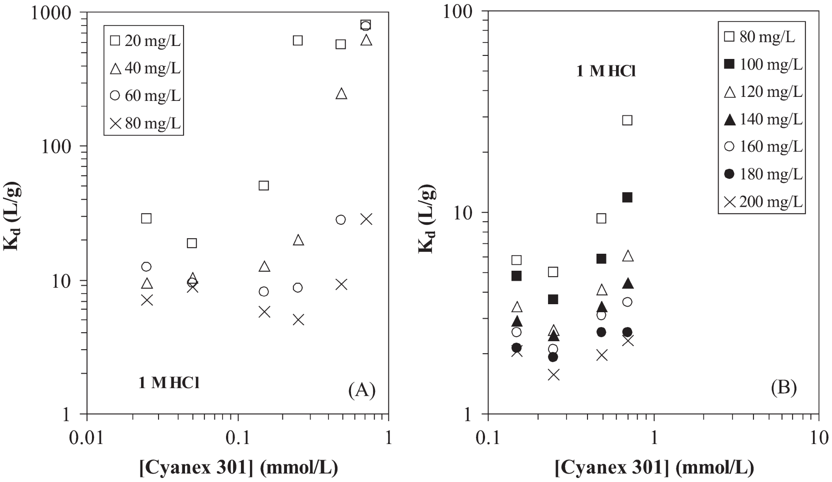


***Figure 5.*** Influence of Cyanex 301 concentration on Pd distribution coefficient for different Pd concentrations – log-log plot (A: low concentration range 20–80 mg Pd $L^{-1}$; B: high concentration range 80–200 mg Pd $L^{-1}$).

containing tri-*n*-octylamine as the extractant, Akita et al. observed that the extractant dependency was close to 2 and they concluded that 2 moles of extractant were involved in the binding of 1 mole of Pd (44). Their sorption isotherms, however, showed that the maximum sorption capacity was less than a half of the extractant content. They concluded, therefore, that a significant fraction of the extractant did not contribute to Pd binding due to steric hindrance or occlusion of the porous network. In the present study, the dispersion of the emulsion in the solution should decrease the negative effect of diffusion limitations in the solid sorbent.

The presence in Fig. 5 of two regions, one where the Pd $K_d$ values are practically independent of the Cyanex 301 concentration ($<0.25$ mmol/L) and the other where a strong functional dependence of $K_d$ on ligand concentration is observed ($>0.25$ mmol/L), indicates that at least two different mechanisms for metal uptake are operative under the experimental conditions used. The first mechanism should not involve the participation of the Cyanex 301 molecules and predominates at very low Cyanex 301 concentrations. At higher extractant concentrations, the second mechanism involving interaction of Pd aqueous species with Cyanex 301 predominates, and metal uptake through the first mechanism becomes negligible.

The data in the present work do not provide sufficient information for a precise identification of the first, Cyanex 301 concentration independent, mechanism. A first possibility could be the physical entrapment of Pd species within the polymeric network of alginate during polymer precipitation. A second possibility consists in the chemical interaction of the Pd species with the protonated carboxylic groups of the polymeric alginate moiety. That one or both of these mechanisms are operative in the uptake of Pd(II) under the conditions used in this work, is demonstrated by the results of experiments in which Pd uptake was measured using the same experimental conditions of selected data points in Fig. 5, but with no Cyanex 301 in the emulsion. Palladium uptake was low (below 4%) but not negligible. Figure 6 shows that the palladium uptake was almost independent of metal concentration at low Cyanex 301 concentration (below 0.05 mmol $L^{-1}$); and metal uptake with the Cyanex 301-free emulsion followed the same trend compared to other low Cyanex 301 experiments. At higher Cyanex 301 concentrations (above 0.05 mmol $L^{-1}$) metal uptake increased linearly with Cyanex concentration, with a slope that decreases with an increase of metal concentration.

