INVESTIGATIONS ON THE RECOVERY OF TITANIUM, VANADIUM AND IRON VALUES FROM THE WASTE CHLORIDE LIQUORS OF TITANIA INDUSTRY

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BY

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled **"INVESTIGATIONS ON THE RECOVERY OF TITANIUM, VANADIUM AND IRON VALUES FROM THE WASTE CHLORIDE LIQUORS OF TITANIA INDUSTRY"** is the result of the investigations carried out by Mrs. JESTY THOMAS under our supervision in the Process Science and Engineering Division of Regional Research Laboratory (CSIR), Thiruvananthapuram, and the same has not been submitted elsewhere for any other degree.

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PREFACE

The thesis entitled **"INVESTIGATIONS ON THE RECOVERY OF TITANIUM, VANADIUM AND IRON VALUES FROM THE WASTE CHLORIDE LIQUORS OF TITANIA INDUSTRY"** embodies the results of the investigations carried out on the solvent extraction separation of iron(III), vanadium(V) and titanium(IV) chlorides from the waste chloride liquors of titanium minerals processing industry by employing tributylphosphate as an extractant. The objective of this work is to generate the knowledge base to achieve the recovery of iron, vanadium and titanium values from multi-metal waste chloride liquors originating from ilmenite mineral beneficiation industries through selective separation and value added material development. The thesis is comprised of six chapters.

The introductory chapter highlights the significance of achieving sustainability in the titanium minerals processing industry through resource recovery (metal values) and its reintegration as value added state-of-art products for use in electronic, pigment, catalysts and environmental industries.

The second chapter deals with a comprehensive review of literature on the recent developments in the solvent extraction of iron(III), vanadium(V) and titanium(IV) from acidic aqueous solutions using various extractants. Recent developments in hydrothermal synthesis of hematite and titania powders have also been included in this chapter.

The investigations on the preparation of hematite powders from waste chloride liquors of titanium minerals processing industry by employing solvent extraction in combination with precipitation stripping and hydrothermal synthesis has been described in chapter 3. The synthesized iron oxide powders have been characterized by state-of-art techniques, namely, XRD, FT-IR, TG/DTA and SEM.

Chapter 4 describes the results on the selective extraction and separation of vanadium(V) from multi-metal chloride solutions using tributylphosphate as the extractant.

The results of studies on the selective separation of titanium chloride and its conversion to TiO_2 powders from titania waste chloride liquors has been incorporated in chapter 5. The synthesized anatase powders have been characterized for their photocatalytic activity and compared with commercial photocatalysts.

The contributions to new knowledge arising out of this thesis have been highlighted in the concluding chapter.

Chapter 1

Introduction

During the 21st century, one of the over riding themes for scientific research is the achievement of sustainable utilization of resources through green chemistry, recycling and reuse of wastes (Lems et al. 2002). The concept of sustainable development has gained widespread acceptance since becoming the central theme of the conference on environment and development in 1992. This theme was also central to the world summit on sustainable development in Johannesburg in 2002. In a nut shell, sustainable development may be defined as the development of processes that meets the needs of the present, without compromising the ability of the future generation to meet their own needs (World commission on environment and development 1987). A life cycle analysis (Fig. 1.1) of the mineral resource conversion to materials, and chemicals needed for the society brings out the crucial role of recycling and reuse towards achieving sustainable development. In the mineral sector, sustainable development occupies a high priority due to extensive generation of solid and liquid wastes by presently employed manufacturing processes (The Mineral Sector and Sustainable Development, Final Report: International Institute for Environment and Development, England, 2004).

The enormous magnitude of waste recycling and reuse with respect to wastes generated in the nonferrous industries in India has recently been reported (Agarwal et al. 2004). India, due to its vast resources of ilmenite mineral deposits accounting for nearly 20% of the world's deposits has an enormous stake in the growth of ilmenite processing industries. Unfortunately, the ilmenite beneficiation process employed by the Indian industries generates solid and liquid wastes accounting to 40-50% of the raw material input, leading to serious environmental problems. A schematic diagram of the process is depicted in Fig. 1.2. Ilmenite minerals whose typical composition is given in Table 1.1 is subjected to carbothermal reduction with coal as a reductant to give a reduced mineral with almost 95% of its iron content in the ferrous form. The reduced ilmenite is then subjected to leaching with HCl at 130-140°C in order to extract the iron values as $FeCl_2$ and $FeCl_3$. However, due to the nonselectivity of the leaching reaction, the leach liquors contain almost all the metal values originally present in the ilmenite minerals as metal chlorides. Typical composition of the waste liquor from the ilmenite beneficiation industries is given in Table 1.2. At present, the highly complex multimetal chloride solution is subjected to pyrohydrolysis to generate HCl and an impure iron oxide.

***Table 1.1.* Percentage of iron, vanadium and titanium present in the ilmenite from different sand deposits in India (Suresh, K. et al. 1991).**

Deposit	TiO_2	FeO	Fe_2O_3	V_2O_5
Chavara	60.00	9.23	25.60	0.15
Manavalakurichi	55.00	20.90	18.90	0.22
Nevra	53.25	23.56	22.5	0.41
Kalpakkam	51.00	30.40	15.96	1.10
Chatrapur	50.20	34.10	12.76	0.24

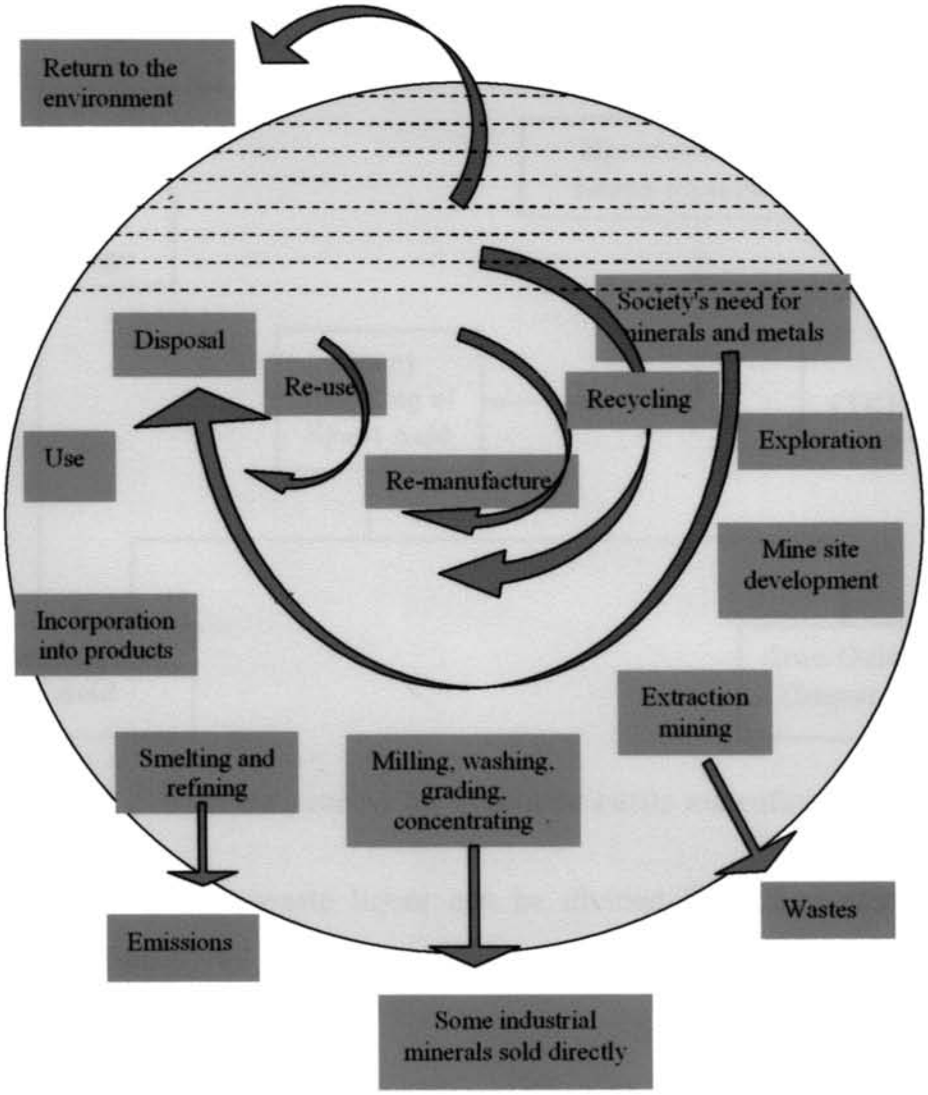


Figure 1.1. **The minerals cycle.**

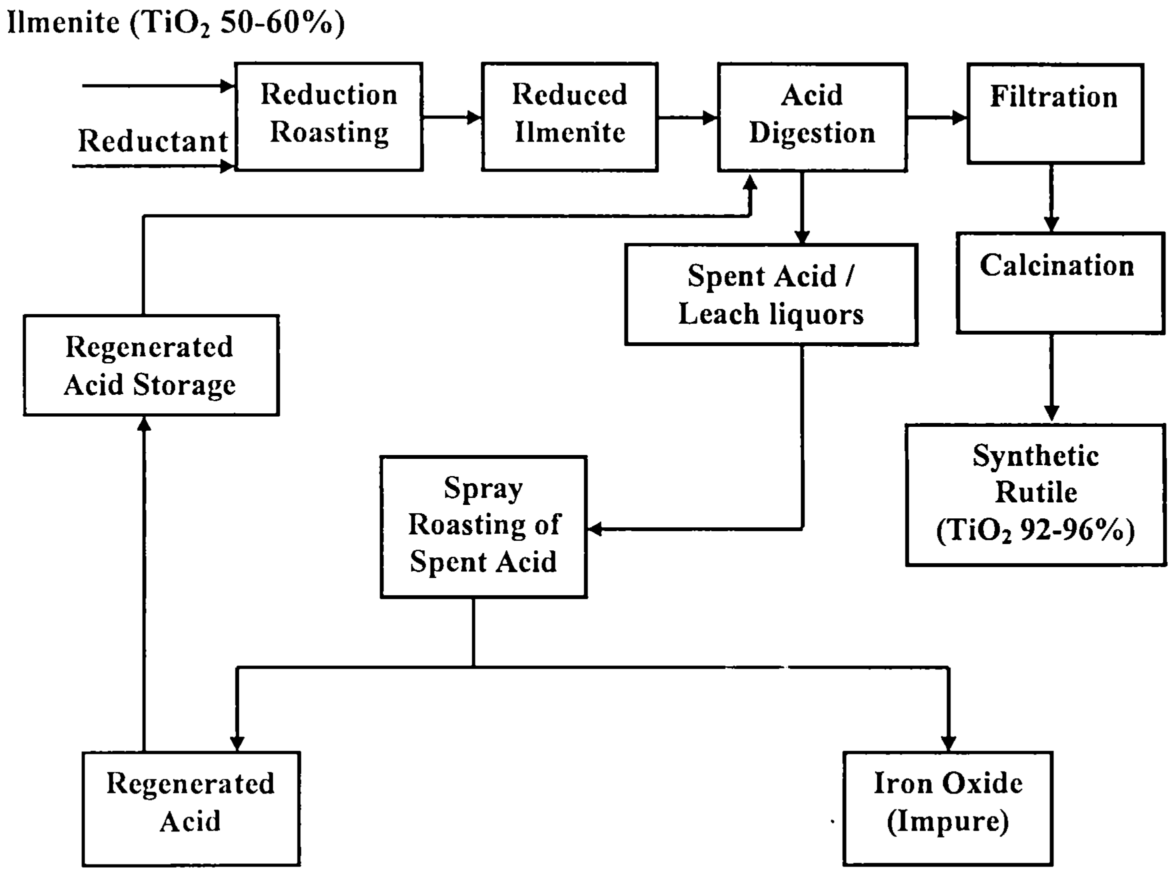


Figure 1.2. **Benelite process for synthetic rutile manufacture.**

The composition of the waste liquor can be divided into three categories which could be recovered and recycled depending on the characteristics of the metallic component.

- Iron chlorides - Valuable as iron oxides or as iron metal due to large volume of the solid waste generated.
- Titanium chloride – Valuable as titanium dioxide.
- Vanadium chloride – Highly valuable and toxic.

This thesis aims to generate the knowledge base to achieve the recovery of iron, vanadium and titanium values from the multimetal waste chloride liquor originating from ilmenite mineral beneficiation industries through selective separation and value added material development.

Table 1.2. **Composition of waste chloride liquor from TiO_2 industry.**

Constituent	**Range** **mol/dm^3**
Fe(II)	1.34 - 1.66
Fe(III)	0.25 - 0.37
Mg(II)	0.16 - 0.17
Mn(II)	0.05 - 0.06
Al(III)	0.02 - 0.04
Ti(IV)	0.02 - 0.03
Cr(III)	0.02 - 0.04
V(V)	0.01 - 0.02
HCl	0.82 - 1.09

Among the various separation options (Fig. 1.3) the solvent extraction process has been chosen for the selective separation based on the concentration of contaminant. The other advantages of the solvent extraction process are namely; simplicity, versatility, easy recovery and ready adaptability towards scale up of the process.

Hydrothermal conversion has been employed to obtain value added materials from iron and titanium chlorides inorder to exploit the advantage of hydrothermal processes to provide novel crystalline materials from amorphous solids.

The potential exploitation of the scientific findings from this work into an existing industrial process through retrofitting is described in the concluding chapter.

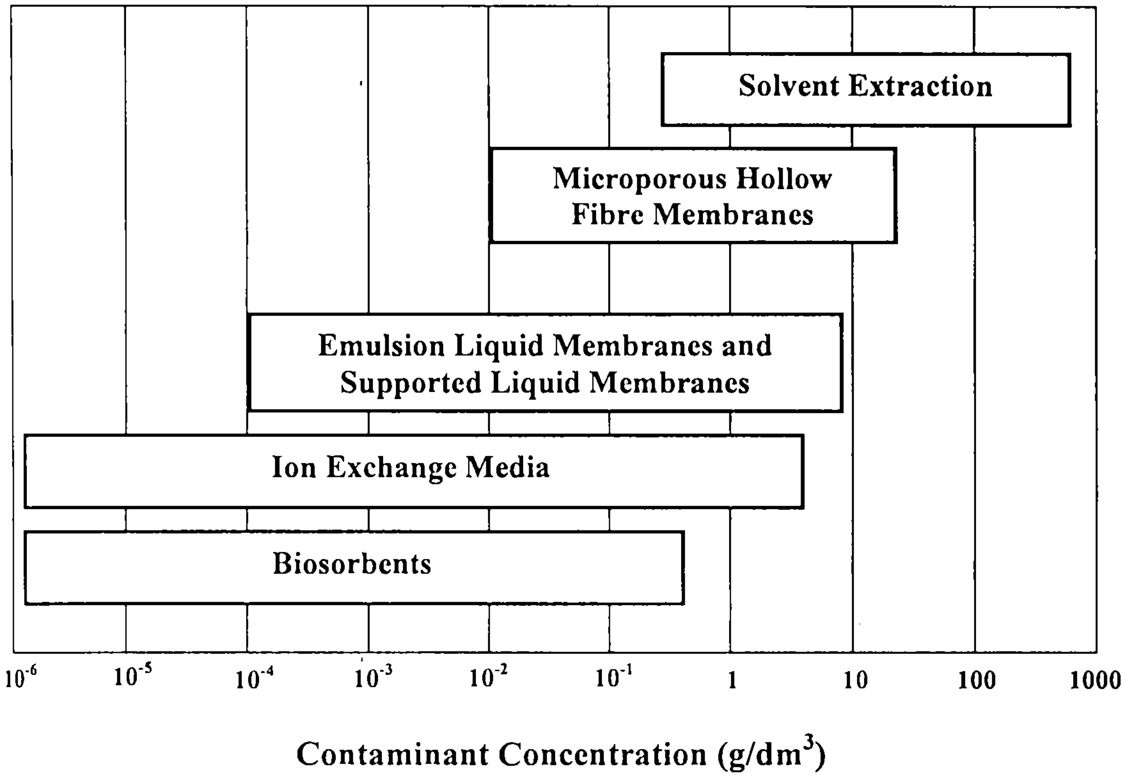


Figure 1.3. **Solute concentration ranges for separation technologies (Kentish and Stevens 2001).**

Chapter 2

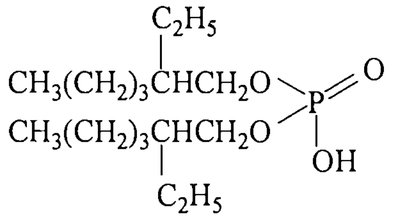
Review of Literature

Solvent extraction of titanium(IV), vanadium(V) and iron(III) from chloride solutions : Literature Review

The review of literature reveals that the metal ions, titanium(IV), vanadium(V) and iron(III) are extracted through three well known classes of extractants viz., acidic extractants, solvating extractants and anion exchangers. The solvent extraction behaviour of tetravalent titanium from chloride solutions with various organophosphorous extractants has been extensively studied and these data are well documented in a recent review article (Reddy and Saji 2002). The influence of acidity on the extraction of titanium(IV) with various extraction systems has been critically reviewed (Kislik and Eyal 1993a).

Extraction by Acidic Extractants

Extraction of titanium(IV) by alkylphosphoric acids: Among the various alkylphosphoric acid extractants used for the extraction of tetravalent titanium, di-2-ethylhexyl phosphoric acid (DEHPA = HX) has proved to be a most versatile reagent for the extraction of titanium(IV) from acidic chloride solutions (Biswas and Begum 1998a; Sato and Keiichi 1992; Islam and Biswas 1978; Islam et al. 1979; Biswas et al. 2002; Sato and Nakamura 1975; Kislik and Eyal 1993b; Islam and Kawnine 1978; Islam et al. 1978).



DEHPA

The extraction behaviour of titanium(IV) from hydrochloric acid solutions with DEHPA in kerosene as an extractant has been investigated over a wide range of aqueous conditions as a function of phase contact time, metal, hydrogen and chloride ion concentrations in the aqueous phase and the extractant concentration in the organic phase (Biswas and Begum 1998a). The results demonstrate that the extraction of titanium occurs via the following reaction:

$$\mathrm{TiO}^{2+}_{\mathrm{aq}} + 2(\mathrm{HX})_{2\,\mathrm{org}} \Leftrightarrow \mathrm{TiOX}_2 \cdot 2\mathrm{HX}_{\mathrm{org}} + 2\mathrm{H}^{+}_{\mathrm{aq}}$$

where $(HX)_2$ refers to the dimeric form of DEHPA. On the other hand, at higher loading of the metal ion, the extraction equilibrium of titanium has been reported as:

$$\mathrm{TiO}^{2+}_{\mathrm{aq}} + (\mathrm{HX})_{2\,\mathrm{org}} \Leftrightarrow \mathrm{TiOX}_{2\ \mathrm{org}} + 2\mathrm{H}^{+}_{\mathrm{aq}}$$

The formation of $TiOX_2$ has been further confirmed by IR spectral data and Ti/P ratio analysis. The loading capacity was found to be 7.31 g of Ti(IV)/100 g of DEHPA. In the later studies, these authors have observed slow kinetics of extraction and stripping processes for titanium(IV) from hydrochloric acid solutions with DEHPA in kerosene as an extractant (Biswas and Begum 2000). Dual extraction behaviour for titanium(IV) (maxima at low acidity, decrease to a minima at medium acidity, and increase at high acidity) has been observed for the extraction of titanium(IV) from hydrochloric acid solutions with DEHPA in benzene or kerosene as an extractant (Sato and Keiichi 1992).

The solvent extraction of titanium(IV) from hydrochloric acid solutions by mixtures of mono- and di-2-ethylhexyl phosphoric acid esters (MEHPA and DEHPA) has been investigated as a function of HCl concentration in the aqueous phase and extractants concentration in the organic phase (Kislik and Eyal 1993b). It was found that MEHPA extracts titanium three orders of magnitude more efficiently than DEHPA and its extraction efficiency is independent of acid concentration in the aqueous phase in the range of 0.1- 8.8 mol/Kg. Further, titanium is effectively extracted by DEHPA at low (<0.1 mol/Kg HCl) and high (>7.5 mol/Kg HCl) aqueous feed acidities.

A solvent extraction process for the recovery of titanium values from ilmenite leach liquors has been described (Tolley and Laughlin 1981). The process involves the roasting of ilmenite ore with a reducing agent, leaching with HCl, and the resultant leach liquor was then subjected to solvent extraction by employing DEHPA in kerosene as a solvent for the extraction of titanium(IV). Titanium(IV) was then recovered from the loaded organic phase by stripping with $H_2SO_4 + H_2O_2$.

Extraction of vanadium(V) by alkylphosphoric acids: DEHPA has been widely used for the extraction of vanadium(IV) and vanadium(V) from acidic aqueous solutions (Hirai et al. 1995; Ho et al. 1994; Tebbe 1982). The extraction behaviour of vanadium(V) from weak acidic chloride solutions has investigated using DEHPA (HX) and di-(2-ethylhexyl)monothiophosphoric acid (DEHTPA=HL) as extractants (Hirai et al. 1995). It has been observed that VO_3^- in the aqueous phase was getting reduced to VO^{2+} on contact with DEHTPA phase, thereby oxidising the extractant to disulfide. The extracted complex has been found to be VOL_2 with DEHTPA. On the other hand, the extracted complex was found to be $VO_2X{\cdot}HX$ with DEHPA. Similar extracted complex for vanadium(V) with DEHPA has also been proposed by others (Nishihama et al. 2000).

Extraction of iron(III) by alkylphosphoric acids: The solvent extraction behaviour of iron(III) from chloride solutions by DEHPA in kerosene has been investigated over a wide range of aqueous acidity as a function of phase contact time, Fe^{3+}, HCl, H^+ and Cl^- concentrations in the aqueous phase, DEHPA concentration in the organic phase and temperature (Biswas and Begum 1998b). The results suggest that the extraction of Fe^{3+} from chloride solution occurs via the following parallel reactions:

$$Fe^{3+}_{aq} + 3(HX)_{2org} \Leftrightarrow FeX_3 \cdot 3HX_{org} + 3H^+_{aq}$$

$$FeCl^{2+}_{aq} + 2(HX)_{2org} \Leftrightarrow FeCl(HX_2)_2(H_2O)_{org} + 2H^+_{aq}$$

$$FeCl^+_{2\,aq} + 3/2(HX)_{2org} \Leftrightarrow FeCl_2X \cdot 2HX_{org} + H^+_{aq}$$

$$FeCl_{3aq} + HCl_{aq} + 3/2(HX)_{2org} \Leftrightarrow H_2XFeCl_4 \cdot 2HX_{org}$$

In the later studies these authors have quantitatively examined the kinetics of the extraction and stripping of Fe(III)-HCl-DEHPA system (Biswas and Begum 1999; Biswas and Begum 2001).

A cation exchange mechanism at lower acidities and a solvating type mechanism at higher acidities has been reported for the extraction of iron(III) from HCl solutions with DEHPA (Sato and Nakamura 1971).

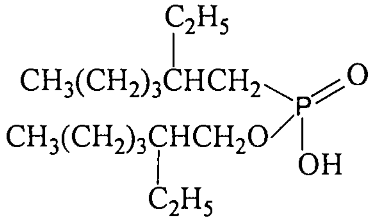
A purification process for iron(III) by solvent extraction has been disclosed (Tsuchiya and Ogata 1992). The process involves dissolution of iron feed in HCl and removing the multivalent metal ions from the resultant acidic solutions by extracting with an organic phase containing a cation exchanger. The raffinate was then oxidized to obtain iron(III) and subjected to a solvent extraction using a cation exchanger to extract iron(III), followed by stripping the loaded organic phase with 0.01-2.0 mol/dm^3 acid to remove trace impurities, and recover iron(III). The ingot from purified iron(III) typically contains < 1.0 ppm of each of Ti, V, Mo, Sb, Cr, Ca, Zn, Ni, C, P.

A solvent extraction process has been described for the recovery of high purity iron oxide from spent liquors of steel making industry (Uchino et al. 1985). The process involves the extraction of iron(III) with DEHPA in paraffin and treating with a fluoride solution to form iron fluoride crystals. Finally the crystals were washed with organic diluent to remove the phosphorus content and calcined at 700-900°C to obtain iron oxide with low phosphorus and fluorine content.

It is well known that the stripping of iron(III) from the loaded organic phase of DEHPA is difficult, since it requires high concentration of HCl. To overcome this limitation, several investigators have used a mixture of DEHPA-TBP-kerosene system for the extraction of iron(III) and observed the ease of iron(III) stripping (Sahu and Das 2000; Hirato et al. 1992). The extraction and stripping behaviour of iron(III) from concentrated acid chloride solutions using a mixed solvent system consisting of DEHPA and TBP or

MIBK has been studied and found that TBP was a better synergist as compared to MIBK (Sahu and Das 2000).

Extraction of titanium(IV) by Dialkylphosphonic acids: Among dialkylphosphonic acids, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA = HX) in kerosene has been used for the extraction of titanium(IV) from hydrochloric acid solutions (Saji and Reddy 2003).



EHEHPA

The results showed that the extraction of titanium(IV) follows the usual cation exchange mechanism.

$$\mathrm{TiO^{2+}_{aq} + 2\,(HX)_{2org} \Leftrightarrow TiO(HX_2)_{2org} + 2\,H^{+}_{aq}}$$

where $(HX)_2$ refers to the dimeric form of EHEHPA. The equilibrium constant of the extracted complex has been deduced by nonlinear regression analysis from the extraction data and found to be $\log K_{ex} = 4.09 \pm 0.03$. Further, the slow kinetics for the extraction of titanium(IV) has been reported. The loading capacity was found to be 5.92 g of Ti^{4+}/100 g of EHEHPA. The separation possibilities of titanium(IV) from other associated multivalent metal ions, which are present in the waste liquors of titanium minerals processing industry has also been discussed.

Extraction of vanadium(V) by Dialkylphosphonic acids: EHEHPA in kerosene has been used as an extractant for the extraction and separation of vanadium(V) from multivalent metal chloride solutions that are present in the waste chloride liquors of titanium minerals processing industry (Saji and Reddy 2002). The results demonstrate that the extraction of vanadium(V) follows the cation exchange mechanism:

$$VO^{+}_{2\,aq} + (HX)_{2\,org} \overset{K_{ex}}{\Leftrightarrow} VO_2X \cdot HX_{org} + H^{+}_{aq}$$

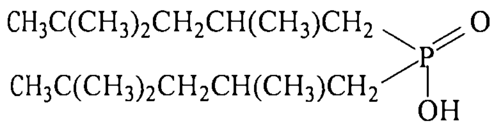
The equilibrium constant of the above extracted complex has been calculated and found to be $K_{exV(V)} = 3.14$. The extracted complex has been further confirmed with the aid of IR spectral data. The loading capacity of EHEHPA for vanadium(V) was found to be 17.7 g of vanadium /dm^3 of the EHEHPA (0.4 mol/dm^3). This study clearly demonstrated that EHEHPA in kerosene can be used as a potential extractant for the recovery of vanadium(V) from the waste chloride liquors of titanium minerals processing industry.

A solvent extraction process for the separation of vanadium(V) from spent catalyst has been described by employing EHEHPA in paraffinic hydrocarbons as an extractant (Shimauchi et al. 1994). The process involves the extraction of vanadium(V) with EHEHPA from a feed solution containing molybdenum and aluminium in the pH range 1.0-4.0 by EHEHPA and back extracting the metal into the aqueous phase with 0.05-2.0 mol/dm^3 mineral acid solution as a stripping agent.

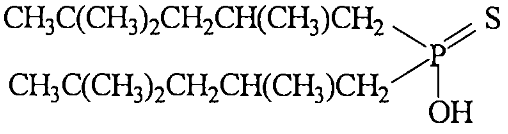
Extraction of iron(III) by Dialkylphosphonic acids: The extraction behaviour of iron(III) from dilute acidic solutions has been studied with EHEHPA in toluene as an extractant and reported quantitative extraction of iron(III) in the pH range 0.75-2.5. The extraction process of iron(III) was found to follow the usual cation exchange mechanism. The differences in extraction and stripping conditions were utilised to establish a selective separation condition for iron(III) from associated metal ions such as titanium(IV), cobalt(II), chromium(VI), zinc(II) and copper(II) (Jayachandran and Dhadke 1997).

The extraction of iron(III) from chloride solutions using DEHPA, EHEHPA, BTMPPA (Cyanex 272) and their mixtures have been investigated and observed synergistic enhancement in the extraction of iron(III) using binary mixtures of the extractants. The results showed that BTMPPA was a better synergist compared to EHEHPA or DEHPA (Sandhibigraha et al. 1996). Later studies by these authors examined the stripping behaviour of iron(III) using H_2SO_4 and HCl from the loaded DEHPA, EHEHPA and BTMPPA phases and found that a higher acid concentration is required for the stripping of iron(III) from loaded DEHPA phase when compared to EHEHPA or BTMPPA (Sandhibigraha et al. 2000). Better stripping efficiencies for iron(III) could be attained using lower acid concentrations when a mixed solvent system consisting of 60% DEHPA and 40% EHEHPA has been used for the extraction.

Extraction of titanium(IV) by Dialkylphosphinic acids: The extraction of titanium(IV) from hydrochloric acid solutions using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272 = BTMPPA = HX) has investigated and the extraction data was compared with bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302 = BTMPTPA = HX) (Saji et al. 2000).



BTMPPA



BTMPTPA

Cyanex 272 was found to be a better extractant for titanium(IV) than Cyanex 302. This has been attributed to the fact that the P=S group of Cyanex 302 forms a weaker complex with titanium compared to the P=O group of Cyanex 272. This is in good agreement with the principle of HSAB concept, which indicates that sulphur is a weaker ligand than oxygen for hard lewis acids like titanium. The results suggest that the extraction of titanium occurs via the following reaction:

$$TiO_{aq}^{2+} + 2(HX)_{2org} \Leftrightarrow TiO(HX_2)_{2org} + 2H_{aq}^{+}$$

Further, a slow kinetics of extraction has been observed with Cyanex 272. On the other hand, fast kinetics has been observed in the case of Cyanex 302. In the later part of their work, these authors have compared the extraction behaviour of titanium with other associated multivalent metal ions, viz., Mg(II), V(V), Mn(II), Fe(III) and Zn(II) that are present in the waste chloride liquors of titanium minerals processing industry and found that none of these multivalent metal ions are being extracted along with titanium(IV).

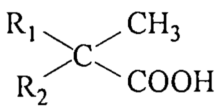
The extraction of titanium(IV) from hydrochloric acid solutions using mono and di-sulphur analogs of bis(2,4,4-trimethylpentyl)phosphinic acid as extractants have been studied to achieve quantitative extraction for titanium at low HCl concentrations (Deep et al. 2001). Further, these authors also reported the extracted complexes as: $Ti(OH)_2R_2$ (HR = Cyanex 301 or 302).

Extraction of vanadium(V) by Dialkylphosphinic acids: A solvent extraction process has been proposed for the selective recovery of vanadium(V) from the aqueous feed solutions containing vanadium(V) and iron(III) by extracting with phosphinic acid compounds (Inoe et al. 1994).

The solvent extraction behaviour of vanadium(V) from hydrochloric acid solution has been investigated using Cyanex 272 = HX in kerosene as extractant (Remya et al. 2004). The results demonstrate that vanadium(V) is extracted into the organic phase as $VO_2X.HX$. The separation and recovery possibilities of vanadium(V) from other associated metal ions which are present in the waste chloride liquors of titanium minerals processing industry has also been discussed.

Extraction of iron(III) by Dialkylphosphinic acids: The solvent extraction behaviour of iron(III) with Cyanex 302 has been investigated and reported quantitative extraction of iron(III) in the pH range 2.0-2.5 (Ajgaonkar and Dhadke 1997). These authors also reported the involvement of three molecules of Cyanex 302 in the extracted complex of iron(III).

Extraction of iron(III) by Carboxylic acids: Monocarboxylic acids such as versatic 10 acid has been well studied for the extraction of iron(III) from acidic solutions.



