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Alkaline Roasting of Ilmenite

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Roasting ilmenite concentrates with alkali metal carbonates and nitrates at 860°C produced a series of M-Fe-Ti oxide phases (M = Na or K) which were readily interconvertible on adding alkali or ilmenite, as appropriate, and reroasting at 860°C. Mixed Na-K compounds were not observed. The M-Ti ratio for maximum formation of each phase was obtained, enabling the upper composition limits for each phase to be determined. The behaviour of these oxide phases with H_2SO_4 and HCl is reported, and an explanation given for the difference in the acid leachability of iron between the Na-Ti and K-Ti systems. No corresponding calcium or magnesium compounds were observed.

Introduction

Much of the ilmenite found on the Eastern coast of Australia is unsuitable as a raw material for the manufacture of pigment-grade titania by the sulphuric acid process because of the presence of separate grains of chromite. Physical methods of removing chromite proved impracticable because of extensive weathering of the grains of chromite-type minerals (*1*), and a study of chemical methods of ilmenite beneficiation was initiated.

Roasting with alkali metal carbonates showed that the chromite fraction could be converted into extractable chromates. However the proportions of alkali needed to effect a high degree of chromium removal were such that considerable decomposition of ilmenite also occurred, making desirable an investigation into the interaction between ilmenite and alkali carbonates. This study forms the subject of the present paper.

Experimental

The ilmenite used throughout the present work, except where otherwise noted, had the composition listed in Table I. A well-mixed quantity of this ilmenite was ground to pass a 200 B.S.S. mesh, and 5-g samples containing 31.5-mg atoms of Ti and 30.2-mg atoms of Fe were used in each experiment.† Calculated quantities of AnalaR anhydrous alkali carbonates or nitrates were mixed loosely with the ilmenite prior to roasting. Each mixture, in a nickel boat, $3 \times \frac{1}{2} \times \frac{1}{2}$ in., was placed in a preheated muffle furnace maintained at 860 ± 20 °C, with free access of air. The temperature of 860 °C was chosen as being the highest at which significant melting or sintering was unlikely to occur. In all cases the roasted products were lightly sintered, but friable and easily removed from the boat. X-ray powder diffraction examination showed that, for a given ilmenite-alkali mixture, roasting for 1 h was sufficient for all phases to have formed, and be identified. One-hour roasts were therefore used when studying phase changes. Extending the roasting period to 4 h gave slightly higher figures for acid-extractable iron, and because of this all acid-solubility data was obtained from the products of 4-h roasts.

TABLE I

COMPOSITION OF THE ILMENITE USED IN THIS WORK

	TiO_2	FeO	Fe_2O_3	Cr_2O_3	MnO	MgO	Ti:Fe
%	50.3	24.5	21.0	1.21	1.37	0.94	1.04:1

To extract water-soluble species, the products were leached with four successive 50-ml portions of boiling water. Whenever calcium or magnesium carbonates had been present during roasting, an additional leach was made with boiling water containing 2–3% of sodium carbonate. The proportion of acid-soluble iron present in the water-insoluble residues was determined by refluxing for 2 h at 110 °C with 10 g of 20% HCl per gram of residue. The solubility of water-insoluble residues in 71% H_2SO_4 was determined by refluxing 0.5-g

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† Throughout this work all ratios quoted are atom ratios.

samples with 71% H_2SO_4 for 2 h at 165°C. Where water-insoluble residues were composed essentially of a single M-Fe-Ti phase, samples were also refluxed with 25% and 43% H_2SO_4. The proportion of acid used in each leach was constant, and always in excess of that required for complete reaction with the sample.

Analyses

For chemical analyses, samples of the various leach residues were fused with analytical-grade $NaHSO_4$, after which iron was determined by the conventional stannous chloride–mercuric chloride method, and titanium by titration with ferric alum after reduction by aluminium to Ti^{3+}. Atomic absorption methods were employed for the determination of alkali metals. In acid-leach liquors iron was determined as above, and titanium spectrophotometrically using hydrogen peroxide.

