

Separation of Ti(IV) and Fe(III) from Aqueous Sulphate Solution by Cyanex 272 [Bis(2,4,4-Trimethylpentyl) Phosphinic Acid] in Kerosene

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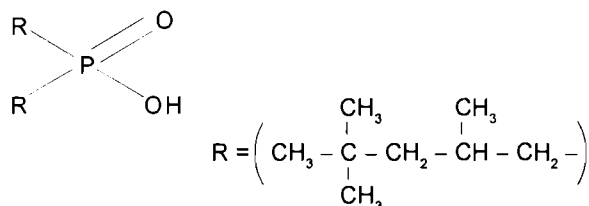
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Abstract. Extraction and separation of Ti(IV) and Fe(III) from aqueous sulphate solution by Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid] in kerosene was investigated. Extraction of Ti(IV) and Fe(III) increased with the increase of extractant concentration and decreased with the increase of aqueous phase acidity. About 95% Ti(IV) and 24% Fe(III) was extracted with 0.20 M Cyanex 272 and 0.25 M H₂SO₄. It was thought that Fe(III) was extracted in the organic phase by the formation of the species FeA₃ or FeA₃(HA)₂ and Ti(IV) as TiO₂·A₂. Data shows that Cyanex 272 can be used as a very effective extractant for Ti(IV) extraction from ilmenite leach solution at high acidity showing large separation coefficient for Ti(IV) from [Ti(IV) and Fe(III)] mixture. The maximum separation factor (β=116.50) was obtained at moderate acidity (0.90 M H₂SO₄) with high extractant (0.20 M Cyanex 272) concentration. The experimental data also suggested that the extraction of Ti(IV) and Fe(III) by Cyanex 272 did not follow simple extraction mechanism for all the acid ranges. It is likely that solvation mechanism may be operative at high acidity of the aqueous phase.

Keywords: solvent extraction, Ti-Fe separation, sulphate solution, Cyanex 272, kerosene

Introduction

Iron(III) coexists as an impurity with other valuable metals, such as titanium, cobalt, copper, nickel, manganese, zirconium etc in leach solutions. It is necessary to remove it before the recovery of pure metals from solutions. The removal of iron by solvent extraction is widely studied as an alternative to solid-liquid separation. Solvent extraction is one of the most effective extraction and separation techniques in hydrometallurgy which has been in use for more than three decades for its versatility and simplicity. The extractant Cyanex 272 is a proprietary technical grade item of Cytec Canada Inc. Its active component is bis [2,4,4-trimethylpentyl] phosphinic acid (Cyanex 272 = HA). The structure of Cyanex 272 is as follows:



This technical grade extractant has been used since 1983 and found to be very effective for the extractive separation of Co(II) from Ni(II) (Parhi *et al.*, 2008a; Gandhi *et al.*, 1993; Tait, 1993; Danesi *et al.*, 1984; Preston, 1983; Chou and Beckstead,

1990). However, other metal ion pairs have also been investigated for separation (Awwad *et al.*, 2009; Bari *et al.*, 2009a,b; Parhi and Sarangi 2008; Da Silva *et al.*, 2008; Deep *et al.*, 2006; Nathsarma and Niharbala 2006). Even though Cyanex 272 is selective for cobalt in the presence of nickel, a variety of several cations such as Fe(III), V(IV), Ni(II), Zn(II), Co(II), Cd(II), Cu(II), Mg(II), Al(III), Ca(II), Mn(II) can also be extracted depending upon the solution pH, from both chloride and sulphate media (Shiau *et al.*, 2005; Fontana *et al.*, 2005; Mandar *et al.*, 1999; Rickelton 1996; Kathryn and Sole 1995; Boyle and Rickelton 1990; Sastre *et al.*, 1990).

Cyanex 272 is totally miscible with common aromatic and aliphatic diluents and is extremely stable to both heat and hydrolysis. There seems to be no report on Ti(IV)/Fe(III) separation by Cyanex 272 in kerosene. Although the extraction of Ti(IV) and Fe(III) by Cyanex 272 has been widely studied from an equilibrium point of view, so far, the system has not been studied from the separation point of view, though separation using carboxylic acids and di-2-ethylhexyl phosphoric acid was attempted in the past.