Versatic 911 acid ($R_1, R_2 = C_4$ -C_5)

Versatic 10 acid ($R_1, R_2 = C_6$)

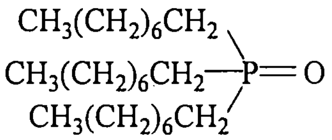
A distinct advantage of carboxylic acid extractants is their acidity and thermal stability to allow the removal of iron(III) at elevated temperatures by direct hydrolysis with water or dilute acids in the hydrolytic and precipitation stripping processes (Doyle 1992). Several studies have been reported for the recovery of hematite powders directly from the iron(III) loaded carboxylate solutions by hydrolytic stripping in a hydrothermal reactor (Monhemius 1985; Monhemius et al. 1985; Monhemius et al. 1993; Konishi et al. 1993; Konishi et al.1994).

Extraction by Solvating Extractants

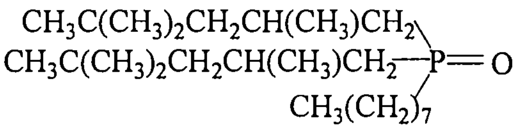
Extraction of titanium(IV) with neutral organophosphorus extractants: Among the neutral organophosphorous extractants, trialkylphophine oxides (Cyanex 923 = TRPO; Cyanex 921 = TOPO; Cyanex 925) have been widely used for the extraction of titanium(IV) from acidic chloride solutions (Remya and Reddy 2004; Saji et al. 1999; Gupta et al. 2002; Shibata and Kurihara 1992; Allal et al. 1997).

$R_3P = O$ $R_2R'P = O$ R = hexyl
$R'_3P = O$ $R'_2RP = O$ R' = octyl

Trialkyl phosphine oxides
(CYANEX 923 TRPO)



CYANEX 921 = TOPO



CYANEX 925

A hydrometallurgical process has been proposed for the production of pigment grade TiO_2 from titaniferrous ores (Duyvesteyn et al. 2002). The process involves a two-step solvent extraction process, first with a mixture of trialkylphosphine oxides (TRPO) for the extraction of titanium and iron from HCl leach liquors, leaving iron(II) in the raffinate and then with alamine 336 in a second-step for the selective removal of iron(III), leaving titanium in the raffinate. However these authors have not disclosed the results concerning the extraction of other associated metal ions.

Recently, a solvent extraction process for the separation of titanium(IV), vanadium(V), and iron(III) from simulated waste chloride liquors of titanium minerals processing industry by TRPO in kerosene as an extractant has been described (Remya and Reddy 2004; Remya et al. 2003). The results demonstrate that titanium(IV), vanadium(V) and iron(III) are extracted into kerosene as: $TiOCl_2 \cdot 2TRPO$, $VO_2Cl \cdot TRPO$ and $HFeCl_4 \cdot 2TRPO$, respectively. On the other hand, magnesium(II), aluminium(III), chromium(III) and manganese(II) are not extracted with TRPO from hydrochloric acid solutions in the range 1.0-4.0 mol/dm^3. The loading capacity of TRPO system with respect to titanium(IV), iron(III) and vanadium(V) has been determined and found to be 7.99 g of iron(III)/100 g of TRPO, 0.53 g of titanium(IV)/100 g of TRPO and 4.88 g of vanadium(V)/100 g of TRPO.

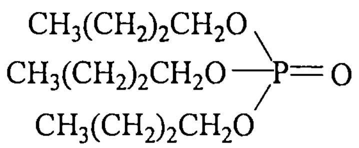
At higher concentrations of HCl, the extraction equilibrium of titanium(IV) with TRPO has been proposed as (Saji et al. 1999; Gupta et al. 2002):

$$Ti^{4+}_{aq} + 4Cl^{-}_{aq} + 2TRPO_{org} \Leftrightarrow TiCl_4 \cdot 2TRPO_{org}$$

Similar extracted complex, $TiCl_4 \cdot 2TPPO$ has been observed with triphenylphosphine oxide (TPPO) in toluene as an extractant (Kakade and Shinde 1995).

The extraction behaviour of titanium(IV) and other metal ions such as Fe(III), Fe(II), Zn(II), Cu(II) and Co(II) from hydrochloric acid solutions has been investigated using a series of trialkylphosphine oxides such as Cyanex 921 (trioctylphosphine oxide), Cyanex 923 (a mixture of four trialkylphosphine oxides) and Cyanex 925 (di-(2,4,4-trimethylpentyl)octylphosphine oxide) and reported that the extraction of titanium(IV) increases with increasing hydrochloric acid concentration (99.0% at 9.0 mol/dm^3 HCl) with simultaneous extraction of other metal ions (Shibata and Kurihara 1992). In the later studies, these authors have developed a computer program for the simulation of counter-current multistage extraction process for the recovery of titanium using Cyanex 923 as an extractant (Shibata et al. 1993).

Allal and co-workers (Allal et al. 1997) have studied the extraction behaviour of tetravalent titanium from hydrochloric acid and calcium chloride solutions using tributylphosphate (TBP) and trioctylphosphine oxide (TOPO) as extractants.



TBP

The results showed that when mixed together, TBP and decanol are suitable for the extraction of titanium(IV), as the kinetics of the extraction reaction is fast and an extraction yield as high as 95% can be obtained from a HCl concentration of 10.0 mol/dm^3. Further, an equilibrium constant value of 0.72

has been reported for TBP extraction and 2.95 for TOPO. These authors have also studied the influence of temperature on the extraction efficiency of titanium using TOPO and reported the extraction process as exothermic. The extraction equilibrium of titanium has been described as:

$$Ti^{4+}_{aq} + 4Cl^{-}_{aq} + 2L_{org} \Leftrightarrow TiCl_4 \cdot 2L_{org}$$

where L = TBP or TOPO. On the other hand, the involvement of three molecules of TBP has also been reported (Narita et al. 1983).

A process for the manufacture of rutile-type TiO_2 has been reported using TBP as an extractant (Chen et al. 1996). This process involves 1) leaching of ilmenite ore with 31% hydrochloric acid and phosphoric acid at 363 K to obtain a pure HCl-Ti liquor; 2) feed adjustment to maintain a free acid concentration >9.0 mol/dm^3, filtering; and 3) extracting with TBP in benzene and the loaded organic phase was then washed with 0.5 mol/dm^3 HCl to remove impurities. Finally the solution is stripped with 4.0 mol/dm^3 HCl to obtain refined HCl-Ti liquor.

A two-step solvent extraction process has been proposed for the recovery of titanium(IV) from acid leach solutions of titanium-iron ore or slag (Watanabe et al. 1989). The process involves treating the acid leach liquor with chlorides of Na, K, Mg or NH_4 and contacted optionally with an oxidant, and then with an organic phase containing TBP in kerosene to extract iron(III) as a chlorinated complex. Titanium(IV) was then extracted from the raffinate with TOPO in kerosene. Finally, the titanium loaded organic phase was stripped with an aqueous solution containing NH_4^+ or together with HF to obtain loaded aqueous solution, which was then contacted with NH_4OH or KOH to precipitate titanium hydroxide or $(NH_4)_2TiF_6$.

Solvent extraction has been used to selectively separate an aqueous mixture of metal chlorides (iron, aluminium and titanium) that is the product from the high temperature chlorination of fly ash by the HiChlor process (Sheng et al. 1983). Tertiaryamines dissolved in xylene or kerosene are used to separate the iron from aluminium and titanium. Iron(III) is stripped from the loaded organic phase using dilute HCl. The recovery of titanium from the aqueous phase containing aluminium after iron removal requires the use of TBP in kerosene at high HCl concentration.

Extraction of vanadium(V) with neutral organophosphorus extractants: The extraction behaviour of vanadium(V) from HCl solutions has been investigated by using TBP in toluene as an extractant and reported the extracted complex as $VO_2Cl{\cdot}(TBP)_{2\text{-}3}{\cdot}2HCl(H_2O)_{2\text{-}3}$ (Tedesco and Rumi 1978).

The solvent extraction of vanadium(V) from HCl solutions has been studied using triphenylphosphine oxide (TPPO) into toluene and identified the extracted complex as $VOCl_3{\cdot}2TPPO$ (Kakade and Shinde 1994).

Tris(2-ethylhexyl)phosphate (TEHP) in toluene has been used as an extractant for vanadium(V) from HCl solutions and proposed the extracted complex as $VOCl_3{\cdot}2TEHP$ (Gaudh and Shinde 1995).

A solvent extraction process has been reported for the recovery of vanadium(V) from an aqueous leach liquor using a mixture of alkylphosphine oxides and fluorinated β-diketones (Lucid 1973).

Extraction of iron(III) with neutral organophosphorus extractants: The extraction of iron(III) from hydrochloric acid solutions using TBP has been studied by many investigators and reported the extracted complexes as $FeCl_3 \cdot 3TBP$ at 2.0-4.0 mol/dm^3 HCl and $HFeCl_4 \cdot 2TBP$ at 6.0-9.0 mol/dm^3 HCl solutions (Saji and Reddy 2001; Reddy and Bhaskara Sarma 1996; Majumdar and De 1960; Narita et al. 1983).

A solvent extraction process for the recovery of high purity iron(III) chloride from titania waste using TBP-MIBK mixed solvent system has been proposed (Saji and Reddy 2001). The process comprises the steps of 1) chlorination of the waste chloride liquor and adjustment of feed acidity, 2) selective extraction of iron(III) chloride from the chlorinated waste chloride liquor using TBP-MIBK mixed solvent system, and 3) stripping of the loaded organic phase using distilled water to recover high purity iron(III) chloride.

TRPO has been used for the extraction of iron(III) from acidic chloride solutions and reported the extracted complex as $HFeCl_4 \cdot 2TRPO$ (Saji et al. 1998). The extraction behaviour of iron(III) has also been compared with other associated metal ions in the ilmenite leach liquors and reported poor selectivity.

A process for the recovery of iron chloride, aluminium chloride and calcium chloride from silicon or ferrosilicon residues has been reported (Andersen et al. 1996). The process involves the leaching with HCl or HCl + $FeCl_3$ solutions and the removal of solid silicon or ferrosilicon residue. Fe(II) in the leach solution is oxidized to Fe(III) where after the solution is subjected to solvent extraction using TBP in hydrocarbon solvent to extract $FeCl_3$ and at least a part of $CaCl_2$, and stripping of $FeCl_3$ and $CaCl_2$ from organic phase by water. Finally by concentrating the remaining solution by evaporation and adding HCl gas to the solution in order to precipitate $AlCl_3 \cdot 6H_2O$ and recovering by filtration.

A solvent extraction process for the recovery of iron oxide from spent pickling liquor has been described (Hasegawa et al. 1987). The process involves air oxidation to convert $FeCl_2$ to $FeCl_3$, followed by solvent extraction with MIBK, and back-extraction with water to transfer the iron from the loaded organic phase. Finally urea was added to the water phase and heated to form iron hydroxide or iron oxide.

Extraction by Anion Exchangers

Extraction of titanium(IV) by anion exchangers: Very few reports are available on the solvent extraction of titanium(IV) using anion exchangers such as amines (Sawant and Khopkar 1983; Chatterjee and Basu 1990; Karve and Khopkar 1994). However their utility was restricted due to the problem of emulsion formation and poor selectivity.

A solvent extraction process for the recovery of titanium(IV) from aqueous solutions containing iron(III), manganese(II), aluminium(III) and chromium(III) has been reported using secondary amines as extractants (Watanabe 1991).

Extraction of vanadium(V) by anion exchangers: Tertiary amines were found to be better extractants for vanadium in the pH range 1.5 to 4.0 (Brooks and Potter 1974). On the other hand, quaternary amines were found to be effective extractants for vanadium in the pH range 1.5 to 12 reaching optimum values between pH 6 to 9 (Wilkomirsky et al. 1985). Tricaprylmethyl ammonium chloride (Aliquat 336), a liquid anion exchanger has been used for the commercial recovery of vanadium and chromium from alkaline leach liquors obtained from titaniferrous magnetite ore (Ritcey and Lucas 1977). Separation is based on preferential extraction of vanadium at pH 9.0 and chromium at pH 13.5. Chromium is first extracted and stripped with NaCl. The raffinate was then used for vanadium extraction using Aliquat 336 followed by stripping with NH_4Cl solution.

The extraction of vanadium(V) from hydrochloric acid solutions using tri-n-octylmethyl ammonium chloride as an extractant has been studied and the extracted species reported as $VO_2Cl{\cdot}2R$ and $(VO_2)_2Cl_2{\cdot}2R$ where R denotes monomeric species of the extractant in benzene diluent (Hirai and Komasawa 1991). Further, these authors have also reported that the extracted species as $VO_2Cl{\cdot}R$ and $VO_2Cl{\cdot}2R$ when chloroform is used as a diluent. Commercially available amines such as ADOGEN 364 (Chatterjee and Basu 1991), Amberlite LA-2 (Rao and Khopkar 1992) and ADOGEN 464 (Chatterjee and Basu 1991) have also been used for the extraction of vanadium.

A process for the recovery of chromium and vanadium from leach liquors of titanomagnetite fraction after the recovery of iron(III) and titanium(IV) from a feed solution containing Cr 2.17, V 0.24 and Al 3.7 g/dm^3 at pH 13.2 with a mixture of Adogen 464, dodecanol and kerosene has been described (Lucas and Ritcey 1982). More than 99.0% of Cr and >95.0% of the vanadium(V) were extracted into the organic phase. The loaded solvent was then scrubbed with sodium chromate solution, and Cr was stripped with NaCl solution. V_2O_5 was recovered subsequently from the scrubbed liquor.

Extraction of iron(III) by anion exchangers: The extraction of iron(III) from hydrochloric acid solution by trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) in benzene has been investigated and proposed the extraction equilibrium expressions on the basis of the results obtained as (Sato et al. 2004):

$$FeCl_{3aq} + R_3NHCl_{org} \Leftrightarrow R_3NHFeCl_{4org} \text{ for TOA and}$$

$$FeCl^-_{4aq} + R_3R'NCl_{org} \Leftrightarrow R_3R'NFeCl_{4org} + Cl^-_{aq} \text{ for TOMAC.}$$

A solvent extraction process has been reported for the preparation of iron oxide (Garcia 1991). Fe_2O_3 was prepared by extracting with Primene 81R in an isodecanol-paraffinic hydrocarbon mixture and simultaneous reextraction-precipitation with an ammoniacal solution of $(NH_4)_2SO_4$. The reextraction of a compound of primary amine and $Fe_2(SO_4)_3$ occurs simultaneously with precipitation of iron as $Fe(OH)_3$ from the ammoniacal solution without prior separation of the organic phase.

Hydrothermal Synthesis of Fe_2O_3 : Literature Review

Several studies have been reported on the synthesis of hematite particles by the hydrothermal reaction of Fe^{3+} ions, not only without additives (Kandori and Ishikawa 2004; Sahu et al. 1997; Li et al. 2002) but also in the presence of additives such as bases (NH_4OH, NaOH) (Sorescu et al. 1998; Demianets et al. 2003; Diamandescu 1999; Sugimoto et al. 1993) or salts (Wang et al. 2004; Chen et al. 1995).

Recently, a hydrothermal route has been proposed for the production of highly ordered cubic particles of hematite with uniform micropores (0.8 nm) from $FeCl_3$ aqueous solutions at 115°C for a reaction time of 7 days (Kandori and Ishikawa 2004). The cubic particles become less uniform with wide pore size distribution with the increase of temperature above 115°C.

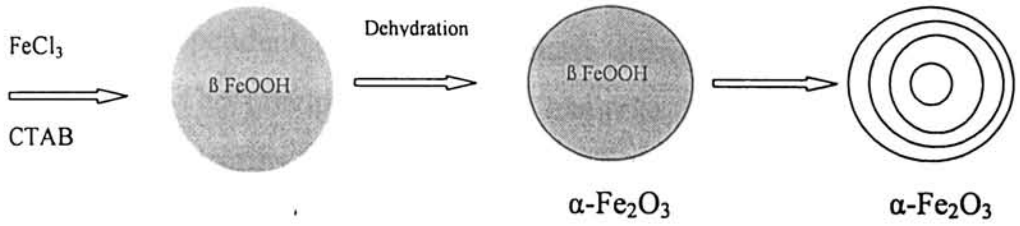
The porous hematite nano-rods have been synthesized by the hydrothermal reaction of $FeCl_3$ and $FeSO_4$ solutions containing urea at 90°C for 10 h, followed by calcination at 600°C for 1h under air atmosphere (Lian et al. 2004). The formation of porous hematite was due to the decomposition of $FeCO_3$ and FeOOH. Urea played a key role in the formation of the iron oxide nano-rods.

Ultra fine α-Fe_2O_3 nano particles (35-100 nm) have been prepared by the hydrothermal reaction of ammonium ferrous sulphate and hydrazine mixtures at 150°C (Li et al. 1998). The following mechanism was proposed to illustrate the formation of α-Fe_2O_3 in the hydrothermal process:

$$N_2H_4 + 2Fe^{2+} + 4H_2O \xrightarrow{\text{pH 3-5}} 2[NH_4]^+ + 2H^+ + 2\alpha\text{-}FeOOH \xrightarrow{150^\circ C} \alpha\text{-}Fe_2O_3 + H_2O$$

A hydrothermal method has been proposed for the synthesis of hematite nanocrystals from amorphous hydrous iron oxides in the absence of alkali at 130°C (Li et al. 2002). When the temperature was lower than 130°C, no product was formed, while above this temperature, the amount of hydrous iron oxides at the surface of hematite nanocrystals was drastically decreased.

The multilayer α-Fe_2O_3 nanoparticles with a closed cage structure have been synthesized by a low temperature (150-180°C) hydrothermal method by employing $FeCl_3$ and cetyltrimethylammonium bromide (CTAB) (Wang et al. 2004). The schematic diagram of the growth process is given below:



A hydrothermal method has been reported for the preparation of hematite particles of four different morphologies: polyhedral, plate like, needlelike and disc shape from various precursors and hydrothermal conditions such as temperature, time and pressure (Sorescu et al. 1998). MÖssbauer spectroscopy studies performed in the temperature range 4.2-300 K revealed the coexistence of the weak ferromagnetic and anti-ferromagnetic phases, in proportions depending on the particle morphology.

Thin films (0.12 μm) of hematite have been synthesized on Si(111) and Si(100) substrates by hydrothermal treatment of a solution of iron nitrate containing urea in the temperature range of 100-200°C for 4-24 h (Chen et al. 1995). The pH and the proportion of Fe^{3+} to urea are the two important factors for the formation of homogeneous films.

A hydrothermal route has been reported for the synthesis of polycrystalline hematite powders with distinct morphology from various precursors in the temperature range of 160-300°C (Diamandescu 1999). By changing and controlling the reaction parameters, oxide powders with desired particle shapes (acicular, polyhedral, plate-like, spherical, hexagonal) and dimensions (0.1-30 μm) were obtained.

Submicrometer, crystalline hematite particles have been synthesized by the hydrolysis of organic carboxylate solutions (Versatic 10) using water at

175°C for 30 min (Sugimoto et al. 1993). The particle size of the hematite was significantly dependent on the liquid phase stirring speed and the organic compositions. The precipitation rate of hematite from the organic solution followed the first order kinetics. At 220°C, the hydrolysis of iron carboxylate led to a mixture of hematite and magnetite.

Hydrothermal synthesis of TiO_2: Literature Review

In the hydrothermal synthesis of nanocrystalline TiO_2, the main attention is paid to the hydrothermal treatment of $TiO_2.nH_2O$ amorphous gels, either in pure distilled water or in the presence of different mineralizers, such as hydroxides, chlorides and fluorides of alkali metals at different pH values (Yanagisawa et al. 1998; Ito et al. 2000; Aruna et al. 2000; Kolen'ko et al. 2003a; Kolen'ko et al. 2003b).

Nanocrystalline powders of anatase and rutile type TiO_2 with different morphology and particle size 13-50 nm have been prepared by the hydrothermal treatment of complex titanyl oxalate acid aqueous solutions (Kolen'ko et al. 2004). The influence of hydrothermal treatment conditions on the formation features, phase composition, particle size, morphology and properties of the products were investigated and discussed. The formation mechanism of mesoporous anatase particles was suggested considering the process as recrystallization of primary grains aggregates.

Recently, titanium oxide nanotubes, nanofibers and nanowires have been synthesized by a simple one-step hydrothermal reaction among TiO_2 powders and alkaline solutions in the temperature range 100-180°C (Yuan et al. 2004). The morphologies of the obtained nanomaterials depend on the process parameters: structure of the raw material, the nature and concentration of the alkaline solution, reaction temperature and time, which suggest that the nanostructure synthesis can be controllable.

A new approach for direct synthesis of well-shaped pure rutile titania nanocrystals by hydrothermal synthesis has been reported (Aruna et al. 2000). The synthesis of 20 nm rutile titania particles from titanium isopropoxide and pH = 0.5 nitric acid is achieved by vigorous stirring of the solution during the hydrothermal treatment. The significance of this method is the elimination of the commonly used mineralizers that can induce impurities to the nanocrystals, in addition to the improved colloid shape in comparison with the standard procedures.

The sol-hydrothermal method provides an alternate approach for preparing uniform, dispersed, nanocrystalline anatase and rutile, respectively, with various particle sizes and morphologies in various acidic media (Wu et al. 2002). Nanocrystals of pure rutile with sizes less than 10 nm was obtained at higher HCl concentrations under mild hydrothermal conditions (140°C). The ability of an acid medium favoring the formation of rutile is as follows: HCl > HNO_3 > H_2SO_4 > HAc. The presence of NaCl salt not only influence the phase formation but also the particle size of TiO_2.

Phase-pure TiO_2 nanocrystallites with narrow particle-size distributions were selectively prepared by a hydrothermal process starting from amorphous TiO_2 (Yin et al. 2001). Autoclaving of amorphous TiO_2 in the presence of HF and HCl lead to the formation of narrow-sized anatase TiO_2 with regular crystalline surface. On the other hand, the use of nitric acid as a cooperative catalyst with HF gave anatase TiO_2 with a narrow size distribution with irregular crystalline surface. Further, in the presence of citric acid and nitric acid, amorphous TiO_2 was lead to the phase-pure rutile TiO_2 nanocrystallites of rod-like shape. The crystal growth of anatase or rutile was proposed to proceed via respective face-sharing and edge-sharing processes through dissolution-precipitation of dissolved TiO_6 octahedra from the amorphous phase.

Nanocrystalline TiO_2 particles were synthesized by hydrothermally treating three titanium alkoxide species, which were derived from i) the hydrolysis of $Ti(OPr)_4$ and $Ti(OBu)_4$ in the presence of HNO_3, tetraethylammoniumhydroxide (TENOH) or $NH_3.H_2O$ ii) water-washed precipitates or iii) sols that were obtained from the precipitates by peptizing with HNO_3 or TENOH. The results showed that HNO_3 peptization favours the formation of rutile, whereas TENOH peptization favours the formation of anatase (Yang et al. 2000).

The catalytic effect of the water on the crystallization of anatase has been demonstrated and the crystallization mechanism has been shown to change from a solid-state type to dissolution precipitation as the temperature is increased (Yanagisawa and Ovenstone 1999). It is shown that the chloride ions accelerate the nucleation of the anatase even under dry conditions. Further, hydrothermal synthesis under acidic conditions result in the formation of anatase, brookite and rutile, whereas basic conditions accelerate the production of anatase.

Microcrystalline TiO_2 powders having high surface area and high crystallinity with photocatalytic activity have been prepared by the high temperature hydrolysis of titanium(IV) alkoxide in organic media (Kominami et al. 1995; Kominami et al. 1999; Aruna et al. 2000).

Porous TiO_2 ceramics having the anatase phase have been prepared below 350°C by hydrothermal hot-pressing of amorphous titania consisting of spherical particles by the hydrolysis of titanium tetraethoxide (Yanagisawa et al. 1997). The porous anatase with open pores was obtained by drying in air after removing water, which had occupied the pores in the compacts during hydrothermal hot-pressing.

A catalyst containing TiO_2 as a primary ingredient has been synthesized hydrothermally by treating meta or ortho-titanic acid in the presence of various flocculents at 180°C, followed by calcination in the temperature range 300-500°C. The proportion of anatase was found to increase in the presence of flocculent such as silicic acid, molybdenum compounds and tungsten compounds (Hums 1990).

A hydrothermal process has been described for the preparation of ultrafine TiO_2 powders from amino titanium oxalate as a precursor in the presence of deionized water at a temperature of 205°C and 400 psig pressure (Bruno 1998).

Chapter 3

Preparation of Hematite Powders from Waste Chloride Liquors of Titanium Minerals Processing Industry

The review of literature presented in the earlier chapter concludes that organophosphorus acid derivatives such as DEHPA, EHEHPA and BTMPPA have been used for the extraction of iron(III) from acidic chloride solutions with better selectivity (Biswas and Begum 1998b; Biswas and Begum 1999; Biswas and Begum 2001; Jayachandran and Dhadke 1997; Sandhibigraha et al. 2000). The main disadvantage with these reagents is the slow kinetics (30-50 min) of extraction for iron(III) and hence long residence time would be necessary to operate these systems on a commercial scale. Further, they require very high acid concentration for the back-extraction of iron(III) from the loaded organic phase. On the other hand, fast kinetics (couple of min) and poor selectivity for iron(III) has been reported with neutral organophosphorus extractants like TRPO (Remya and Reddy 2004). Recently, TBP in combination with MIBK has been employed for the selective extraction of iron(III) from titania waste chloride liquors (Saji and Reddy 2001). However, the practical application of the above process has some limitations, since it employs MIBK. As is well known, MIBK suffers from drawbacks such as low flash point, high vapour pressure and solubility in the aqueous phase. Further, it requires high acid concentration (>6.0 mol/dm^3) for the extraction of iron(III). Although few studies concerning the extraction equilibrium of iron(III) with TBP at low concentration of metal ion is known (Narita et al. 1983), no attempts have been made to recover iron(III) as marketable products from the waste chloride liquors of titanium minerals processing industry. Hence in the present work, investigations have been carried out to recover iron as pure hematite powder by solvent extraction using TBP in kerosene as an extractant followed by precipitation stripping and hydrothermal synthesis.

3.1 Experimental

Reagents

Tributylphosphate supplied by Aldrich Chemical Company, USA, was used in the present study. Decanol supplied by Merck, Germany, was used as a modifier. Distilled kerosene (boiling range 433-473 K, composed of aliphatic hydrocarbons: 96.4% and aromatic hydrocarbons: 3.6%) was used as a diluent in the present work. All other chemicals used were of analytical reagent grade.

Iron(III) stock solution was prepared by dissolving 324.42 g of $FeCl_3$ in concentrated hydrochloric acid and diluted to 1.0 dm^3 with distilled water. Titanium(IV) solutions were prepared from $TiCl_4$ (Spectrochem, India; Purity = 99.0%) by diluting to the required concentration with hydrochloric acid. Vanadium(V) stock solution was prepared by dissolving 5.85 g of ammonium monovanadate in hydrochloric acid and diluting to 1.0 dm^3 with distilled water. Freshly prepared solutions of vanadium(V) were used in all the experimental studies to prevent partial reduction to tetravalent vanadium in hydrochloric acid solutions with respect to time (Tedesco and Rumi 1978). Stock solutions of magnesium(II), aluminium(III), chromium(III) and manganese(II) were prepared by dissolving 10.16 g of $MgCl_2.6H_2O$, 18.75 g of $Al(NO_3)_3.9H_2O$, 25 g of $CrK(SO_4)_2.12H_2O$ and 8.45 g of $MnSO_4.H_2O$ in 1.0 dm^3 of distilled water, respectively. Suitably diluted stock solutions (standardized) of the above metal ions were used in the extraction and analytical studies.

Apparatus

A Hitachi 220 double beam microprocessor-controlled spectrophotometer (Tokyo, Japan) was used for measuring absorbances. An Orion 720A Ion Analyzer (Beverly, USA) was used for the pH measurements. A Perkin Elmer AAnalyst 100 atomic absorption spectrophotometer (Norwalk, USA) was used for the analysis of metal ions in multicomponent mixtures. A Parr 4842 reactor (USA) was used for the hydrothermal synthesis (Fig. 3.0). The X-ray diffraction patterns were recorded by a Philips X' Pert X-ray diffractometer (Netherlands) using Nickel filtered CuK_α radiation. A Nicolet impact 400D IR spectrometer using KBr (Madison WI, USA) was used for IR spectra. A Jeol JSM 5600LV scanning electron microscope (Tokyo, Japan) was used for SEM studies. A Sedigraph 5100 X-ray based particle size analyzer (Micromeritics, USA) was used for the particle size analysis. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed using a Shimadzu thermogravimetric analyzer (Japan). Diffusion reflectance spectra of the iron oxide was carried out with a Shimadzu UV-2401 spectrophotometer operating in the range 400-800 nm range and the color coordinates were determined using CIE-LAB 1976 scales.

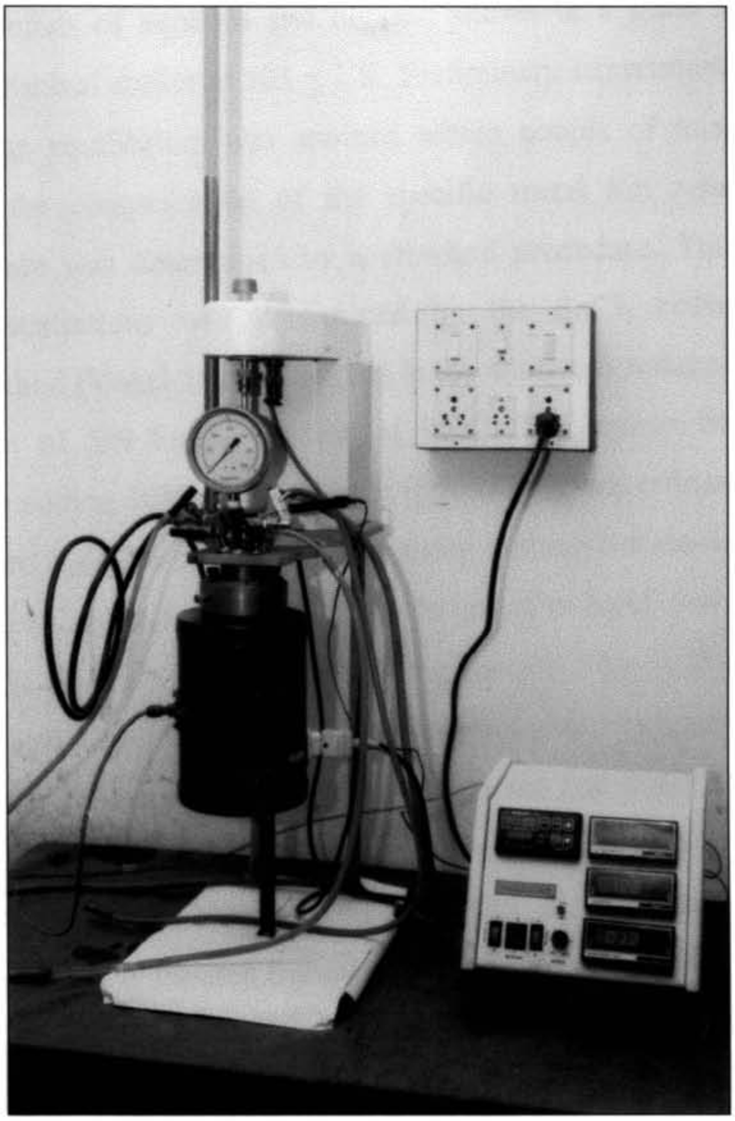


Figure 3.0 **Hydrothermal reactor**

Solvent extraction and analytical procedures

Solvent extraction and stripping experiments were carried out by shaking required volumes of aqueous and organic phases in a glass stoppered vial using a mechanical shaker at 303 ± 1 K. Preliminary experiments showed that the extraction equilibrium was attained within couple of min. After phase separation, the concentration of the specific metal ion remaining in the aqueous phase was determined by a standard procedure. Thus, iron(III) at higher concentrations was determined by the $SnCl_2$ reduction–$K_2Cr_2O_7$ titration method (Vogel 1978). Iron(III) in the analyte is reduced to iron(II) by the addition of 5% $SnCl_2$ solution at 90°C. The excess $SnCl_2$ was then removed by adding 10% $HgCl_2$ and the ferrous iron was estimated by titrating with standard $K_2Cr_2O_7$ (0.1 N) solution using diphenylamine-4-sulphonic acid (0.01% in con. H_2SO_4) as an indicator. On the other hand, low concentrations of iron(III) was assayed spectrophotometrically by 1,10-phenanthroline method (Vogel 1996a). Iron(III) in the aqueous phase sample was reduced to iron(II) using 10% hydroxylammonium chloride and complexed with 1,10-phenanthroline (0.25%) in sodium acetate buffer (0.2 mol/dm^3) solutions of pH = 5.0. The absorbances were recorded at 515 nm and the metal concentration was computed from the calibration plot.

