Manufacture of Pure Titanium(IV) Oxide by the Chloride Process. II. Selective Extraction of Titanium(IV) and Iron(III) from Hydrochloric Acid Leach Liquor of Ilmenite Ore by Tributyl Phosphate

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The selective recoveries of titanium(IV) and iron(III) from the synthetic hydrochloric acid leach liquor of ilmenite, *i.e.*, 1.8—11 M (1 M=1 mol dm^{-3}) hydrochloric acid solutions containing 0.25—0.57 M titanium(IV) and 0.27—0.29 M iron(III), or each single metal ion, were investigated by solvent extraction with benzene solutions of various tributyl phosphate (TBP) concentrations under the volume ratio (Org/Aq) of unity at 25 °C. Iron(III) was extracted into the TBP phase over a wide concentration range of hydrochloric acid studied, and the extraction was considerably accelerated by the salting-out effect of the coexisting titanium(IV). Since no extraction of titanium(IV) was observed at hydrochloric acid concentrations lower than 6 M, iron(III) could be recovered selectively from 3—6 M hydrochloric acid solutions under the conditions of the molar ratio $[\mathrm{TBP}]_{\mathrm{org}}/[\mathrm{Fe(III)}]_{\mathrm{init\ aq}} \leqq 3.0$. On the other hand, titanium(IV) in the residual aqueous phase was also extracted as $\mathrm{TiCl_4 \cdot 3TBP}$ at a concentration range of chloride ion higher than 7 M. The coextractions of other metal ions and free hydrochloric acid could be prevented by controlling the TBP concentration in the organic phase as $[\mathrm{TBP}]_{\mathrm{org}}/[\mathrm{Ti(IV)}]_{\mathrm{init\ aq}} \leqq 3.5$. The problem in applying the solvent extraction technique to actual leach liquor is discussed, as well as the recovery of free hydrochloric acid from the residual leach liquor.

Although titanium(IV) oxide has been produced industrially by the sulfate process and by the vapor phase oxidation of titanium(IV) tetrachloride, both processes have serious disadvantages, such as the treatments of byproducts in the former and the lack of raw rutile minerals in the latter.[1,2] The authors have endeavored to develop a new manufacturing process for titanium(IV) oxide, which would be based on the leaching of ilmenite ore in concentrated hydrochloric acid solution and the selective recovery of titanium(IV) from the resulting leach liquor by solvent extraction with neutral organophosphorus compounds. In this process ilmenite ore, which occurs abundantly in nature, can be used. One other important feature is that the hydrochloric acid used as the leachant allows easier recovery of reusable acid from the waste solution than does sulfuric acid. Therefore, the manufacturing process that we have proposed may solve the serious disadvantages of most methods for the production of titanium(IV) oxide. It is well known that the dissolution of titanium and iron in ilmenite ore can be achieved satisfactorily by using concentrated hydrochloric acid solution over a temperature range of 70—90 °C.[3-5]

A solvent extraction technique has been applied extensively to a hydrometallurgical process not only of highly valuable metals but of nonferrous metals such as Cu, Ni, and Co[6-8] and is becoming more and more common, even for the extraction of iron from the waste solution of steel cleansing,[9] the acid leach liquor of clay,[10] and the waste solution of the sulfate process of titanium(IV) oxide production[11,12] because of the higher selectivity of the solvent extraction operation. For the production of titanium(IV) oxide by leaching ilmenite ore in hydrochloric acid, the preferential removal of iron from the resulting leach liquor has been attempted using trialkyl phosphates,[13] trialkylamines,[13] and organic ketones,[14] However, no attempt has been made to extract titanium(IV) from the leach liquor by solvent extraction with neutral organophosphorus compounds, although several reports concerning solvent extraction of iron(III)[15,16] and titanium(IV)[17-21] with tributyl phosphate (TBP) have been published.

This paper deals with the selective recoveries of titanium(IV) and iron(III) from the synthetic hydrochloric acid leach liquor of ilmenite ore by solvent extraction with TBP in benzene under practical conditions in which the concentrations of metal ions and acid in the leach liquor are sufficiently high.

Experimental

Reagents. All the reagents were of analytical reagent grade. Synthetic hydrochloric acid leach liquor was prepared by dissolving titanium(IV) chloride and/or iron(III) chloride in hydrochloric acid solution. In one part of the experiment, other metal ions incorporated generally to ilmenite ore were also dissolved in the synthetic leach liquor. Since no differences between the extraction results using the commercial and purified TBP were observed, TBP was used without further purification.