The extraction and separation of titanium and iron by carboxylic acids, carbolic acid and carpic acid (Islam *et al.*, 1988) is very low. Though the reports on bis (2-ethylhexyl) phosphoric acid (Islam *et al.*, 1979) had been satisfactory, complete removal of iron was not achieved in a single operation. There are numerous reports on the extraction, separation

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and study of mechanism of different metal ions by other Cyanex type extractants such as Cyanex 301, Cyanex 302 Cyanex 471 and Cyanex 923.

The present work reports the extractive behaviour of titanium and iron as well as their separation from the mixture by Cyanex 272, as most of the titanium ores are associated with iron in nature. One of the chief ore of titanium is ilmenite (FeTiO_3). During processing for the production of pure TiO_2 from ilmenite leach solution, the separation of iron from titanium is a great problem. High purity TiO_2 can be obtained if all iron can be removed from the leach solution. Many methods are available but only few solvent extraction processes are reported with commercial extractants. Present work examines the efficacy of Cyanex 272 for separation of Ti and Fe from the aqueous phase.

Materials and Methods

Standard solution of Ti(IV) was prepared by fusing 0.5 g of analytically pure TiO_2 with 10.0 g of KHSO_4 in a suitable platinum crucible with heating until the oxide is dissolved. It was then cooled and dissolved in 15% H_2SO_4 by gentle heating and diluted to 500 cc by 15% H_2SO_4 . Another stock solution of Fe(III) was prepared by dissolving exactly 0.864 g of A.R grade ferric ammonium sulphate in distilled water to which 10 cc conc. H_2SO_4 was added. The resulting solution was then diluted to 1000 cc and mixed thoroughly. The solutions were standardized by the following methods.

The extractant Cyanex 272 having 85% purity was used without further purification. All other chemicals were of reagent grade and used without further purification. The diluent, kerosene, was purchased from the local market and distilled to collect the colourless fraction obtained in the range of 200-260 °C.

A stock solution of Cyanex 272 (1 M) was prepared by weighing out exactly 290 g of Cyanex 272 in a 1 litre volumetric flask and diluting with distilled kerosene. Extractant solutions of different concentrations were prepared by proper dilution of this stock solution by distilled kerosene.

A definite aliquot of an aqueous phase 20 ml was taken in a 125 ml reagent bottle and to it the same aliquot of organic phase, 20 ml, was added. The bottle was stoppered and shaken vigorously for a definite time (40 min) period in a thermostatic water bath at $30 \pm 1^\circ\text{C}$ (otherwise stated in the temperature dependence study). After attainment of equilibrium, the phases were allowed to settle and were disengaged. The aqueous phase was used to measure the metal ion content. The equilibrium organic phase metal ion concentrations were estimated by the method of difference (the organic phase Ti(IV)/Fe(III)

concentration was determined by the formula: aqueous phase initial concentration – aqueous phase concentration of Ti(IV)/Fe(III) after extraction). The distribution ratio (D) of a metal ion was calculated as the ratio of metal ion concentration in the organic phase to that in the aqueous phase at equilibrium. In the case of loading test, the organic phase was repeatedly contacted with fresh equal volume of aqueous solutions until the saturation of organic phase with the metal was attained. Metal contents [Ti(IV) and Fe(III)] in the aqueous phase were estimated by the hydrogen peroxide colorimetric method at $\lambda=410$ nm for Ti(IV) (Vogel, 1989a) and the thiocyanate method at $\lambda=480$ nm for Fe(III) (Vogel, 1989b) using spectrophotometer ANA-75 (Tokyo Photoelectric Company, Japan).

Results and Discussion

Effect of phase contact time on the extraction of Ti(IV) and Fe(III). Figure 1 represents contact time in minutes and the distribution ratio. It is evident from the figure that extraction ratio of Ti(IV) and Fe(III) increases continuously with the contact time. Near the equilibrium point the increase of extraction ratio with respect to time is much slower. No appreciable extraction of Ti(IV) and Fe(III) took place after 35 and 18 min, respectively. Therefore, it is concluded that the equilibrium is reached at 40 min, for Ti(IV) and at 20 mins for Fe(III) and there is no further extraction of metal ions. Previously, the phase contact time of Ti(IV) extraction was reported to be 180 min (Biswas and Begum, 1998) by D2EHPA in kerosene system. The equilibrium time for Fe(III) extraction was reported