X-Ray Characterisation

Solid products were examined by means of a proportional counter X-ray diffractometer, using CuK_α radiation. Powder diffraction patterns of the tertiary titanates encountered in this work are shown in Fig. 1. Rutile, α-Fe_2O_3, and binary titanates such as Na_2TiO_3 were identified from patterns listed in the ASTM index. The minimum amount of a minor phase that could be detected in the roasted products was found to be between 7% and 10%. However acid-insoluble phases present in amounts below this limit could often be identified in the residues after acid leaching. Where the alkali content of the initial charges was low, the excess of 20% HCl used in leaching was found to dissolve up to 4% of the total TiO_2. This raised the effective level at which rutile was detected in the residue.

The proportions of different phases present in solid reaction products were determined by comparing the peak heights of the strongest diffraction lines characteristic of each phase with the heights obtained when only that particular phase was detected. This method of assessing the quantity of a component in a mixture is not as precise as using standardized mixtures, but even so good and reproducible estimates of the positions of maximum incidence of all phases were obtained.

Results and Discussion

Roasting with Sodium Carbonate

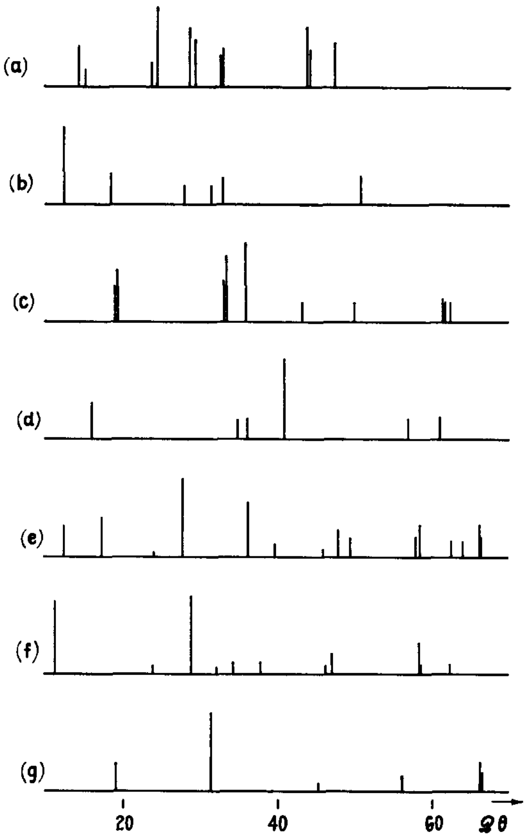

FIG. 1. Powder diffraction patterns of tertiary titanates, CuK_α radiation: (a) $Na_xFe_xTi_{8-x}O_{16}$, (b) $Na_xFe_xTi_{2-x}O_4$, (c) $NaFeTiO_4$, (d) $Na_xFe_xTi_{1-x}O_2$, (e) $K_xFe_xTi_{8-x}O_{16}$, (f) $K_xFe_xTi_{2-x}O_4$, and (g) $K_xFe_xTi_{1-x}O_2$.

Ilmenite containing no ferric species reacted only slightly with sodium carbonate when heated at 860°C for 1–4 hours in an argon atmosphere. However, upon heating natural ilmenites with sodium carbonate in the presence of air, i.e., roasting, rapid reaction occurred at 860°C to give products containing one or more of the Na-Fe-Ti oxide phases listed in Table II. In addition, whenever the over-all Fe-Ti atom ratio in the Na-Fe-Ti oxide phases formed was less than 1:1 the surplus iron was present as HCl-soluble α-Fe_2O_3, and whenever the ratio was greater than 1:1 the surplus titania was converted to a mixture of simple titanates, mainly Na_2TiO_3.

The ternary phases formed from ilmenite at 860°C were found to be quite reactive and readily interconvertible on adding appropriate amounts of alkali or ilmenite and reroasting. The results, summarized graphically in Fig. 2(a) and (b), demonstrate the reversibility of the system. At equilibrium the phases present in the final product were independent of the number of reagent additions

TABLE II

PHASES IDENTIFIED IN THE PRODUCTS OF ROASTING ILMENITE WITH SODIUM CARBONATE

Initial Na-Ti Atom Ratio	Phase				Solubility in 71% H_2SO_4[a]
	Formula of Phase	x (Composition range)	Structure	References	
< 0.1:1–0.87:1	$Na_xFe_xTi_{8-x}O_{16}$	1.20–2.00	Isomorphous with Na_xTiO_2, (sodium titanium bronze)	(*2*), (*7*), and (*8*)	Soluble after two hours
0.39:1–0.75:1[b]	$Na_xFe_xTi_{2-x}O_4$	0.75–0.90	A unique structure recently reported	(*3*)	Immediately soluble
0.27:1–2.1:1	$NaFeTiO_4$	Stoichiometric	Isomorphous with $CaFe_2O_4$, calcium ferrite	(*4*)	Immediately soluble
0.99:1–> 2.1:1	$Na_xFe_xTi_{1-x}O_2$	0.67–1.00	α-$NaFeO_2$-type, with deficiency of sodium	(*5*)	Immediately soluble

[a] Refluxed for 2 h, see text.

