



Solvent Extraction of Titanium(IV) with Organophosphorus Extractant from Chloride Solutions

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The organophosphorus extractants for extraction of Ti(IV) from chloride solutions were introduced, mainly including acidic organophosphorus extractants such as D2EHPA, EHEHPA, Cyanex 272, Cyanex 302, Cyanex 301 and neutral organophosphorus extractants like Cyanex 923 (TRPO), tri-octyl phosphine oxide (TOPO) and tri-*n*-butyl phosphate (TBP). The extraction behaviours like extraction mechanism, extraction equilibrium, loading capacity, stripping behaviour and selectivity were reviewed, along with the effect of acidity, diluent and metal concentration to Ti(IV) extraction. The Ti(IV) extraction equilibrium time with acidic organophosphorus extractants is more than 1 h except Cyanex 302 and Cyanex 301 with which less than 5 min are required to reach equilibrium. The Ti(IV) extraction kinetics with neutral organophosphorus extractant is also fast: the extraction reaches equilibrium within 3-5 min. Stripping Ti(IV) from loaded acidic organophosphorus extractants is difficult, while from neutral ones is much easier. Compared to neutral organophosphorus extractants, the practical application of acidic organophosphorus compound is difficult for Ti(IV) extraction due to their slow extraction equilibrium and difficulty in stripping and neutral organophosphorus extractants could be used to separate both Fe(III) and Ti(IV) from other metal impurities. TBP could be used for separation Fe(III) from Ti(IV) and other metal ions.

Keywords: Titanium, Solvent extraction, Organophosphorus extractant, Chloride solution.

INTRODUCTION

Ilmenite supplies 90 % of the world demand for titanium minerals. The widest application of titanium is producing TiO₂ which has a wide range of applications such as pigment, sunscreen and food coloring. Titanium dioxide is considered as the best white pigment in the world. The manufacture of the pigment grade titanium dioxide is based on two processes *i.e.*, sulphate process and chloride process. The sulphate process is the first commercialized technology to convert ilmenite to titanium dioxide and is based on the digestion of ilmenite or titanium slag in concentrated sulphuric acid¹. The disadvantages of this process include relatively inferior product quality, long processing time, high input of energy, large volumes of waste iron sulfate and waste sulphuric acid. The chloride process relies on chlorination of high grade titanium slag or rutile, then oxidation of TiCl₄ to TiO₂. The chloride process is better than the sulphate process and has dominated the pigment industry. The disadvantages of the chloride process are that low grade ilmenite ores can't be chlorinated directly and high grade titanium slag or rutile is needed. Another disadvantage of chloride process is that the use of the harmful chlorine gas is not environmentally friendly and requires complicated equipment.

Recovery of Ti(IV) from industry waste chloride liquors or extraction and separation Ti(IV) from ilmenite using solvent extraction technology has been investigated. Producing pigment grade TiO₂ by solvent extraction technology could overcome the drawbacks of the two processes mentioned above due to its simplified facilities, less operation procedures and low operating costs. A hydrometallurgical process has been proposed for the production of pigment TiO₂ from titaniferous mineral ores². The process embodies two steps of solvent extraction process, first extraction of Fe(III) and Ti(IV) with TRPO, leaving Fe(II) and other metal ions in the raffinate and second selective removal of Fe(III) from Ti(IV) with Alamine 336, leaving Ti(IV) in the raffinate. Since then, many investigations have been conducted. Sole³ has reviewed the extraction behaviour of Ti(IV) from sulphate media. In this paper, an attempt has been made to review the recent reports on the solvent extraction and separation of titanium from other metal ions in the chloride solutions.

Extraction by acidic organophosphorus extractants:

Acidic organophosphorus compounds are the most widely used extractants in solvent extraction technology for metal separation and recovery. Among them, D2EHPA⁴⁻⁸ and EHEHPA⁹⁻¹³ has been proved to be the most versatile reagent for the extraction of Ti(IV) from acidic chloride solutions. Their molecular formulae are listed in Table-1.

TABLE-1
MOLECULE FORMULA OF DIFFERENT ACIDIC ORGANOPHOSPHORUS EXTRACTANTS

Extractant	Chemical name	Formula	Reference
D2EHPA	Di(2-ethylhexyl)phosphoric acid (D2EHPA)		14
EHEHPA	2-Ethylhexyl phosphonic acid mono-2-ethylhexyl phosphoric ester (EHEHPA)		14
Cyanex 301	Di-2,4,4-trimethylpentyl dithiophosphinic acid (Cyanex 301)		14,15
Cyanex 272	Di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272)		16
Cyanex 302	Di-2,4,4-trimethylpentyl monothiophosphinic acid (Cyanex 302)		16

Extraction mechanism: The extraction of Ti(IV) by acidic organophosphorus extractants from chloride medium results from the exchange of TiO^{2+} or $\text{Ti}(\text{OH})_2^{2+}$ in aqueous phase and H^+ in organic phase when the acidity of the solutions is relatively low. The solvent extraction of Ti(IV) occurs *via* eqn. 1^{8-10,14,16}:



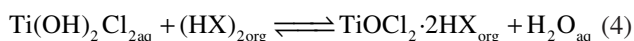
where $(\text{HX})_2$ refers to the dimeric form of the acidic organophosphorus extractants and at higher Ti(IV)/HX ratio when using D2EHPA, extraction mechanism could be expressed as eqn. 2⁸:



But when Ti(IV) is extracted by the form of $\text{Ti}(\text{OH})_2^{2+}$, the extraction occurs following eqn. 3⁵:



Sato^{5,12} found that the extraction of Ti(IV) at low aqueous acidity is governed by cation-exchange reaction and at higher acidity by solvating reaction. The extraction mechanism at higher aqueous acidity is expressed as eqn. 4:



Extraction equilibrium: According to the extraction mechanism of cation exchange, the Ti(IV) extraction equilibrium constant K_{ex} ¹⁰ with acidic organophosphorus extractants under relatively high ratio of Ti(IV)/HX could be expressed as eqn. 5:

$$K_{\text{ex}} = \frac{[\text{TiO}(\text{HX}_2)_2][\text{H}^+]^2}{[\text{TiO}^{2+}][(\text{HX})_2]^2} \quad (5)$$

The equilibrium constants K_{ex} of Ti(IV) extraction with different extractants are listed in Table-2:

The results obtained with EHEHPA in kerosene and in xylene were different. The discrepancy may be due to the difference in diluent. But it is clear that the extraction efficiencies of Ti(IV) with EHEHPA and D2EHPA are greater than Cyanex 272. From the value of $\log K_{\text{ex}}$, it is evident that the extraction capabilities of D2EHPA and EHEHPA for Ti(IV) are close to each other. The equilibrium time for Ti(IV) extraction reported by different authors are listed in Table-3. From these results,

TABLE-2
EQUILIBRIUM CONSTANTS OF Ti(IV)
EXTRACTION FOR DIFFERENT EXTRACTANTS

Extractant name	Diluent	Log K_{ex}	Reference
D2EHPA	Kerosene	3.95 ± 0.02	8
EHEHPA	Xylene	4.77 ± 0.02	9
–	Kerosene	4.09 ± 0.03	10
Cyanex 272	Xylene	2.27 ± 0.02	16
Cyanex 302	Toluene	1.85 ± 0.02	17
Cyanex 301	Toluene	1.93 ± 0.02	17

TABLE-3
EQUILIBRIUM TIME FOR Ti(IV) EXTRACTION

Extractant	Time (min)	HCl (M)	Diluent	Reference
D2EHPA	120	0.5, 1.0	Kerosene	8
EHEHPA	<5	0.2-1.5	Xylene	9
–	90	1-2	Kerosene	10
–	60	0.5	Kerosene	11
–	50	0.5-4.0	Kerosene	13
Cyanex 272	120	0.14	Xylene	16
Cyanex 302	2	0.01-5	Toluene	17
Cyanex 301	2	0.01-5	Toluene	17

it is obvious that long time is needed to reach equilibrium for Ti(IV) extraction with acidic organophosphorus extractant from HCl solutions.

The saturated loading capacities reported for Ti(IV) extraction with acidic organophosphorus extractants under different conditions are listed in Table-4:

Although each extractant was investigated under different conditions, including metal concentration, extractant concentration and HCl concentration, the results demonstrated the loading capacities for titanium with different organophosphorus extractants were roughly consistent with the order of equilibrium constants (Table-2).

Effect of HCl concentration: The extraction of Ti(IV) from HCl solutions at various HCl concentrations with D2EHPA in kerosene or benzene was carried out by Sato⁵. The results showed that the distribution coefficient decreased with aqueous acidity increasing below 3 M and rose with acidity above this acidity. This tendency was not greatly influenced by varying the kind of the diluent: although the extraction efficiency for Ti(IV) with D2EHPA in kerosene was higher than that in benzene, the shape of the extraction curves resembled each other.

TABLE-4
SATURATED LOADING CAPACITY OF ACIDIC ORGANOPHOSPHORUS EXTRACTANTS

Extractant name	Ti(IV) loading (g/mol)	Ti(IV) (g/L)	Diluent	HX (M)	HCl (M)	Reference
D2EHPA	23.6	1.00	Kerosene	0.2	0.2	8
EHEHPA	18.1	0.48	Kerosene	1.0	2.0	10
Cyanex 272	17.6	–	Xylene	–	0.25	16
Cyanex 301	4.79	>5.0	Toluene	0.1	2	17
Cyanex 302	7.58	>5.0	Toluene	0.1	2	17

Fig. 1 showed a very slight minimum in the distribution values at 1 M HCl concentration¹¹. It indicated that extraction of Ti(IV) with EHEHPA was much less dependent on the HCl concentration; probably because TiO^{2+} was still the dominating species while the concentration of HCl was less than 4 M.