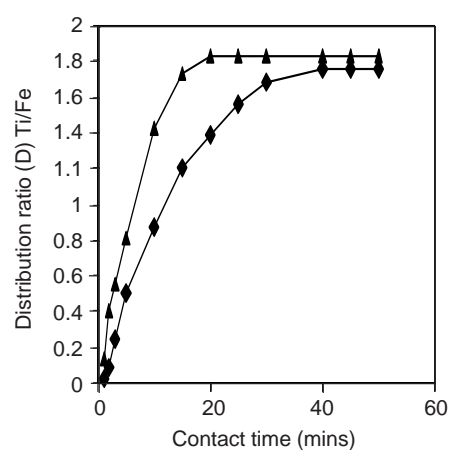


Fig. 1. Effect of contact time to reach equilibrium for Ti(IV) and Fe(III).

◆ = $[\text{Ti(IV)}]_{(ini)} = 1.1 \text{ g/dm}^3$, Acidity = $0.60 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; $[\text{HA}] = 0.10 \text{ M}$ Cyanex 272; ▲ = $[\text{Fe(III)}]_{(ini)} = 1.1 \text{ g/dm}^3$, acidity = $0.005 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; temperature = $(30 \pm 1)^\circ\text{C}$; phase ratio (A/O) = 1:1

to be 210 min (Islam *et al.*, 1979) by D2EHPA in benzene system. Therefore the equilibrium attainment was obtained much faster with Cyanex 272 in kerosene system than with D2EHPA for Ti(IV) and Fe(III) extraction. This may be advantageous as less time is required for the solvent extraction operation. Thus, in subsequent experiments, 40 min mixing have been used to ensure equilibrium for both the aqueous [Ti(IV) and Fe(III)] mixture.

Effect of extraction of Ti(IV) and Fe(III) from Ti(IV) - Fe(III) mixture on aqueous phase acidity and extractant concentration. The extraction data are plotted as log D vs. log $[H_2SO_4]$, M in Figs. 2 and 3. These figures represent the variation of distribution ratio on its aqueous phase acidity at different extractant concentrations. The plot shows that the extraction decreases with increasing aqueous phase acidity both for Ti(IV) and Fe(III) extraction within the range of 0.25 to 0.90 M H_2SO_4 . The extraction of Ti(IV) is higher than that of Fe(III). About 95% Ti(IV) is extracted at 0.25 M H_2SO_4 with 0.20 M Cyanex 272 and about 24% of Fe(III) is extracted at the same condition indicating that comparatively larger separation of the metal ions Ti(IV) and Fe(III) is possible at higher acidity. The extraction of Ti(IV) and Fe(III) is higher with 0.20 M Cyanex 272 than with 0.05 M Cyanex 272 extractant. At 0.90 M H_2SO_4 concentration, the extraction of Fe(III) is very low (about 1.82 %) and almost similar with different extractant concentrations (0.05, 0.10, 0.15 and 0.20 M Cyanex 272), and for 0.60 M H_2SO_4 concentration, the extraction of Fe(III) is also similar to the extractant concentrations of 0.10, 0.15 and 0.20 M Cyanex 272.

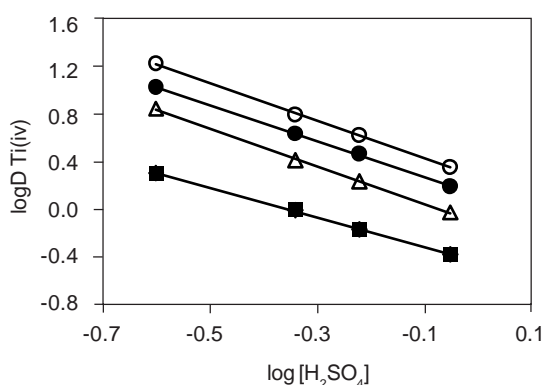


Fig. 2. Effect of extraction of Ti(IV) from Ti(IV) and Fe(III) mixture on aqueous phase acidity. $[Ti(IV)]_{(ini)} = 1.1 \text{ g/dm}^3$; $[Fe(III)]_{(ini)} = 1.1 \text{ g/dm}^3$; temperature = $(30 \pm 1)^\circ\text{C}$; contact time = 40 min; phase ratio (A/O) = 1:1; ■: 0.05 M HA; slope = 1.24; △: 0.10 M HA; slope = 1.50; ●: 0.15 M HA; slope = 1.50; ○: 0.20 M HA; slope = 1.57