Procedure. A 20 cm^3 portion of the hydrochloric acid leach liquor containing known amounts of metal ions was transferred to a 100 cm^3 pear shaped separatory funnel, together with 20 cm^3 portions of benzene solution of various TBP concentration. The extraction was carried out by shaking it vigorously for 10 min at 25 °C, and then leaving it until the phases separated clearly. The metal ions in the aqueous phase were analyzed by colorimetry and atomic absorption spectroscopy. The percentage extractions and distribution coefficients of the metals were calculated from the metal concentrations in the aqueous phase before and after the extraction. In one part of the experiment, the extraction behaviors of acid and chloride ion were also investigated by neutralization and the Volhard method, respectively.

Results and Discussion

Recovery of Iron. The extraction behavior of iron(III) and iron(II) in the presence of titanium(IV) as a function of the initial concentration of hydrochloric

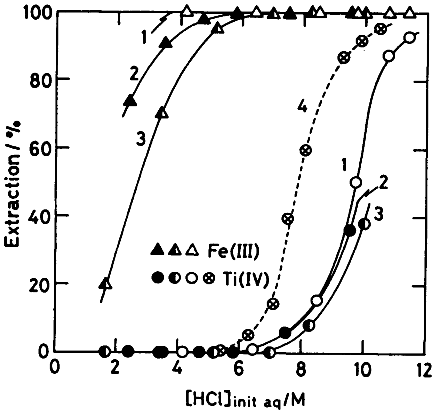

Fig. 1. Extraction of Fe(III) and Ti(IV) *vs.* concentration of HCl in aqueous phase.
1: 0.29 M Fe(III)+0.55 M Ti(IV), 1.8 M TBP, 2: 0.29 M Fe(III) +0.55 M Ti(IV), 0.92 M TBP, 3: 0.29 M Fe(III)+0.29 M Ti(IV), 0.92 M TBP, 4: 0.55 M Ti(IV), 1.8 M TBP.

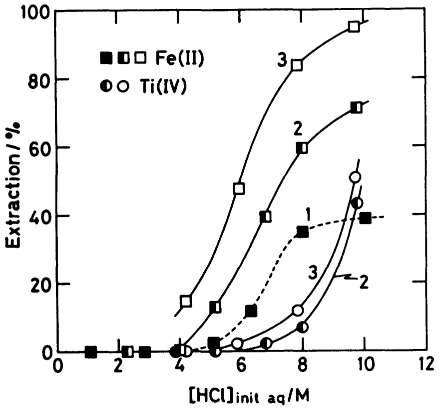

Fig. 2. Extraction of Fe(II) and Ti(IV) *vs.* concentration of HCl in aqueous phase.
1: 0.28 M Fe(II), 2: 0.28 M Fe(II)+0.26 M Ti(IV), 3: 0.28 M Fe(II)+0.57 M Ti(IV), 1, 2, 3: 0.92 M TBP.

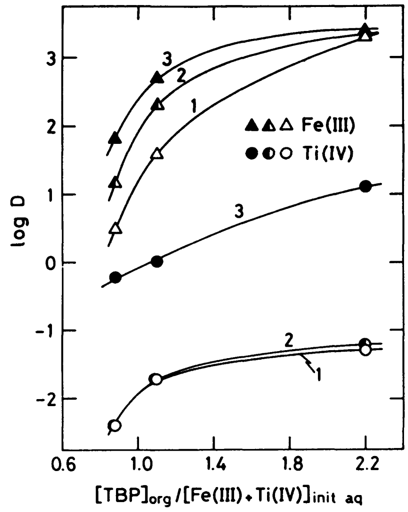

Fig. 3. Dependence of distribution ratios of Fe(III) and Ti(IV) on TBP concentration in organic phase.
1, 2, 3: 0.29 M Fe(III)+0.54 M Ti(IV), HCl(M)—1: 4.2, 2: 6.0, 3: 11.4.

acid is shown in Figs. 1 and 2, respectively. The percentage extraction of iron(III) was increased with increasing concentration of hydrochloric acid in the aqueous phase and TBP in the organic phase. Another important feature is that the coexisting titanium(IV) accelerated the extraction of iron(III) by the salting-out effect. Although similar behavior was observed in the extraction of iron(II), the percentage extraction was much lower than that of iron(III). Since the selective recovery of iron(II) was difficult, as can be seen in Fig. 2, iron(II) should be oxidized to iron(III) before applying solvent extraction. Titanium(IV) and minor constituents of ilmenite ore such as manganese(II), aluminum(III), magnesium(II), and chromium(III) were not extracted along with iron(III) from the leach liquor at hydrochloric acid concentrations lower than 6 M. Therefore, it was concluded that the selective recovery of iron from 3—6 M hydrochloric acid leach liquor was possible by solvent extraction with TBP after the oxidation of all iron(II) to iron(III).