Titanium(IV) and vanadium(V) were determined spectrophotometrically as their H_2O_2 complexes in 1.0 mol/dm^3 sulphuric acid solutions at 410 and 450 nm, respectively (Vogel 1996b; Vogel 1996c). The metal concentrations in the aqueous phase were then computed from the respective calibration graphs.

Chromium(III) was analysed spectrophotometrically as chromium(VI) complex with diphenylcarbazide in 0.1 mol/dm^3 H_2SO_4 solutions after oxidation using potassium permanganate (Vogel 1996d). The absorbances were recorded at 540 nm and the metal concentrations were then computed from the calibration graph.

The determination of aluminium(III) was carried out spectrophotometrically using Eriochrome Cyanine R indicator (0.1%) as the complexing agent in dilute sodium acetate buffer solutions of pH = 6.1 (Vogel 1996e). Absorbances were measured at 535 nm after allowing 30 min for colour development. The metal concentration was then read from the calibration plot.

Magnesium(II) was determined colourimetrically as its complex with Eriochrome black T indicator (0.1% in methanol) in ammonia buffer solutions of pH = 10.1 (Vogel 1996f). Absorbances were recorded at 520 nm and the corresponding metal concentrations were calculated from the calibration graph.

Analysis of manganese(II) was carried out volumetrically by titration with standard EDTA, after the addition of 0.5 g of hydroxylammonium chloride to prevent oxidation (Vogel 1996g). Aqueous NH_3/NH_4Cl solution of pH = 10 was used as a buffer and Eriochrome black T in KCl was employed as an indicator. The concentrations of the above metal ions in both simulated and actual waste chloride liquors were determined by AAS.

The concentration of metal ion in the organic phase was then obtained by material balance. The distribution ratio, *D*, was taken as the ratio of the concentration of metal ion in the organic phase to that present in the aqueous phase. The percentage extraction of metal ion was calculated using the formula:

% E = $D \times 100 / D + V_{aq.}/V_{org.}$, where $V_{aq.}$ = Volume of the aqueous phase and $V_{org.}$ = Volume of the organic phase.

The solvent extraction data was analysed by "slope analysis" method to find out the nature of the extracted complexes. The batch type counter-current extraction and stripping studies were performed at a laboratory scale using separatory funnels of suitable volume. 20% Decanol was used as a modifier in all the solvent extraction experiments along with TBP in kerosene to prevent the third phase formation. All the extraction and stripping experiments were performed in duplicate and the general agreement of the distribution ratio values obtained was within ± 5%.

Hydrothermal synthesis procedure

A pressure reactor with monel alloy as material of construction and lined with teflon (capacity of 600 cm^3) was used for hydrothermal synthesis of iron oxide powders. Temperatures were varied from 393 to 453 K (under autogeneous pressure corresponding to the temperature) with constant stirring (200 rpm). The heating time in the hydrothermal reactor was varied between 30 min to 120 min. The precursor, ferric hydroxide used in the hydrothermal transformation was prepared by the following procedure: The iron hydroxide was prepared from the ferric chloride loaded organic phase obtained from the solvent extraction process by precipitation-stripping using sodium hydroxide with concentrations in the range 1.5-3.0 mol/dm^3. The alkaline suspension containing iron hydroxide was then separated from the organic phase and transferred into a hydrothermal reactor. After hydrothermal reaction, the powders were filtered, washed with deionised water and acetone, dried at 373

K and stored in the desiccator. The powders were characterized by X-ray diffraction analysis (XRD), thermogravimetry (TG), differential thermal analysis (DTA) and FT-IR. The purity of the powders was also checked by chemical analysis after dissolving the powder in HCl solution and analysed by AAS. The morphological analysis was performed using scanning electron microscopy (SEM).

3.2 Results and discussion

Effect of hydrochloric acid concentration

The extraction behaviour of magnesium(II) (0.04 mol/dm^3), aluminium(III) (0.03 mol/dm^3), titanium(IV) (0.03 mol/dm^3), vanadium(V) (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.03 mol/dm^3) and iron(III) (1.0 mol/dm^3) present in the waste chloride liquors of titanium minerals processing industry was investigated as a function of hydrochloric acid concentration (0.2-6.0 mol/dm^3) using 2.5 mol/dm^3 TBP in kerosene as an extractant and the results are shown in Fig. 3.1. The extraction of iron(III) was found to increase with increasing hydrochloric acid concentration in the aqueous phase. On the other hand, magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III) and manganese(II) were found not to be extracted into the organic phase between 0.2-2.0 mol/dm^3 hydrochloric acid concentrations. However, vanadium(V) was found to be extracted into the organic phase above 2.5 mol/dm^3 HCl. In view of the better extraction efficiency and selectivity observed between iron(III) and other associated metal ions, in the present study, 2.0 mol/dm^3 hydrochloric acid was chosen as the feed acidity in the subsequent experiments.

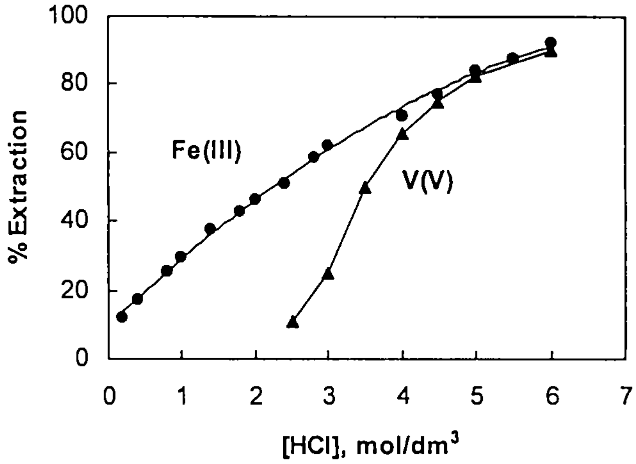


Figure 3.1. Effect of hydrochloric acid concentration on the extraction of iron(III). $[FeCl_3]$ = 1.0 mol/dm^3 and vanadium(V) = 0.02 mol/dm^3 using 2.5 mol/dm^3 TBP in kerosene.

The effect of hydrogen ion concentration (2.0-4.0 mol/dm^3) on the extraction of iron(III) was studied with 2.5 mol/dm^3 TBP in kerosene as an extractant at constant chloride (5.0 mol/dm^3) and metal (1.0 mol/dm^3) ion concentrations using HCl + NaCl mixtures (Fig. 3.2). The extraction of iron(III) was found to increase linearly with an increase in hydrogen ion concentration in the aqueous phase. The Log D versus Log $[H^+]$ plot gave a slope of 1.0 ± 0.1, indicating the involvement of one hydrogen ion in the extracted complex.

The effect of chloride ion concentration (4.5-6.0 mol/dm^3) was also investigated at a given hydrogen (2.0 mol/dm^3) and metal (1.0 mol/dm^3) ion concentrations using 2.5 mol/dm^3 TBP in kerosene as an extractant and the results are depicted in Fig. 3.3. It is clear from the results that the extraction of iron(III) increases with increase in chloride ion concentration in the aqueous phase. From the slope of the plot Log D versus Log $[Cl^-]$, it can be inferred that four chloride ions are involved in the extracted complex.

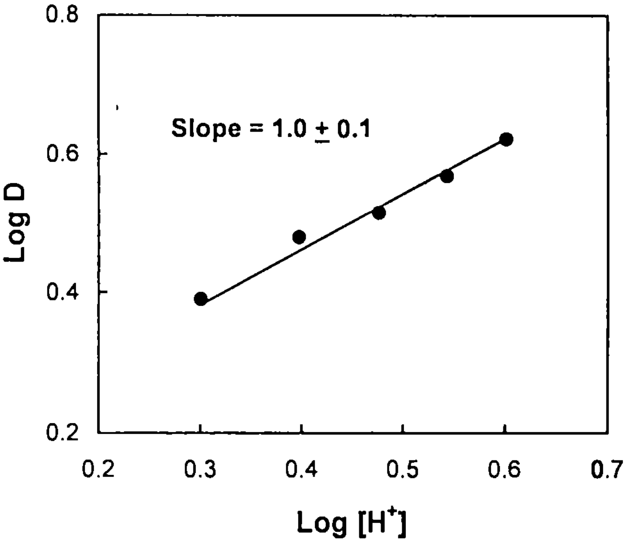


Figure 3.2. Effect of hydrogen ion concentration on the extraction of iron(III) at constant Cl^- concentration. $[FeCl_3]$ = 1.0 mol/dm^3; $[Cl^-]$ = 5.0 mol/dm^3; [TBP] = 2.5 mol/dm^3.

Effect of TBP concentration

The effect of TBP concentration (1.5-3.3 mol/dm^3) on the extraction efficiency of iron(III) was investigated at constant metal ion (1.0 mol/dm^3) and hydrochloric acid (2.0 mol/dm^3) concentrations and the results are shown in Fig. 3.4. It is evident from the results that the extraction efficiency of iron(III) increases with increasing TBP concentration in the organic phase. From the slope of the plot, Log D versus Log [TBP], it is clear that two molecules of TBP are involved in the extracted complex of iron(III).

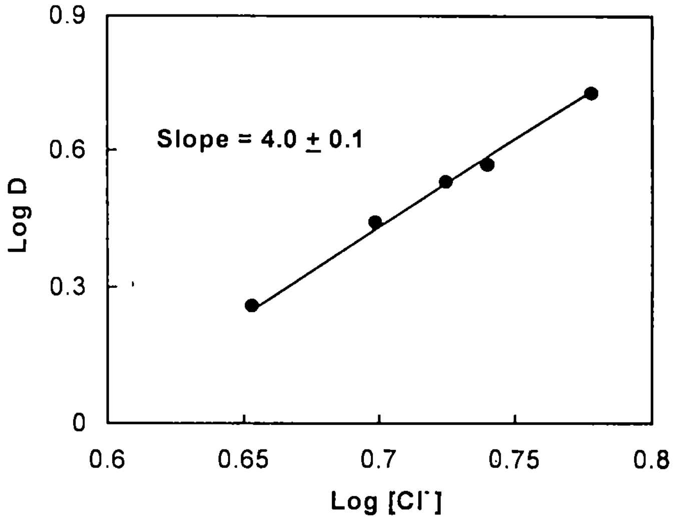


Figure 3.3 Effect of chloride ion concentration on the extraction of iron(III) at constant H^+ concentration. $[FeCl_3]$ = 1.0 mol/dm^3; $[H^+]$ = 2.0 mol/dm^3; [TBP] = 2.5 mol/dm^3.

Effect of metal ion concentration

The effect of metal ion concentration (0.008-2.0 mol/dm^3) on the extraction of iron(III) was investigated from 2.0 mol/dm^3 hydrochloric acid solutions by employing 2.5 mol/dm^3 TBP in kerosene as an extractant. It is clear from the results that the extraction of iron(III) decreases with the increase of initial metal ion concentration in the aqueous phase. The log–log plot (Fig. 3.5) of equilibrium organic-phase iron(III) concentration against aqueous-phase iron(III) concentration is linear with a slope of unity up to 1.0 mol/dm^3 iron(III) concentration, indicating the extraction of mononuclear species into the organic phase.

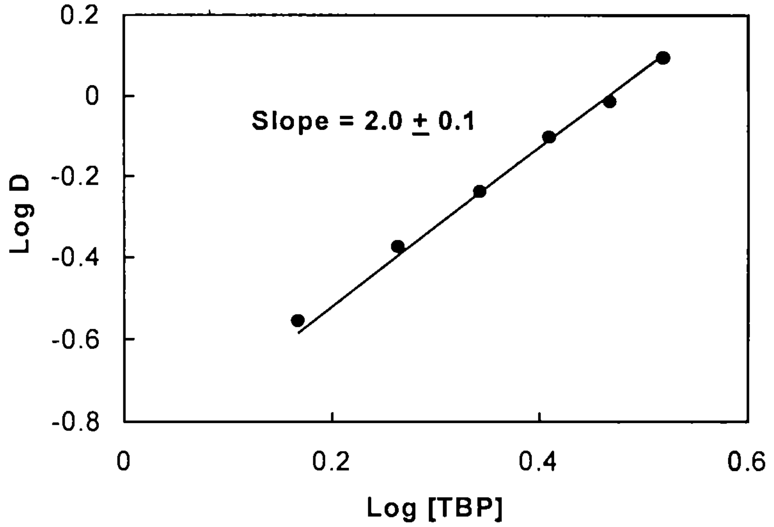


Figure 3.4. Effect of TBP concentration on the extraction of iron(III). $[FeCl_3] = 1.0$ mol/dm^3; $[HCl] = 2.0$ mol/dm^3.

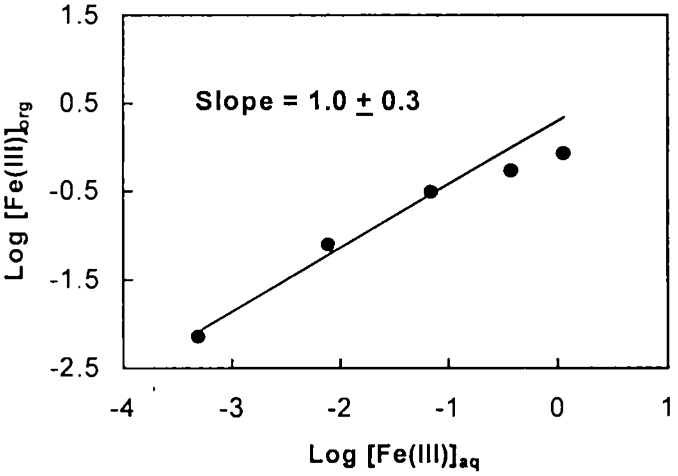


Figure 3.5. Effect of metal ion concentration on the extraction of iron(III). $[HCl] = 2.0$ mol/dm^3, $[TBP] = 2.5$ mol/dm^3 in kerosene.

Extraction equilibrium

Based on the above results, the extraction equilibrium of iron(III) using TBP as an extractant can be represented as:

$$Fe^{3+}_{aq} + H^{+}_{aq} + 4Cl^{-}_{aq} + 2TBP_{org} \overset{Kex}{\Leftrightarrow} HFeCl_4 \cdot 2TBP_{org}$$

$$K_{ex} = \frac{[HFeCl_4 \cdot 2TBP]_{org}}{[Fe^{3+}]_{aq}[H^{+}]_{aq}[Cl^{-}]^{4}_{aq}[TBP]^{2}_{org}}$$

where K_{ex} is the equilibrium constant. The above extraction equilibrium is in good agreement with the earlier reports for the extraction of iron(III) from HCl solutions with TBP (Sahu and Das 1997) or TRPO (Remya and Reddy 2004) as extractant. Similar extracted complex has also been observed for the extraction of iron(III) from 2.0 mol/dm^3 HCl solutions with mixed solvent system consisting of TBP (70 vol. %) and MIBK (30 vol. %) (Saji and Reddy 2001). Contrary to the above reports, it has been reported the extracted complex as $FeCl_3 \cdot 3TBP$ with 100% TBP from 2.0 mol/dm^3 HCl (Majumdar and De 1960). However, these authors have also observed $HFeCl_4 \cdot 2TBP$ at 6.0 mol/dm^3 HCl.

Effect of diluent

The extraction efficiency of iron(III) (1.0 mol/dm^3) from 2.0 mol/dm^3 HCl solutions was investigated using 2.5 mol/dm^3 TBP in various diluents and the results are shown in Table 3.1. The results clearly demonstrate that diluents such as benzene, xylene, toluene, and kerosene, which have low dielectric constants, show higher extraction efficiency for iron(III). On the other hand, diluents with higher dielectric constants, such as chloroform, gave poor extraction. This may be due to the strong interaction between TBP and chloroform through hydrogen bonding (Sekine and Hasegawa 1997). However, in the present work, MIBK, which has high dielectric constant, shows high extraction efficiency for iron(III). This can be attributed to the synergistic effect of the mixed-solvent system (Saji and Reddy 2001). In view of the commercial availability, kerosene was used as the diluent in the present study.

Table 3.1. Effect of nature of diluent on the extraction of iron(III) chloride (1.0 mol/dm^3) from 2.0 mol/dm^3 HCl by 2.5 mol/dm^3 TBP.

Diluent	Dielectric constant (ε)	% Extraction
Kerosene	2.00	46.3
Cyclohexane	2.02	47.3
Xylene	2.26	48.4
Toulene	2.24	47.3
Benzene	2.28	47.3
Chloroform	4.90	38.0
Methyl isobutyl ketone	13.11	54.7

Loading capacity

Aliquots of 10 cm^3 of 2.5 mol/dm^3 TBP in kerosene were repeatedly extracted with equal volumes of the aqueous phase containing 1.0 mol/dm^3 of iron(III) chloride in 2.0 mol/dm^3 hydrochloric acid at 303 ± 1 K for 10 min. The aqueous phases were analyzed for iron(III) after each stage of extraction and the amount of iron(III) content transferred into the extractant phase was calculated. The cumulative concentration of iron(III) in the organic phase after each stage of extraction was determined and plotted against the number of stages of extraction (Fig. 3.6). The loading capacity of 2.5 mol/dm^3 TBP in kerosene for the extraction of iron(III) from 2.0 mol/ dm^3 hydrochloric acid solutions was calculated and found to be 40.5 g of iron(III)/ dm^3 of the solvent.

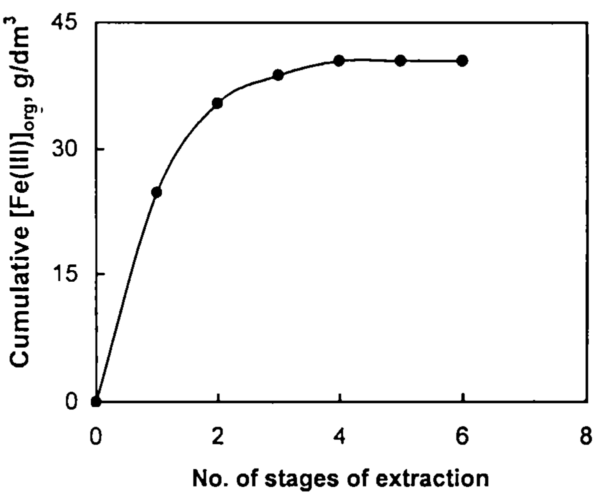


Figure 3.6. Loading capacity of the solvent system 2.5 mol/dm^3 TBP in kerosene for the extraction of iron(III) chloride. [HCl] = 2.0 mol/dm^3.

IR spectra of iron(III) - TBP complex

The IR spectra of the extracted complex, $HFeCl_4 \cdot 2TBP$ show that the stretching frequency of the P=O in TBP has shifted from 1276 cm^{-1} to 1243 cm^{-1} (Fig. 3.7). These spectral changes confirm the nature of the extracted complex formed via the coordination of lone pair of electrons of oxygen in the P=O group of TBP to the metal ion.

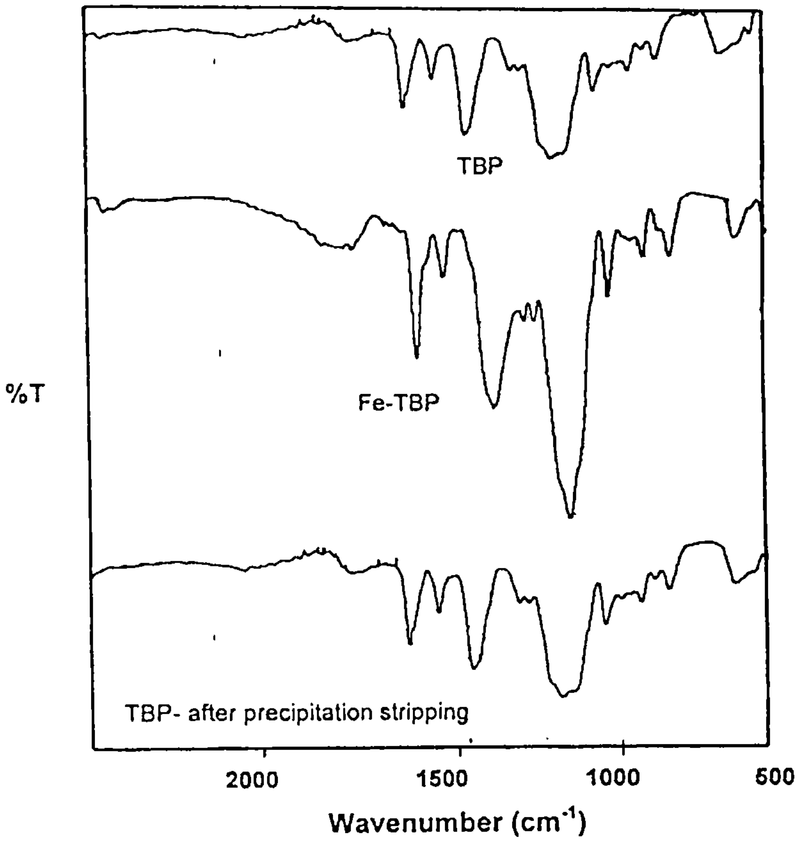


Figure 3. 7. IR spectra of pure TBP, Fe-TBP complex and TBP after precipitation-stripping.

Extraction isotherm

Extraction isotherms were obtained using a typical feed solution containing 1.0 mol/dm^3 of iron(III) chloride and 2.0 mol/dm^3 of HCl using 2.5 mol/dm^3 of TBP in kerosene as an extractant at different aq : org (A : O) phase ratios and the results are depicted in Figs. 3.8-3.9. The McCabe-Thiele plot for a feed solution containing 1.0 mol/dm^3 of iron(III) chloride showed that almost quantitative extraction of iron(III) was possible in three counter-current extraction stages at an A : O of 1 : 1.5. On the other hand, two counter-current stages of extraction was found to be sufficient to achieve quantitative extraction at A : O ratio of 1 : 2.

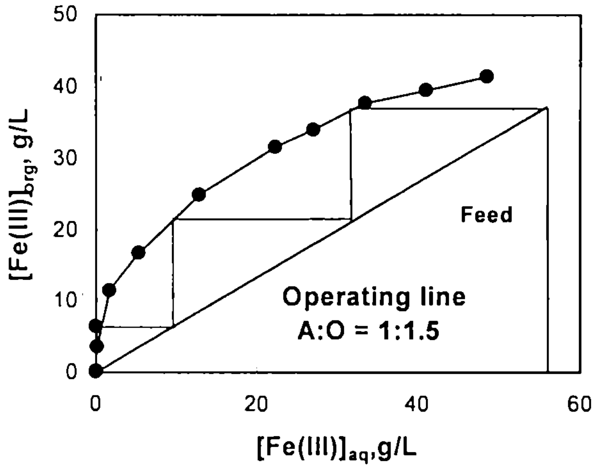


Figure 3.8. McCabe-Thiele plot for Iron(III) Extraction. [$FeCl_3$] = 1.0 mol/dm^3; [HCl] = 2.0 mol/dm^3, A : O = 1 : 1.5; [TBP] = 2.5 mol/dm^3.

Effect of hydrochloric acid concentration on the stripping behavior of iron(III) chloride

The effect of HCl concentration on iron(III) stripping from a loaded organic solvent system consisting of 2.5 mol/dm^3 of TBP in kerosene and 0.5 mol/dm^3 Fe(III) was investigated and the results are shown in Fig. 3.10. It is clear from the results that the percentage stripping of iron(III) decreases with increasing HCl concentration. In view of the better stripping efficiency, 0.1 mol/dm^3 HCl was chosen as a stripping agent for the recovery of iron(III) chloride from the loaded organic phase.

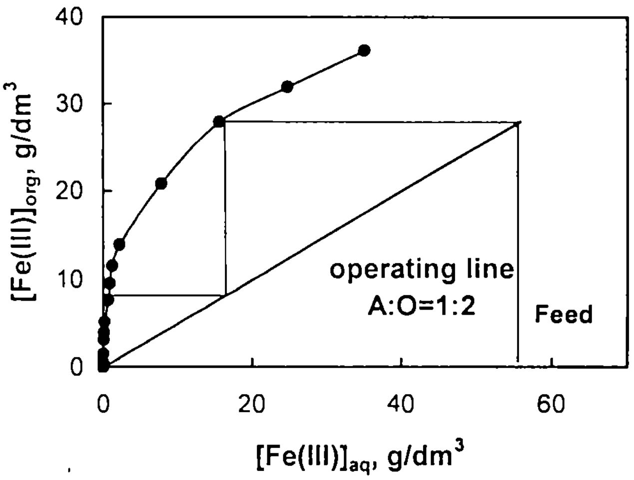


Figure 3.9. McCabe-Thiele plot for Iron(III) Extraction. [$FeCl_3$] = 1.0 mol/dm^3; [HCl] = 2.0 mol/dm^3, A : O = 1 : 2; [TBP] = 2.5 mol/dm^3.

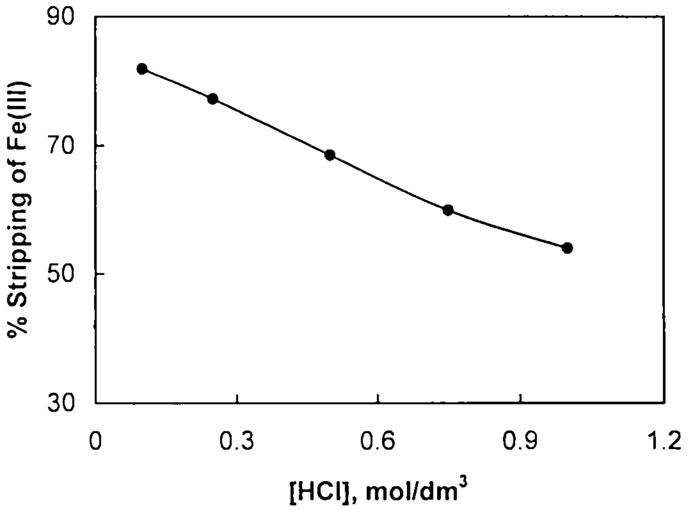


Figure 3.10. Stripping behaviour of iron(III) using hydrochloric acid.

Stripping isotherm

Stripping isotherm was obtained using a typical strip feed solution containing 27.92 g/dm^3 iron(III) in 2.5 mol/dm^3 of TBP in kerosene and 0.1 mol/dm^3 HCl as the stripping agent and the results are shown in Fig. 3.11. It is clear from the McCabe-Thiele plot that the quantitative stripping is possible in three counter-current stages with an org : aq phase ratio of 1 : 1.5.

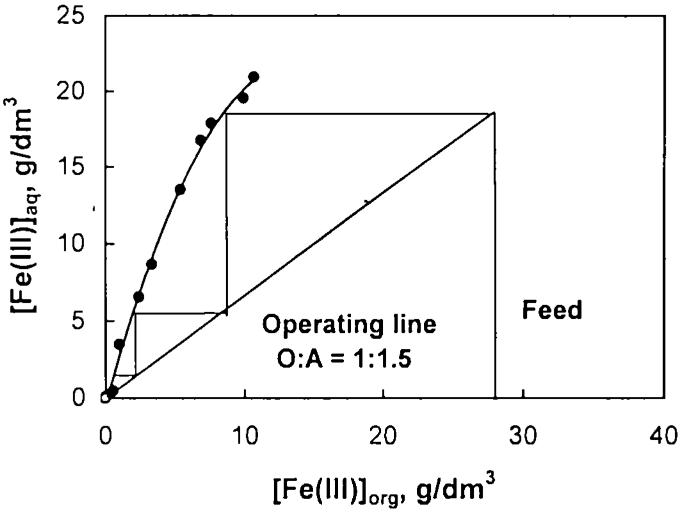


Figure 3.11. McCabe-Thiele plot for Iron(III) Stripping. [$FeCl_3$] = 0.5 mol/dm^3; O : A =1 : 1.5; [TBP] = 2.5 mol/dm^3.

Extraction and separation of iron(III) from simulated waste chloride liquors of titanium minerals processing industry

Based on the above results, a simulated waste chloride liquor consisting of iron(III) (1.03 mol/dm^3), magnesium(II) (0.04 mol/dm^3), aluminium(III) (0.03 mol/dm^3), titanium(IV) (0.03 mol/dm^3), vanadium(V) (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3) and manganese(II) (0.03 mol/dm^3) in various HCl concentrations (1.75; 2.0 and 2.25 mol/dm^3) was prepared and subjected to a batch-type counter-current extraction process using 2.5 mol/dm^3 TBP in kerosene as an extractant (A : O = 1 : 2). Batch type counter-current extraction and stripping studies were performed at laboratory scale using separatory funnels of suitable volume at 303 ± 1 K. The loaded organic phase was then subjected to three stages of counter-current stripping by employing deionised water of pH = 1 at an O : A phase ratio of 1 : 1.5. Typical results of the process are given in Tables 3.2-3.4. It is clear from the results that with increasing HCl concentration in the feed from 1.75-2.25 mol/dm^3, the purity of the product has not affected. However, it has marginal effect on the yield of the product.

Table 3.2. Extraction of iron(III) chloride from simulated waste liquors of titanium minerals processing industry using 2.5 mol/dm^3 TBP in kerosene as an extractant. A : O = 1 : 2 for extraction; O : A = 1 : 1.5 for stripping.

Constituent	Feed (mol/dm^3)	Raffinate (mol/dm^3)	Strip Liquor (mol/dm^3)
Fe(III)	1.03	0.06	0.32
Ti(IV)	0.03	0.03	N.D.
Mn(II)	0.03	0.03	N.D.
Mg(II)	0.04	0.04	N.D.
Al(III)	0.03	0.03	N.D.
Cr(III)	0.01	0.01	N.D.
V(V)	0.02	0.02	N.D.
HCl	1.75	0.97	0.36

N.D. = Not detectable

Purity of iron(III) chloride = 99.9%, Yield = 94.0%

Selective extraction of iron(III) chloride from waste chloride liquors of titania industry (KMML)

The developed solvent extraction process was applied for the recovery of high purity iron(III) chloride from the waste liquors of titanium minerals processing industry (Kerala Minerals and Metals Ltd. Quilon; KMML). The typical composition of the waste chloride liquor from KMML is given in Table 3.5.

Table 3.3. Extraction of iron(III) chloride from simulated waste liquors of titanium minerals processing industry using 2.5 mol/dm^3 TBP in kerosene as an extractant. A : O = 1 : 2 for extraction; O : A = 1 : 1.5 for stripping.

Constituent	Feed (mol/dm^3)	Raffinate (mol/dm^3)	Strip Liquor (mol/dm^3)
Fe(III)	1.03	0.01	0.34
Ti(IV)	0.03	0.03	N.D.
Mn(II)	0.03	0.03	N.D.
Mg(II)	0.04	0.04	N.D.
Al(III)	0.03	0.03	N.D.
Cr(III)	0.01	0.01	N.D.
V(V)	0.02	0.02	N.D.
HCl	2.00	1.20	0.36

Purity of iron(III) chloride = 99.9%, Yield = 99.0%

Table 3.4. Extraction of iron(III) chloride from simulated waste liquors of titanium minerals processing industry using 2.5 mol/dm^3 TBP in kerosene as an extractant. A : O = 1 : 2 for extraction; O : A = 1 : 1.5 for stripping.