## Tentative Explanation for the Pd-Cyanex 301 Interaction

With respect to the Cyanex 301 concentration dependent mechanism, based on the results discussed above, the solvation reaction between the Pd(II) species and the undissociated dithiophosphinic acid ligand should be independent from acid and chloride ion concentrations. Also, the solvation number of Cyanex 301 in the metal-ligand complex should be 1 or 2. At high $Cl^-$ concentrations such as those used in the present study, Pd(II) exists mainly as the $PdCl_4^{2-}$ chloropalladate species (48). The simplest reaction between Cyanex 301 and $PdCl_4^{2-}$ can be written as:

$$nC301 + PdCl_4^{2-} \leftrightarrow (C301)_nPdCl_2 + 2Cl^- \qquad (3)$$

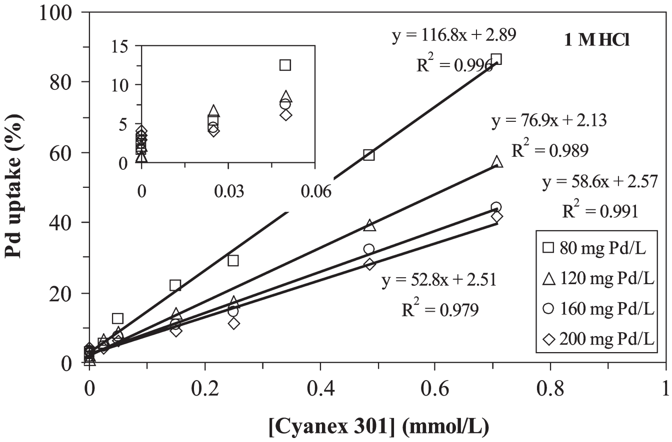


***Figure 6.*** Influence of Cyanex 301 concentration on Pd uptake at different initial metal concentrations (80–200 mg Pd $L^{-1}$).

where C301 represents Cyanex 301 and the ligand solvation number, n, is 1 or 2. Similar equilibriums have been proposed in various studies of Pd(II) solvent extraction systems (46, 47). In the case of reaction (3), however, a log-log plot of Pd $K_d$ vs. $Cl^-$ concentration should exhibit a slope value close to $-2$, which is in contrast with the data in Fig. 3 exhibiting a slope of about $-0.5$ at $[Cl^-]$ lower than 1 M.

An alternative equilibrium that takes into account our slope analysis results is the following:

$$nC301 + H_2PdCl_4 \leftrightarrow (C301)_n H_2PdCl_4 \tag{4}$$

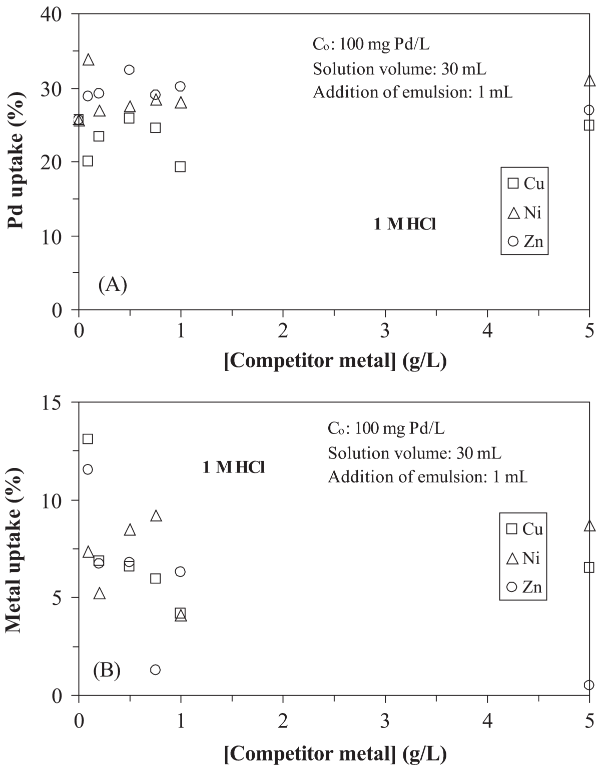
for which no acid or $Cl^-$ dependency is expected in log-log plots of $K_d$ vs. [HCl] or $[Cl^-]$. Under the experimental conditions of this work (high acidity and chloride concentrations), the presence of the $H_2PdCl_4$ species in solution can always be assumed and is practically independent of the specific HCl and $Cl^-$ concentrations. The value of the Cyanex 301 solvation number in reaction (4). depends on the ratio of Cyanex 301 to Pd(II) concentrations. Two complexes are formed, one with $n = 1$, predominant at low ligand excess compared to the metal, and the other with $n = 2$, predominant at high ligand excess (low Pd and high Cyanex 301 concentrations in Fig. 5).