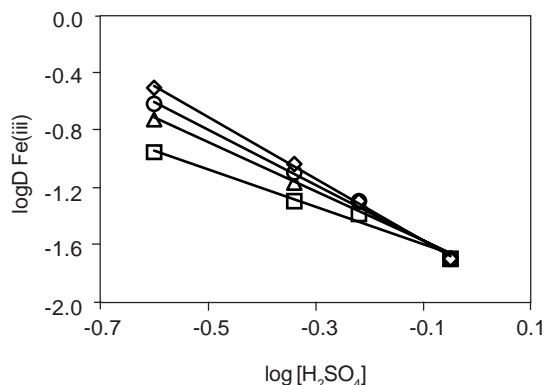


Fig. 3. Effect of extraction of Fe(III) from Ti(IV) and Fe(III) mixture on aqueous phase acidity. $[Ti(IV)]_{(ini)} = 1.1 \text{ g/dm}^3$; $[Fe(III)]_{(ini)} = 1.1 \text{ g/dm}^3$; Temperature = $(30 \pm 1)^\circ\text{C}$; contact time = 40 min; phase ratio (A/O) = 1:1; □: 0.05 M HA, slope = 1.29; △: 0.10 M HA, slope = 1.72; ○: 0.15 M HA, slope = 1.94; ◇: 0.20 M HA, slope = 2.15

At low aqueous acidity, the extractant molecules ionize in the aqueous phase boundary or its ionizing tendency becomes predominant forming a neutral extractable species with the metal ions. In a highly acidic solution, the above tendency is suppressed due to common ion effect and metal ion extraction is decreased. At a very high acidic solution, ionization of the extractant does not occur at all and it behaves like a neutral phosphate ester. In such a case, if any extraction occurs, the solvation by the extractant becomes the principal governing factor. The distribution ratio decreases with the increase of hydrogen ion concentration in the aqueous phase (Peppard *et al.*, 1962). It is observed that the distribution ratio of both Ti(IV) and Fe(III) increases with the increase of extractant concentration. In the case of Ti(IV) extraction, the slopes of acid dependence curves are 1.24, 1.58, 1.50 and 1.57 with the extractant concentrations of 0.05, 0.10, 0.15 and 0.20 M Cyanex 272; respectively; in the case of Fe(III) extraction, the acid dependence slopes are 1.29, 1.72, 1.94 and 2.15 with the extractant concentration of 0.05, 0.10, 0.15 and 0.20 M Cyanex 272, respectively. These values are much lower than the theoretical value of 3 as discussed below. Thus, it is concluded that simple ion exchange is not the principal extraction mechanism.

Fig. 4 and 5 represent the variation of distribution ratios of Ti(IV) and Fe(III) on extractant concentration using the same data. It is seen that the extraction of Ti(IV) increases linearly with the increase of extractant concentration. The slopes of the lines are 1.50, 1.31, 1.30 and 1.20 for the aqueous phase acidities of 0.25, 0.46, 0.60 and 0.90 M H_2SO_4 , respectively. In the case of Fe(III), at low acidities of 0.25, 0.46 and 0.60 M

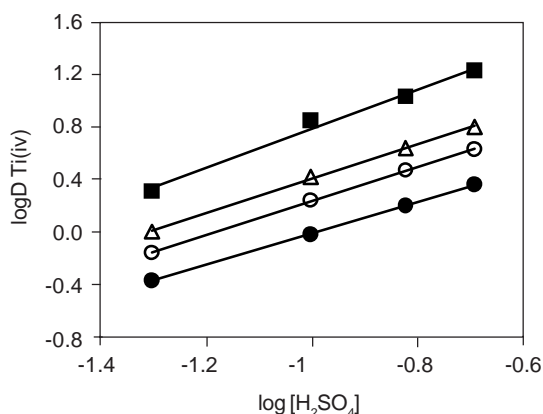


Fig. 4. Effect of extraction of Ti(IV) from Ti(IV) and Fe(III) mixture on extractant concentration.