The concentration of TBP in organic phase is an important factor in extracting iron(III) without contamination by titanium(IV). Figure 3 shows the plots of log *D*, distribution coefficient, *versus* log $[\mathrm{TBP}]_{\mathrm{org}}/[\mathrm{Fe(III)}+\mathrm{Ti(IV)}]_{\mathrm{init\ aq}}$. As expected from Fig. 1, the selectivity, $\beta = D_{(\mathrm{Fe})\mathrm{III}}/D_{\mathrm{Ti(IV)}}$, was low at high concentrations of hydrochloric acid in aqueous phase because of the coextraction of titanium(IV). At hydrochloric acid concentrations lower than 6 M, β became as high as 1×10^3—1×10^4. The purity of the extracting iron(III) could be increased by controlling TBP concentration in the organic phase as $[\mathrm{TBP}]_{\mathrm{org}}/[\mathrm{Fe(III)}]_{\mathrm{init\ aq}} \leq 3.0$, which was obtained from the result in Fig. 3. Islam *et al.*[22] have reported that the reverse selectivity, $\beta' = D_{\mathrm{Ti(IV)}}/D_{\mathrm{Fe(III)}}$, by solvent extraction with bis(2-ethylhexyl) hydrogenphosphate (B2EHP) was about 60. For the mutual separation of titanium(IV) and iron(III), TBP was superior to B2EHP.

Hydrochloric acid is extracted by an excess of TBP in organic phase.[23,24] The effect of the TBP concentration in the organic phase on the extraction of hydrochloric acid and iron(III) is shown in Fig. 4, which

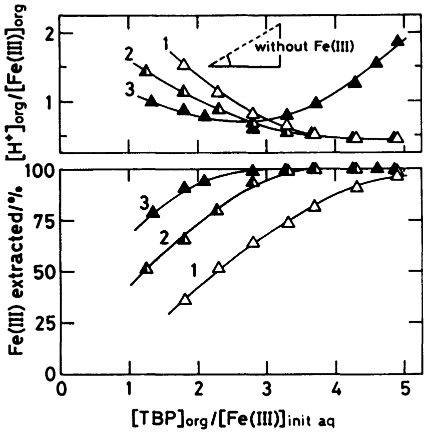

Fig. 4. Dependence of extraction of Fe(III) and acid on TBP concentration in organic phase.
1: 0.27 M Fe(III)+4.9 M HCl, 2: 0.27 M Fe(III)+6.1 M HCl, 3: 0.27 M Fe(III)+10.1 M HCl.

Table 1. The effect of salts added on the extraction of Ti(IV) with 0.92 M TBP in benzene

Concentration in initial solution		Extraction of Ti(IV)/%									
Ti(IV)	Salt	$[H^+]$/M					$[Cl^-]$/M				
M	M	6	8	9	10	11	7	9	10	11	12
0.25	—	1	20	65	87	96	1	20	65	87	96
0.25	KCl 0.25	1	25	70	90	93	1	20	64	86	97
0.25	NaCl 0.25	2	27	73	90	92	1	21	66	87	96
0.25	$MgCl_2$ 0.34	4	47	92	93	98	1	18	68	87	97
0.25	$MnCl_2$ 0.27	1	23	74	88	94	1	17	62	83	94
0.25	$AlCl_3$ 0.33	6	63	83	94	99	2	17	63	83	96

gives the percentage extraction of iron(III) and the molar ratio of $[H^+]/[Fe(III)]$ in the organic phase in tests conducted for the leach liquor containing only iron(III). At 4.9—6.1 M acid concentration, the ratio of $[H^+]_{org}/[Fe(III)]_{org}$ decreased with increasing TBP concentration, whereas the percentage extraction of iron(III) increased. This result indicates that the competitive extractions of $FeCl_3$ and HCl would occur at moderate acid concentrations as follows:

$$n[HCl]_{aq} + [TBP]_{org} = [nHCl\cdot TBP]_{org} \quad n=1,2 \tag{1}$$

$$[FeCl_3]_{aq} + 2[TBP]_{org} = [FeCl_3\cdot 2TBP]_{org}. \tag{2}$$

At 10.1 M acid concentration, the ratio of $[H^+]_{org}/[Fe(III)]_{org}$ were approximately constant as 0.75—1.0; which means that iron(III) is extracted mainly as $HFeCl_4$:

$$[H^+]_{aq} + [FeCl_4^-]_{aq} + 2[TBP]_{org} = [HFeCl_4\cdot 2TBP]_{org}. \tag{3}$$