Constituent	Feed (mol/dm^3)	Raffinate (mol/dm^3)	Strip Liquor (mol/dm^3)
Fe(III)	1.03	0.007	0.34
Ti(IV)	0.03	0.03	N.D.
Mn(II)	0.03	0.03	N.D.
Mg(II)	0.04	0.04	N.D.
Al(III)	0.03	0.03	N.D.
Cr(III)	0.01	0.01	N.D.
V(V)	0.02	0.02	N.D.
HCl	2.25	1.4	0.38

Purity of iron(III) chloride = 99.9%, Yield = 99.3%

Table 3.5. Composition of waste chloride liquor from titania industry (KMML).

Constituent	mol/dm^3
Fe(II)	1.92
Fe(III)	0.11
Mg(II)	0.10
Mn(II)	0.03
Al(III)	0.06
Ti(IV)	0.05
Cr(III)	0.002
V(V)	0.02
HCl	1.24

As is well known, the ferrous iron is less extractable than ferric iron when extracted with TBP, in the present study, the waste chloride liquor was chlorinated to convert ferrous to ferric iron by passing chlorine gas (in a stoichiometric amount to the divalent iron ions).

$$2FeCl_2 + Cl_2(g) \rightarrow 2FeCl_3$$

The extraction process for the recovery of iron(III) chloride from the waste liquor comprises the steps of

- Chlorination of waste chloride liquor, dilution (to half) and adjustment of feed acidity to 2.0 mol/dm^3 HCl;
- Selective extraction of iron(III) chloride from the chlorinated waste chloride liquor in three stages of counter-current extraction (aq. : org. = 1 : 2) using 2.5 mol/dm^3 TBP in kerosene as an extractant; and
- Stripping of loaded organic phase using distilled water (pH = 1.0) in three stages (org. : aq. = 2 : 3) to recover high purity iron(III) chloride.

Typical results of the process are given in Table 3.6. The present study clearly shows that TBP can be used as a selective extractant for the recovery of high purity iron(III) chloride (99.9 %) with an yield of 99.0 % from a multivalent metal chloride feed, present in the waste chloride liquors of titanium minerals processing industry.

Table 3.6. Extraction of iron(III) chloride from waste liquors of titanium minerals processing industry using 2.5 mol/dm^3 TBP in kerosene as extractant. A : O = 1 : 2 for extraction; O : A = 1 : 1.5 for stripping.

Constituent	Feed (mol/dm^3)	Raffinate (mol/dm^3)	Strip Liquor (mol/dm^3)
Fe(III)	1.016	0.008	0.336
Ti(IV)	0.025	0.025	N.D.
Mn(II)	0.014	0.014	N.D.
Mg(II)	0.051	0.051	N.D.
Al(III)	0.030	0.030	N.D.
Cr(III)	0.001	0.001	N.D.
V(V)	0.010	0.010	N.D.
HCl	2.000	1.200	0.366

Purity of iron(III) chloride = 99.9%, Yield = 99.2%

Hydrothermal synthesis and characterization of iron oxide powders

The preparation of iron oxide powders comprises the steps of

- Chlorination of waste chloride liquor for converting ferrous iron to ferric iron, dilution to the required concentration and adjustment of the feed acidity to 2.0 mol/dm^3 HCl;
- Selective extraction of iron(III) chloride from the simulated or actual waste chloride liquor in three stages of counter-current

extraction (A : O = 1 : 2) using 2.5 mol/dm^3 TBP in kerosene as an extractant;

- Precipitation stripping of ferric hydroxide from the loaded organic phase obtained from the solvent extraction stream using sodium hydroxide in an org.:aq. phase ratio of 1:2; and
- Hydrothermal synthesis of iron oxide powders using the alkaline suspension containing iron hydroxide as the precursor. The ferric hydroxide will transform into α-$Fe_2O_3(s)$ as follows:

$$2\,Fe(OH)_3\,(aq) \longrightarrow \alpha\text{-}Fe_2O_3(s) + 3H_2O$$

The schematic diagram of the process is shown in Fig.3.12. The iron oxide powders were characterized by XRD and FT-IR. The purity of the iron oxide powders were confirmed by chemical analysis with AAS and found that the powders are free from other associated metal ions, which are present in the waste chloride liquors of titanium minerals processing industry. The formation of hematite powder was confirmed by FT-IR spectrum embedded in KBr as shown in Fig. 3.13. The spectrum of Fe_2O_3 showed two bands at 564 and 480 cm^{-1} (Kandori et al. 1998).

The XRD patterns of the iron oxide powders synthesized at different temperatures (393-453 K) and reaction times (30 min, 60 min and 120 min) are shown in Figs. 3.14 and 3.15, respectively. The diffraction patterns at 393-453 K are typical to the standard pattern of hematite powders (α-Fe_2O_3) (Konishi et al. 1994). It is clear from the Fig. 3.14 that the intensities of the peaks increase with increase in temperature indicating the growing volume fraction of the crystalline hematite. However, the reaction time has only a marginal effect on the crystallinity of the hematite from 60 min to 120 min

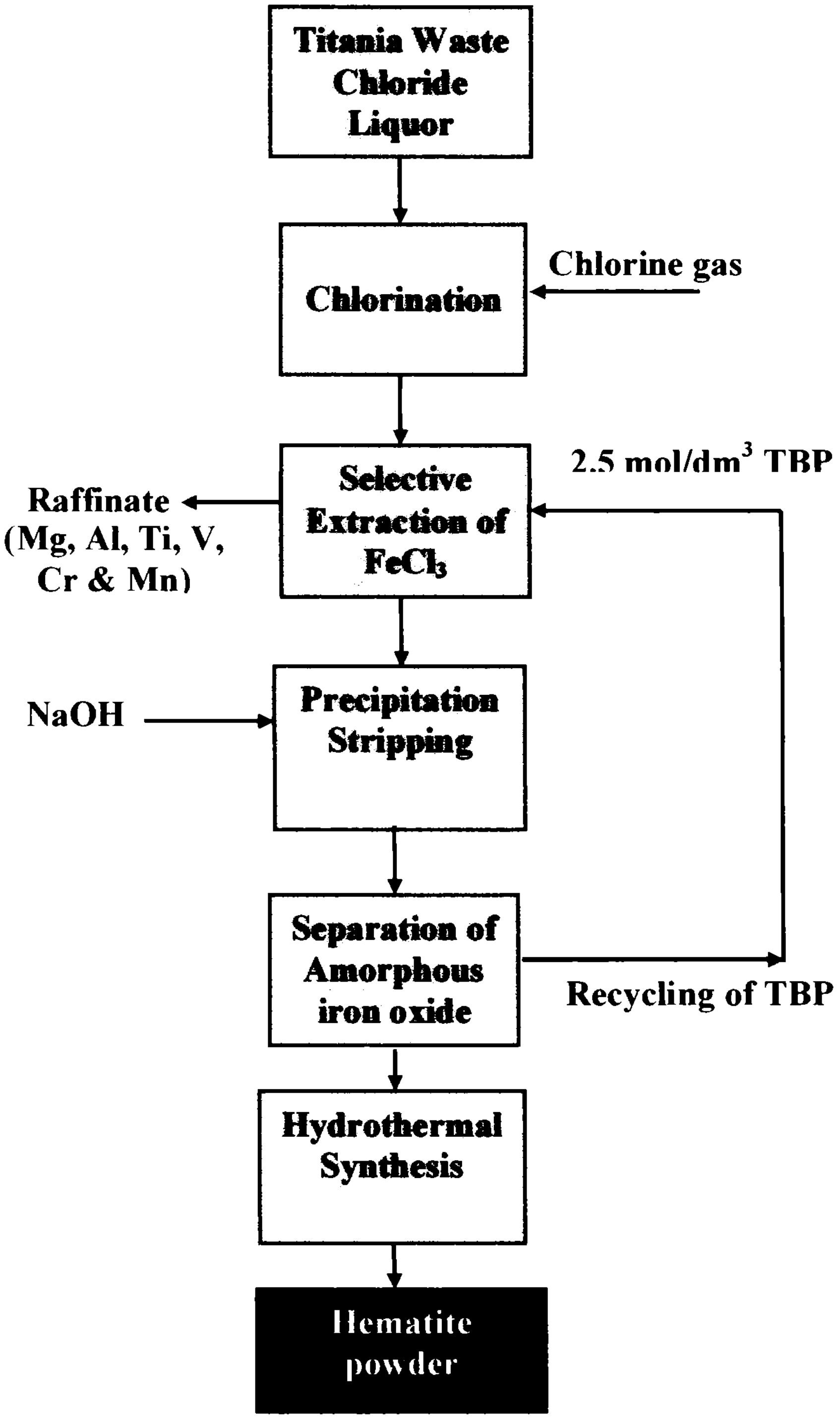


Figure 3.12. **Schematic flow diagram of the process for the preparation of hematite powders.**

(Fig. 3.15). On the other hand, poor crystallinity was observed when the heating time was 30 min.

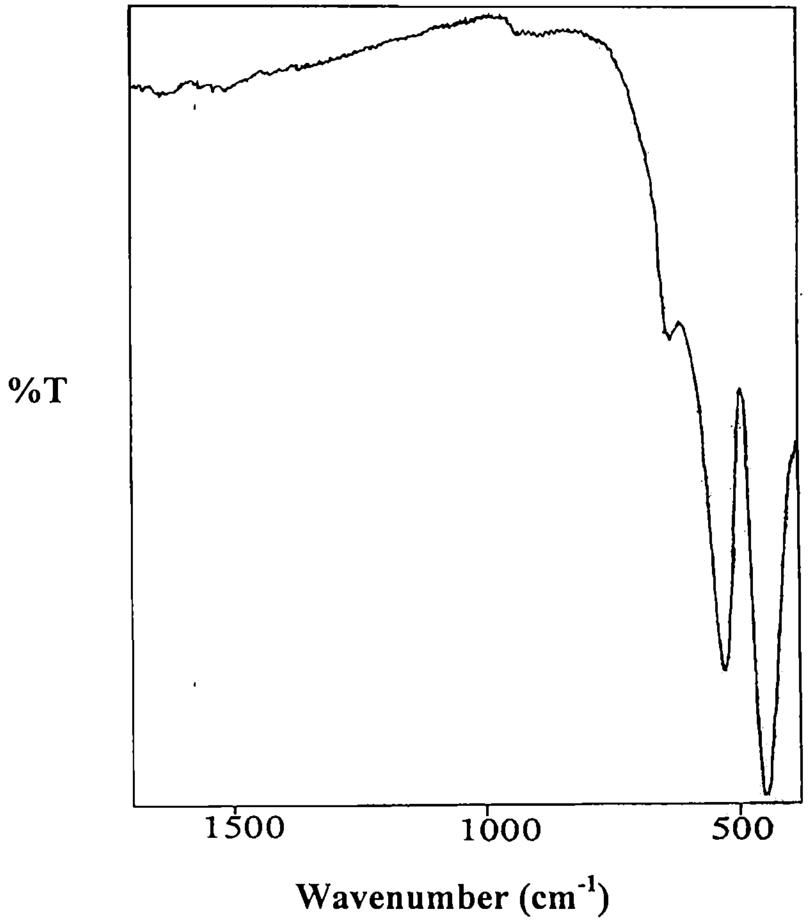


Figure 3.13. IR spectrum of hematite powder synthesised at 453 K at a reaction 120 min using 3.0 mol/dm^3 sodium hydroxide for precipitation stripping.

Fig. 3.16 shows the XRD patterns of the hematite powders obtained by using different sodium hydroxide concentrations (1.5-3.0 mol/dm^3) for precipitation-stripping at 413 K and heating time of 120 min. The diffraction pattern obtained at 1.5 mol/dm^3 sodium hydroxide contains some iron hydroxide peaks, which indicates the poor conversion of iron hydroxide into hematite powders.

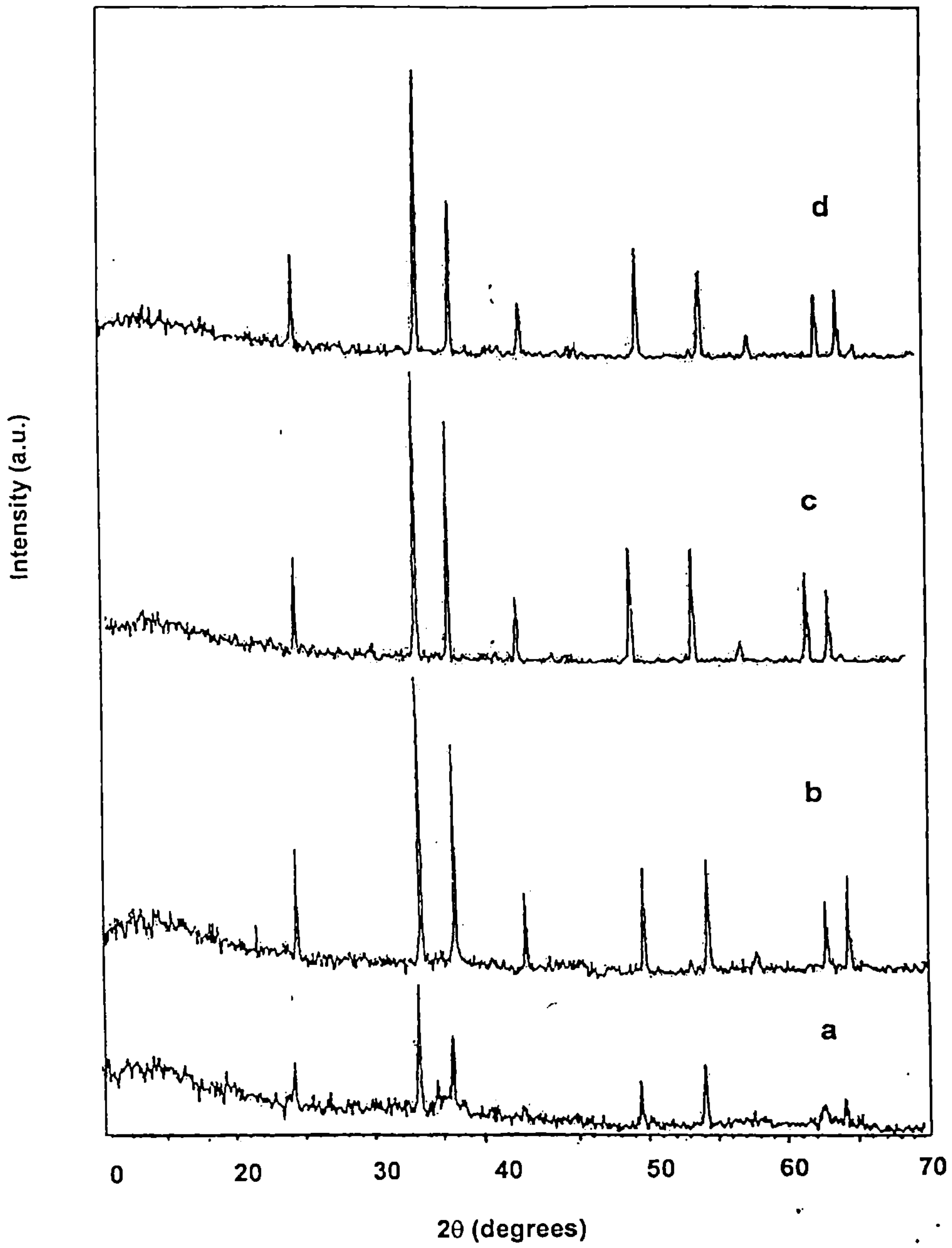


Figure 3.14. X-ray diffraction pattern of hematite powders at different temperatures using 3.0 mol/dm^{3}sodium hydroxide for precipitation stripping. Reaction time = 120 min; a = 393 K, b = 413 K, c = 433 K, d = 453 K.

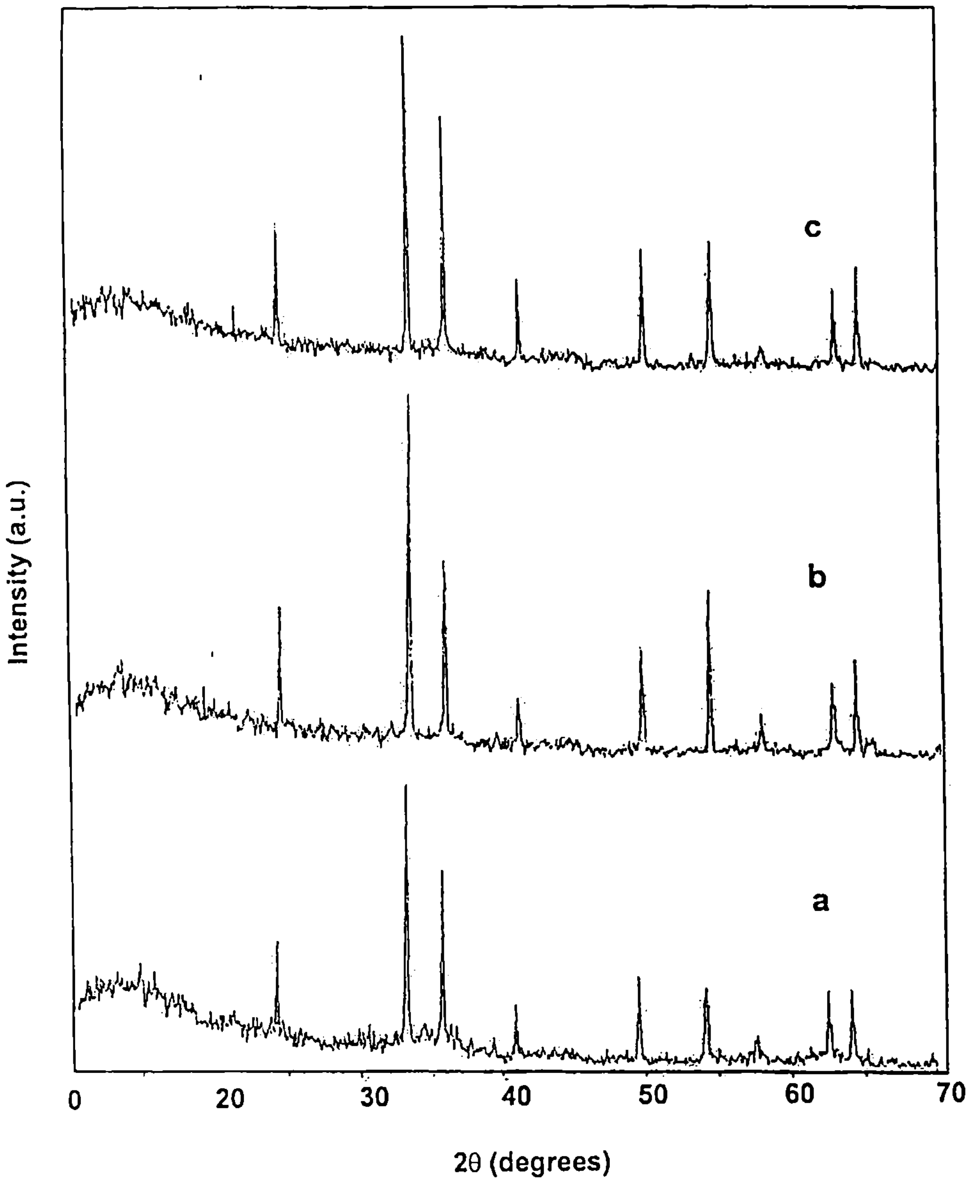


Figure 3.15. X-ray diffraction pattern of hematite powders synthesised at different reaction times using 3.0 mol/dm^3 sodium hydroxide for precipitation stripping. Reaction temperature = 413 K; a = 30 min, b = 60 min, c = 120 min.

Figs. 3.17-3.19 show the scanning electron micrographs of hematite powders prepared at different temperatures (393-453 K), reaction times (30 min, 60 min and 120 min) and sodium hydroxide concentrations (1.5-3.0 mol/dm^3). Fig. 3.20 shows the SEM of hematite powder synthesized from KMML waste chloride liquor at 453 K for 120 min using 3.0 mol/dm^3 sodium hydroxide for precipitation stripping. The SEM picture of powders synthesized at 393 K shows the presence of amorphous precipitate. On the other hand, the SEM pictures of powders synthesized at 413 K, 433 K and 453 K show the plate-like morphology. The plate-like morphology has also been observed for the SEM pictures of hematite powders synthesised at different reaction times and sodium hydroxide concentrations.

Table 3.7 gives the particle diameter of the hematite powders synthesised at different hydrothermal reaction conditions. The average particle diameter of the hematite powders varies in the range 2.75 μm-5.0 μm.

Table 3.7. Effect of hydrothermal reaction conditions on the particle diameter of the hematite powders.

Hydrothermal reaction conditions	Particle diameter (μm)
393 K, 120 min, 3.0 mol/dm^3 NaOH	4.00
413 K, 120 min, 3.0 mol/dm^3 NaOH	4.40
433 K, 120 min, 3.0 mol/dm^3 NaOH	4.60
453 K, 120 min, 3.0 mol/dm^3 NaOH	5.00
413 K, 30 min, 3.0 mol/dm^3 NaOH	3.00
413 K, 60 min, 3.0 mol/dm^3 NaOH	3.75
413 K, 120 min, 1.5 mol/dm^3 NaOH	2.75
413 K, 120 min, 2.5 mol/dm^3 NaOH	4.25

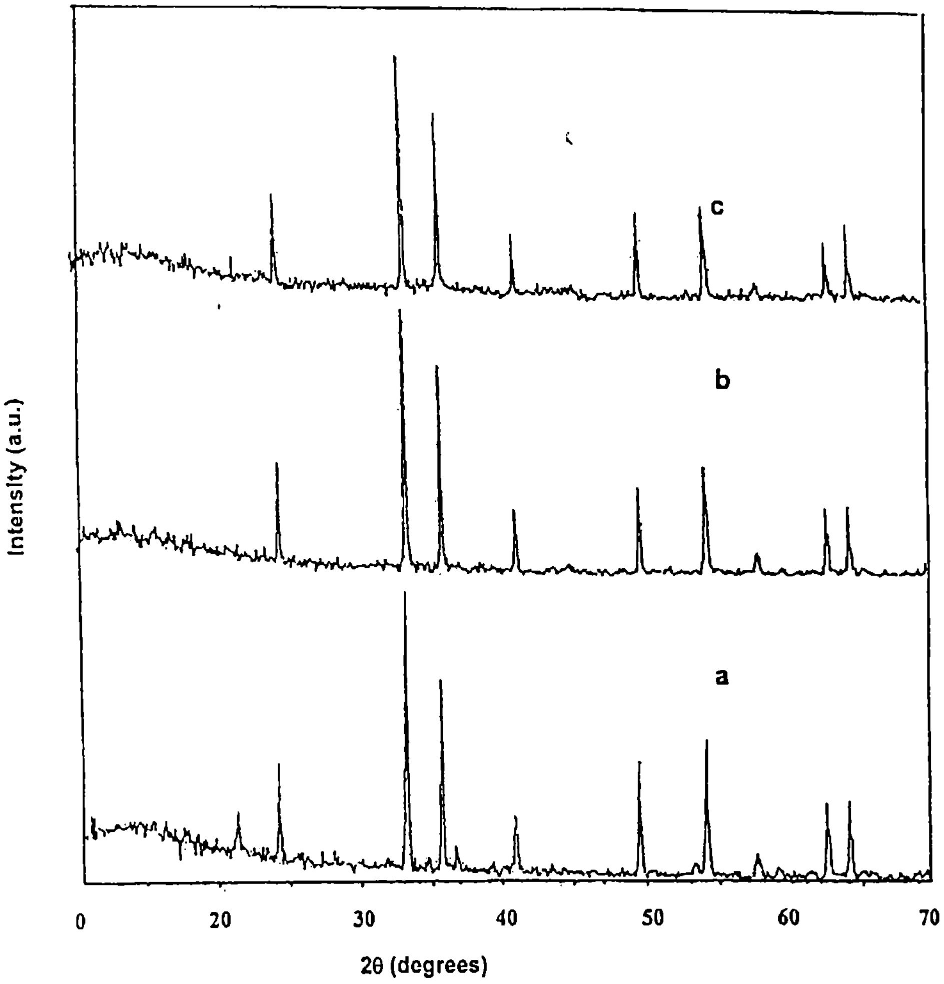


Figure 3.16. X-ray diffraction pattern of hematite powders synthesised using different sodium hydroxide concentrations for precipitation stripping at 413 K. Reaction time = 120 min; a) = 1.5 mol/dm^3, b) = 2.5 mol/dm^3, c) = 3.0 mol/dm^3.

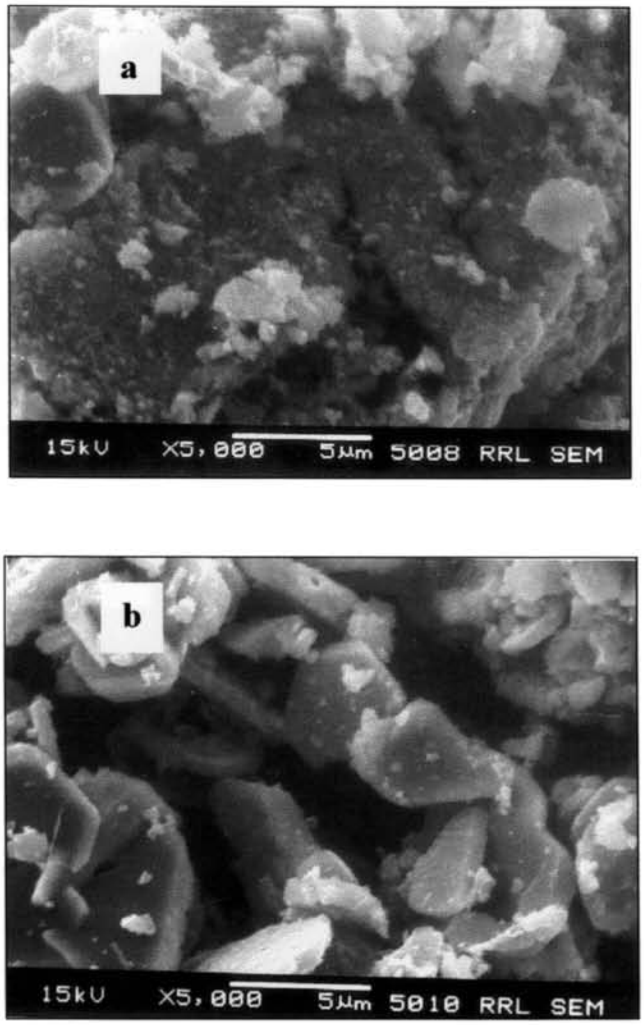


Figure. 3.17. Scanning electron micrographs of hematite powders prepared at different temperatures for 120 min using 3.0 mol/dm^3 sodium hydroxide. a) = 393 K, b) = 413 K.

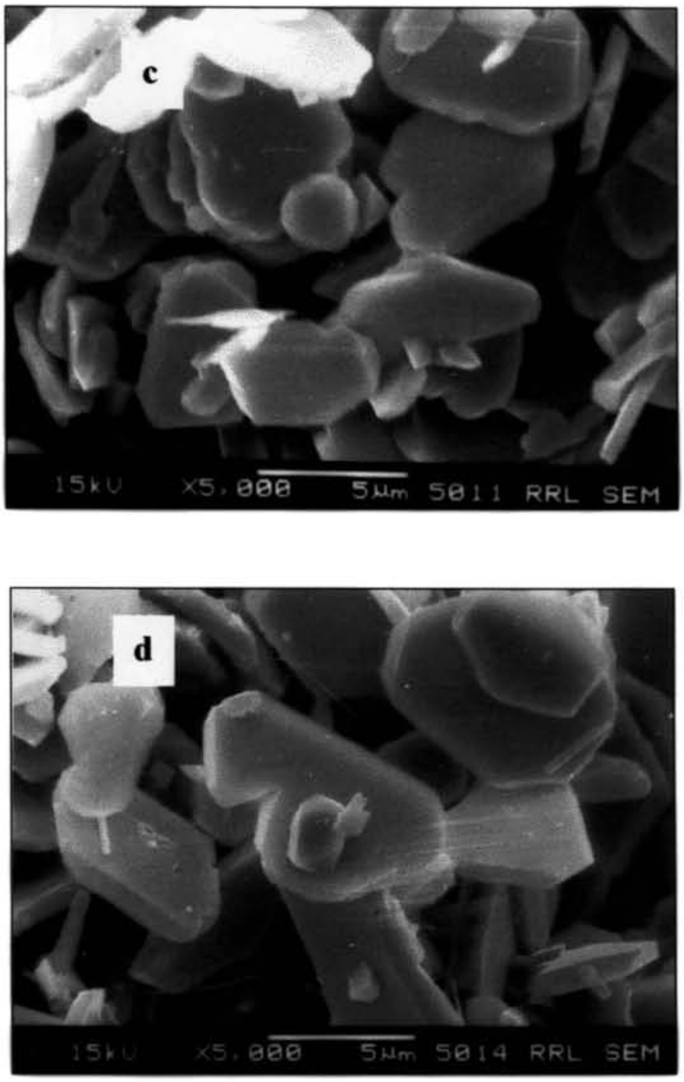


Figure. 3.17. Scanning electron micrographs of hematite powders prepared at different temperatures for 120 min using 3.0 mol/dm^3 sodium hydroxide. c) = 433 K, d) = 453 K.

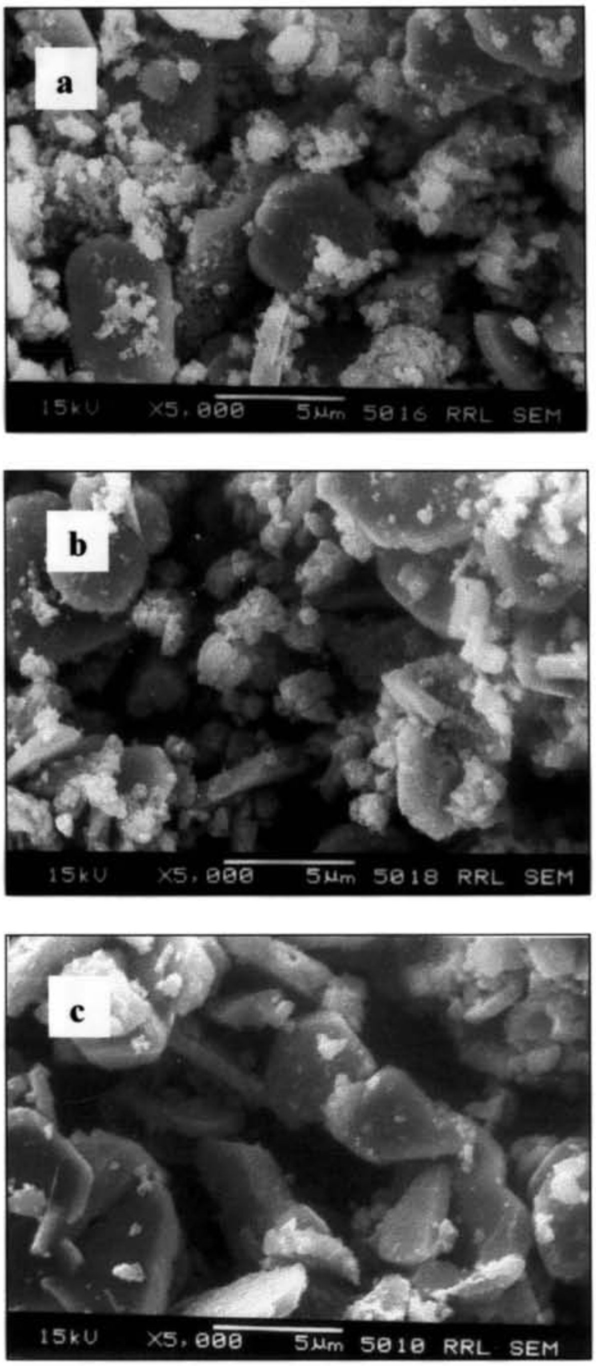


Figure. 3.18. Scanning electron micrographs of hematite powders synthesised at different reaction times using 3.0 mol/dm^3 sodium hydroxide for precipitation stripping. Reaction temperature = 413 K; a = 30 min., b = 60 min, c = 120 min.