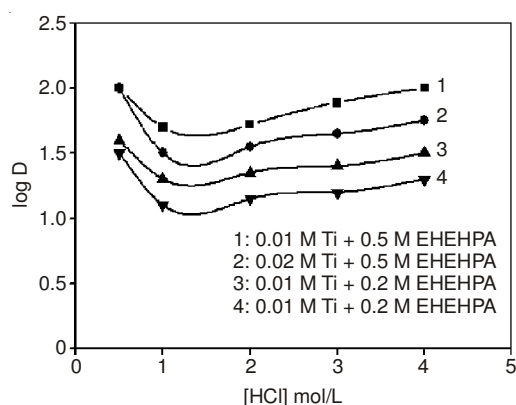


Fig.1. Effect of HCl concentration on Ti(IV) extraction with EHEHPA in kerosene [Ref. 11]

Effect of diluent on Ti(IV) extraction: Polarities of diluents have significant effect on Ti(IV) extraction with acidic organophosphorus extractants. John *et al.*⁹ and Saji & Reddy¹⁰ investigated the relationship between dielectric constant and percentage of extraction or distribution coefficient with EHEHPA. He found with the dielectric constant increasing, the percentage of extraction decreased. Also distribution coefficient has been investigated the same tendency. The percentage of extraction was found to be 98 % for diluent cyclohexane with a dielectric constant of 2.02 while 32 % for diluent methyl isobutyl ketone with a dielectric constant of 13.11. The distribution coefficient was found to be 5.27 for kerosene with a dielectric constant of 2.00 while 1.15 for chloroform with a dielectric constant of 4.90. The relationship between dielectric constant and distribution coefficient has been investigated by Saji *et al.*¹⁶ when using Cyanex 272 as an extractant in different kinds of diluents under the same conditions. Also the result showed the same tendency with EHEHPA. Diluents such as kerosene, benzene, toluene and xylene having lower dielectric constant showed higher extraction efficiency of Ti(IV). But with methyl isobutyl ketone with a dielectric constant of 13.11

as the diluent for Cyanex 272, the distribution coefficient of Ti(IV) extraction reached as high as 10.11 unexpectedly. This could be attributed to the synergistic effect of the mixed-ligand system. Strong interactions of diluent with the extractant could result in lower extraction efficiency of metal ions.

Effect of Ti(IV) concentration on extraction: Biswas and Begum⁸ found that the distribution coefficient was independent of initial Ti(IV) concentration in aqueous phase up to 1 g/L Ti(IV) and after that it decreased appreciably when the equilibrium acidity and concentration of D2EHPA remained constant. This behaviour indicated the formation of non-extractable TiO^{2+} species in aqueous phase at higher Ti(IV) concentration. Saji *et al.*¹⁰ and Fontana *et al.*¹¹ found that the extraction of Ti(IV) was independent of metal ion concentrations with EHEHPA. The log-log plot of the equilibrium organic phase metal concentration against the aqueous phase metal concentration was linear with the slope equal to 1, indicating that only mononuclear species were extracted into the organic phase. The different conditions during the investigations of the effect of different Ti(IV) concentration on extraction are listed in Table-5.

Stripping behaviour of Ti(IV): Saji *et al.*¹⁶ have investigated stripping behaviour of Ti(IV) from a loaded organic solvent system consisting of Cyanex 272 in xylene using various mineral acids such as sulphuric acid, hydrochloric acid and nitric acid and found that the stripping of Ti(IV) from loaded organic phase was not quantitative even at higher acid concentrations. Trial experiments showed that complete stripping of Ti(IV) from the loaded organic phase was possible in a single stage extraction using a solution containing 2 M H_2SO_4 and 1 % H_2O_2 . Saji and Reddy¹⁰ found that stripping was impractical with HCl alone and a mixture of 2 M H_2SO_4 and 2 % H_2O_2 was found to be an effective stripping agent for Ti(IV) in a single stage. Fontana *et al.*¹¹ and Borsalini *et al.*¹³ reported that a single stage experiment with 3 M sulphuric acid, hydrochloric acid and nitric acid showed very slow kinetics of titanium stripping. But using sodium carbonate as stripping agent, the stripping of titanium was very fast with the yield of 100 %.

The reason for the slow kinetics may be due the strong Ti(IV)-EHEHPA complex. But when using a mixture of H_2O_2 and sulphuric acid solution as stripping solutions, high yield

TABLE-5
EFFECT OF DIFFERENT Ti(IV) CONCENTRATION ON EXTRACTION

Extractant	HCl (M)	Extractant (M)	Diluent	Ti(IV) (mM)	References
D2EHPA	2.00	0.075	Kerosene	0.5-50	8
EHEHPA	1.37	0.100	Xylene	0.4-2	9
–	1.00	0.100	Kerosene	2-10	10
–	1.00	0.500	Kerosene	6-20	11
Cyanex 272	0.18	0.050	Xylene	2.5-10	16

was achieved. It is probably because that the chemical bond energy formed between Ti(IV) and stripping agents are stronger than those in Ti(IV)-EHEHPA complex. From Table-6, it is obvious that the mixtures of H₂SO₄ with certain amounts of H₂O₂ and Na₂CO₃ are the effective stripping agents for Ti(IV) with the acidic organophosphorus extractants. It demonstrated that using the mixture of H₂SO₄ and H₂O₂, the optimum concentration could be 2 M H₂SO₄ and 2 % H₂O₂. The stripping efficiency also significantly improved using a mixture of HCl and H₂O₂ as stripping solution.

Comparison of extraction behaviour of Ti(IV) with other associated metal ions: Reddy *et al.*⁹ studied Ti(IV) selectivity over other associated metal ions of 0.36 mM Fe(III), 0.83 mM Mg(II), 0.25 mM V(V), 0.1 mM Cr(VI), 1 mM Mn(II), 1 mM Zn(II) and 0.55 mM Zr(IV) in the HCl concentration range of 0.03-1.46 M with 0.05 M EHEHPA in xylene as an extractant. It was found that the extraction of Ti(IV) and Fe(III) decreased with increasing HCl concentration and Zr(VI) was quantitatively extracted and Cr(VI) was extracted moderately under these conditions. High separation factor of 8333 between Ti(IV) and Fe(III) was observed at 0.2 M HCl. Fig. 2 showed the effect of HCl concentration on extraction of Zr(IV), Ti(IV), Fe(III) and Cr(VI).

