Chapter 1

Introduction
During the 21st century, one of the overriding 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 nutshell, 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).
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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 FeCl₂ and FeCl₃. 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).

<table>
<thead>
<tr>
<th>Deposit</th>
<th>TiO₂</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>V₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chavara</td>
<td>60.00</td>
<td>9.23</td>
<td>25.60</td>
<td>0.15</td>
</tr>
<tr>
<td>Manavalakurichi</td>
<td>55.00</td>
<td>20.90</td>
<td>18.90</td>
<td>0.22</td>
</tr>
<tr>
<td>Nevra</td>
<td>53.25</td>
<td>23.56</td>
<td>22.5</td>
<td>0.41</td>
</tr>
<tr>
<td>Kalpakam</td>
<td>51.00</td>
<td>30.40</td>
<td>15.96</td>
<td>1.10</td>
</tr>
<tr>
<td>Chatrapur</td>
<td>50.20</td>
<td>34.10</td>
<td>12.76</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Figure 1.1. The minerals cycle.
Ilmenite (TiO$_2$ 50-60%)

Reduction Roasting → Reduced Ilmenite → Acid Digestion → Filtration

Spent Acid / Leach liquors → Calcination

Spray Roasting of Spent Acid → Synthetic Rutile (TiO$_2$ 92-96%)

Regenerated Acid Storage

Regenerated Acid → Iron Oxide (Impure)

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.
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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.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Range mol/dm^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>1.34 - 1.66</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>0.25 - 0.37</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>0.16 - 0.17</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>0.05 - 0.06</td>
</tr>
<tr>
<td>Al(III)</td>
<td>0.02 - 0.04</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>0.02 - 0.03</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>0.02 - 0.04</td>
</tr>
<tr>
<td>V(V)</td>
<td>0.01 - 0.02</td>
</tr>
<tr>
<td>HCl</td>
<td>0.82 - 1.09</td>
</tr>
</tbody>
</table>

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).

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:

\[
\text{TiO}^{2+}_{\text{aq}} + 2(\text{HX})_{2\text{org}} \Leftrightarrow \text{TiOX}_2 \cdot 2\text{HX}_{\text{org}} + 2\text{H}^+_{\text{aq}}
\]

where \((\text{HX})_2\) 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:

\[
\text{TiO}^{2+}_{\text{aq}} + (\text{HX})_{2\text{org}} \Leftrightarrow \text{TiOX}_2 \cdot 2\text{H}^+_{\text{aq}}
\]

The formation of \(\text{TiOX}_2\) 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 H₂SO₄ + H₂O₂.

**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$_2$X-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:

$$\text{Fe}^{3+}_{\text{aq}} + 3(\text{HX})_{2\text{org}} \Leftrightarrow \text{FeX}_3 \cdot 3\text{HX}_{\text{org}} + 3\text{H}^+_{\text{aq}}$$

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

$$\text{FeCl}^+_{2\text{aq}} + 3/2(\text{HX})_{2\text{org}} \Leftrightarrow \text{FeCl}_2\text{X} \cdot 2\text{HX}_{\text{org}} + \text{H}^+_{\text{aq}}$$

$$\text{FeCl}_3\text{aq} + \text{HCl}_{\text{aq}} + 3/2(\text{HX})_{2\text{org}} \Leftrightarrow \text{H}_2\text{XFeCl}_4 \cdot 2\text{HX}_{\text{org}}$$

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/dm³ 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](image)

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

\[
\text{TiO}^{2+} + 2(HX)_{2\text{org}} \rightleftharpoons \text{TiO(HX}_2)^{2+} + 2H^+_{\text{aq}}
\]

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 \(\log K_{\text{ex}} = 4.09 \pm 0.03\). 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.
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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:

\[ \text{VO}_2^{+} + (\text{HX})_{2\text{org}} \overset{K_{\text{ex}}}{\leftrightarrow} \text{VO}_2^{+} \cdot \text{HX}_{\text{org}} + \text{H}^+_\text{aq} \]

The equilibrium constant of the above extracted complex has been calculated and found to be \( K_{\text{exV(v)}} = 3.14 \). 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$_2$SO$_4$ 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).
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:

\[
\text{TiO}^{2+} + 2\text{HX}_{\text{org}} \leftrightarrow \text{TiO(HX)_2}_{\text{org}} + 2\text{H}^+_{\text{aq}}
\]

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)R$_2$(HR = Cyanex 301 or 302).
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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 VO₂X.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.

\[
\begin{align*}
&\text{Versatic 911 acid (} R_1, R_2 = C_4 - C_5 \text{)} \\
&\text{Versatic 10 acid (} R_1, R_2 = C_6 \text{)}
\end{align*}
\]
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, trialkylyphosphate 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).

\[
\begin{align*}
R_3P &= O \\
R'R_2P &= O \\
R'P &= O
\end{align*}
\]