$[\text{Ti(IV)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; $[\text{Fe(III)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; contact time = 40 min; phase ratio(A/O) = 1:1; temperature = $(30 \pm 1)^\circ\text{C}$;

■: $0.25 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 1.50; Δ : $0.46 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 1.31; \circ : $0.60 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 1.30; \bullet : $0.90 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 1.20

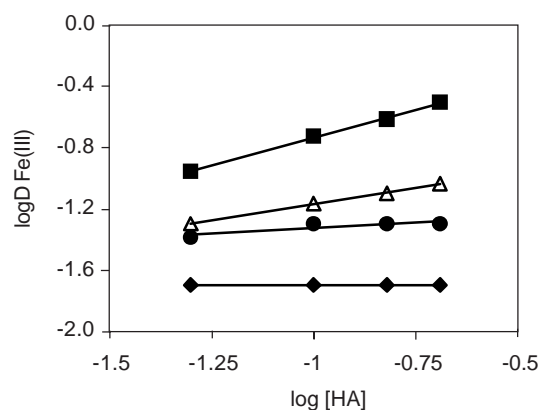


Fig. 5. Effect of extraction of Fe(III) from Ti(IV) and Fe(III) mixture on extractant concentration.

$[\text{Ti(IV)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; $[\text{Fe(III)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; contact time = 40 min; phase ratio(A/O) = 1:1; temperature = $(30 \pm 1)^\circ\text{C}$;

■: $0.25 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 0.73; Δ : $0.46 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 0.42; \bullet : $0.60 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 0.15; \blacklozenge : $0.90 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = 0.00

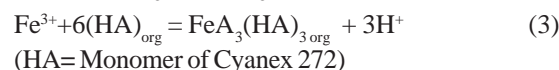
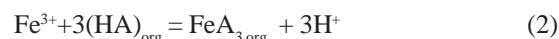
H_2SO_4 , the extraction of Fe(III) increases linearly with the increase of extractant concentration. The slopes of the lines are 0.73, 0.42 and 0.15 for the aqueous phase acidities of 0.25, 0.46 and 0.60 M H_2SO_4 , respectively. On the contrary, at 0.90 M H_2SO_4 , the extraction of Fe(III) is constant with different extractant concentrations and distribution ratio is very low or constant for 0.10, 0.15 and 0.20 M Cyanex 272 concentrations. In other words, the extraction does not increase with the extractant concentration but with 0.05 M Cyanex 272 is much lower than with extractant concentration of 0.20 M Cyanex 272.

In the case of Ti(IV), the extraction reaction is represented as follows by assuming the presence of TiO_2 in solution.



This extraction reaction suggested that the extractant dependence and inverse hydrogen ion dependence is 2. However, the failure to confirm the extraction equation as suggested for the above reaction points to the fact that other phenomena such as the existence of polymerized TiO_2 ion may be responsible for such discrepancy. Low hydrogen ion dependency suggests that solvation mechanism may be operative at high acidity.

The extraction of Fe(III) by Cyanex 272 is also noteworthy. The slope for extractant dependence decreases with increasing acidity. The maximum slope obtained in the acidity range studied is 0.72, which is much less than the theoretical value as given by the general equation:



Similar observation was made by Miralles *et al.* (1992), wherein extractant dependence of 3 and inverse hydrogen ion dependence of 3 is suggested. Fe(III) does not follow the simple extraction mechanism for all the acid ranges. It is likely that solvation mechanism may be operative at high acidity of the aqueous phase.

Effect of extraction of Ti(IV) and Fe(III) from [Ti(IV) and Fe(III)] mixture on temperature. Figures 6 and 7 represent $\log D$ vs. inverse of absolute temperature, showing the variation of distribution ratio on temperature. It is seen that the extraction of Ti(IV) increases linearly with the increase of temperature at all acidities. On the contrary, the extraction of Fe(III) at different acidities show different extraction behaviour. At acidity 0.46 M H_2SO_4 , the extraction rate increased with the increase of temperature up to 40°C and then decreased with the increase of temperature. At acidities 0.60 and 0.90 M H_2SO_4 concentration, the extraction of Fe(III) increased with the increase of temperature and at 50°C , it was maximum for these two acidities and then the extraction decreased. The extraction became equal at 60°C for all the three acidities. The lower extraction above 50°C at acidities 0.60 and 0.90 M H_2SO_4 may be explained on the basis of the formation of unextractable hydrolyzed Fe(III) species with the increase of temperature. The slope of the lines has been calculated by Vant-Hoff equation (Islam *et al.*, 1988) giving the average enthalpy change (ΔH) as 5.34 kcal/mol for Ti(IV) and 20.14 kcal/mol for Fe(III) for the portion at which the distribution ratio increases with the increase of temperature. The extrac-