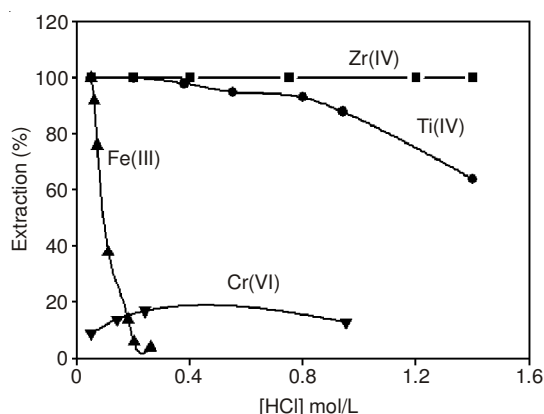


Fig. 2. Ti(IV) extraction selectivity over associated metals with EHEHPA [Ref. 9]

The extraction behaviours of Mg(II), Al(III), Ti(IV), V(V), Cr(III), Mn(II) and Fe(III) have been investigated as a function

of HCl concentration and the results are shown in Fig. 3¹⁰. The same tendency with the result obtained by Saji⁹, with HCl concentration increasing the percentage of the extraction of Ti(IV), Fe(III) and V(V) decreased. The extraction of Mg(II), Al(III), Cr(III) and Mn(II) were found to be negligible under these experimental conditions and V(V) and Fe(III) was also negligible at 2 M HCl concentration.

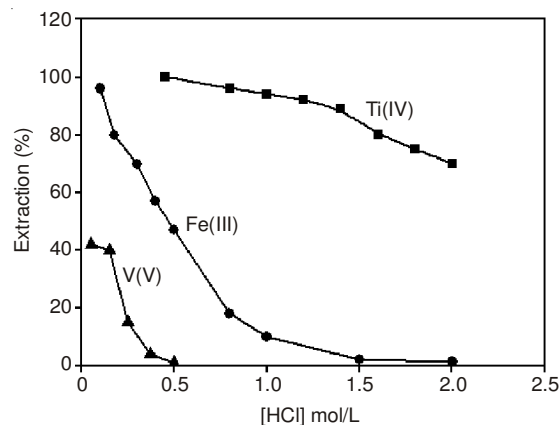


Fig. 3. Ti(IV) extraction selectivity over associated metals with EHEHPA [Ref 10]

Saji *et al.*¹⁶ investigated the separation of Ti(IV) from various synthetic binary mixtures [Ti(IV)/Fe(III), Ti(IV)/Mn(II), Ti(IV)/Zn(II), Ti(IV)/Mg(II), Ti(IV)/V(V)] and ternary mixtures [Ti(IV)/Mn(II)/Zn(II)/Fe(III)/Mg(II)/V(V)] by extraction with Cyanex 272 in xylene from HCl solutions. With the aqueous solutions containing 0.5-2.5 mM metal ions and 0.3 M HCl and the organic solution containing 0.2 M Cyanex 272, almost entire Ti(IV) was extracted into the organic phase while little Mn(II), Zn(II), Fe(III), Mg(II) and V(V) were extracted. The results indicated that Cyanex 272 demonstrated excellent selectivity of Ti(IV) over other associated metals. Deep *et al.*¹⁷ reported the poor selectivity of Ti(IV) with Cyanex 302 or Cyanex 301 as extractant. Pospiech *et al.*¹⁸, Jayachandran and Dhadke¹⁹ investigated separation of Fe(III) from other metal ions with D2EHPA and EHEHPA as extractant, respectively. The results showed that other metal ions were more or less co-extracted with Fe(III), indicating the poor selectivity of D2EHPA and EHEHPA.

TABLE-6
STRIPPING FROM LOADED ACIDIC ORGANOPHOSPHORUS EXTRACTANTS AT AN A/O RATIO OF 1

	Concn. (M)	Diluent	Stripping solutions	Stripping (%)	Reference
EHEHPA	0.2	Kerosene	4 M HCl	11.7	10
			2 M HCl + 1 % H ₂ O ₂	61.2	
			2 M HCl + 2 % H ₂ O ₂	95.5	
			2 M H ₂ SO ₄ + 1 % H ₂ O ₂	68.2	
	0.5	Kerosene	2 M H ₂ SO ₄ + 2 % H ₂ O ₂	>99.9	11
			3 M H ₂ SO ₄	6.7	
			3 M H ₂ SO ₄ + 1 % H ₂ O ₂	52.6	
			3 M H ₂ SO ₄ + 3 % H ₂ O ₂	81.7	
	0.5	Kerosene	1 M Na ₂ CO ₃	Complete	13
			2 M H ₂ SO ₄	20.1	
			2 M H ₂ SO ₄ + 2 % H ₂ O ₂	60.5	
			2 M H ₂ SO ₄ + 4 % H ₂ O ₂	82.0	
			2 M Na ₂ CO ₃	99.0	
Cyanex 272	0.2	Xylene	2 M H ₂ SO ₄ + 1 % H ₂ O ₂	Complete	16
Cyanex 302	0.1	Toluene	0.5 M H ₂ SO ₄ + 3 % H ₂ O ₂	99.1	17
Cyanex 301	0.1	Toluene	0.5 M H ₂ SO ₄ + 3 % H ₂ O ₂	98.2	17