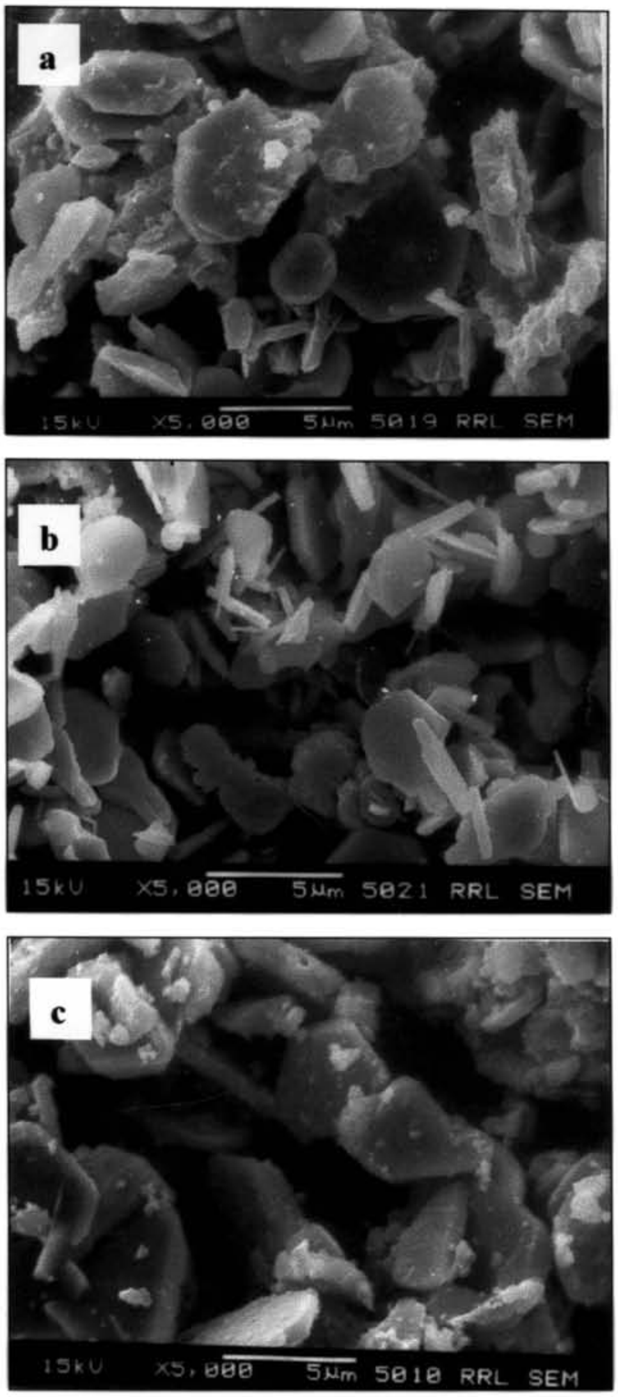


Figure. 3.19. SEM of hematite powders synthesised using different sodium hydroxide concentrations for precipitation stripping at 413 K. Reaction time = 120 min; a) = 1.5 mol/dm^3, b) = 2.5 mol/dm^3, c) = 3.0 mol/dm^3.

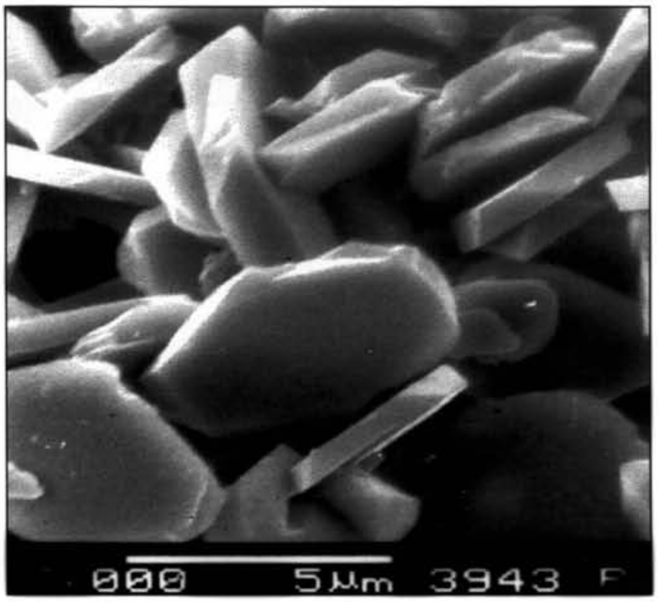


Figure. 3.20. SEM of hematite powders synthesised from KMML waste chloride liquor. Hydrothermal conditions: Sodium hydroxide concentration for precipitation stripping = 3.0 mol/dm^3, Temperature = 453 K, Reaction time = 120 min.

The TG-DTA data for the hematite powders prepared from hydrothermal synthesis at 453 K are shown in Figs. 3.21 and 3.22, respectively. It is clear from the data that there is no weight loss and phase transformations for the hematite powders in the temperature range 313-1273 K.

Fig. 3.23 shows the reflectance spectrum corresponding to hematite powder prepared from KMML waste chloride liquors by hydrothermal synthesis at 453 K. The high reflectance lies in the region 700-800 nm and shows a maximum of 20 R%. The colour coordinates of the hematite powder were determined by CIE-LAB 1976 colour data. The moderate **'a'** (5.68) and low **'b'** (1.58) values suggest the brown-red colour of the iron oxide powder. The lightness (L) of the iron oxide powder was found to be 28.28.

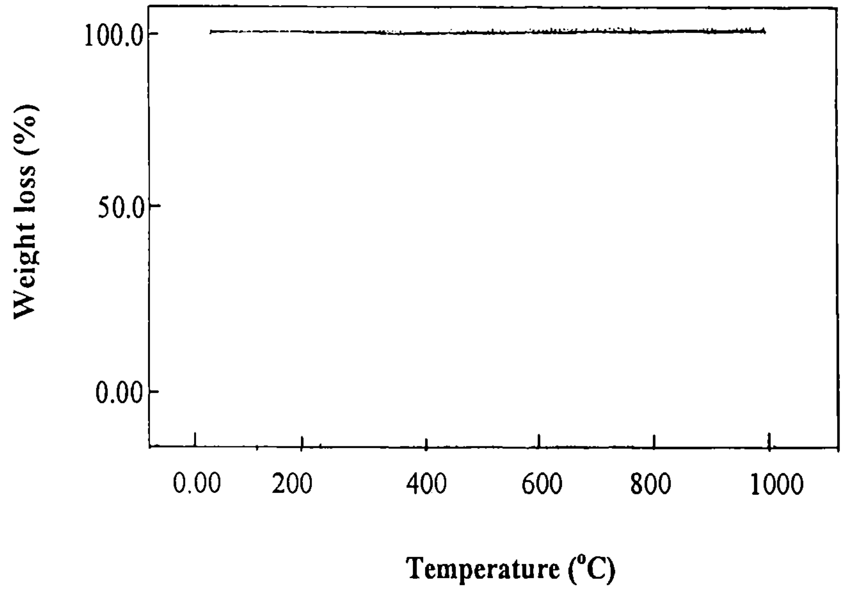


Figure. 3.21. Thermogravimetric analysis of hematite powder synthesised from KMML waste chloride liquor at 453 K at a reaction time of 120 min using 3.0 mol/dm^3 sodium hydroxide for precipitation-stripping.

In the literature there have been several reports concerning the synthesis of hematite powders by various methods (González-Carreño et al. 1993; Domingo et al. 1994; Bermejo et al. 1995; Ding et al. 1997; Dong et al. 1995; Chhabra et al. 1996). However, the use of hydrothermal techniques shows versatility for generating hematite powders of different shapes, such as acicular, plate-like, spherical and polyhedral, which would have potential applications in magnetic recording media, pigment for anticorrosive protection, soft ferrites, inorganic pigment, catalysis etc. (Diamandescu et al. 1999). The shape and the size of hematite powders obtained through hydrothermal synthesis has been shown to depend on the precursor composition, the neutralizing media, temperature, reaction time and the concentration ratio of Fe to OH. The role of various process conditions cited has not been investigated in detail by earlier workers.

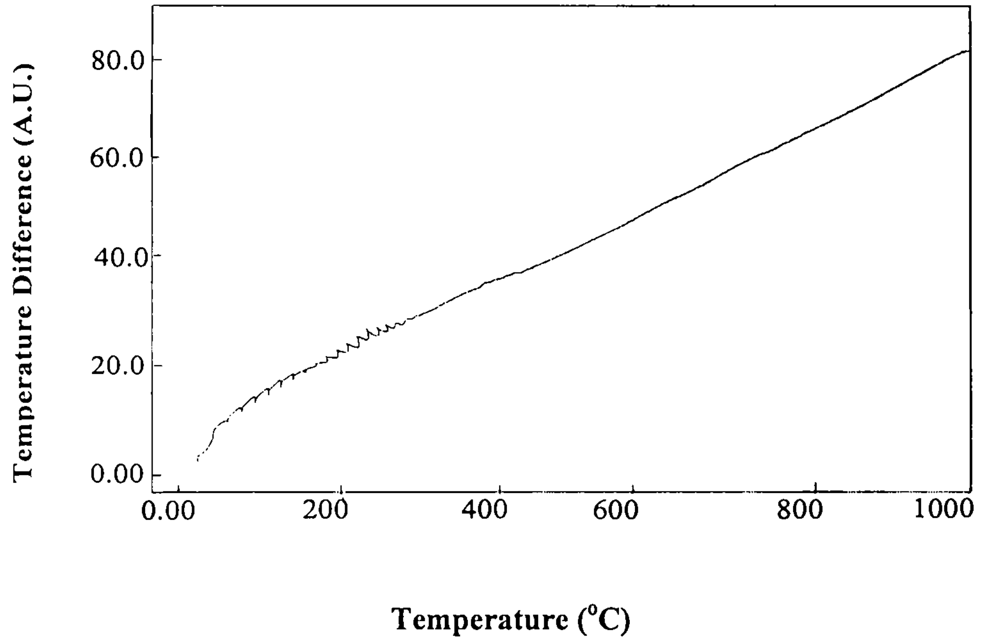


Figure 3.22. Differential thermal analysis of hematite powder synthesised from KMML waste chloride liquor at 453 K at a reaction of 120 min using 3.0 mol/dm^3 sodium hydroxide for precipitation-stripping.

In the present study, by varying the reaction temperature in the range 393-453 K, it was observed that plate-like morphology could be obtained even at a low temperature of 413 K with constant stirring and without additives. As a comparison, the plate-like structures at a temperature of 453 K have been reported in presence of urea or excess alkali (Diamandescu et al. 1999).

Further the present study has shown the plate-like morphology could be achieved at a much lower NaOH concentration (2.5 mol/dm^3), in comparison with earlier report (Diamandescu et al. 1999) (4.0 mol/dm^3).

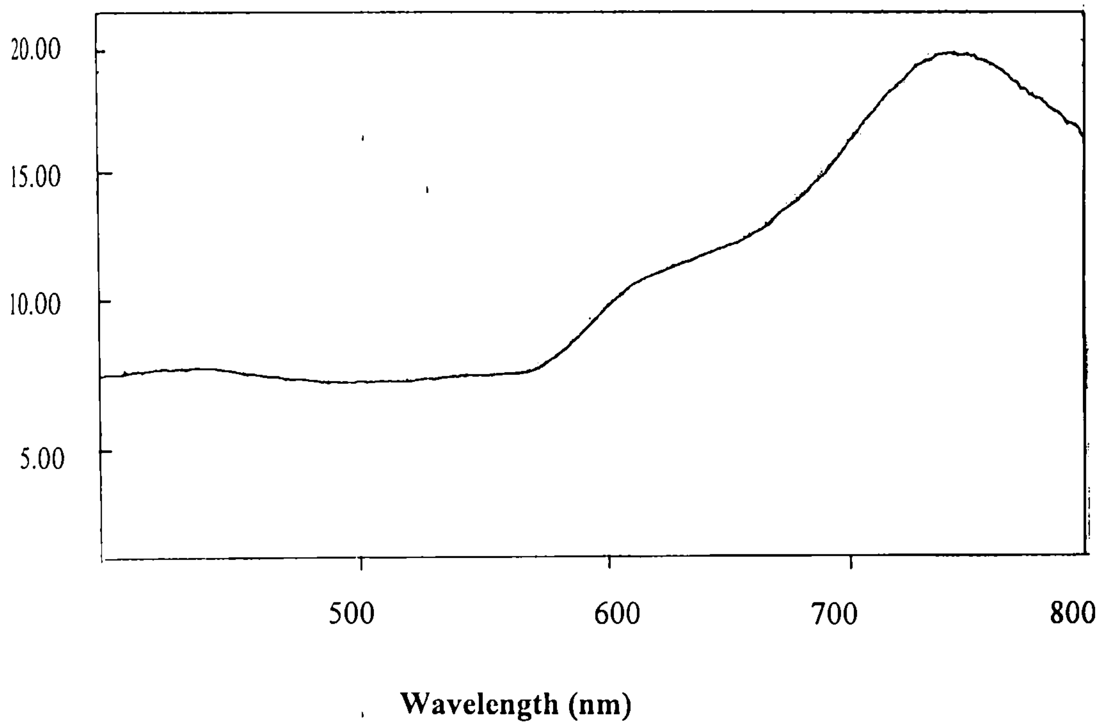


Figure. 3.23. Reflectance spectrum of hematite powder synthesised from KMML waste chloride liquor at 453 K at a reaction of 120 min using 3.0 mol/dm^3 sodium hydroxide for precipitation-stripping.

Submicrometer particles of crystalline hematite powders were also prepared by the hydrolysis of iron-loaded Versatic 10 acid using water at temperatures between 403-478 K (Konishi et al. 1994). The main draw back of this process is the difficulty in the separation of the solid phase from the organic phase. On the other hand, the present investigations demonstrate that hematite powders of plate-like morphology can be prepared from the loaded organic phase of the solvent extraction stream by adopting the precipitation stripping coupled with hydrothermal synthesis. Further, the present investigation provides an optimum set of hydrothermal process conditions for the synthesis of hematite powders at relatively low temperature and alkali concentration as compared to the previous reports.

Recycling capacity of the solvent

The recycling capacity of the extractant was tested, first by extracting iron(III) using 2.5 mol/dm^3 TBP from 2.0 mol/dm^3 of hydrochloric acid solutions containing 1.0 mol/dm^3 ferric chloride and then stripping with 3.0 mol/dm^3 sodium hydroxide in an org : aq. phase ratio of 1 : 2. The stripped organic phase was reused for extraction. The extraction efficiency was found to be the same as that of fresh extractant. Further, the recycling capacity was also confirmed by IR spectral data (Fig. 3.7). It is clear from the IR data that the P=O stretching frequency of TBP was not changed even after precipitation-stripping. The results revealed practically insignificant change in the extraction efficiency of the solvent even after five cycles of extraction and stripping processes.

Chapter 4

Solvent Extraction Separation of Vanadium(V) from Multimetal Chloride Solutions Using Tributylphosphate

Vanadium is commercially important as a constituent of several alloys and catalysts. Nowadays, vanadium production is limited to its recovery from industrial wastes or low grade ores such as vanadium-bearing ferrophosphorus slag, iron slag, fly ash, spent catalysts and titaniferrous magnetite ore. Selective separation and recovery of vanadium from titania waste streams for its potential use is of paramount importance in view of the depleting resources of vanadium. Further, the more our economy recovers and recycles useful metals from industrial wastes, the less mining will be needed and less environmental damage will result from waste disposal. Hence, in the present work, an attempt has been made to develop a solvent extraction-based separation method to recover vanadium from multivalent metal chloride solutions present in the waste chloride liquors of titanium minerals processing industry.

A survey of literature showed that acidic organophosphorus extractants have been widely used for the extraction of vanadium(V) from acidic chloride solutions (Biswas et al. 1985; Hirai et al. 1995; Brunette et al. 1979; Nishihama et al. 2000; Saji and Reddy 2002). However, as compared with acidic organophosphorus extractants, studies on the extraction of vanadium(V) from hydrochloric acid solutions using neutral organophosphorus extractants are limited (Tedesco and Rumi 1978; Remya et al. 2003). The separation and recovery possibilities of vanadium(V) from other associated metal ions such as magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), and iron(III), present in the waste streams of titanium minerals processing industry, were investigated using trialkylphosphine oxide (Cyanex 923) in kerosene as an extractant and reported poor selectivity (Remya et al. 2003). The extraction equilibrium involved in the extraction of vanadium(V) from hydrochloric acid solutions, especially with tributylphosphate (TBP), is not well understood (Tedesco and Rumi 1978). Further, no attempts have been made to recover vanadium(V) from titania waste chloride liquors by employing TBP as an extractant. Hence in the present study, TBP has been explored for the extraction of vanadium(V) from acidic chloride solutions to elucidate the nature of the complex extracted into the organic phase and also to investigate the selectivity between vanadium(V) and other associated multivalent metal ions present in the titania waste chloride liquors.

4.1 Experimental

The preparation of stock solutions of metal ions, apparatus used and solvent extraction and analytical procedures followed in this work are the same as described in chapter 3. Freshly prepared solutions of vanadium(V) were used in all the experimental studies to prevent partial reduction to tetravalent vanadium in hydrochloric acid solutions with respect to time

(Tedesco and Rumi 1978). The initial vanadium(V) concentration was maintained at 0.02 mol/dm^3 in all the experiments.

Solvent extraction and analytical procedures

The solvent extraction and analytical procedures for the determination of metal ions are the same as described in chapter 3. Preliminary experiments showed that the extraction equilibrium for vanadium(V) was attained within 5 min.

4.2 Results and Discussion

Effect of hydrochloric acid concentration

The extraction of vanadium(V) (0.02 mol/dm^3) and other associated metal ions, viz., magnesium(II) (0.03 mol/dm^3), aluminium(III) (0.02 mol/dm^3), titanium(IV)' (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.03 mol/dm^3) and iron(III) (0.01 mol/dm^3) was examined as a function of hydrochloric acid concentration (1.0 - 5.0 mol/dm^3) using 1.47 mol/dm^3 TBP in kerosene as an extractant and the results are depicted in Fig. 4.1. It is clear from the results that iron(III) is co-extracted along with vanadium(V) into the organic phase. On the other hand, magnesium(II), aluminium(III), titanium(IV), chromium(III) and manganese(II) were not extracted under the present experimental conditions. The extraction of vanadium(V) and iron(III) was found to increase with an increase in hydrochloric acid concentration.

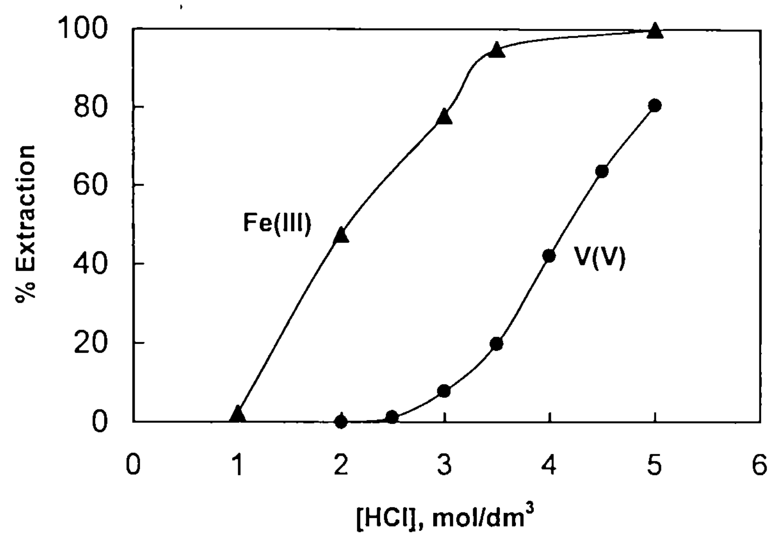


Figure 4.1. Effect of hydrochloric acid concentration on the extraction of vanadium(V) (0.02 mol/dm^3), magnesium(II) (0.03 mol/dm^3), aluminium(III) (0.02 mol/dm^3), titanium(IV) (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.03 mol/dm^3) and iron(III) (0.01 mol/dm^3) using 1.47 mol/dm^3 TBP in kerosene.

The effect of hydrogen (3.5-5.1 mol/dm^3) and chloride (4.0-5.5 mol/dm^3) ion concentrations on the extraction of vanadium(V), respectively, was investigated from HCl + NaCl mixtures using 1.47 mol/dm^3 TBP in kerosene as an extractant and the results are depicted in Figs. 4.2 and 4.3. From the slopes of the log-log plots, it is clear that vanadium(V) was extracted as $VO_2Cl.2HCl$ into the organic phase. The activity coefficients of hydrogen and chloride ions in the aqueous phase were calculated using Bromley's formulation (Bromley 1973).

$$\mathrm{Log}\,\gamma_{ij} = \frac{-A\; Z_iZ_j\; I^{1/2}}{1 + I^{1/2}} + \frac{(0.06 + 0.6\,B)\; Z_iZ_j\; I}{\left(1 + \dfrac{1.5\,I}{Z_iZ_j}\right)^2} + BI$$

where, γ_{ij} = mean activity coefficient, A = Debye-Huckel constant, B = ionic interaction parameter, I = Ionic strength, Z_i, Z_j = absolute value of ionic charge of ions.

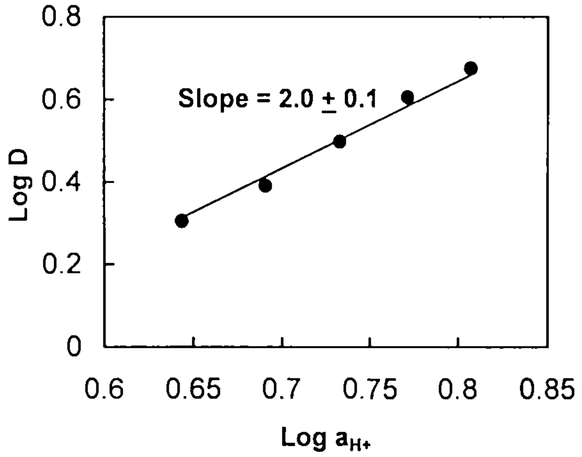


Figure 4.2. Effect of hydrogen ion concentration on the extraction of vanadium(V) at constant chloride ion concentration. $[Cl^-]$ = 5.1 mol/dm^3, [V(V)] = 0.02 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Effect of extractant concentration

The effect of TBP concentration (0.5-2.5 mol/dm^3) on the extraction of vanadium(V) was studied at constant metal ion (0.02 mo/dm^3) and hydrochloric acid (5.0 mol/dm^3) concentrations and the results are shown in Fig. 4.4. The distribution ratio, D, of vanadium(V) increased linearly with increased TBP concentration and the slope of the log-log plot shows that two molecules of TBP were associated with the extractable complexes. However, the involvement of two and three molecules of TBP in the extracted complexes of vanadium(V) from hydrochloric acid solutions at higher concentrations of the extractant was reported (Tedesco and Rumi 1978). The involvement of two molecules of TRPO has also been reported for the extraction of vanadium(V) from hydrochloric acid solutions (Remya and Reddy 2004).

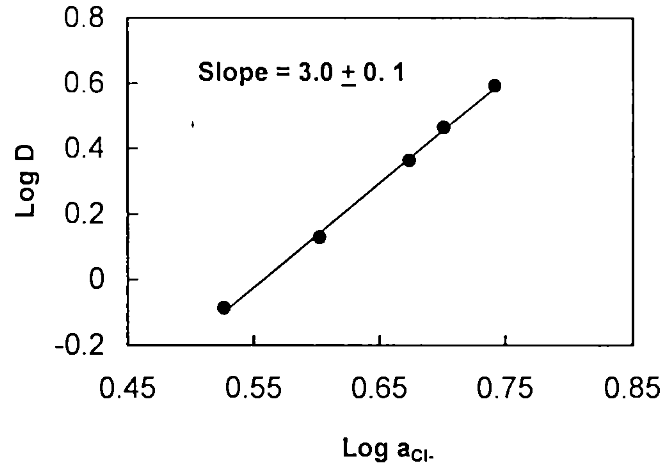


Figure 4.3. Effect of chloride ion concentration on the extraction of vanadium(V) at constant H^+ concentration. $[H^+]$ = 4.0 mol/dm^3, [V(V)] = 0.02 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Effect of metal ion concentration

The effect of metal ion concentration (0.004-0.05 mol/dm^3) on the extraction of vanadium(V) was investigated from 5.0 mol/dm^3 hydrochloric acid solutions by employing 1.47 mol/dm^3 TBP in kerosene as an extractant. The log–log plot (Fig. 4.5) of equilibrium organic-phase vanadium(V) concentration against aqueous-phase vanadium(V) concentration is linear with a slope of unity, indicating that only mononuclear species are extracted into the organic phase.

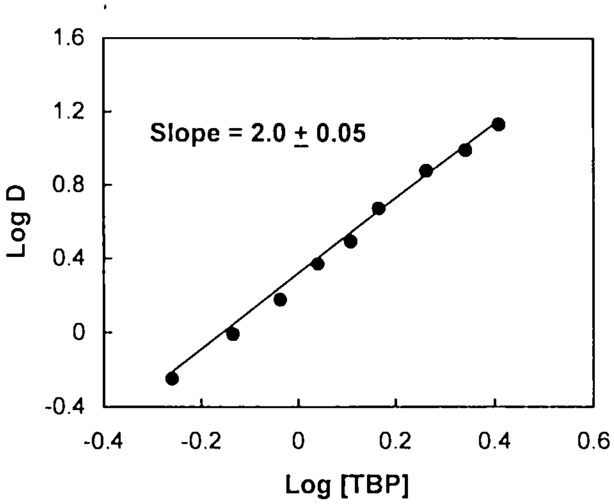


Figure 4.4. Effect of TBP concentration on the extraction of vanadium(V). $[V(V)] = 0.02\ \mathrm{mol/dm^3}$, $[HCl] = 5.0\ \mathrm{mol/dm^3}$.

Extraction Equilibrium

Based on the preceding results, the extraction equilibrium for vanadium(V) from hydrochloric acid solutions with TBP as an extractant can be represented by:

$$\mathrm{VO_{2\,aq}^{+} + 2H_{aq}^{+} + 3Cl_{aq}^{-} + 2TBP_{org}} \overset{K_{ex}}{\Leftrightarrow} \mathrm{VO_2Cl\cdot 2HCl\cdot 2TBP_{org}}$$

where, K_{ex}, denotes the equilibrium constant.

$$K_{ex} = \frac{[\mathrm{VO_2Cl \cdot 2HCl\cdot 2TBP}]}{[\mathrm{VO_2^+}][\mathrm{H^+}]^2[\mathrm{Cl^-}]^3[\mathrm{TBP}]^2}$$

The Eq. (2) may also be represented in terms of concentrations and activity coefficients as:

$$K_{ex} = \frac{D\ \gamma_{\mathrm{VO_2Cl\cdot 2HCl\cdot 2TBP}}}{[\mathrm{H^+}]^2[\mathrm{Cl^-}]^3[\mathrm{TBP}]^2\,\gamma_{\mathrm{H^+}}^2\,\gamma_{\mathrm{Cl^-}}^3\,\gamma_{\mathrm{TBP}}^2}$$

where, γ, represents the activity coefficient and the parentheses represent the concentration of each species. However, in the present experiments the concentration of metal ion (0.02 mol/dm^3) used is low as compared to the concentration of TBP (0.5-2.5 mol/dm^3) in the organic phase and hydrogen ion (3.5-5.1 mol/dm^3) and chloride ion (4.0-5.5 mol/dm^3) concentrations in the aqueous phase. Further, due to the non-availability of the activity coefficient data of TBP in kerosene system, in the present study the activities of the metal complex and TBP in the organic phase have been considered as equal to their equilibrium concentration in the organic phase. The activity coefficients of the hydrogen ion and the chloride ion in the aqueous phase were calculated by Bromley's formulation (Bromley 1973). The equilibrium constant was calculated from the distribution data and found to be 4.72 x 10^{-4}.

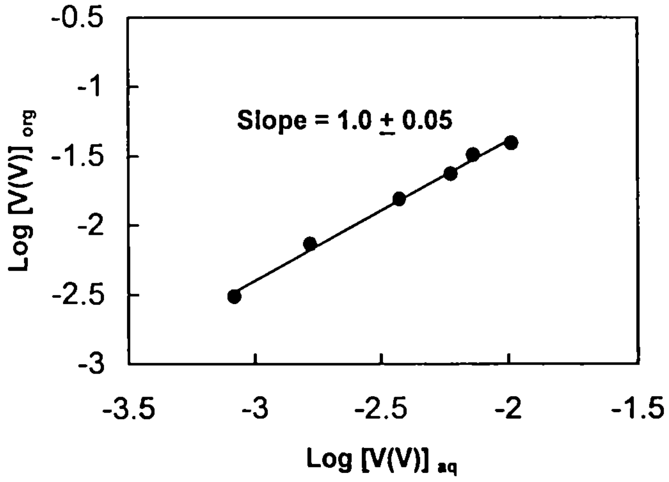


Figure 4.5. Effect of metal ion concentration on the extraction of vanadium(V). [HCl] = 5.0 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Effect of diluent

The extraction efficiency of vanadium(V) from 5.0 mol/dm^3 hydrochloric acid solutions was studied using 1.47 mol/dm^3 TBP in various diluents and the results are shown in Table 4.1. The results clearly demonstrate that diluents such as benzene, xylene, toluene and kerosene, which have low dielectric constants, show higher extraction efficiency for vanadium(V). On the other hand, diluents having higher dielectric constants, such as chloroform, gave poor extraction. This may be due to the strong interaction between TBP and chloroform through hydrogen bonding (Sekine and Hasegawa 1997). Among aromatic hydrocarbons, the extraction efficiency of vanadium(V) varies in the order: benzene < toluene < xylene. In view of the commercial availability and high extraction efficiency, kerosene was chosen as the diluent in the present study.

Table 4.1. Effect of nature of diluent on the extraction of vanadium(V) (0.02 mol/dm^3). [HCl] = 5.0 mol/ dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Diluent	Dielectric constant (ε)	D
Kerosene	2.00	3.56
Cyclohexane	2.02	3.17
Xylene	2.24	1.75
Toluene	2.26	1.60
Benzene	2.28	1.51
Chloroform	4.90	0.01

Loading Capacity

Aliquots of 10 cm^3 of 1.47 mol/dm^3 TBP in kerosene were repeatedly extracted at 303 ± 1 K for 10 min with equal volumes of the aqueous phase containing 0.02 mol/dm^3 vanadium(V) in 5.0 mol/dm^3 hydrochloric acid. The aqueous phases were analysed for vanadium(V) after each stage of extraction and the cumulative vanadium(V) content transferred into the extractant phase was calculated. The plot of cumulative vanadium(V) in the organic phase per 100 g of TBP versus the number of stages of contact is presented in Fig. 4.6. It is clear that the loading capacity of TBP in kerosene for the extraction of vanadium from hydrochloric acid solutions is 1.0 g of vanadium(V) per 100 g of TBP.

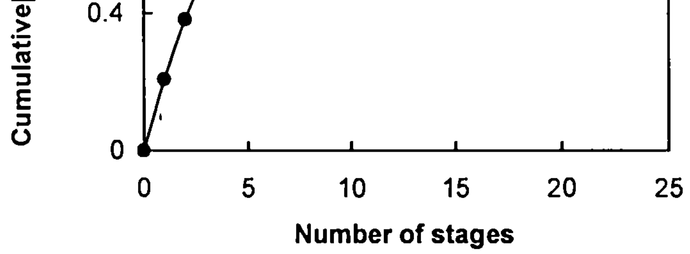


Figure 4.6. Loading capacity of TBP by vanadium(V). [HCl] = 5.0 mol/dm^3, [TBP] = 1.47 mol/dm^3.