In the Pd separation system proposed in this work, in analogy with conventional coagulation-flocculation systems, the strong agitation of the Cyanex 301-based emulsion with the Pd solution during the first minutes of contact, allows the dispersion of the emulsion and the homogenization of the solution. The tetrachloropalladate species are solvated by the thiophosphoryl group of the ligand according to equilibrium (4). The alginate moiety that coagulates in the presence of multicharged cations by ionotropic gelation, also forms a gel in the presence of very acidic solutions. After reacting with the Pd species, the Cyanex 301-Pd complex is incorporated into the alginate gel in acidic media.

## Selectivity of Pd Uptake from Multi-Component Solutions

An important challenge for the development of Pd recovery systems is the selectivity of the binding process. Indeed, in most cases the leachate solutions contain a great variety of metals including other precious metals (such as Pt) or base metals (such as Cu, Ni, Zn, etc.). To verify the possibility of using the materials proposed in this study for the treatment of real industrial solutions, several experiments were performed with multi-component solutions containing Cu, Ni and Zn at increasing concentrations (from 1 to 5 g metal $L^{-1}$) in 1 M HCl.

Figure 7 shows that the presence of these metals in the solution did not affect Pd binding: under the experimental conditions used, Pd uptake remained close to 26% (within experimental error), regardless of the



| | Reference | Cu | Ni | Zn |
|---|---|---|---|---|
| Pd uptake (%) | 26.4 ± 1.2 | 23.0 ± 2.7 | 29.3 ± 2.6 | 29.4 ± 1.8 |
| $K_d$ | 3.90 ± 0.25 | 3.19 ± 0.53 | 4.59 ± 0.66 | 4.60 ± 0.43 |

***Figure 7.*** Influence of increasing concentration of competing metal (Cu, Ni, Zn) on Pd (A) and competing metal (B) uptake.

concentration of the competing metals. The Pd distribution coefficient was also almost unchanged in the presence of the competing ions. The most significant effect was observed in the presence of copper. Analytical determinations of the competing metal ions also showed that a small fraction of the metals initially present (less than 10%) was removed from the solution. Although the Pd sorption process was not really selective, the presence of base metals within the concentration range used did not decrease the Pd binding performance.

Figure 8 shows the effect of the presence of platinum on the uptake of palladium from 1 M HCl. Pd uptake was not affected by increasing concentrations of Pt. Under our experimental conditions, the Pd uptake remained at about 27–28% and the binding capacity remained close to 320 mg Pd $g^{-1}$ Cyanex 301. The change in Pd uptake was less than 5%, regardless of

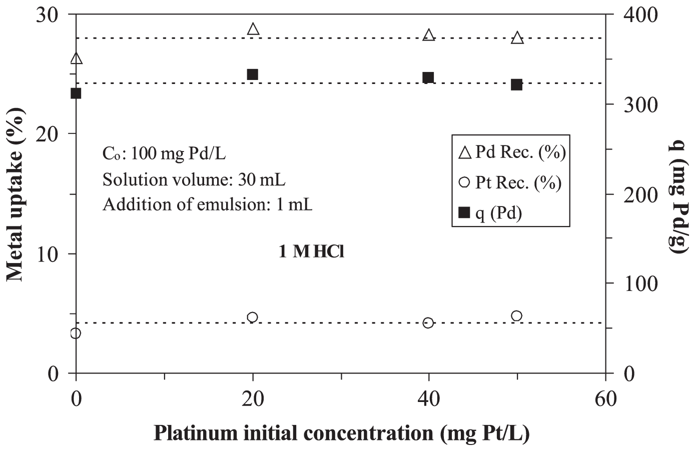


*Figure 8.* Pd uptake from Pd/Pt binary solutions – Influence of Pt concentration on Pd and Pt uptake and Pd binding capacity.

the concentration of Pt in the 0–50 mg Pt $L^{-1}$ concentration range. Pt uptake did not exceed 5%, showing that the Cyanex 301 emulsion has a marked preference for Pd compared to Pt. This is confirmed by the data in Table 3 showing the selectivity coefficient S ($S = K_d(Pd)/K_d(Pt)$) as a function of different Pd/Pt molar ratios. The selectivity coefficient increased with the molar excess of Pd. It exceeded 1200 when the initial Pd concentration was 7 times the concentration of Pt, but decreased to 7 when the concentration of Pt was 3 times that of Pd. These results indicate that the Cyanex 301 emulsion-based process allows improving the separation of the metals although it is not possible to collect Pd separately from Pd/Pt mixed solutions.