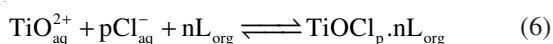
TABLE-7
WIDELY USED NEUTRAL ORGANOPHOSPHORUS EXTRACTANTS

Extractant	Chemical name	Formula
TBP	Tri- <i>n</i> -butyl phosphate	(RO) ₃ P=O, R = butyl
TOPO	Tri-octyl phosphine oxide	R ₃ P=O, R = octyl
Cyanex 923(TRPO)	Tri-alkyl phosphine oxide	A mixture of R ₃ P=O, R ₂ R'P=O and RR' ₂ P=O, R = octyl, R' = hexyl

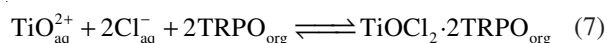
Extraction by neutral organophosphorus extractant:

Neutral organophosphorus extractants are other important compounds for Ti(IV) extraction. Among them, tri-*n*-butyl phosphate (TBP)²⁰⁻²⁴, tri-octyl phosphine oxide (TOPO)²⁵⁻²⁹ and Cyanex 923 (TRPO)³⁰⁻³² have been widely used for Ti(IV) extraction. Compared with acidic organophosphorus extractants, neutral organophosphorus extractants have no H⁺ for ion exchange, so the extraction mechanism is solvating reaction. Ti(IV) is extracted in the form of neutral molecule consisting of associated anions. The formulae of the three widely used extractants are showed in Table-7.

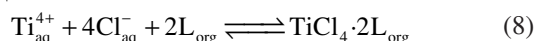
Extraction mechanism: Allal *et al.*²⁰ have studied the extraction behaviour of tetravalent titanium from HCl and calcium chloride solutions with TBP and TOPO as the extractant. They proposed the extraction mechanism (eqn. 6) for Ti(IV):



where L is the extractant (TBP or TOPO); n and p equal to 2. A very similar equation was given by Remya and Reddy³², the extraction mechanism for Cyanex 923 (TRPO) could be expressed as eqn. 7:



Thomas *et al.*¹⁴ and John *et al.*³¹ investigated Ti(IV) extraction from acidic chloride solutions with Cyanex 923 and TBP, respectively. In their studies, the extraction mechanism of Ti(IV) with neutral organophosphorus extractants can be represented as:



where L is TBP¹⁴, TOPO²⁵ or Cyanex 923³¹.

Extraction equilibrium: When the neutral molecule involved in the extraction complex is TiCl₄, the extraction equilibrium constant K_{ex} could be calculated with eqn. 9^{14,25,31}, while the neutral molecule is TiOCl₂, K_{ex} could be expressed as eqn. 10^{20,32}:

$$K_{\text{ex}} = \frac{[\text{TiCl}_4 \cdot 2\text{L}]}{[\text{Ti}^{4+}][\text{Cl}^{-}]^4[\text{L}]^2} \quad (9)$$

$$K_{\text{ex}} = \frac{[\text{TiOCl}_2 \cdot 2\text{L}_2]}{[\text{TiO}^{2+}][\text{Cl}^{-}]^2[\text{L}]^2} \quad (10)$$

The equilibrium constants of Ti(IV) extraction with different kinds of neutral organophosphorus extractants are listed in Table-8.

Several authors^{20,25,31,32} reported that the extraction equilibrium with neutral organophosphorus extractants was very fast

and taking less than 5 min were required to reach equilibrium. The saturated loading capacities reported for Ti(IV) with neutral organophosphorus extractants under different conditions are listed in Table-9.

TABLE-8
K_{ex} OF Ti(IV) EXTRACTION WITH DIFFERENT NEUTRAL ORGANOPHOSPHORUS EXTRACTANTS

Extractant name	Diluent	K _{ex}	Reference
TBP	Dodecane	0.72	20
TOPO	Dodecane	2.95	20
Cyanex 923	Xylene	0.59	31
-	Xylene	2.85	31
-	Kerosene	1.34	32

The results demonstrate the loading capacities of different neutral organophosphorus extractants for titanium are lower than that of acidic organophosphorus extractants.

Effect of acidity and chloride ion concentration: Many investigations showed that the Ti(IV) extraction efficiency increased with the concentration of HCl or the total chloride increasing using TBP^{14,20}, TOPO^{20,25} and Cyanex 923^{31,32}.

To confirm the effect of chloride ion concentration on Ti(IV), the experiments were carried out varying chloride ion concentration with HCl and CaCl₂²⁰. Fig. 4 showed the extraction efficiency of Ti(IV) from CaCl₂ solution was better than from HCl solution. The results demonstrated that the concentration of chloride ion played an important role in Ti(IV) extraction. In fact, the increase HCl concentration played an undesirable role in Ti(IV) extraction. During the extraction of Fe(III) from acidic chloride solutions by Cyanex 923³⁰, it was found with the HCl concentration increasing, the Ti(IV) extraction efficiency decreased at the HCl concentration of 0.2-2.0 M. This was attributed to the fact that HCl was extracted by neutral organophosphorus extractants, leading to a decrease in the number of free molecules of TRPO available to extract Ti(IV).