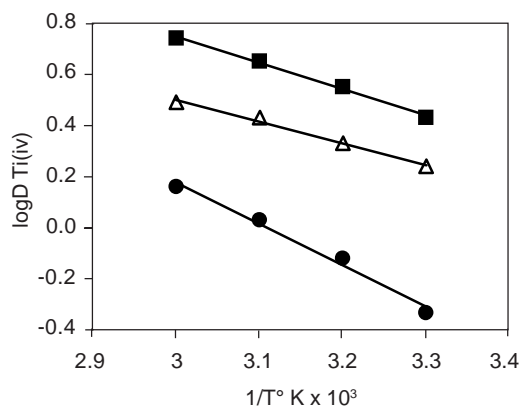


Fig. 6. Effect of temperature on Ti(IV) extraction from Ti(IV) and Fe(III) mixture.

$[\text{Ti(IV)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; $[\text{Fe(III)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; $[\text{HA}] = 0.1 \text{ mol/dm}^3$ cyanex 272 in kerosene; contact time = 40 min; phase ratio (A/O) = 1:1;
 ■: $0.46 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = -1.03 ; △: $0.60 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = -0.85 ; ●: $0.90 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = -1.62

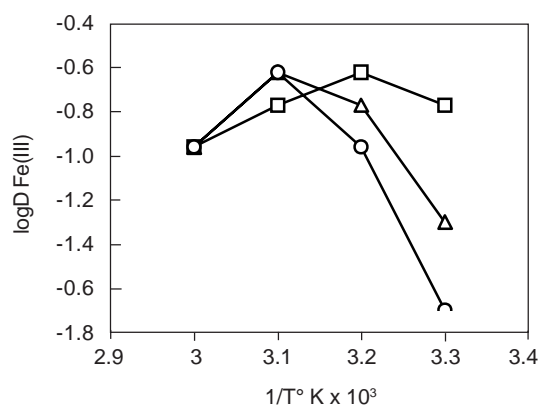


Fig. 7. Effect of temperature on Fe(III) extraction from Ti(IV) and Fe(III) mixture.

$[\text{Ti(IV)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; $[\text{Fe(III)}]_{(\text{ini})} = 1.1 \text{ g/dm}^3$; $[\text{HA}] = 0.1 \text{ M}$ cyanex 272 in kerosene; contact time = 40 min; phase ratio, A/O = 1:1;
 □: $0.46 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; △: $0.60 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = -3.4 ; ○: $0.90 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; slope = -5.4

tion of Ti(IV) is endothermic up to 60°C and Fe(III) extraction is also endothermic up to 50°C by 0.10 M Cyanex 272. Thus extraction of Ti(IV) and Fe(III) by 0.10 M Cyanex 272 in kerosene system is strongly influenced by temperature.

Loading capacity of Cyanex 272 for Ti(IV) and Fe(III). The loading capacity is defined as the amount of metal content in grams extracted per 100 g of pure extractant. It is an important factor for the study of mechanism of extraction and also for the industrial evaluation of the extractant. High values of loading capacity are desirable for any particular extractant

metal system for industrial applications. Loading capacity is influenced by a number of factors including aqueous phase acidity, diluents, temperature, ions present in the aqueous phase and nature of the extractant etc.

The organic phase (20 ml) was repeatedly contacted for 40 min at $30 \pm 1^\circ\text{C}$ with fresh equal volumes of aqueous solution containing fixed concentration of metal ions [$3.50 \text{ g/dm}^3 \text{ Ti(IV)}$ and $2.0 \text{ g/dm}^3 \text{ Fe(III)}$ mixture with $0.32 \text{ M H}_2\text{SO}_4$]. After equilibration, the phases were disengaged and the aqueous phases were analysed for Ti(IV) and Fe(III) contents. The amount of metal ions [Ti(IV) and Fe(III)] transferred into the organic phase for each contact was then determined by subtracting the determined aqueous concentration after extraction from the initial aqueous concentration, and the cumulative concentration of Ti(IV) and Fe(III) in the organic phase after each stage of contact was estimated.