Extraction isotherm

The extraction isotherm for a typical feed solution containing 1.1 g/dm^3 of vanadium(V) and 5.0 mol/dm^3 hydrochloric acid using 1.47 mol/dm^3 TBP in kerosene as an extractant was generated and the results are shown in Fig. 4.7. The McCabe–Thiele plot for a feed solution containing 1.1 g/dm^3 of vanadium(V) showed that almost quantitative extraction of vanadium(V) is possible in three counter-current stages at an A : O (aq : org) ratio of 1 : 1.

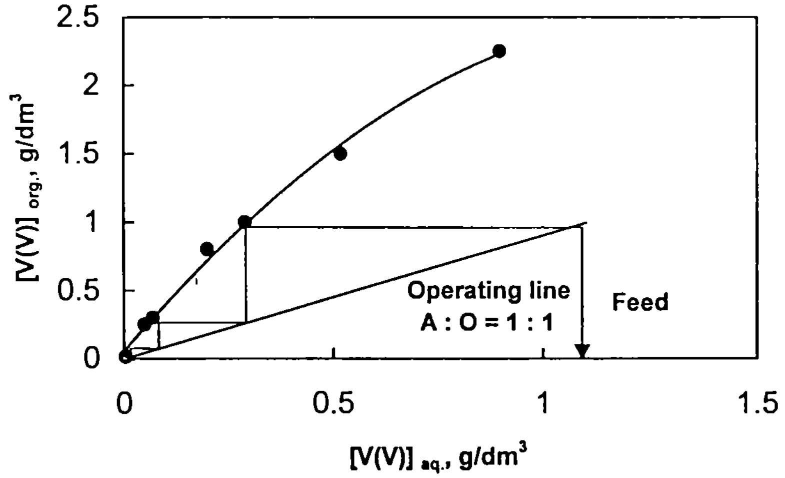


Figure 4.7. McCabe-Thiele plot for vanadium(V) extraction. [V(V)] = 1.1 g/dm^3, [HCl] = 5.0 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Comparison of extraction and stripping behaviour of vanadium(V) with other associated metal ions

It is clear from Fig. 4.1 that iron(III) is co-extracted with vanadium(V). On the other hand, magnesium(II) (0.03 mol/dm^3), aluminium(III) (0.02 mol/dm^3), titanium(IV) (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3) and manganese(II) (0.03 mol/dm^3) were not extracted under the present experimental conditions. To develop a selective separation method for the recovery of vanadium(V) from the loaded organic phase, the stripping behaviour of vanadium(V) and iron(III) from the loaded organic phase was examined as a function of hydrochloric acid concentration and the results are shown in Fig. 4.8. The results show that vanadium(V) can be selectively recovered from the loaded organic phase using 4.0 mol/dm^3 hydrochloric acid. On the other hand, the stripping of iron(III) was found to be negligible under this condition. Thus vanadium(V) can be selectively separated from the loaded organic phase containing vanadium(V) and iron(III) using 4.0 mol/dm^3 hydrochloric acid as a stripping agent in four stages. Subsequently, iron(III) can be recovered from the organic phase using deionized water of pH = 2.

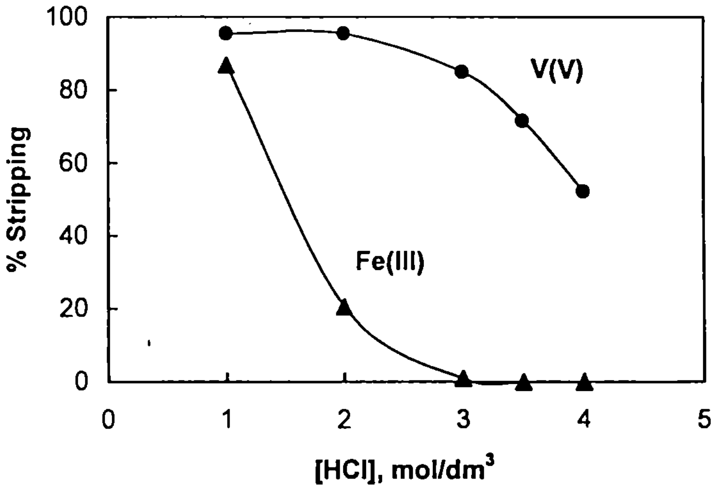


Figure 4.8. Stripping behaviour of vanadium(V) (0.02 mol/dm^3) and iron(III) (0.01 mol/dm^3) from loaded TBP phase (1.47 mol/dm^3 in kerosene) using hydrochloric acid.

Stripping isotherm

The McCabe–Thiele plot (Fig. 4.9) for a loaded organic phase containing 1.1 g/dm^3 vanadium(V) showed that quantitative stripping of vanadium(V) is possible in four counter-current stages using 4.0 mol/dm^3 hydrochloric acid as the stripping agent (O : A = 2 : 3).

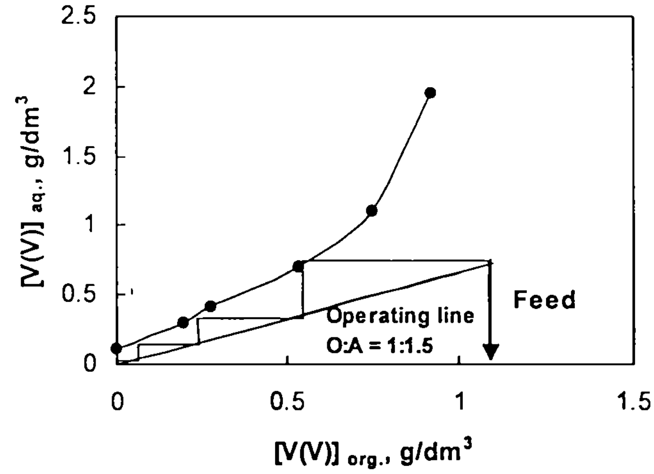


Figure 4.9. McCabe-Thiele plot for vanadium(V) stripping. $[V(V)]_{org}$ = 1.1 g/dm^3, [HCl] = 4.0 mol/dm^3.

Separation of vanadium(V) from simulated waste chloride liquors

Based on the above results, a simulated waste chloride liquor consisting of magnesium(II) (0:03 mol/dm^3), aluminium(III) (0.02 mol/dm^3), titanium(IV) (0.02 mol/dm^3), vanadium(V) (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.03 mol/dm^3) and iron(III) (0.01 mol/dm^3), similar to the raffinate stream of the solvent extraction process-1 (after the removal of iron(III) as shown in chapter 3) in 5.0 mol/dm^3 hydrochloric acid was prepared and subjected to a batch-type counter-current extraction process using 1.47 mol/dm^3 TBP in kerosene as an extractant. The results show that vanadium(V) and iron(III) are co-extracted into the organic phase whereas other metal ions remain unextracted in the raffinate stream. Vanadium(V) was then selectively stripped from the loaded TBP phase in four stages of counter-current stripping using 4.0 mol/dm^3 hydrochloric acid as a stripping agent (O : A = 2 : 3). Subsequently, iron(III) was recovered from the organic phase using deionized water of pH = 2 in a single stage (O : A = 1 : 1). The schematic diagram of the process and the typical results are shown in Fig. 4.10 and Table 4.2, respectively. These results show that vanadium(V) can be selectively recovered from waste chloride liquors containing multivalent metal chlorides using TBP in kerosene as an extractant.

Table 4.2. Extraction and separation of vanadium(V) from simulated waste chloride liquor using 1.47 mol/dm^3 TBP in kerosene. Extraction = 4 stages; O : A = 1 : 1, Stripping agent-1 for vanadium recovery = 4.0 mol/dm^3 HCl; A : O = 2 : 3, Stripping agent-2 for iron recovery = 0.01 mol/dm^3 HCl; A : O = 1 : 1.

Metal ion	Feed (mol/dm^3)	Raffinate (mol/dm^3)	Strip liquor-I (mol/dm^3)	Strip liquor-II (mol/dm^3)
V(V)	0.022	N.D.	0.0146	N.D.
Fe(III)	0.011	N.D.	N.D.	0.011
Mg(II)	0.028	0.028	N.D.	N.D.
Al(III)	0.021	0.021	N.D.	N.D.
Ti(IV)	0.020	0.020	N.D.	N.D.
Cr(III)	0.010	0.010	N.D.	N.D.
Mn(II)	0.030	0.030	N.D.	N.D.
HCl	5.00	4.10	4.06	0.55

N.D. = not detectable

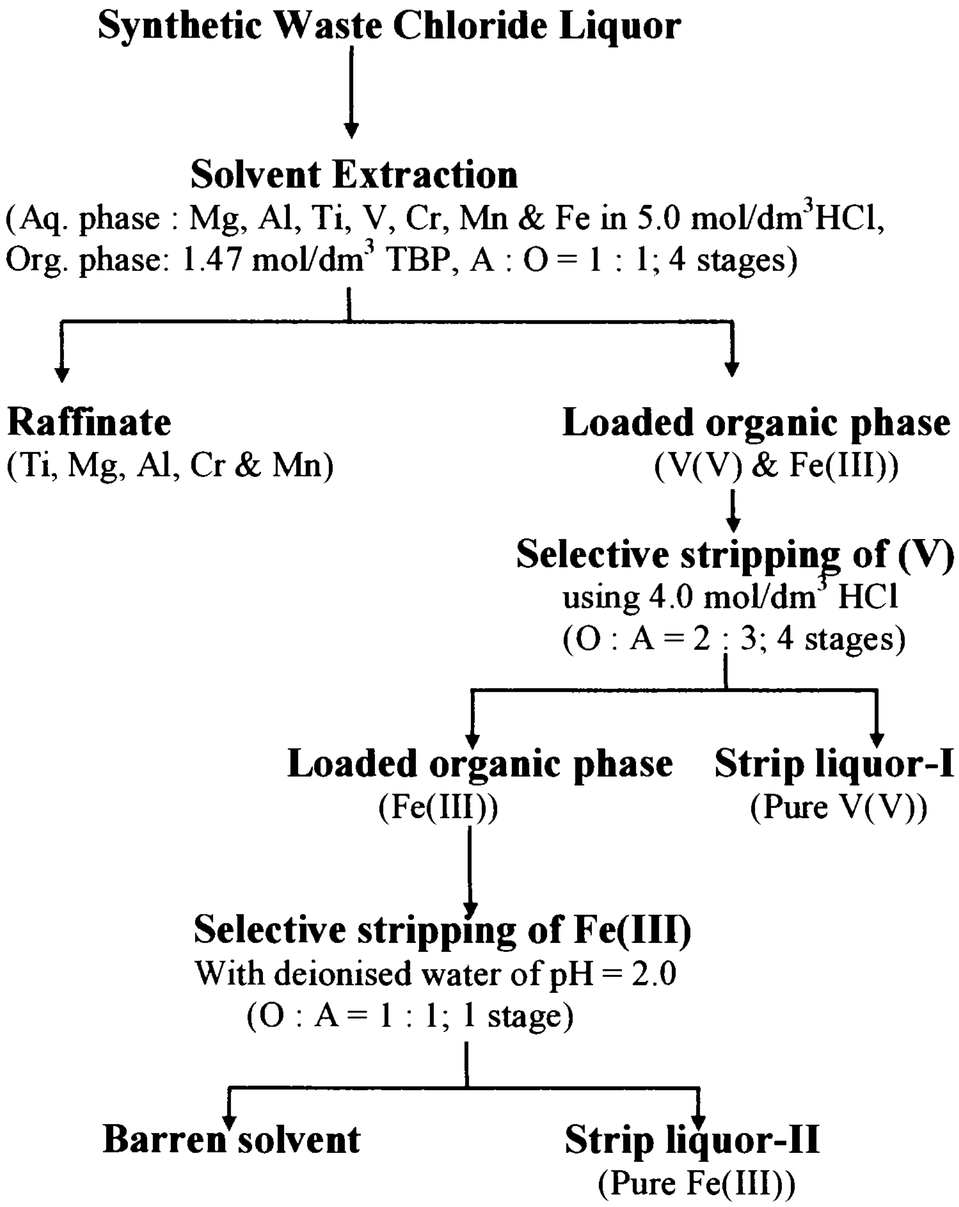


***Figure 4.10.* Separation Scheme for the Recovery of Vanadium from Simulated Waste Chloride Liquor.**

Chapter 5

Selective Separation of Titanium Chloride and its Conversion to TiO_2 Powders

Solvent extraction of tetravalent titanium has been extensively investigated using commercially available acidic organophosphorus extractants such as DEHPA, EHEHPA and BTMPPA from acidic chloride solutions (Biswas and Begum 1998a; Reddy and Saji 2002; Saji et al. 2000; Saji and Reddy 2003). The major disadvantage with these reagents is the relatively slow kinetics of extraction (60-120 min). This has been attributed to the slow rate at which the $(-Ti-O-)_n$ polymeric chains are broken down prior to being extracted as simple ions (Biswas and Begum 1998a). Hence, longer residence time would be necessary to operate these systems on a commercial scale for the separation of titanium from leach liquors. However, better selectivity can be achieved by employing acidic organophosphorus extractants between titanium and other associated multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry. On the other hand, neutral organophosphorus extractants such as TRPO exhibit rapid extraction kinetics (couple of min) but poor selectivity for the extraction of titanium(IV) from the waste chloride liquors of titanium minerals processing industry (Remya and Reddy 2004, Duyvesteyn et al. 2002). Although preliminary studies on the extraction of titanium(IV) from hydrochloric acid with TBP are known (Narita et al. 1983), systematic efforts have not been made to employ TBP for the extraction and separation of titanium(IV) either from the leach liquors of titanium minerals processing industry or from titania waste chloride liquors. Hence, in the present work, TBP has been chosen as an extractant for the separation of titanium(IV) from the waste chloride liquors of titanium minerals processing industry. In the present study efforts have also been made to recover titanium as phase-pure titania powders by adopting a low temperature hydrothermal synthesis route.

5.1 Experimental

The preparation of stock solutions of metal ions, apparatus used and solvent extraction and analytical procedures followed in this work are the same as described in chapter 3. Preliminary experiments showed that the extraction equilibrium was attained within couple of min.

Hydrothermal synthesis procedure

The hydrothermal synthesis of TiO_2 powders was performed in a pressure reactor with monel alloy as the material of construction and with a teflon liner (600 cm^3). The autoclaving temperatures were varied between 413 to 453 K (under autogeneous pressure corresponding to its temperature) with constant stirring (200 r.p.m.). The precursor amorphous titania powder was prepared by the following procedure: The amorphous titania was prepared from the $TiCl_4$ loaded organic phase (2.5 mol/dm^3 TBP in kerosene containing

0.2 mol/dm^3 $TiCl_4$) obtained from solvent extraction process by precipitation-stripping by the addition of sodium hydroxide (2.0 mol/dm^3) with constant stirring. The white amorphous precipitate was then separated from the organic phase, washed with deionised water and acetone, respectively. The amorphous titania precipitate was then dispersed in deionised water (100 cm^3), adjusted the pH of the suspension to the desired value (4-7) and autoclaved for varying lengths of time (60-180 min) and temperatures (413-453 K). After the completion of the autoclaving treatment, the powders were filtered, washed with water and acetone, respectively, dried at 353 K and then stored in a desiccator. The powders were characterized by X-ray diffraction analysis (XRD), thermogravimetry (TG), differential thermal analysis (DTA) and FT-IR. Scherrer's equation ($D = 0.9\ \lambda/\beta\ \cos\theta$, where D is the crystallite size, λ is the wavelength of X-ray used, β and θ are half width of XRD diffraction lines and half diffraction angle 2θ, respectively) was applied to determine the crystallite size of the anatase TiO_2 to find out the effects of various preparation parameters on the crystal growth. The specific surface area of the powders was measured via nitrogen adsorption, using a surface area analyzer (Micromeritics, Gemini, USA). The average particle size, d_{BET} was calculated based on the BET specific surface area analysis. The morphological analysis was performed using scanning electron microscopy.

Photocatalytic activity

The photocatalytic activity of the synthesized anatase TiO_2 was assessed by photocatalytic degradation of methyl orange. The synthesized anatase TiO_2 (1.0 g/dm^3) was suspended in aqueous solution of methyl orange (250 cm^3

containing 50 $\times 10^{-6}$ mol/dm^3 methyl orange) and photoirradiated using 450W medium pressure mercury lamp under air oxygen at 303 ± 1.0 K with vigorous magnetic stirring. The samples were withdrawn at different time intervals and centrifuged at 6000 r.p.m. to remove the TiO_2 powders. The absorbance of the methyl orange was measured at 462 nm using a Shimadzu scanning spectrophotometer, UV-3101 PC UV-VIS-NIR. There was no loss of dye observed when the irradiation was carried out in the absence of TiO_2. On the other hand, some loss of dye occurred due to the adsorption of TiO_2 in the unirradiated blank solution.

5.2 Results and Discussion

Effect of hydrochloric acid concentration

The extraction of titanium(IV) (0.03 mol/dm^3) and other associated metal ions, viz., magnesium(II) (0.04 mol/dm^3), aluminium(III) (0.03 mol/dm^3), chromium(III) (0.01 mol/dm^3) and manganese(II) (0.03 mol/dm^3) present in the waste chloride liquors of titanium minerals processing industry was investigated as a function of hydrochloric acid concentration (4.0-10.0 mol/dm^3) using 1.47 mol/dm^3 TBP in kerosene as an extractant. The results are depicted in Fig. 5.1. The extraction of titanium(IV) was found to be negligible at hydrochloric acid concentrations below 6.0 mol/dm^3. On the other hand, the extraction efficiency increases with increasing acidity in the aqueous phase at hydrochloric acid concentrations above 6.0 mol/dm^3. The investigations also reveal that magnesium(II), aluminium(III), chromium(III) and manganese(II), present in the raffinate stream after the removal of iron(III) and vanadium(V) (as described in chapters 3 and 4, respectively) were not extracted under the present experimental conditions.

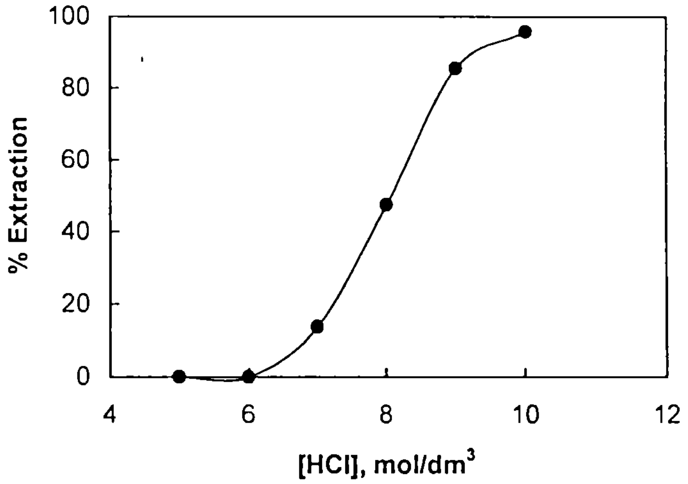


Figure 5.1. Effect of hydrochloric acid concentration on the extraction of titanium(IV) (0.03 mol/dm^3), magnesium(II) (0.04 mol/dm^3), aluminium(III) (0.03 mol/dm^3), chromium(III) (0.01 mol/dm^3) and manganese(II) (0.03 mol/dm^3) using 1.47 mol/dm^3 TBP in kerosene.

The effect of hydrogen ion concentration on the extraction of titanium(IV) was studied using 1.47 mol/dm^3 TBP in kerosene as an extractant at constant chloride (8.0 mol/dm^3) and metal (0.03 mol/dm^3) ion concentrations using HCl + $CaCl_2$ mixtures and the results are depicted in Fig. 5.2. The extraction of titanium(IV) was found to be independent of hydrogen ion concentration under the present experimental conditions. It is evident from the above results (Figs. 5.1 and 5.2) that the extraction efficiency of titanium(IV) was dependent only on the chloride ion concentration in the aqueous phase. It can be concluded from the slope of the plot Log D versus Log a_{HCl} that (Fig. 5.3) four chloride ions are involved in the extracted complex. The activity coefficients of the species H^+ and HCl in the aqueous phase were calculated using Bromley's formulation (Bromley 1973).

Effect of metal ion concentration

The effect of metal ion concentration (5.0×10^{-4} to 4.0×10^{-2} mol/dm^3) on the extraction efficiency of titanium(IV) was investigated from 8.0 mol/dm^3 HCl by employing 1.47 mol/dm^3 TBP in kerosene as an extractant. The Log–Log plot (Fig. 5.4) of equilibrium organic-phase titanium(IV) concentration against aqueous-phase titanium(IV) concentration is linear with a slope of unity, indicating that only mononuclear species are extracted into the organic phase.

Effect of extractant concentration

The effect of concentration of TBP (0.7-1.8 mol/dm^3) on the extraction of titanium(IV) was studied at constant metal ion (0.03 mo/dm^3) and hydrochloric acid (8.0 mol/dm^3) concentrations and the results are shown in Fig. 5.5. The extraction efficiency of titanium(IV) increases linearly with increasing TBP concentration in the organic phase. From the slope of the plot of Log D versus Log [TBP], it can be inferred that two molecules of TBP are involved in the extracted complex.

IR spectra of titanium(IV) - TBP complex

The IR spectrum of the extracted complex shows that the stretching frequency of P=O was shifted from 1276 cm^{-1} in TBP to 1265 cm^{-1} in $TiCl_4\cdot$

2TBP, indicating the interaction between the oxygen of the P=O group in TBP with the metal ion (Fig. 5.6).

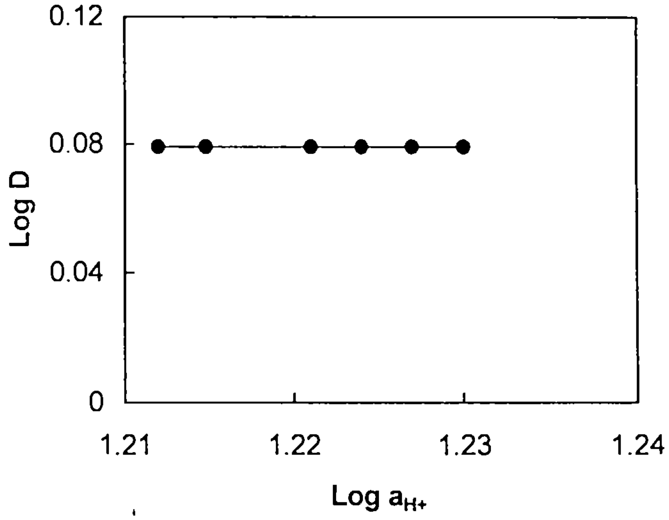


Figure 5.2. Effect of hydrogen ion concentration on the extraction of titanium(IV) (0.03 mol/dm^3) at constant chloride ion concentration. [Cl$^-$] = 8.0 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

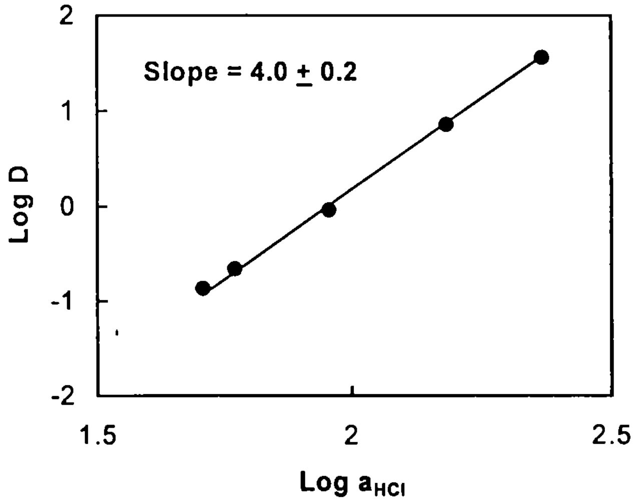


Figure 5.3. Effect of HCl concentration on the extraction of titanium(IV) (0.03 mol/dm^3), [TBP] = 1.47 mol/dm^3 in kerosene.

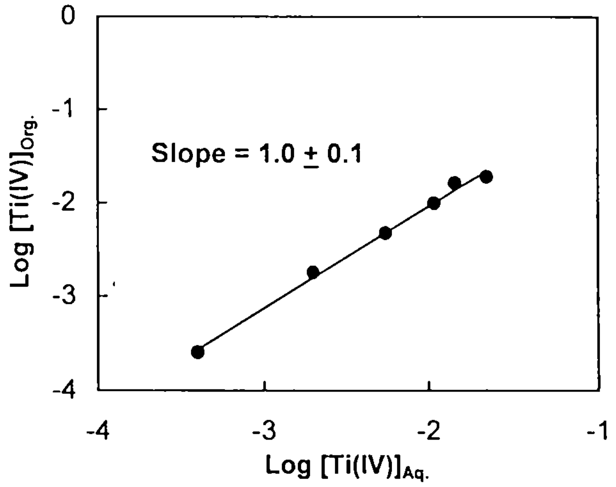


Figure 5.4. Effect of metal ion concentration on the extraction of titanium(IV). [HCl] = 8.0 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

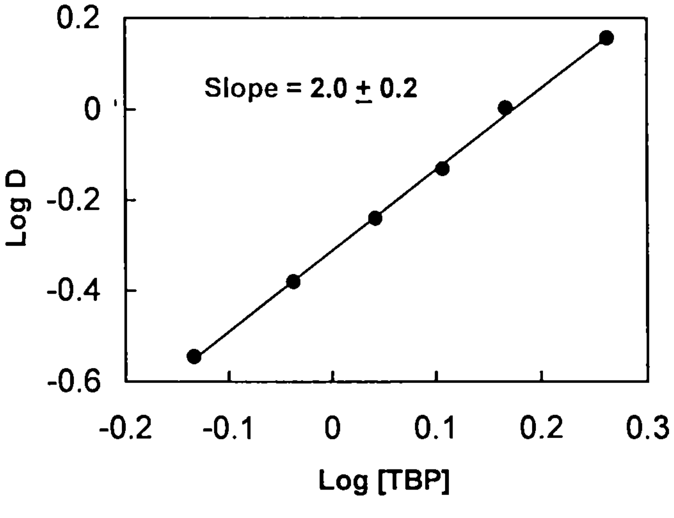


Figure 5.5. Effect of TBP concentration on the extraction of titanium(IV) (0.03 mol/dm^3), [HCl] = 8.0 mol/dm^3.

Extraction equilibrium

Based on the above results, the extraction equilibrium of titanium(IV) using TBP as an extractant can be represented as:

$$\mathrm{Ti}^{4+}_{aq} + 4\mathrm{Cl}^{-}_{aq} + 2\mathrm{TBP}_{org} \overset{\mathrm{Kex}}{\Leftrightarrow} \mathrm{TiCl}_4 \cdot 2\mathrm{TBP}_{org}$$

$$K_{ex} = \frac{[\mathrm{TiCl}_4 \cdot 2\mathrm{TBP}]_{org}}{[\mathrm{Ti}^{4+}]_{aq}[\mathrm{Cl}^-]^4_{aq}[\mathrm{TBP}]^2_{org}}$$

where K_{ex} is the equilibrium constant. Similar extraction equilibrium was proposed for the extraction of titanium(IV) from hydrochloric acid solutions with various alkyl phosphine oxides (Kakade and Shinde 1995; Saji et al. 1999; Allal et al. 1997). On the other hand, the involvement of two or three molecules of TBP in the extracted complex of titanium(IV) was also reported elsewhere at different HCl and TBP concentrations (Narita et al. 1983). The co-extraction of HCl along with the metal complex by TBP is also known (Narita et al. 1983; De et al. 1970; Marcus and Kertes 1967).

Effect of nature of the diluent on the extraction of titanium(IV)

The extraction efficiency of titanium(IV) from 8.0 mol/dm^3 hydrochloric acid solutions was studied using 1.47 mol/dm^3 TBP in various diluents. The results are shown in Table 5.1. The results demonstrate that diluents such as benzene, xylene, toluene and kerosene, which have low dielectric constants, show higher extraction efficiency for titanium(IV). On the other hand, diluents having higher dielectric constants, such as chloroform, exhibit poor extraction. This may be due to the strong interaction between TBP and chloroform through hydrogen bonding (Sekine and Hasegawa 1997). In view of the commercial availability and good extraction efficiency, kerosene was chosen as the diluent in the present study.

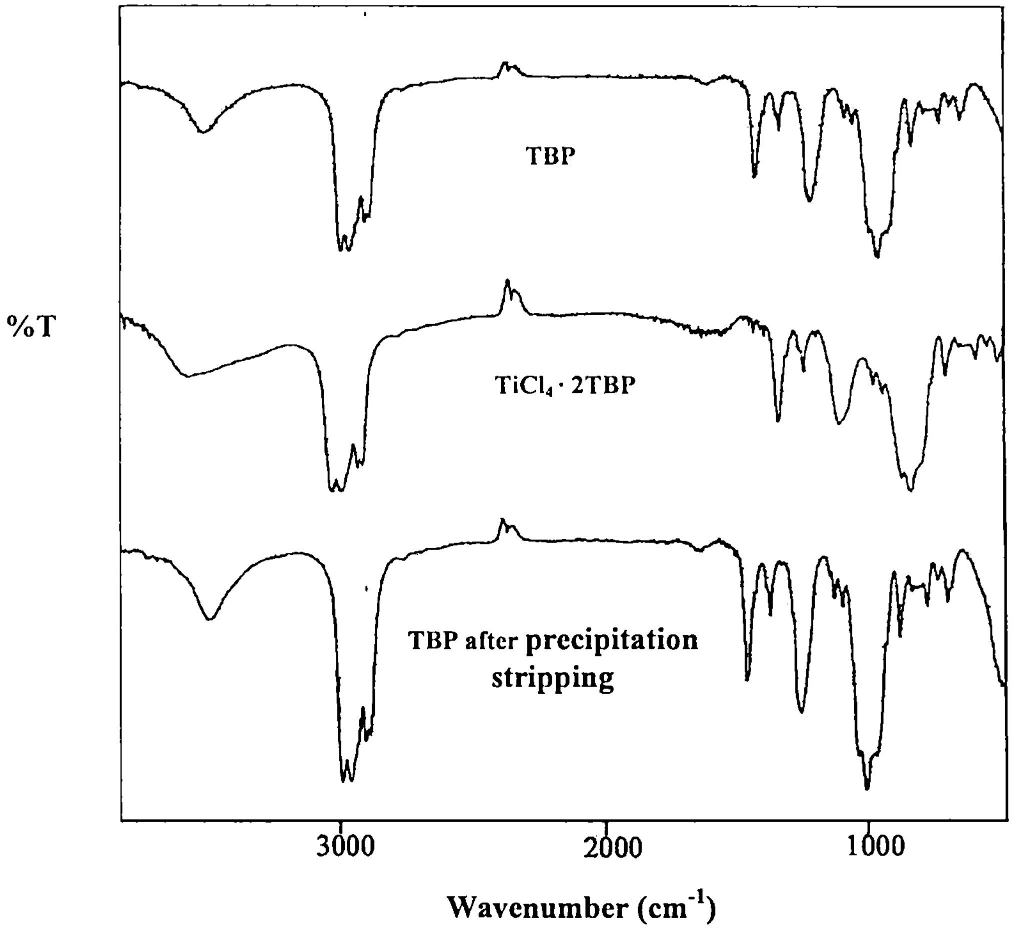


Figure 5.6. IR spectra of pure TBP, $TiCl_4 \cdot 2TBP$ complex and TBP after precipitation-stripping.