It is obvious that compared with TBP and TOPO seems to be a better extractant and the extraction efficiency increased with the concentration of extractant increasing (Fig. 5). Ti(IV) was almost completely extracted at the chloride concentration of 6 M, but extraction with TBP only occurred while the concentration of chloride ion was greater than 6 M. The extraction of Ti(IV) found to be negligible at the HCl concentrations below 6 M was also reported by Thomas *et al.*¹⁴. Cyanex 923 also had strong extraction ability for Ti(IV) (Fig. 6). The extraction efficiency of Ti(IV) reached as high as 95 % with 0.4 M Cyanex 923 from 6.3 M HCl solution.

TABLE-9
SATURATED LOADING CAPACITY OF NEUTRAL ORGANOPHOSPHORUS EXTRACTANTS

Extractant name	Diluent	Ti(IV) (g/L)	L (M)	HCl (M)	Ti(IV) loading (g/100 g)	Reference
TBP	Kerosene	1.44	1.47	8.0	0.90	14
Cyanex 923	Kerosene	1.00	1.0	3.0	0.53	32

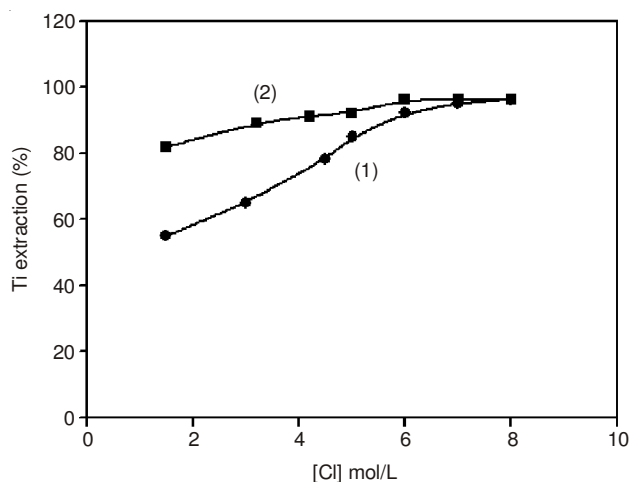


Fig. 4. Effect of the total chloride concentration on Ti(IV) extraction with 0.5 M TOPO in dodecane. (1) = HCl; (2) = 0.1 M HCl + x M CaCl₂ [Ref. 20]

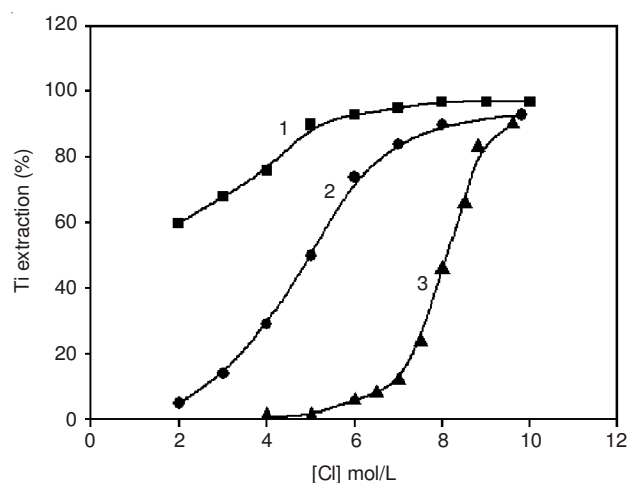


Fig. 5. Extraction of Ti(IV) from chloride media with TBP and TOPO in dodecane. Ti(IV) = 0.01 M; [Cl] = 0.1 M [HCl] + x M [CaCl₂]; 1 = 0.5 M TOPO; 2 = 0.1 M TOPO; 3 = 1 M TBP [Ref. 20]

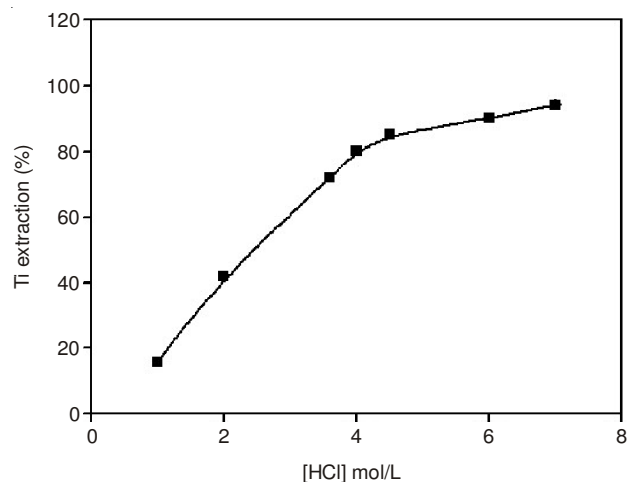


Fig. 6. Effect of HCl concentration on Ti(IV) extraction with 0.4 M Cyanex 923 in xylene. Ti(IV) = 1 mM [Ref. 31]