Trialkyl phosphine oxides
(CYANEX 923 TRPO)

\[
\begin{align*}
CH_3(CH_2)_6CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3(CH_2)_6CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3(CH_2)_6CH_2
\end{align*}
\]

\[
\begin{align*}
CYANEX 921 = TOPO
\end{align*}
\]

\[
\begin{align*}
CH_3C(CH_3)_2CH_2CH(CH_3)CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3C(CH_3)_2CH_2CH(CH_3)CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3C(CH_3)_2CH_2CH(CH_3)CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3C(CH_3)_2CH_2CH(CH_3)CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3C(CH_3)_2CH_2CH(CH_3)CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3C(CH_3)_2CH_2CH(CH_3)CH_2
\end{align*}
\]

\[
\begin{align*}
CYANEX 925
\end{align*}
\]
A hydrometallurgical process has been proposed for the production of pigment grade TiO\textsubscript{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\textsubscript{2}\cdot2TRPO, VO\textsubscript{2}Cl\cdotTRPO and HFeCl\textsubscript{4}\cdot2TRPO, 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\textsuperscript{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):

\[
\text{Ti}_{\text{aq}}^{4+} + 4\text{Cl}_{\text{aq}}^- + 2\text{TRPO}_{\text{org}} \rightleftharpoons \text{TiCl}_4 \cdot 2\text{TRPO}_{\text{org}}
\]
Similar extracted complex, TiCl₄·2TPPO 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 (triocetylphosphine 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/dm³ 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.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{O} \\
\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{O} \xrightarrow{P=O} \text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{O} \\
\text{TBP}
\end{align*}
\]

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/dm³. 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:

\[ Ti^{4+}_{aq} + 4Cl^{-}_{aq} + 2L_{org} \rightleftharpoons TiCl_4 \cdot 2L_{org} \]

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\(_4\)OH 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$_2$Cl·(TBP)$_2$·2HCl(H$_2$O)$_2$·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$_3$·2TPPO (Kakade and Shinde 1994).

Tris(2-ethylhexyl)phosphosphate (TEHP) in toluene has been used as an extractant for vanadium(V) from HCl solutions and proposed the extracted complex as VOCl$_3$·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
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studied by many investigators and reported the extracted complexes as FeCl₃·3TBP at 2.0-4.0 mol/dm³ HCl and HFeCl₄·2TBP at 6.0-9.0 mol/dm³ 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 HFeCl₄·2TRPO (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 + FeCl₃ 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 FeCl₃ and at least a part of CaCl₂, and stripping of FeCl₃ and CaCl₂ from organic phase by water. Finally by concentrating the remaining solution by evaporation and adding HCl gas to the solution in order to precipitate AlCl₃·6H₂O 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 NH₄Cl 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 VO₂Cl·2R and (VO₂)₂Cl₂·2R 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 VO₂Cl·R and VO₂Cl·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/dm³ 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. V₂O₅ 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, R₃N) and
triocetyltrimethylammonium chloride (TOMAC, R₃R'NCl) in benzene has been investigated and proposed the extraction equilibrium expressions on the basis of the results obtained as (Sato et al. 2004):

\[
\text{FeCl}_3^{aq} + R_3\text{NHCl}^{org} \leftrightarrow R_3\text{NHFeCl}_4^{org} \quad \text{for TOA and}
\]

\[
\text{FeCl}_4^{aq}^{-} + R_3R'NCl^{org} \leftrightarrow R_3R'NFeCl_4^{org} + Cl^{-}_{aq} \quad \text{for TOMAC.}
\]

A solvent extraction process has been reported for the preparation of iron oxide (Garcia 1991). Fe₂O₃ was prepared by extracting with Primene 81R in an isodecanol-paraffinic hydrocarbon mixture and simultaneous reextraction-precipitation with an ammoniacal solution of (NH₄)₂SO₄. The reextraction of a compound of primary amine and Fe₂(SO₄)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 Fe₂O₃: Literature Review**

Several studies have been reported on the synthesis of hematite particles by the hydrothermal reaction of Fe³⁺ 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 (NH₄OH, 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 FeCl₃ 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.
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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$_2$O$_3$ 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$_2$O$_3$ in the hydrothermal process:

\[
\text{pH 3-5} \quad \text{150°C} \\
N_2H_4 + 2Fe^{2+} + 4H_2O \rightarrow 2[\text{NH}_4]^+ + 2H^+ + 2\text{α-FeOOH} \rightarrow \alpha-\text{Fe}_2\text{O}_3 + H_2O
\]

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$_2$O$_3$ 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 TiO₂: Literature Review

In the hydrothermal synthesis of nanocrystalline TiO₂, the main attention is paid to the hydrothermal treatment of TiO₂.nH₂O 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 TiO₂ 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 TiO₂ 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 > HNO₃ > H₂SO₄ > HAc. The presence of NaCl salt not only influence the phase formation but also the particle size of TiO₂.

Phase-pure TiO₂ nanocrystallites with narrow particle-size distributions were selectively prepared by a hydrothermal process starting from amorphous TiO₂ (Yin et al. 2001). Autoclaving of amorphous TiO₂ in the presence of HF and HCl lead to the formation of narrow-sized anatase TiO₂ with regular crystalline surface. On the other hand, the use of nitric acid as a cooperative catalyst with HF gave anatase TiO₂ 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$_2$O 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\textsubscript{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\textsubscript{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\textsubscript{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).