## Recycling of the Separation System

The possibility of material recycling is of fundamental importance, especially in the case of base metal recovery. In general, for the practical viability of a

*Table 3.* Pd and Pt separation from 0.1 M HCl bi-component solutions: influence of Pd/Pt molar ratio on the selectivity coefficient, S

| [Pd] (mg $L^{-1}$) | [Pt] (mg $L^{-1}$) | [Pd]/[Pt] (molar units) | S $K_d$(Pd)/ $K_d$(Pt) |
|---|---|---|---|
| 74.6 | 19.0 | 7.2 | 1244 |
| 75.6 | 38.8 | 3.6 | 24 |
| 75.1 | 49.6 | 2.8 | 37 |
| 38.2 | 49.2 | 1.4 | 20 |
| 19.4 | 47.8 | 0.74 | 28 |
| 19.5 | 96.6 | 0.37 | 7 |

separation system, the cost of the extractant, the value of the recovered metal, and the possibility to reuse the extractant are the key parameters. In the case of PGMs, the value of the target metal changes the approach to the problem. Although reuse of materials is always preferable, the economic constraints are less acute.

The stripping of Pd from the metal loaded Cyanex 301-emulsion was tested using common stripping agents, such as acids, ammonia and thiourea. 0.1 M thiourea (at neutral pH and in HCl solutions at pH 2) and 0.5 M ammonia allowed to recover between 20 and 35% of Pd. Palladium chelation to thiourea is not favorable for the following steps of metal separation. Hydrochloric acid (8 M) and nitric acid (5 M) were also tested. Although a considerable fraction of the Pd was removed from the polymer phase, the desorption yield remained quite low (below 30% with HCl and no more than 50% with nitric acid). The relatively low metal recovery is due to the strong interaction of the metal with the components of the emulsion. Also, the physical entrapment of Pd in the polymer gel probably limits the accessibility of the loaded internal sites to the stripping agent. The better performance of nitric acid can be explained by a change in the chemical speciation of Pd: nitric acid destroys the chloro-complexes and brings the metal back to its $Pd^{2+}$ cationic state that is much less extractable by Cyanex 301 from acidic solutions.

It is possible that the recovery of Pd by stripping with nitric acid might be further improved by finding the optimum acid concentration for stripping. However, even if total metal strip were achieved, the polymeric material after stripping would still be in a gel state, and, as such, it would not be compatible with reuse for a new reactive precipitation/stripping cycle. It seems therefore that the most appropriate treatment of the loaded polymeric phase should consist in incinerating the material, followed by further purification of the concentrated palladium residue using one of the conventional processes that are effective for more concentrated feeds.

## CONCLUSIONS

Cyanex 301 was used for the preparation of a stable emulsion in the presence of gelatin and alginate. This stable emulsion efficiently removes Pd from HCl solution by solvating interaction with the thiophosphoryl group of the ligand, followed by precipitation of the emulsification matrix (i.e., alginate) in the acidic medium. The sorption of palladium by the Cyanex 301-based emulsion was practically independent of HCl and $Cl^-$ concentrations. The ligand to metal ratio at emulsion saturation was close to 1:1. Logarithmic slope analysis of the Pd distribution ratios between the liquid and gel phases vs. the Cyanex 301 concentration also indicated the formation of complexes with a ligand solvation number of 2 when the ligand is in large excess over the metal. However, the data also suggested that other metal uptake mechanisms are operative under the conditions used in this study.

The binding capacities reached values as high as 330 to 350 mg Pd $g^{-1}$ Cyanex 301, almost independent of HCl and $Cl^-$ concentrations. The binding isotherm was very favorable (almost irreversible) as indicated by the initial slope of the curve. High sorption capacities were reached with residual Pd concentrations as low as 10 to 15 mg Pd $L^{-1}$. The maximum binding capacities obtained with the emulsion-based separation procedure were significantly higher (by ~20%) than the values obtained with the same material in the form of capsules (i.e., in solid form). The accessibility of the reactive groups when the ligand is in a soluble form is improved compared to when a solid-like form (capsules) is used.

The presence of Cu, Ni, Zn at concentrations as high as 5 g metal $L^{-1}$ did not significantly affect the Pd uptake, although the simultaneous uptake of a fraction of these metals did not allow complete separation of Pd from base metals. A similar preference of the Cyanex 301 emulsion was observed for Pd in the presence of increasing concentrations of Pt. The selectivity coefficient depended on the initial Pd/Pt molar ratio.

Complete stripping of palladium from the precipitated polymeric alginate phase was not achieved. The most appropriate treatment of the palladium loaded alginate phase should consist in incineration.

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