Effect of diluent on Ti(IV) extraction: Diluents have significant effect on Ti(IV) extraction with neutral organophosphorus extractants. Several authors^{14,20,31} investigated the relationship between dielectric constant and the extraction

efficiency or distribution coefficient of TBP and Cyanex 923. The tendency turned out to be the same with that of acidic organophosphorus extractants. With the dielectric constant increasing, the extraction efficiency and distribution coefficient decreased. The extraction efficiency was found to be 80 % for diluent cyclohexane with a dielectric constant of 2.02 while 40 % for diluent chloroform with a dielectric constant of 4.9. Diluents having lower dielectric constant showed higher extraction efficiency of Ti(IV). Aromatic diluents had relatively low extraction efficiency due to their strong interactions with the extractant than that of non-aromatic diluents. However, MIBK (methyl isobutyl ketone), which also had a high dielectric constant, showed high extraction efficiency for Ti(IV) unexpectedly. This could be attributed to the synergistic effect of the mixed solvent system³². For Cyanex 923, aromatic compound like xylene and mesitylene may be a better diluent than kerosene considering the viscosity of the organic phase³³.

It has to be mentioned that the third phase is formed during the extraction process with the neutral organophosphorus extractants^{20,23}. A third phase was formed with TBP or TOPO in dodecane as the extractant for Ti(IV) extraction, but no third phase was observed with xylene as diluent²⁰. This could be explained by the formed compound TBP-HCl and TOPO-HCl was insoluble in dodecane but soluble in xylene. This indicates that diluents have significant effect on Ti(IV) extraction with neutral organophosphorus extractants.

Stripping behaviour of Ti(IV): Allal *et al.*²⁰ reported that Ti(IV) was easily stripped from the loaded organic phase with 1 M HCl from loaded TBP and TOPO in decanol. The effect of HCl concentration on Ti(IV) stripping from the loaded organic solvent system consisting of 0.2 M Cyanex 923 in xylene [0.009 M of Ti(IV); temperature 303 ± 1 K] has been investigated by Saji³¹ and the results are shown in Fig. 7. Trial experiments showed that almost complete stripping of Ti(IV) from the loaded organic phase was possible in two stages of batch type countercurrent extraction at an A/O ratio of 3:1 with 1.0 M HCl solution. At a low A/O ratio of 1:1, only 70 % of Ti(IV) was stripped with HCl solution.

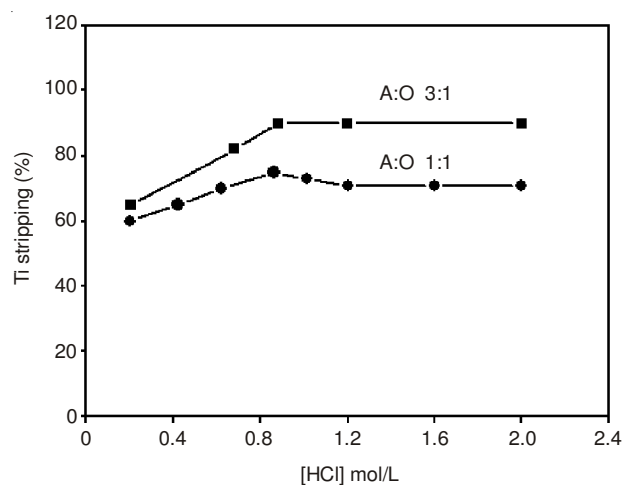


Fig. 7. Effect of HCl concentration on Ti(IV) stripping from loaded Cyanex 923 [Ref. 31]

Stripping of 0.015 M Ti(IV) loaded in 1.47 M TBP in kerosene was investigated by Thomas *et al.*¹⁴ with varying HCl

concentration in the stripping solution (Fig. 8). The results showed that quantitative stripping of Ti(IV) was realized with HCl concentration in the range of 1.0-5.0 M at an A:O ratio of 1:1.

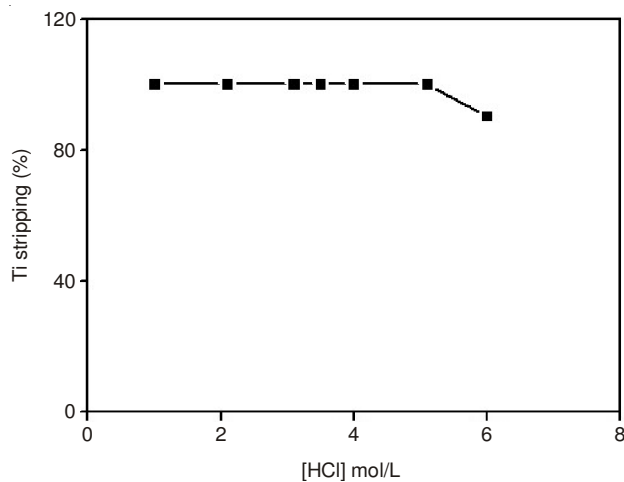


Fig. 8. Effect of HCl concentration on Ti(IV) stripping from loaded TBP [Ref. 14]

Comparison of extraction behaviour of Ti(IV) with other associated metal ions: The effect of HCl on the extraction of 1 mM Ti(IV), 0.358 mM Fe(III), 0.1 mM Cr(VI) and 0.252 mM V(V) has been studied with 0.1 M Cyanex 923 in xylene³¹. The results showed that the extraction of Ti(IV) and Fe(III) increased with increasing HCl concentration with Cyanex 923. Below the HCl concentration of 6.0 M, Cyanex 923 showed stronger extraction ability of Fe(III) over Ti(IV). Remya and Reddy³² investigated solvent extraction separation of Ti(IV), V(V) and Fe(III) from simulated waste chloride liquors with Cyanex 923 (Fig. 9). Mg(II), Cr(III), Mn(II) and Al(III) could not be extracted under experimental conditions. Duyvesteyn *et al.*² reported that Fe(III) was co-extracted with Ti(IV) using Cyanex 923 in kerosene leaving Fe(II) behind in the aqueous phase.