Loading Capacity

Aliquots of 10 cm^3 of 1.47 mol/dm^3 TBP in kerosene were repeatedly extracted at 303 ± 1 K for 10 min with equal volumes of the aqueous phase containing 1.44 g/dm^3 of titanium(IV) in 8.0 mol/dm^3 hydrochloric acid. The aqueous phases were analysed for titanium(IV) after each stage of extraction and the cumulative titanium(IV) content transferred into the extractant phase was calculated. The plot of cumulative titanium(IV) in the organic phase per 100 g of TBP versus the number of stages of contact is presented in Fig. 5.7. It shows that the loading capacity of TBP in kerosene for the extraction of titanium(IV) from hydrochloric acid solutions is 0.9 g of titanium(IV) per 100 g of TBP.

Table 5.1. Effect of nature of diluent on the extraction of titanium(IV) (0.03 mol/dm^3). [HCl] = 8.0 mol/ dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Diluent	Dielectric constant (ε)	D
Kerosene	2.00	1.23
Cyclohexane	2.02	1.40
Xylene	2.24	1.58
Toluene	2.26	1.58
Benzene	2.28	1.58
Chloroform	4.90	0.95

Extraction isotherm

The extraction isotherm for a typical feed solution containing 1.44 g/dm^3 of titanium(IV) and 8.0 mol/dm^3 hydrochloric acid using 1.47 mol/dm^3 TBP in kerosene as an extractant was generated and the results are depicted in Fig. 5.8. The McCabe–Thiele plot for a feed solution containing 1.44 g/dm^3 of titanium(IV) showed that almost quantitative extraction of titanium(IV) is possible in four counter-current stages using an A : O ratio of 1 : 2.

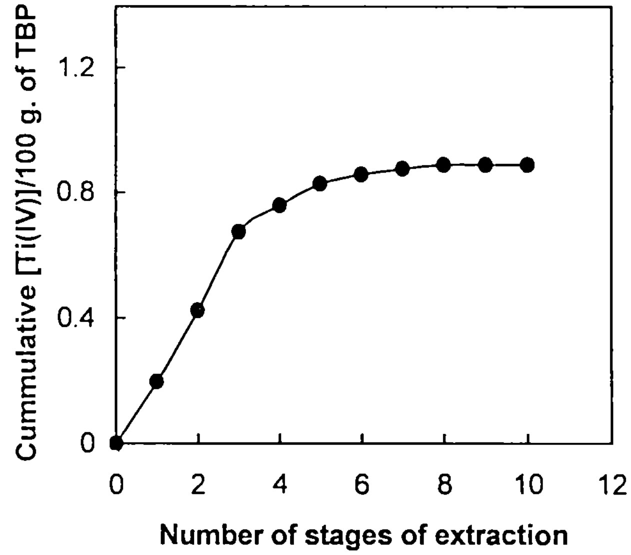


Figure 5.7. Loading capacity of TBP by titanium(IV). [HCl] = 8.0 mol/dm^3, [TBP] = 1.47 mol/dm^3.

Effect of hydrochloric acid concentration on the stripping behavior of titanium(IV)

The effect of HCl concentration on the stripping behaviour of titanium(IV) from a loaded organic solvent system consisting of 1.47 mol/dm^3 TBP in kerosene and 0.72 g/dm^3 titanium(IV) was investigated and the results are shown in Fig. 5.9. It is clear from the results that quantitative stripping of titanium(IV) is possible in a single stage with hydrochloric acid concentration in the range 1.0 to 5.0 mol/dm^3. Thus in the present study, 1.0 mol/dm^3 hydrochloric acid was chosen as a stripping agent for the recovery of titanium(IV) from the loaded organic phase.

The McCabe–Thiele plot (Fig. 5.10) for a loaded organic phase containing 0.72 g/dm^3 of titanium(IV) showed that quantitative stripping of titanium(IV) is possible in a single stage of counter-current stripping using 1.0 mol/dm^3 hydrochloric acid as the stripping agent (O : A = 1 : 1).

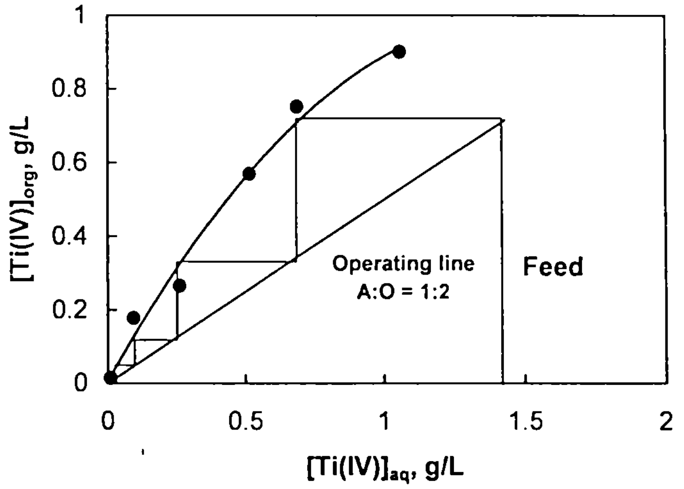


Figure 5.8. McCabe-Thiele plot for titanium(IV) extraction. [Ti(IV)] = 1.44 g/dm^3, [HCl] = 8.0 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Extraction and separation of titanium(IV) from simulated waste chloride liquors of titanium minerals processing industry

Based on the above results, a simulated waste chloride liquor consisting of magnesium(II) (0.04 mol/dm^3), aluminium(III) (0.03 mol/dm^3), titanium(IV) (0.03 mol/dm^3), chromium(III) (0.01 mol/dm^3) and manganese(II) (0.03 mol/dm^3) in 8.0 mol/dm^3 hydrochloric acid, similar to the raffinate stream of the solvent extraction process II (after the removal of vanadium(V)), was prepared and subjected to a batch-type counter-current extraction process using 1.47 mol/dm^3 TBP in kerosene as an extractant (A : O = 1 : 2; Number of stages = 4). Batch type counter-current extraction and stripping studies were performed at laboratory scale using separatory funnels of suitable volume at 303 ± 1 K. The loaded organic phase was then subjected to counter-current stripping by employing 1.0 mol/dm^3 hydrochloric acid as a stripping agent at an O : A phase ratio of 1 : 1 (Number of stripping stages = 1).

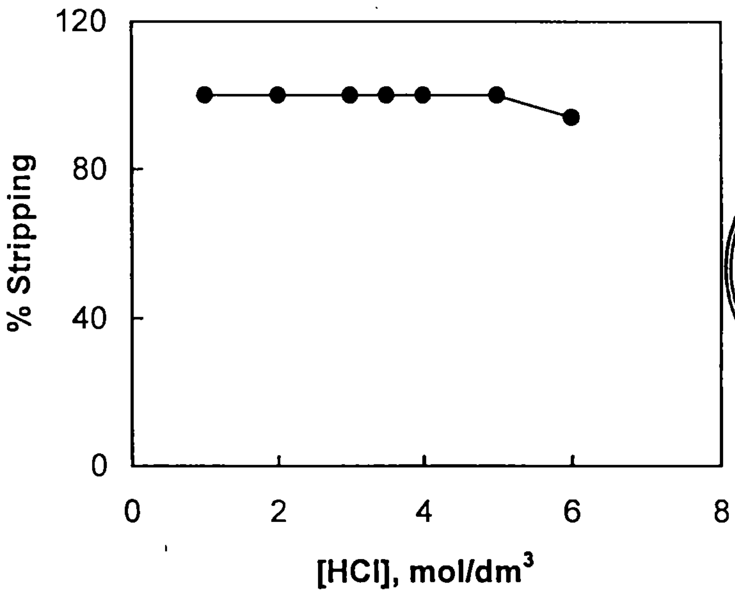


Figure 5.9. Stripping behaviour of titanium(IV) from the loaded TBP phase using hydrochloric acid. Strip feed = 1.47 mol/dm^3 TBP in kerosene containing 0.72 g/dm^3 titanium(IV).

Typical results of the process are given in Table 5.2. The above results demonstrate that titanium(IV) chloride can be selectively separated from the waste chloride liquors of titania manufacturing industry by employing TBP as an extractant.

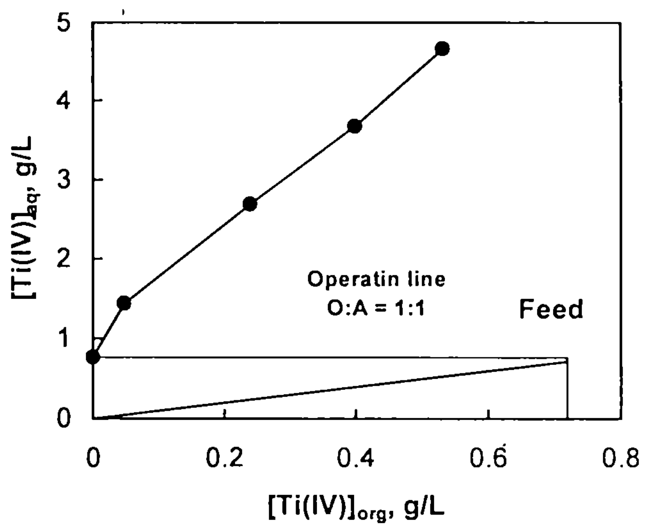


Figure 5.10. McCabe-Thiele plot for titanium(IV) stripping. Strip feed = 1.47 mol/dm^3 TBP in kerosene containing 0.72 g/dm^3 titanium(IV). Stripping agent = 1.0 mol/ dm^3 HCl.

Table 5.2. Extraction and separation of titanium(IV) from simulated waste chloride liquor using 1.47 mol/dm^3 TBP in kerosene. Extraction: Number of stages = 4; A : O = 1 : 2, Stripping: Number of stages = 1; Stripping agent = 1.0 mol/ dm^3 HCl; O : A = 1 : 1.

Metal ion	Feed (mol/dm^3)	Raffinate (mol/dm^3)	Strip liquor (mol/dm^3)
Mg(II)	0.036	0.036	N.D.
Al(III)	0.035	0.035	N.D.
Ti(IV)	0.028	N.D.	0.014
Cr(III)	0.014	0.014	N.D.
Mn(II)	0.031	0.031	N.D.
HCl	8.050	6.260	1.895

Hydrothermal synthesis of TiO_2 powders and characterization

The preparation of TiO_2 powders comprises the steps of:

- Precipitation of amorphous titania from the $TiCl_4$ loaded TBP phase by employing sodium hydroxide (2.0 mol/dm^3);
- Separation of amorphous titania from the TBP phase and washing with deionized water and acetone, respectively, to remove excess alkali, chloride ions and organic solvent impurities;
- Dispersion of amorphous titania powders in deionized water and adjustment of the pH of the reaction suspension to the desired value;
- Hydrothermal synthesis of titania powders by using the above precursor;
- Separation of the synthesized products by filtration or centrifugation, washing with deionized water and acetone, respectively, and drying at 353 K.

The schematic diagram of the process is shown in Fig. 5.11. The products were characterized by XRD and FT-IR. The morphological analysis was performed by SEM. The thermal studies were carried out by TG/DTA analysis. The specific surface area of the powder was measured using the three point BET method. Photocatalytic activity of the titania powders was also investigated.

Effect of pH on the hydrothermal synthesis

It is evident from the XRD patterns (Fig. 5.12c) that phase-pure anatase TiO_2 powders having crystallite size 15 nm (Table 5.3) was formed when the pH of the reaction suspension was 7.0 (at 453 K for a reaction time of 120

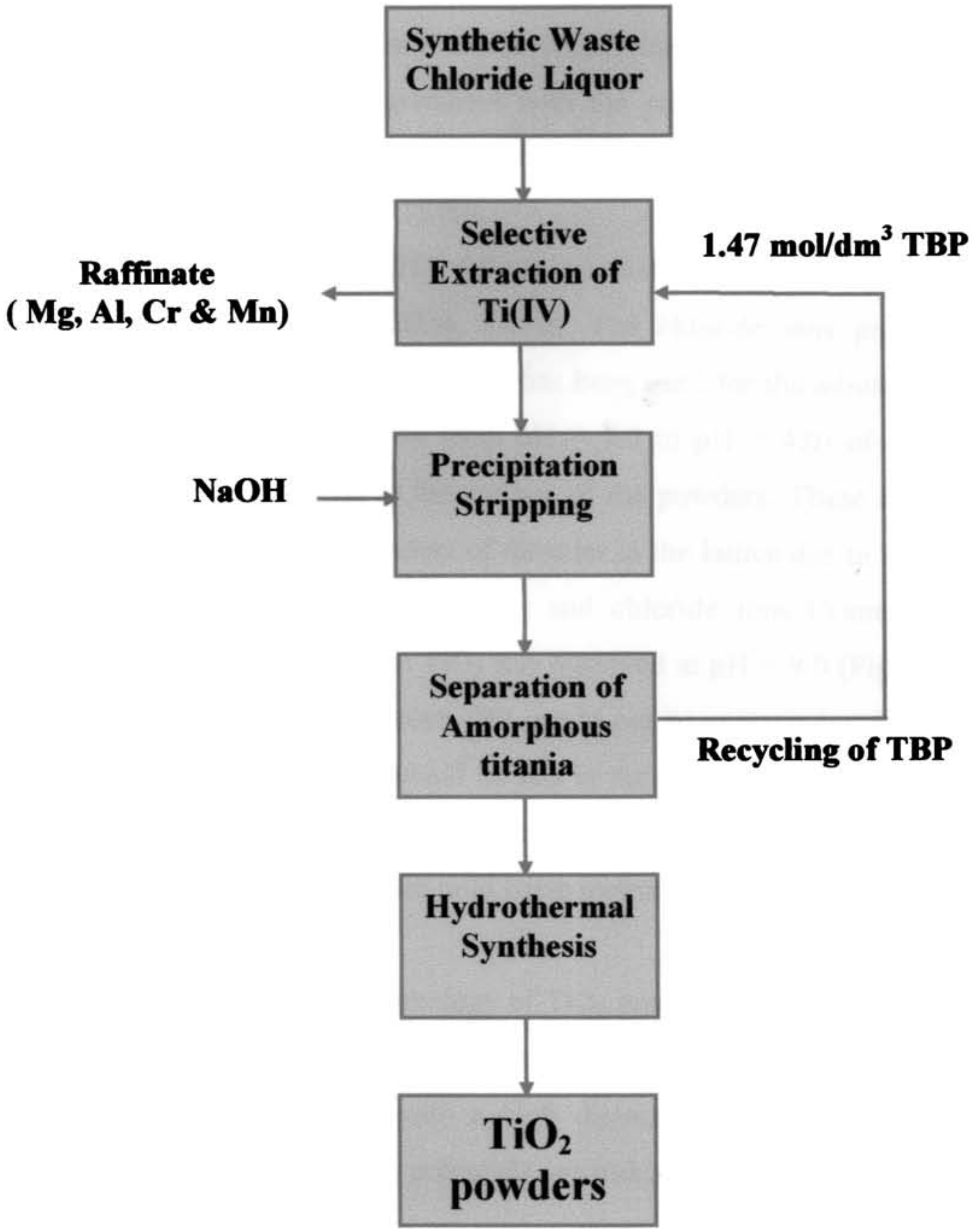


Figure 5.11. **Schematic representation of the process for the preparation of TiO_2 powders.**

min). Further, it is clear from the XRD patterns that neither rutile nor brookite phases are present. The results demonstrate that the presence of water in the reaction atmosphere catalyses the crystallization step for the formation of anatase. This is in good agreement with the previous results published for anatase, crystallized from amorphous titania using the hydrothermal technique (Yanagisawa and Ovenstone 1999).

On the other hand, at pH = 4.0 poor crystal growth with small crystallite size (5 nm) was observed (Fig. 5.12b). The chloride ions present in the amorphous powder at pH = 4.0 (HCl has been used for the adjustment of the pH of the reaction suspension from pH = 7.0 to pH = 4.0) of the reaction suspension may be bound to the surface of the powders. These chemisorbed species will cause certain amount of disorder in the lattice due to the differing charge and size between the oxygen and chloride ions (Yanagisawa and Ovenstone 1999). Amorphous TiO_2 was observed at pH = 9.0 (Fig. 5.12a). At higher pH values, the amorphous TiO_2 could not be separated well due to less protonation, and TiO_6 units would be still in the aggregate form via hydrogen bonding. This finding is consistent with the earlier reports that the formation of amorphous phase TiO_2 under mild basic hydrothermal conditions (Yin et al. 2001).

Fig.5.13 shows the morphology of TiO_2 powder synthesized at pH = 7.0 of the reaction suspension. The particles are found to be very fine and highly agglomerated. In a solvent with a high dielectric constant such as water, precipitates with high surface potentials are stable for relatively small particle sizes (Park et al. 1997).

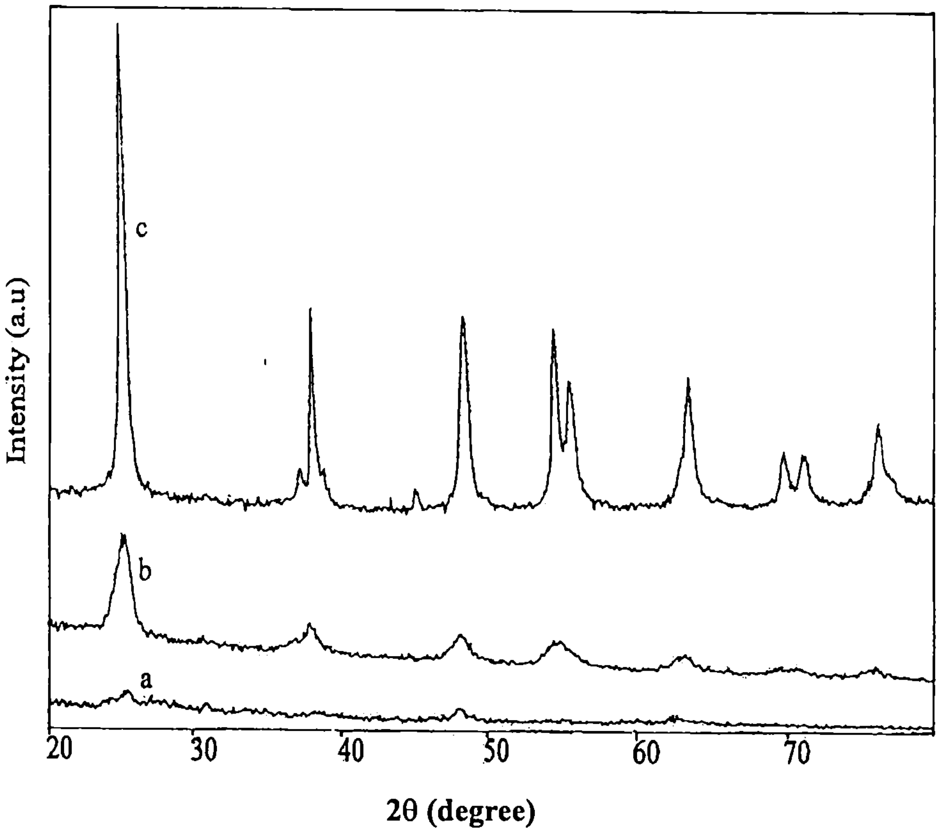


Figure 5.12. XRD patterns of TiO_2 powders synthesised at various pH values of the reaction suspension. Reaction temperature = 453 K; Reaction time = 120 min. a) pH = 9.0, b) pH = 4.0, c) pH = 7.0.

Effect of temperature on the hydrothermal synthesis

It is clear from Fig. 5.14 that the growth of the titania particles with anatase phase increases with increasing hydrothermal reaction temperature from 413 to 453 K (crystallite size increases from 6 to 15 nm). The changes in the crystallite size suggests that a shift in the growth mechanism from solid-state epitaxy to dissolution precipitation, since in this region the ionic product of the crystallization medium increases rapidly, allowing for greater solubility of the amorphous titania as well as faster transport kinetics. On the other hand, the specific surface area of the anatase powders decreases drastically with increase in the reaction temperature as shown in Table 5.3. Similar behaviour has also been reported elsewhere (Yanagisawa et al. 1997). Hence it could be concluded that crystallization was prompted by increasing the autoclaving temperature under the present experimental conditions. The remarkable decrease in surface area with an increase in reaction temperature from 413-453 K indicates that a large amount of amorphous content remained in the compacts at 413 K, as evidenced by the negligible increase in Vickers hardness with increase in reaction temperature.

Table 5.3. Effect of various hydrothermal reaction conditions on the surface area, particle size and crystallite size of the anatase powder.

Hydrothermal reaction conditions			Surface area (m^2/g)	Particle size (nm)	Crystallite size (nm)
pH	Temperature (K)	Time (min)			
4.0	453	120	291	5	5
7.0	453	120	85	18	15
9.0	453	120	-	-	-
7.0	413	120	247	6	6
7.0	433	120	167	9	9
7.0	453	60	88	17	13
7.0	453	180	84	18	15
7.0 (calcined)	453	120	40	38	19

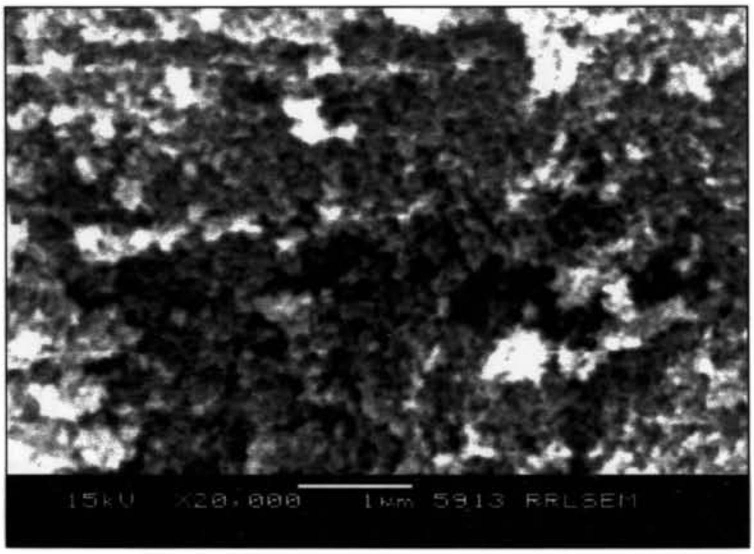


Figure 5.13. **SEM micrograph of anatase TiO_2 powder synthesised from a reaction suspension of pH = 7.0; Reaction temperature = 453 K; Reaction time = 120 min.**

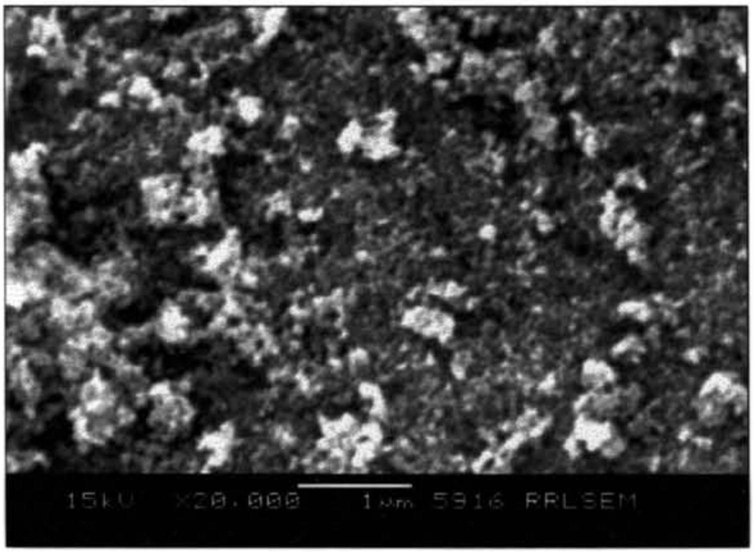


Figure 5.13c. **SEM micrograph of calcined (773 K) anatase TiO_2 powder. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0.**

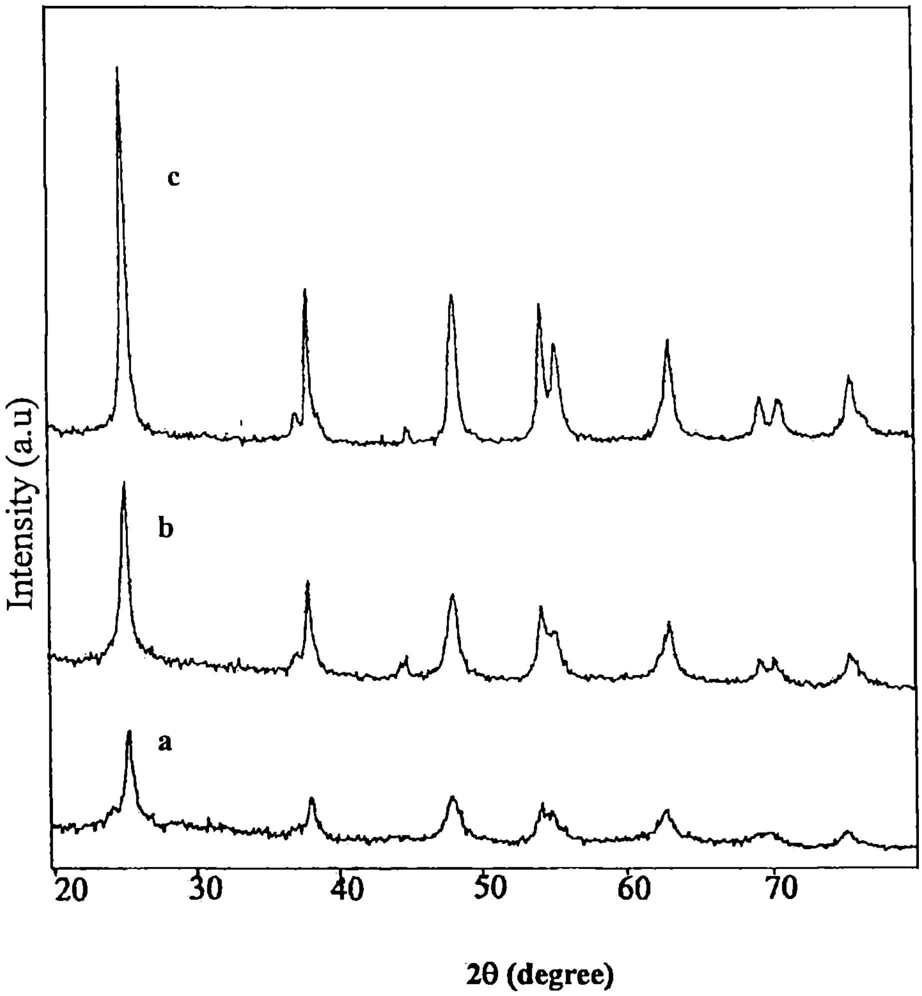


Figure 5.14. X-ray diffraction patterns of TiO_2 powders synthesised at various reaction temperatures. pH = 7.0; Reaction time = 120 min. a) 413 K, b) 433 K c) 453 K.

Effect of hydrothermal reaction time on the hydrothermal synthesis

It is evident from Fig.5.15 that a marginal increase in crystallite size occurs with increasing autoclaving time from 60 to 180 min. This is also consistent with the results obtained from the BET surface area analysis as can be seen from Table 5.3.

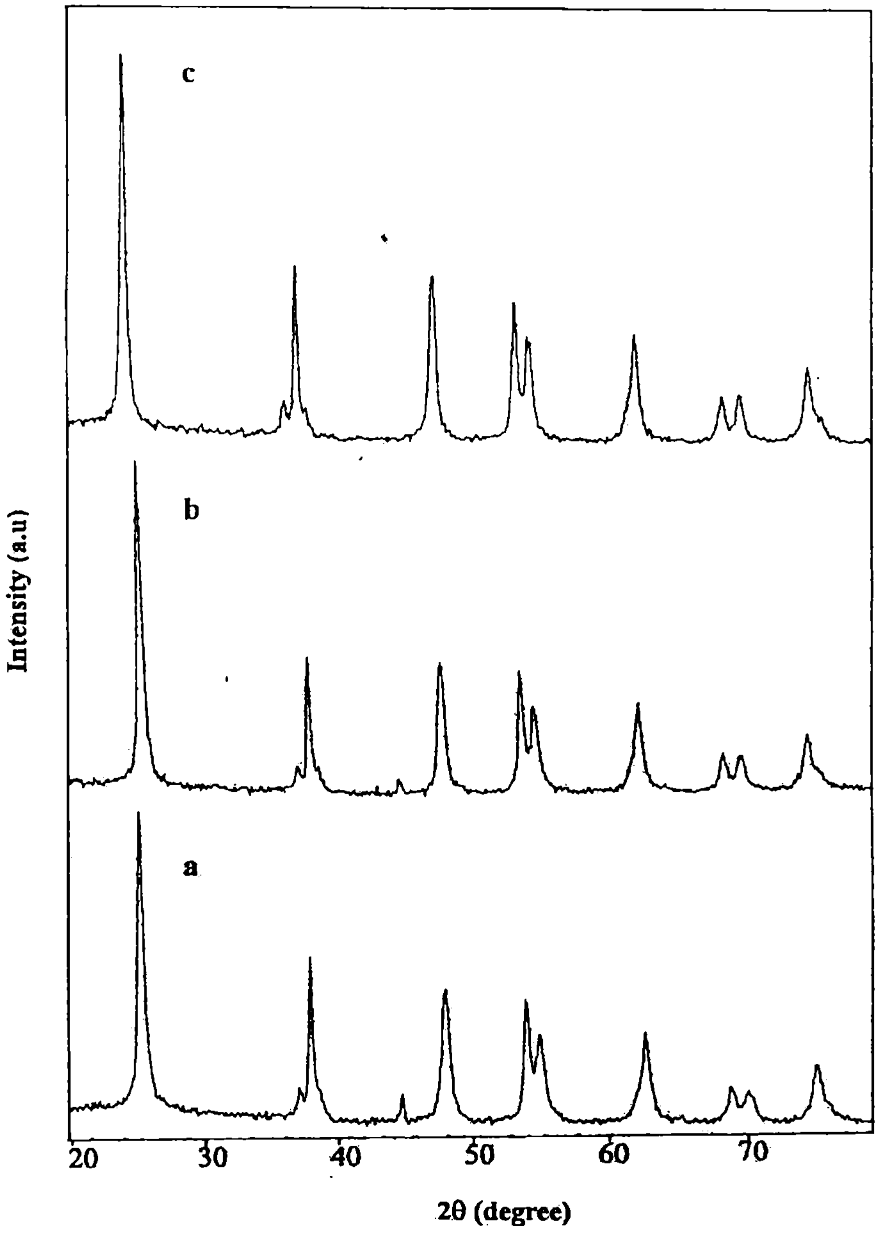


Figure 5.15. X-ray diffraction patterns of TiO_2 powders synthesised at various reaction times. pH = 7.0; Reaction temperature = 453 K by a) 60 min b) 120 min c) 180 min.

TG/DTA analysis of the synthesized TiO_2 powders

The peak at 553 K in the DTA curve (Fig. 5.16) indicates the removal of absorbed water (Lee and Zuo 2004). This is also consistent with the loss of weight (2.5%) as can be seen from the TG analysis data (Fig. 5.17). Further, it is also evident from the TG/DTA data that no phase transformation was observed for anatase phase TiO_2 in the temperature range from 313 to 1273 K.