Since the slopes of log $D_{Fe(III)}$/log TBP obtained from the results in Fig. 4 were 1.90—1.95, two extractive species of iron(III) such as $FeCl_3\cdot 2TBP$ and $HFeCl_4\cdot 2TBP$ have been postulated. On the other hand, the ratio of $[H^+]_{org}/[Fe(III)]_{org}$ became greater than unity under the conditions that the acid concentration was 10.1 M and the ratio of $[TBP]_{org}/[Fe(III)]_{init\ aq}$ was greater than 3.5. The dependence of the acid extraction behavior on the TBP concentration was approximately identical with that obtained without iron(III). Therefore, it is reasonable to assume that the extraction of free hydrochloric acid occurs at high TBP concentration as Eq. 1.

Recovery of Titanium. As shown in Fig. 1, the recovery of titanium(IV) can be performed by increasing the hydrochloric acid concentration in the residual aqueous phase and by extracting with fresh TBP in benzene. The shift of the extraction curve of titanium(IV) toward the low acid side by the removal of iron(III) makes it possible to extract titanium(IV) from the leach liquor at hydrochloric acid concentrations higher than 8 M.

The effect of various chlorides in the leach liquor on the extraction behavior of titanium(IV) is given in Table 1. The extraction of titanium(IV) was apparently accelerated in the presence of these chlorides judged from the same acid concentration, but not accelerated judged from the same chloride ion concentration. This was deduced by following the extraction curves based on the data in the left column in Table 1. This result indicates that these cations did not contribute to the salting-out effect. Under the conditions in which these experiments were conducted, all metal ions listed in Table 1 were not extracted. This result also indicates that the extraction of titanium(IV) will be accelerated by the addition of chlorides of magnesium(II) and aluminum(III) into the leach liquor of acid concentration range of 8—9 M.

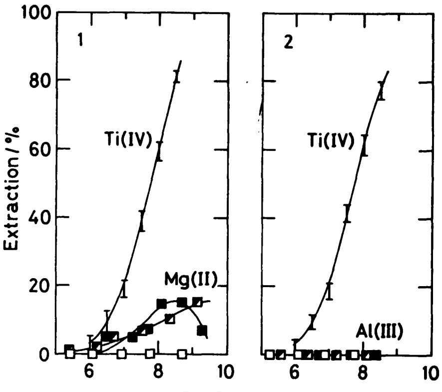

Fig. 5. Extraction of Ti(IV) and other metal ions *vs.* concentration of chloride in aqueous phase.
1: 0.56 M Ti(IV), 1.8 M TBP, 2: 0.27 M Ti(IV), 0.92 M TBP, HCl(M) —□: 4.0, ▨: 5.0, ■: 6.0.

Figure 5 shows the extraction behavior of titanium(IV) from 4—6 M hydrochloric acid solutions as a function of chloride ion concentration when $MgCl_2$ or $AlCl_3$ was added. The extraction of titanium(IV) was accelerated with increasing chloride ion; behavior quite similar to that observed in changing only hydrochloric acid concentration as shown in Fig. 1. The acceleration effect by these compounds was apparently dependent upon the increase of chloride ion. The salting-out effect by chlorides such as $MgCl_2$[25] and $CaCl_2$[20] on the extraction of titanium(IV) into the TBP phase had previously been investigated.

Figure 6 shows the plots of log *D* *versus* log $[TBP]_{org}$ in tests conducted for 7.0—10.3 M hydrochloric acid solution containing only titanium(IV). The slope of log $D_{Ti(IV)}$/log TBP was about unity at 7 M acid concentration, and increased with increasing acid concentration in aqueous phase; the value of which became 2.7 at 10.3 M acid concentration. It means that the ratio of TBP to titanium(IV) in the extracted

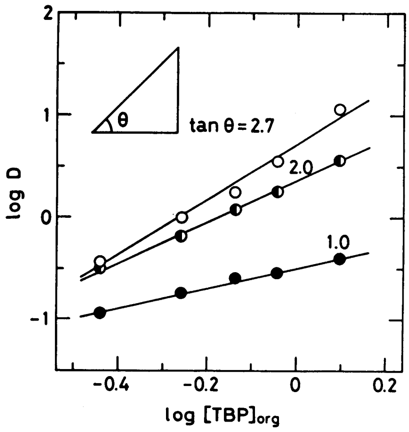

Fig. 6. Dependence of distribution ratio of Ti(IV) on TBP concentration in organic phase.
0.51 M Ti(IV), HCl(M) —●: 7.0, ◐: 8.8, ○: 10.3.