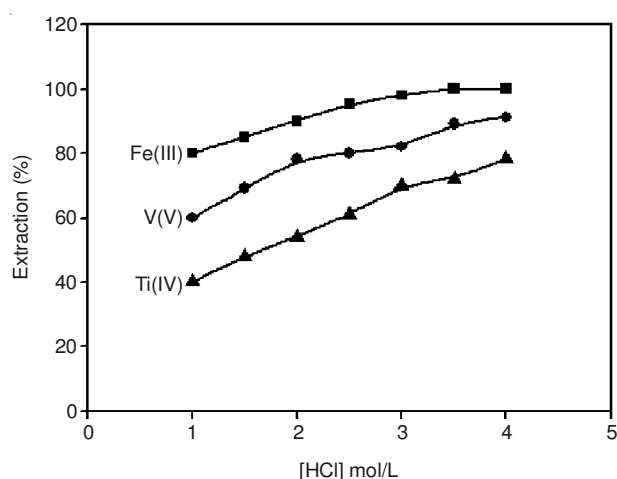


Fig. 9. Extraction behaviour of Mn(II), Al(III), Ti(IV), V(V), Cr(III), Mg(II) and Fe(III) from HCl solutions with 0.5 M TRPO [Ref. 32]

Ti(IV) extraction selectivity in a simulated wasted chloride liquor consisting of 0.04 M Mg(II), 0.03 M Al(III), 0.03 M Ti(IV), 0.01 M Cr(III), 0.03 M Mn(II) in 8.0 M HCl has been investigated by Thomas *et al.*¹⁴ using 1.47 M TBP in kerosene

(A:O = 1:2). Ti(IV) was detected 0.014 M while other metal ions couldn't be detected in the stripping liquor under the experimental conditions, indicating that Ti(IV) could be selectively separated from the waste chloride liquors of titanium manufacturing industry by employing TBP as an extractant. Seyfi found that the poor selectivity of TBP for Ti(IV) led to co-extraction of Fe(III) up to 65 %²³. Extraction and separation of Fe(III) from chloride solutions has been investigated³⁴⁻³⁷ and the results demonstrated that TBP showed higher selectivity of Fe(III) over Ti(IV).

Conclusion

- The extraction of Ti(IV) with acidic organophosphorus extractants proceeds *via* cation exchange mechanism in low HCl concentration solutions, while it proceeds *via* solvating mechanism in high HCl concentration solutions. With neutral organophosphorus extractant, the extraction mechanism is solvating reaction.

- The extraction equilibrium time of Ti(IV) with acidic organophosphorus extractants like D2EHPA, EHEHPA and Cyanex 272 is long *i.e.*, more than 1 h is required to reach equilibrium, while the equilibrium time with Cyanex 301 and Cyanex 302 is short behaviour of the extraction reaches equilibrium within 5 min. The Ti(IV) extraction kinetics with neutral organophosphorus extractants is also fast: 3-5 min is required to reach equilibrium.

- Stripping Ti(IV) from loaded acidic organophosphorus extractants is difficult, especially with mineral acids alone. High stripping efficiency could be obtained with special stripping solutions containing H₂SO₄-H₂O₂ mixtures or Na₂CO₃. Comparatively, stripping Ti(IV) from loaded neutral organophosphorus extractants is much easier with diluted HCl solutions.

- The diluents with low dielectric constants favour Ti(IV) extraction. Aromatic diluents have relatively low extraction efficiency because of their stronger interactions with the extractant than that of non-aromatic diluents. The diluent is very important for neutral organophosphorus extractants due to the formation of the third phase. Choosing a diluent which could dissolve the HCl-L (the neutral organophosphorus extractant) compound can eliminate the third phase.

- Acidic organophosphorus extractants show poor selectivity for Ti(IV) over V(V) and Fe(III) except Cyanex 272. Neutral organophosphorus extractants have better extraction capacity for Fe(III) than for Ti(IV).

- The extraction efficiency for Ti(IV) with the acidic organophosphorus extractants was found in the order of D2EHPA~EHEHPA > Cyanex 272 > Cyanex 302~Cyanex 301. Acidic organophosphorus extractants are not suitable for commercial application of Ti(IV) extraction because of their slow extraction equilibrium, poor selectivity and difficulty in stripping.

- The capacity for Ti(IV) extraction of the three widely used neutral organophosphorus extractants was found in the order of TOPO~TRPO > TBP. The extraction efficiency reached as high as 80 % at the HCl concentration of 4 M when the concentration of TOPO and TRPO were 0.5 M and 0.4 M, respectively. But with 1 M TBP, the extraction efficiency was less than 10 % although the concentration of HCl was 7 M. It is suggested that neutral organophosphorus could be used for

separation both Fe(III) and Ti(IV) from other metal ions and TBP could be used for separation Fe(III) from Ti(IV) and other metal ions. Then Ti(IV) can be separated from Fe(III) with other extractants.

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