[b] Only small proportions obtained at 860°C.

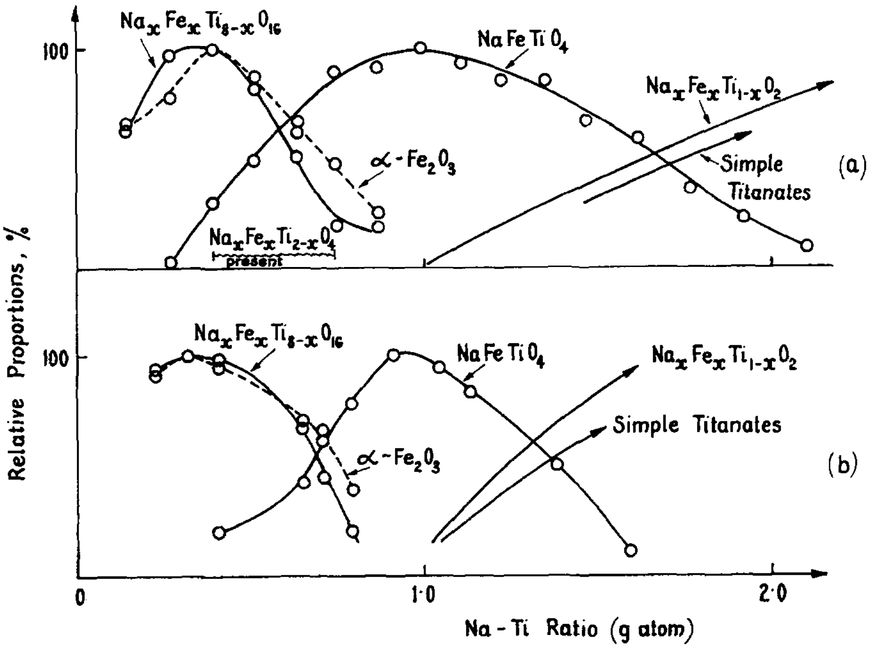

FIG. 2. Regions of occurrence of tertiary titanates from the roasting of ilmenite with sodium carbonate. (a) Phases formed on successive additions of Na_2CO_3 to the same sample of ilmenite, reroasting for 1 hour after each addition. (b) Phases formed on successive additions of ilmenite to an initial sample of Na_2CO_3, reroasting for 1 h after each addition.

and roasting stages, depending only on the terminal Na-Ti ratio. Prior formation of appreciable amounts of pseudobrookite, by roasting ilmenite for 1 h at 860°C in the absence of alkali, had little effect on the establishment of equilibrium in the Na-Fe-Ti oxide system.

Maximum formation of the sodium titanium bronze-type phase was observed at Na-Ti ratios of 0.34:1–0.35:1, and from these values the upper limit for x in $Na_xFe_xTi_{8-x}O_{16}$ was estimated to be 2.03–2.07, in good agreement with the upper limit of 2.00 allowed by the structure (*2*), (*7*), and (*8*). Similarly, the maximum formation of $NaFeTiO_4$ was observed to occur at Na-Ti ratios of 0.95:1–

1.01:1, also in good agreement with structural requirements (*4*). The phase $Na_xFe_xTi_{2-x}O_4$, $0.75 < x < 0.90$, recently shown by Mumme and Reid (*3*) to be structurally related to $NaFeTiO_4$ was observed only infrequently at 860°C, but at 1040°C could be obtained at the expense of $NaFeTiO_4$ for Na-Ti ratios approaching 1:1.