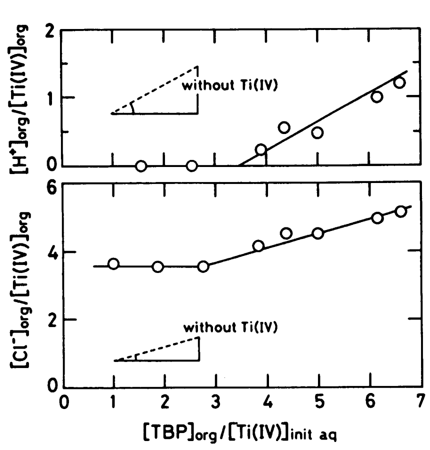

Fig. 7. Dependence of extraction ratio of H+/Ti(IV) and Cl-/Ti(IV) on TBP concentration in organic phase.
0.54 M Ti(IV)+10.3 M HCl.

species in organic phase was changed from 1 to 3 according to the acid concentration. Under the conditions conducted here, no free acid was extracted.

The effect of TBP concentration in the organic phase on the extraction of acid and chloride together with titanium(IV) is shown in Fig. 7, which gives the molar ratio of $[H^+]/[Ti(IV)]$ and $[Cl^-]/[Ti(IV)]$ in organic phase in tests conducted for 10.3 M hydrochloric acid solution containing only titanium(IV). At ratios of $[TBP]_{org}/[Ti(IV)]_{init\ aq}$ lower than 3, the ratio of $[Cl^-]_{org}/[Ti(IV)]_{org}$ was constant at 3.6; which suggests that titanium(IV) is extracted as a 1 : 3 complex of $TiCl_4$ and TBP:

$$[TiCl_4]_{aq} + 3[TBP]_{org} = [TiCl_4\cdot 3TBP]_{org}. \qquad (4)$$

As a minor species of titanium(IV) in organic phase, $TiOCl_2$ was inferred. At such high TBP concentration in organic phase as the ratio of $[TBP]_{org}/[Ti(IV)]_{init\ aq}$ ≥ 3.5, the equal amounts of Cl^- and H^+ were extracted together with titanium(IV). Because the dependence of acid extraction behavior on TBP concentration in the organic phase was identical with that obtained without titanium(IV), hydrochloric acid would be extracted with an excess of TBP in the organic phase as Eq. 1. According to Startsev *et al.*,[19,21] titanium(IV) was extracted as $H_2TiCl_6\cdot 3TBP$, *i.e.*, $[TiCl_4\cdot 2TBP][2HCl\cdot TBP]$ at high concentrations of hydrochloric acid in aqueous phase and of TBP in organic phase. Our results on the extracted species of titanium(IV) agreed with that reported by Startsev *et al.*

Conclusion

It is generally known that the optimum conditions which realize an effective dissolution of ilmenite ore are as follows: grain size of ore, under 150 mesh; concentration of HCl, higher than 10 M; amount of HCl to ore, 2—4 times in weight; temperature, 70—90 °C.[3,13,14] As can be seen from Eq. 5, the concentration

$$FeTiO_3 + 4HCl = TiOCl_2 + FeCl_2 + 2H_2O \qquad (5)$$

of hydrochloric acid decreases with the progress of the leaching reaction, finally becoming 4—6 M. Thus the extraction with TBP can be applied to the leach liquor after the oxidation of iron(II) to iron(III) to recover iron selectively. By the thermal decomposition method,[26,27] iron(III) oxide of higher than pigment grade can be recovered with free hydrochloric acid from the back-extracted solution. This technique is now being applied to the upgrading of ilmenite ore[28] and steel cleansing.[29,30]

Titanium(IV) extracted in organic phase as $TiCl_4\cdot 3TBP$ should be back-extracted by using 4—6 M hydrochloric acid solutions. The significant acid concentration dependence of the extraction behavior of titanium(IV) was preferable for the back-extraction because titanium(IV) tends to be hydrolyzed easily in weak acid solutions. Since the resulting aqueous solution containing titanium(IV) was not contaminated with any impurities, highly pure titanium(IV) oxide can also be obtained by the thermal decomposition method[28,29] or by the thermal hydrolysis.[31,32] The recovery of free hydrochloric acid from the residual solution after the extractions of iron(III) and titanium(IV) is now a feasible operation.[29,30,33]

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