The plot of cumulative $[\text{Ti(IV)/Fe(III)}] \text{ g/dm}^3$ vs. contact number is given in Fig. 8; it is seen that the organic phase is saturated with Ti(IV) after the 9^{th} contact and with Fe(III) after the 13^{th} contact for the stated experimental condition [$3.50 \text{ g/dm}^3 \text{ Ti(IV)}$, $2.00 \text{ g/dm}^3 \text{ Fe(III)}$, $0.32 \text{ M H}_2\text{SO}_4$ and 0.40 M Cyanex 272]. The loading capacity for Ti(IV) is 18 g/litre , for Fe(III) 3.65 g/litre at $0.32 \text{ M H}_2\text{SO}_4$ and 0.40 M Cyanex 272 concentration; 7.70 g/litre for Ti(IV) and 3.64 g/litre for Fe(III) at $0.32 \text{ M H}_2\text{SO}_4$ and 0.20 M Cyanex 272 concentration. It is observed that the maximum loading of Cyanex 272 for Fe(III) is almost same for both 0.40 and 0.20 M Cyanex 272. Therefore, 0.20 M Cyanex 272 is satisfactory for Fe(III) loading of Cyanex 272. Loading data indicates Ti(IV) : Cyanex 272 ratio of $1:1.25$ and

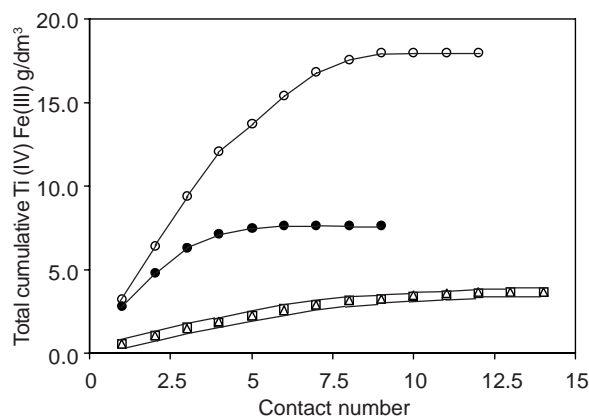


Fig. 8. Loading of Cyanex 272 in the extraction of Ti(IV)-Fe(III).

Contact time = 40 min ; temperature = $(30 \pm 1)^\circ\text{C}$; acidity = $0.32 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; $[\text{Ti(IV)}]_{(\text{ini})} = 3.50 \text{ g/dm}^3$, $[\text{Fe(III)}]_{(\text{ini})} = 2.00 \text{ g/dm}^3$; Ti(IV): ○: 0.40 M HA ; ●: 0.20 M HA ; Fe(III); △: 0.40 M HA ; □: 0.20 M HA

Fe(III) : Cyanex 272 ratio of 1:2.86 at 0.20 M Cyanex 272, indicating almost 1:1 metal complexes in the organic phase saturation for Ti(IV) and 1:3 complex for Fe(III) if monomeric species for extractant is assumed. However, this is not supported by acidity dependence slopes.

In the case of Fe(III), the loading test ratio is nearly equal to the theoretical value and at 0.40 M Cyanex 272, the loading test ratio is 1:5.72, which shows that less Fe(III) is extracted than the theoretical value at higher extractant concentration; it indicates the difference of extraction mechanism at different extractant concentrations. It may be concluded that solvation may be responsible for this discrepancy for extra molecules of Cyanex 272 may be solvated to the central Fe(III) ion.

Separations study. Effect of aqueous phase acidity and extractant concentration on separation factor. The separation factor (β) for [Ti(IV) and Fe(III)] system has been calculated for each extractant concentration of 0.05, 0.10, 0.15 and 0.20 M Cyanex 272. It is seen from the plots (Fig.9) that the separation factor increases with the increase of aqueous phase acidities at all concentrations of Cyanex 272. As the acidity increases, the separation factor differs for different extractant concentration in the following sequences: 0.20 M > 0.15 M > 0.10 M > 0.05 M Cyanex 272. The maximum separation factor is noted for extraction with 0.20 M Cyanex 272 from highly acidic (0.90 M H_2SO_4) Ti(IV)-Fe(III) mixed (1:1) solution. It is concluded that the maximum separation factor for [Ti(IV)-Fe(III)] system is achieved at high aqueous acidity with high extractant concentration (0.20 M Cyanex 272).