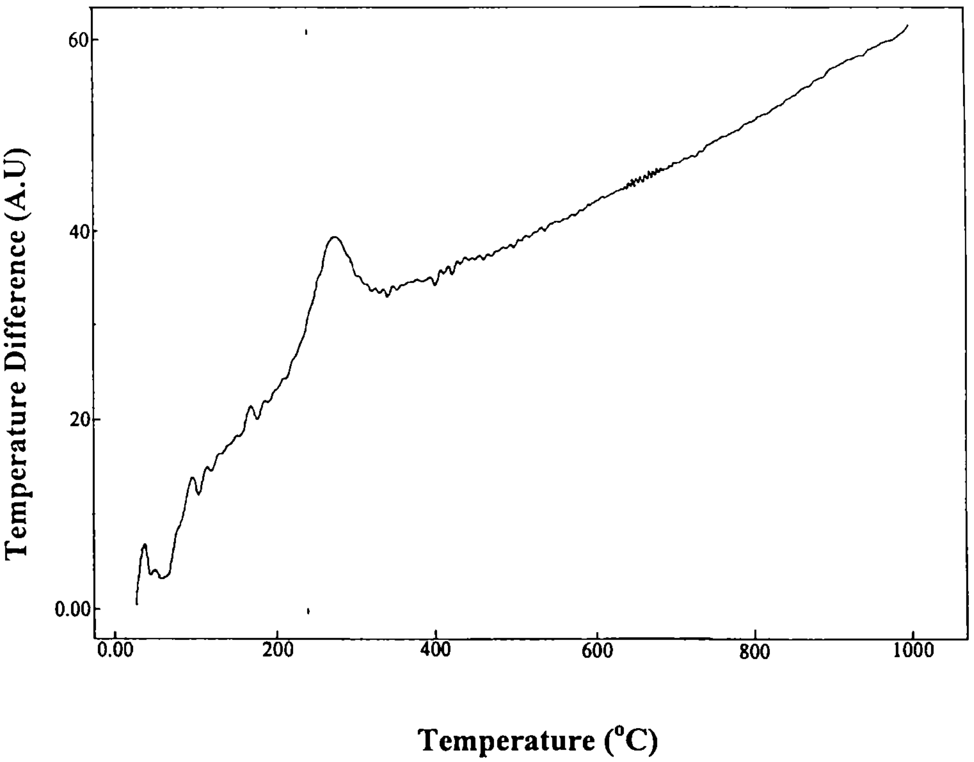


Figure. 5.16 Differential thermal analysis of TiO_2 powders. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0.

FT-IR spectrum of anatase TiO_2

The broad absorption peak at 3400 cm^{-1} and the peaks at 1627 cm^{-1} and 650 cm^{-1} present in the FT-IR spectrum of the synthesized anatase powder

(Fig. 5.18) corresponds to the absorbed molecular water present in the anatase powder. The absence of P=O stretching frequency of TBP (at 1276 cm^{-1}) clearly indicates that the synthesized powder is free from contamination by the extractant used for the preparation of the precursor.

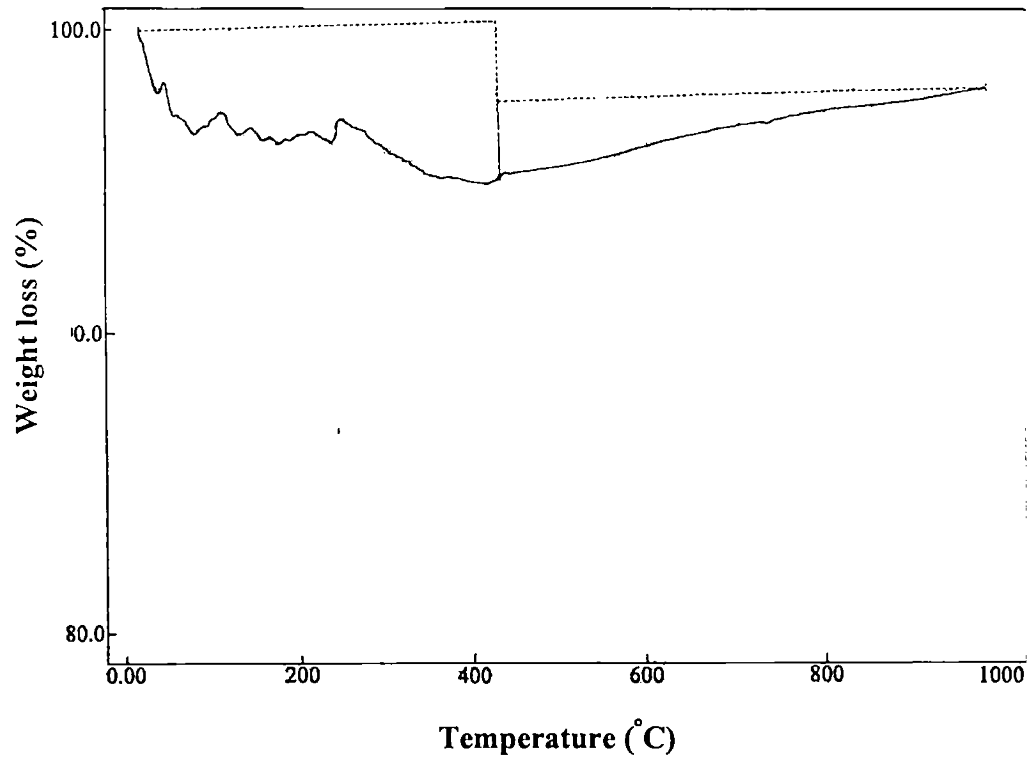


Figure. 5.17 Thermogravimetric analysis of TiO_2 powders. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0.

Mechanism of anatase crystallization

Anatase consists of TiO_6 octahedra, which share faces, and the phase transformation is accomplished by the rearrangement of these octahedra. For anatase, the rearrangement under hydrothermal conditions of these octahedra from the amorphous state proceeds by a solid-state reaction, where water molecules form bridges between surface OH groups of different octahedra which share only one common vertex, using the two lone pairs of electrons on oxygen. Due to the size of the water bridges, it is possible for two bridges to form between the two octahedra, thus linking them by triangular face. Having thus aligned the octahedra correctly, dehydration occurs, and the original two water molecules are lost, along with two further water molecules, leaving the two titanium ions linked by two further oxygen ion vertexes, thus sharing a face (anatase). Several investigators have proposed the similar mechanism for anatase cystallisation (Yanagisawa and Ovenstone 1999; Yin et al. 2001).

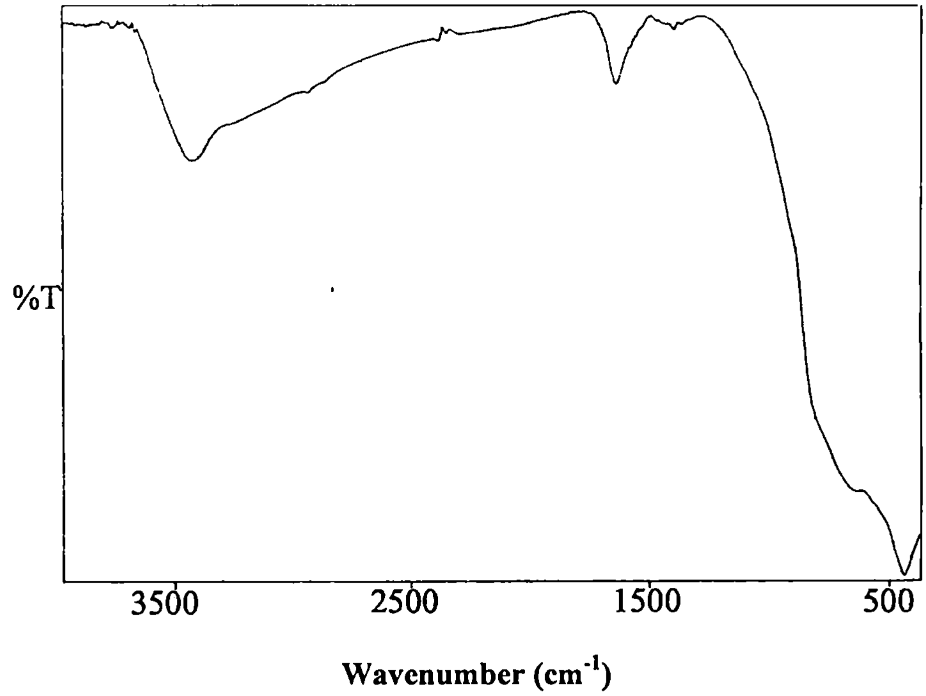


Figure. 5.18 IR spectrum of TiO_2 powders. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0.

Photocatalytic activity

The excellent photocatalytic activity of titania has been well documented (Fox and Dulay 1993) and is well known that it is the anatase polymorph rather than the brookite or rutile polymorph that has the highest photocatalytic activity. The most active commercially available photocatalyst (Degussa P25) has an anatase content of 75% and 25% of rutile content (Sudhadevi et al. 2003). The difficulty in producing an extremely active phase-pure anatase photocatalyst stems from the fact that rutile is the thermodynamically stable polymorph, and although anatase is kinetically stable, it is readily converted into rutile phase in the temperature range of 873-1273 K. It is therefore desirable to find a low-temperature route for the synthesis of anatase phase to avoid conversion to rutile. Further more, control of the physical properties of anatase itself is important in determining its photocatalytic activity. It is widely regarded that anatase powder with a high surface area and also with high degree of crystallinity, with a large crystallite size is desirable to enhance the photocatalytic activity, since such a powder will have relatively few disruptions in its electronic band structure. Hence, in the present study, an attempt has been made to test the photocatalytic activity of the synthesized phase-pure anatase titania by investigating the photocatalytic degradation of methyl orange. For comparison, studies also have been performed with commercially available photocatalysts, Degussa P25 (consists of 75% anatase and 25% rutile with a specific BET surface area of 50 m^2/g and particle size 30 nm) and Hombikat UV 100 (consists of 100% pure anatase with a specific BET surface area of 250 m^2/g and particle size of 5 nm).

Fig. 5.19 shows the change in the absorption intensity on irradiation of an aqueous solution of methyl orange (50.0×10^{-6} mol/dm^3) containing 1.0 g/dm^3 TiO_2 (hydrothermally synthesized anatase at 453 K for 120 min at pH = 7.0) in the presence of air oxygen using 450W medium pressure mercury lamp. Control experiments were carried out by employing unirradiated blank solution. It is evident from the results that the absorption intensity decreases with increasing irradiation time and nearly total decolourisation was observed within 180 min. On the other hand, total decolourisation of methyl orange was obtained within 30 min in the presence of Degussa P25 and within 60 min in the presence of Hombikat UV 100 (Fig. 5.20). The more time required for the decolourisation of methyl orange with the synthesized anatase TiO_2 may be due to the presence of absorbed water in titania powder, as is evident from the TG/DTA analysis data. To achieve the full photocatalytic potential of the synthesized sample, calcination of the powder may be required as documented in the literature (Kominami et al. 1995; Kominami et al. 1999).

Hence the synthesized anatase powder (at 453 K for 120 min at pH = 7.0) has been subjected to calcination at 773 K for 120 min with a view to improve its photocatalytic property. It is evident from the XRD pattern (Fig. 5.21) that the calcined anatase powder contains neither rutile nor brookite phases. Enhancement in the crystallite size (15 nm to19 nm) and decrease in the BET specific surface area (85 to 40 m^2/g) was noticed for the calcined anatase TiO_2 powder. The typical SEM micrograph of the calcined sample is shown in Fig. 5.13c. The particles are found to be very fine and highly agglomerated. The DTA analysis of the calcined sample indicates the absence of absorbed water molecules (Fig. 5.22).

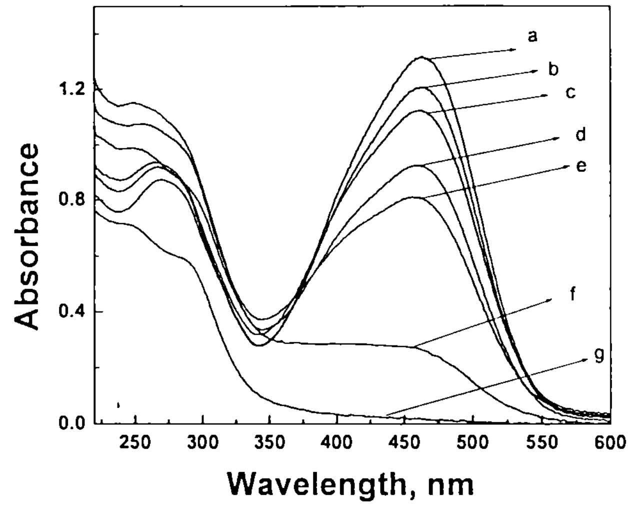


Figure. 5.19 Change in absorption spectrum on irradiation of aqueous suspension of the synthesised TiO_2 (1.0 g/dm^3) (Reaction temperature = 453 K; Time = 120 min; Suspension pH = 7.0) containing methyl orange (50.0 × 10^{-6} mol/dm^3). a) blank, b) 5 min, c) 10 min, d) 20 min, e) 30 min, f) 90 min, g) 180 min.

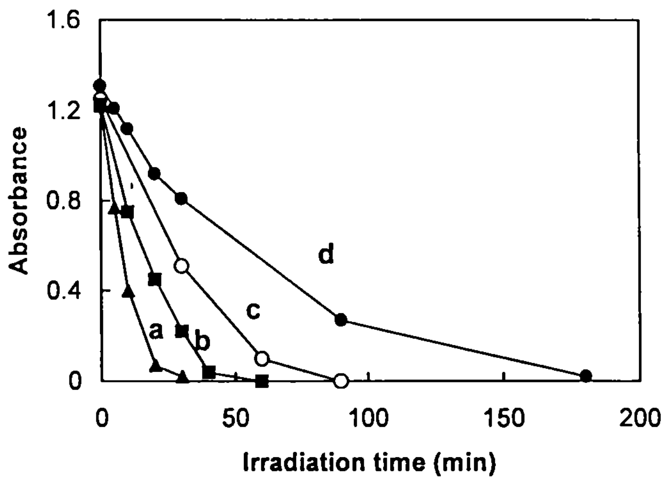


Figure. 5.20 Change in intensity at 462 nm versus irradiation time for the aqueous solution of methyl orange (50.0×10^{-6} mol/dm^3). a) in presence of Degussa P25 ((1.0 g/dm^3). b) in presence of Hombikat UV 100. c) in presence of calcined TiO_2 at 773 K. d) in the presence of TiO_2, (Reaction Temperature = 453 K; Time = 120 min; Suspension pH = 7.0).

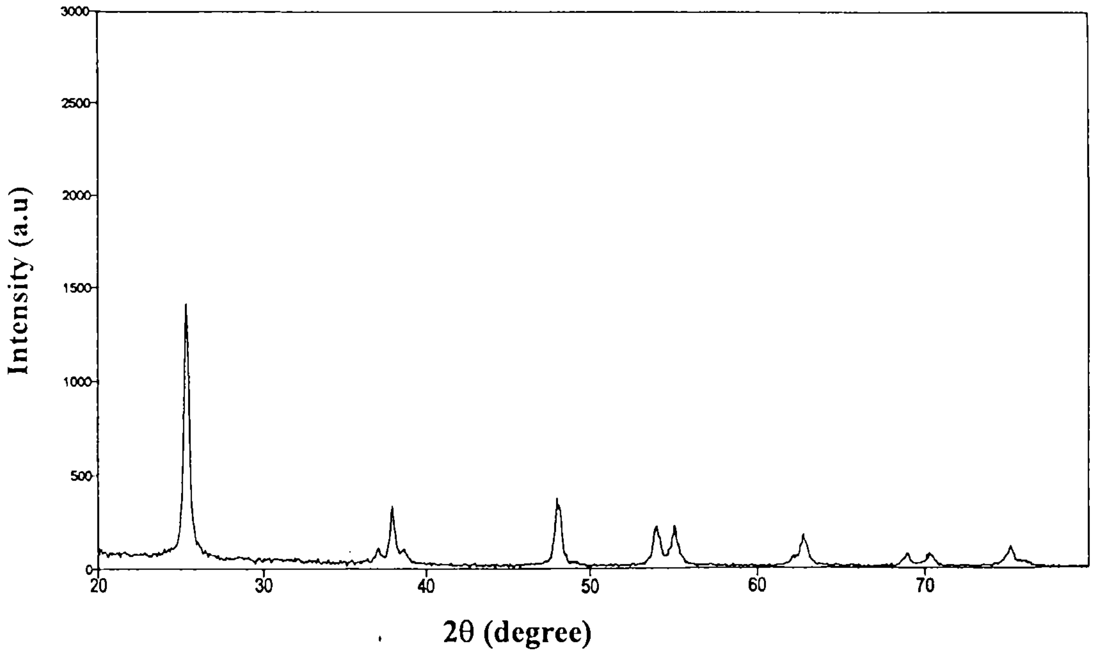


Figure 5.21. X-ray diffraction pattern of calcined (773 K) TiO_2 powder. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0

Figs. 5.20c and 5.23 show the change in the absorption intensity on irradiation of an aqueous solution of methyl orange (50.0×10^{-6} mol/dm^3) containing 1.0 g/dm^3 calcined TiO_2 anatase powder. The photocatalytic activity of the calcined sample was significantly improved as compared to the uncalcined sample.

The results demonstrate that phase-pure anatase TiO_2 nanocrystallites can be synthesized hydrothermally at relatively low temperatures (413-453 K) and reaction times (1-2 hr) as compared to the earlier reports (reaction time 12-48 hr; reaction temperature 473-623 K). Further, the results also reveal that photocatalytic anatase powders can be prepared without the addition of mineralizers and additives.

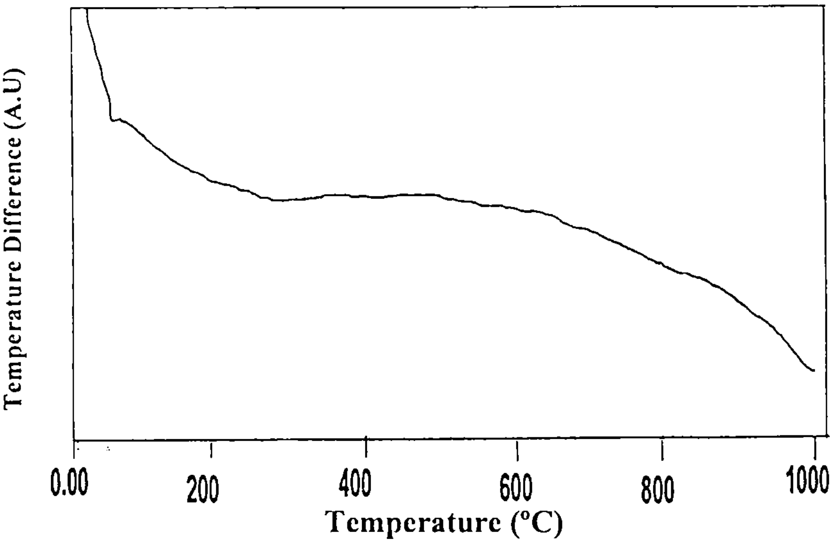


Figure. 5.22 Differential thermal analysis of calcined (773 K) TiO_2 powders. Reaction temperature = 453 K; Time = 120 min; Suspension pH = 7.0.

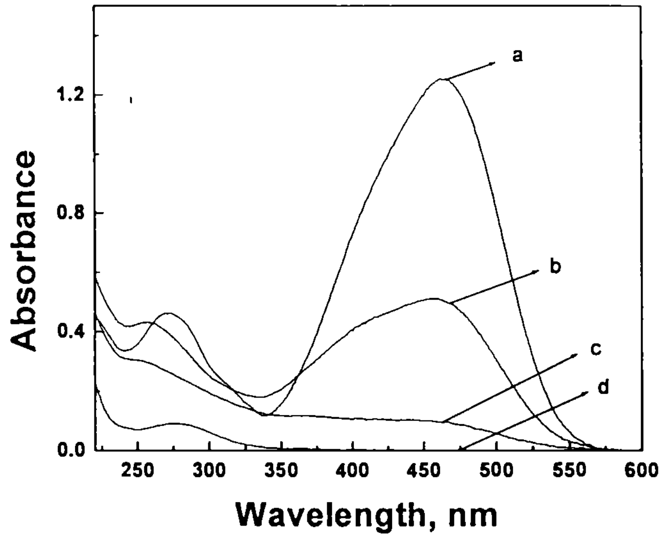


Figure. 5.23. Change in absorption spectrum on irradiation of aqueous suspension of calcined (773 K) TiO_2 ((1.0 g/dm^3) (Reaction Temperature = 453 K; Time = 120 min; Suspension pH = 7.0) containing methyl orange (50.0×10^{-6} mol/dm^3). a) blank, b) 30 min, c) 60 min, d) 90 min.

Recycling capacity of the solvent

The recycling capacity of the extractant was tested, first by extracting titanium(IV) using 1.47 mol/dm^3 TBP from 8.0 mol/dm^3 of hydrochloric acid solutions containing 0.03 mol/dm^3 titanium(IV) and then stripping with 2.0 mol/dm^3 sodium hydroxide in an org : aq. phase ratio of 1 : 2. The stripped organic phase was reused for extraction. The extraction efficiency was found to be the same as that of fresh extractant. Further, the recycling capacity was also confirmed by IR spectral data (Fig. 5.6). It is clear from the IR data that the P=O stretching frequency of TBP was not changed even after precipitation-stripping. The results revealed practically insignificant change in the extraction efficiency of the solvent even after five cycles of extraction and stripping processes.

Chapter 6

Conclusions

Recovery of iron(III), vanadium(V) and titanium(IV) from titania waste chloride liquors: A commercially available extractant namely, tributylphosphate has been experimentally found to be an ideal solvent for achieving the selective separation of iron(III), vanadium(V) and titanium(IV) as chlorides from the typical waste (spent acid) liquors of titanium minerals processing industry. This novel finding aims at achieving the selective separation by variation of concentration of HCl in the respective feed streams viz., 1.0 to 2.0 mol/dm^3 for iron(III), 4.0 to 6.0 mol/dm^3 for vanadium(V) and 8.0 to 10.0 mol/dm^3 for titanium(IV). The new findings reported in this thesis are depicted schematically in Fig. 6.1. The potential application of this novel process enabling the recycling and recovery of valuable components from waste liquors is schematically represented in Fig. 6.2. However, the practical utility of the new findings reported in this work requires further techno-economic optimization of the various process parameters.

- The extracted complexes have been elucidated as: $HFeCl_4 \cdot 2TBP$, $VO_2Cl \cdot 2HCl \cdot 2TBP$ and $TiCl_4 \cdot 2TBP$ for iron(III), vanadium(V) and titanium(IV), respectively.
- The loading capacity of TBP has been evaluated and found to be 5.9 g of iron(III), 1.0 g of vanadium(V) and 0.9 g of titanium(IV) per 100 g of TBP.
- The effect of nature of diluent on the extraction efficiency of iron(III), vanadium(V) and titanium(IV) has been investigated. The results demonstrate that diluents such as benzene, xylene, toluene and kerosene, which have low dielectric constants show higher extraction efficiency. On the other hand, chloroform which has a high dielectric constant exhibits poor extraction efficiency.
- The extraction and stripping isotherms have been investigated to find out the number of stages required for quantitative extraction and stripping of iron(III), vanadium(V) and titanium(IV) from the waste liquors of titanium minerals processing industry.
- High purity ferric chloride (>99.9%) has been recovered from titania waste chloride liquors, which may find potential applications in water purification as flocculating agent and also as a precursor for generating pure iron oxides for electronic and materials industry. HCl also can be recovered from the ferric chloride through known state-of-art techniques like pyrohydrolysis.
- Recovered high purity vanadium oxychloride for use in the preparation of various vanadium compounds.
- High purity titanium chloride has been recovered for applications in pigment and catalyst industries as precursor.

- One of the major attractions towards the developed process is the recycling of the spent solvent system, TBP.

Hydrothermal synthesis in combination with solvent extraction for the recovery of valuable products:

- Thermally stable hematite powders of plate-like morphology have been prepared hydrothermally at relatively low temperatures (413-453 K) and reaction times (30-120 min). Plate-like morphology powders may find applications as anticorrosive pigments.
- Phase-pure anatase nano-powders (6-20 nm) have been synthesized hydrothermally at relatively low temperatures (413-453 K) and reaction times (60-180 min).
- The synthesized anatase powders were found to be thermally stable in the range 313-1273 K.
- The crystal growth of TiO_2 to phase-pure anatase has been proposed to proceed via face-sharing process through dissolution-precipitation of the dissolved TiO_6 octahedra from the amorphous phase.
- The calcined anatase powders (773 K) were found to have enhanced photocatalytic activity than the uncalcined powders.

The materials described above have been characterized with the state-of-art techniques namely, XRD, FT-IR, TG/DTA, SEM, BET surface area and photocatalytic activity.

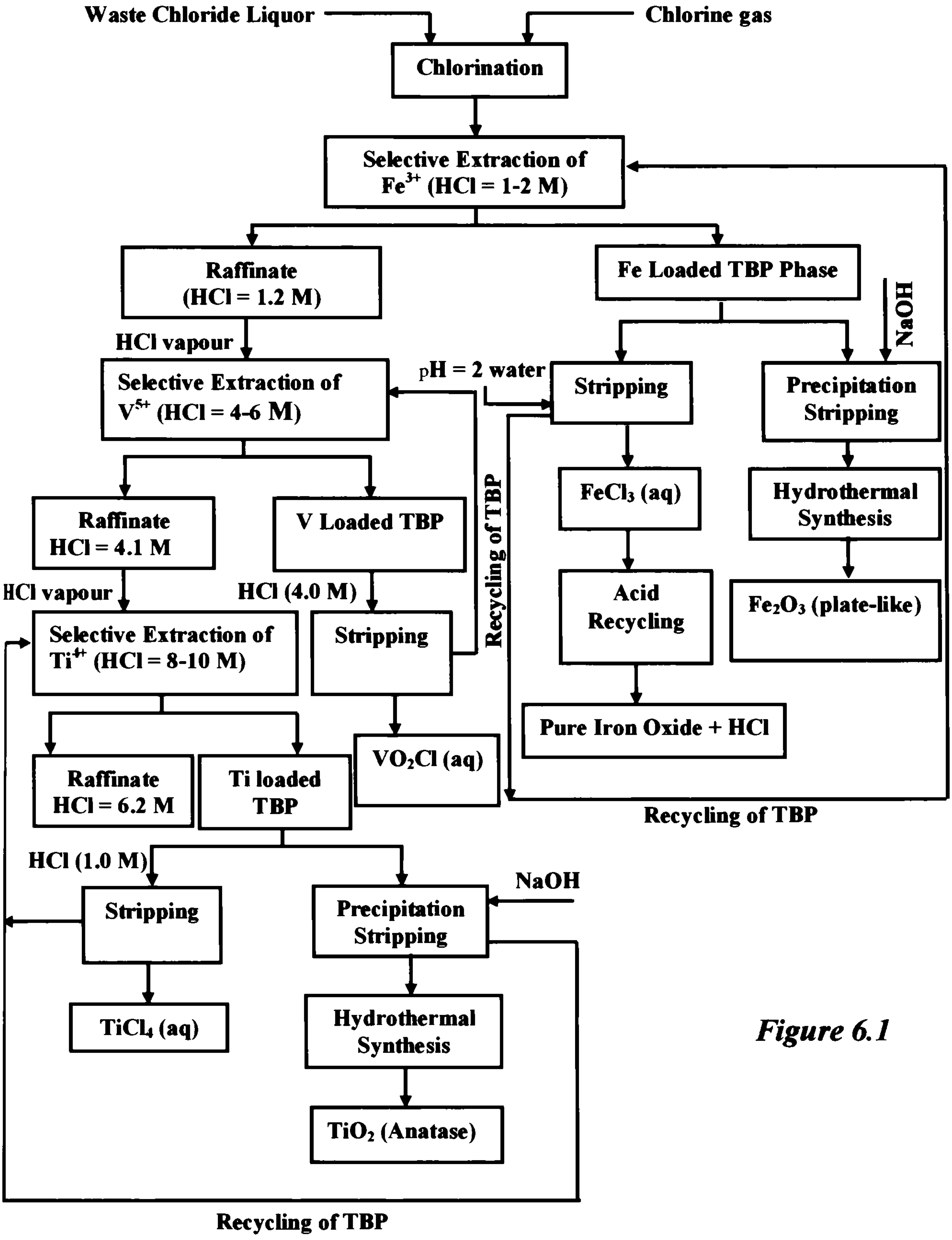

Waste Chloride Liquor
Chlorine gas
Chlorination
Selective Extraction of Fe^{3+} (HCl = 1-2 M)
Raffinate (HCl = 1.2 M)
Fe Loaded TBP Phase
NaOH
HCl vapour
Selective Extraction of V^{5+} (HCl = 4-6 M)
pH = 2 water
Stripping
Precipitation Stripping
Raffinate HCl = 4.1 M
V Loaded TBP
Recycling of TBP
$FeCl_3$ (aq)
Hydrothermal Synthesis
HCl vapour
HCl (4.0 M)
Selective Extraction of Ti^{4+} (HCl = 8-10 M)
Stripping
Acid Recycling
Fe_2O_3 (plate-like)
Pure Iron Oxide + HCl
Raffinate HCl = 6.2 M
Ti loaded TBP
VO_2Cl (aq)
Recycling of TBP
HCl (1.0 M)
NaOH
Stripping
Precipitation Stripping
$TiCl_4$ (aq)
Hydrothermal Synthesis
TiO_2 (Anatase)
Recycling of TBP

Figure 6.1

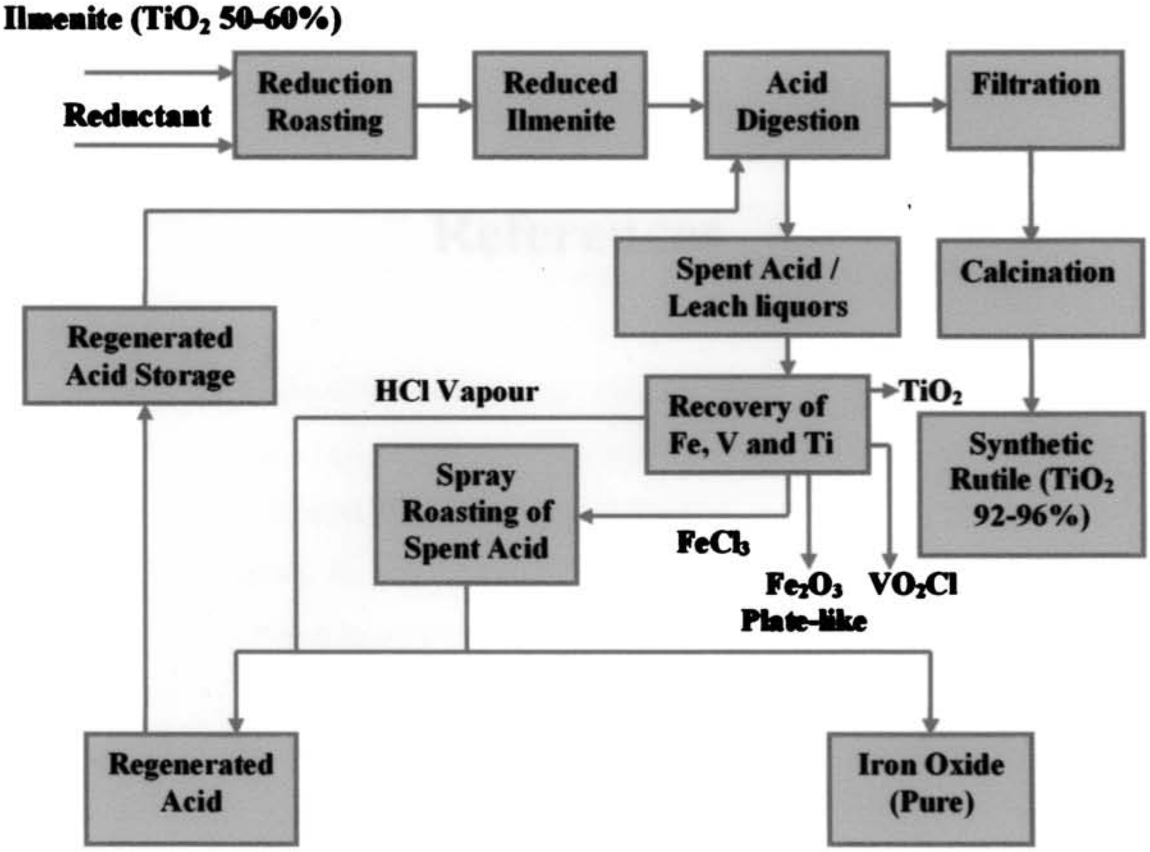


Figure 6.2. **Benelite process with recovery of iron, vanadium and titanium from leach liquor.**

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