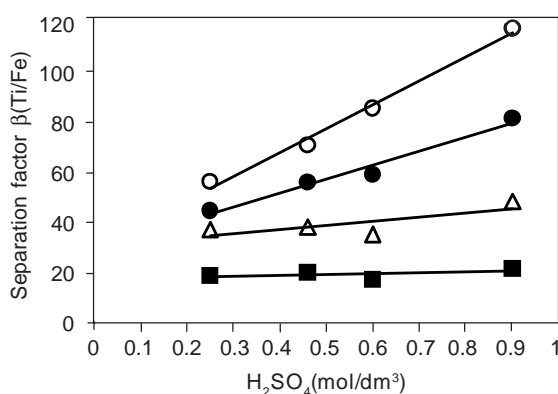


Fig. 9. Effect of aqueous phase acidity on separation factor (β).

[Ti(IV)]_(ini) = 1.1 g/dm³; [Fe(III)]_(ini) = 1.1 g/dm³; phase ratio, A/O = 1:1 contact time = 40 min; temperature = (29±1)°C; ■: 0.05 M HA; △: 0.10 M HA; ●: 0.15 M HA; ○: 0.20 M HA

Effect of temperature on separation factor. The separation factor (β) at acidities 0.46, 0.60 and 0.90 M is graphically represented as a function of temperature (Fig.10). In all cases, the separation factor decreases with the increase of temperature, then it increased again with the increase of temperature. Maximum separation factor ($\beta \sim 116.50$) was obtained at higher aqueous acidity and higher temperature. The separation factor increases in the following order: 0.46 M > 0.60 M > 0.90 M H_2SO_4 at 0.10 M Cyanex 272. Thus the separation factor (β) is markedly temperature dependent. From the plots, it may be concluded that: (a) Ti(IV) can be separated from Fe(III) at all (0.46, 0.60 and 0.90 M H_2SO_4) acidities; (b) the maximum separation of Ti(IV) from Fe(III) is possible at 60°C with 0.46 M Cyanex 272 concentration.

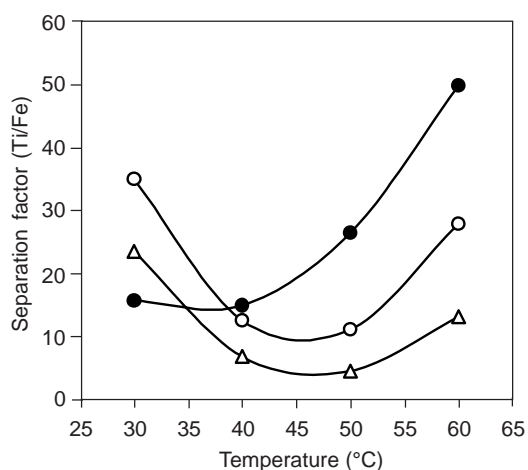


Fig. 10. Effect of temperature on separation factor (β).

[Ti(IV)]_(ini) = 1.1 g/dm³; [Fe(III)]_(ini) = 1.1 g/dm³; [HA] = 0.10 M cyanex 272 in kerosene; phase ratio, A/O = 1:1; contact time = 40 min; ●: 0.46 mol/dm³ H_2SO_4 ; ○: 0.60 mol/dm³ H_2SO_4 ; △: 0.90 mol/dm³ H_2SO_4

Conclusion

Cyanex 272 is a very effective extractant for the extraction and separation of Ti(IV) and Fe(III) from an aqueous sulphate solution containing Ti(IV) and Fe(III). The equilibrium is reached within 40 min for Ti(IV) and 20 min for Fe(III). The loading capacity of Ti(IV) and Fe(III) are 18 g/litre and 3.65 g/litre, respectively, for 0.40 M Cyanex 272 and 0.32 M H_2SO_4 concentration. Separation factor (β) of Ti(IV) with respect to Fe(III) is 116.50 at the experimental conditions [temperature = 30±1°C, [HA] = 0.20 M Cyanex-272 in kerosene, phase ratio = 1:1 and 0.90 M H_2SO_4], suggesting good separation from Fe(III). The extraction data suggests that Fe(III) is extracted in organic phase by the formation of the species FeA_3 or $\text{FeA}_3(\text{HA})_3$ and for Ti(IV) is $\text{TiO}_2 \cdot \text{A}$. The positive ΔH value

suggests that the extraction process is endothermic and the average enthalpy change (ΔH) values are 5.34 and 20.14 kcal/mol for Ti(IV) and Fe(III), respectively, for 0.10 M Cyanex 272. The temperature dependence data shows that Ti(IV)/Fe(III) separation is strongly influenced by the temperature of extraction.

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