Where the quantity of sodium carbonate was insufficient to convert all the ilmenite to the phase of lowest sodium content, i.e., the sodium titanium bronze-type, the remainder of the ilmenite was oxidised to a pseudobrookite phase, Fe_2TiO_5, together with a small quantity of another oxidation product as yet unidentified. This latter phase was formed also in the absence of alkali, on roasting chromium-free ilmenite at 860°C for short periods, and was completely converted to pseudobrookite on heating in air for 2 h. Because of the broad medium-intensity X-ray diffraction peaks at 3.38, 2.88, and 2.72 Å which characterize this phase, it is unlikely to be a partial oxidation product in the solid solution series, $FeTi_2O_5$–Fe_2TiO_5 (*9*).

Acid Solubility of Roast Products. Published works on these Na-Fe-Ti oxide phases have dealt only with their crystal structures, and their preparation in the pure state at temperatures at or above 1000°C from appropriate mixtures of simple components (*2*)–(*7*). They give no information regarding the behaviour of these phases in acid media. Safiullin and Belyaev (*10*) examined the products of roasting ilmenites with a Ti-Fe ratio of 2.4:1 with sodium carbonate, but did not relate the composition of their products to the observed behaviour in refluxing 20% HCl.

During the present work it was observed that the acid solubility of the Na-Fe-Ti oxide phases, as indicated by the proportions of soluble iron and titanium, decreased as the sodium content was decreased. Thus, after a 6-h leach with a twofold excess of boiling 25% H_2SO_4, 70% of both the titania and iron content of samples of $NaFeTiO_4$ were soluble. After a similar treatment of samples containing the sodium titanium bronze-type phase and α-Fe_2O_3, only 6–10% of the titania content was soluble, and prolonged refluxing with fresh reagent had little further effect. However about 80% of the free α-Fe_2O_3 in any sample was soluble in 25% H_2SO_4. Similar behaviour was observed in 43% H_2SO_4, in which 15% of the bronze-type phase and 98% of the original free α-Fe_2O_3 were soluble. $NaFeTiO_4$ was found to be slightly soluble in hot 1:1 HNO_3, whereas the bronze-type phase appeared to be unaffected.

Both $NaFeTiO_4$ and the sodium-deficient α-$NaFeO_2$-type phase, $Na_xFe_xTi_{1-x}O_2$, were rapidly soluble in 71% H_2SO_4 once reflux conditions were established, and samples containing the bronze-type phase plus α-Fe_2O_3 were more than 90% soluble after refluxing for 2 h.

In boiling 20% HCl only 1–4% of the total titania content of any roast product was found to be in solution, whilst the iron contents of $Na_xFe_xTi_{1-x}O_2$, $NaFeTiO_4$, $Na_xFe_xTi_{2-x}O_4$, and α-Fe_2O_3 were largely soluble. The sodium titanium bronze-type phase was unaffected, in agreement with the observations of Safiullin and Belyaev (*11*), indicating that this lattice, like that of pseudobrookite, is apparently a very stable one. Thus, leaching with 20% HCl provided an alternative method of characterizing the roast products.

Figure 3 shows the effect of varying the sodium carbonate-ilmenite ratio on the proportion of iron extracted by boiling 20% HCl. At sufficiently low Na-Ti ratios pseudobrookite was the dominant phase and for this reason the proportion of HCl-soluble iron was small. The solubility of the α-Fe_2O_3 in HCl, and its formation alongside the sodium titanium bronze-type phase, caused the proportion of HCl-soluble iron to rise as the Na-Ti ratio was increased to 0.35:1. As shown in Fig. 2(a) and (b), in conjunction with Fig. 3, the region of maximum formation of the sodium titanium bronze-type phase and α-Fe_2O_3, at a Na-Ti ratio of 0.35:1, corresponds to the disappearance of detectable amounts of pseudobrookite from the HCl-insoluble residues. At this point, assuming complete conversion of the titanium to $Na_2Fe_2Ti_6O_{16}$, 65.2% of the total iron should have been present as HCl-soluble α-Fe_2O_3. The experimental solubility figure of $64 \pm 2\%$ was in good agreement with this calculated value, suggesting that little, if any, of the iron component of the bronze-type phase had been attacked by 20% HCl. Beyond this point Na-Fe-Ti oxide phases from which the iron can be dissolved in 20% HCl were being formed progressively, thus accounting for the steady increase in the proportion of HCl-soluble iron.

Effect of Variations in the Ti-Fe Ratio. The effect of variations in the Ti-Fe ratio was studied briefly, since in natural ilmenites extensive weathering and chemical substitution may cause the Ti-Fe ratio to be altered considerably. A decrease in the ratio below 1:1 was thought unlikely to affect the behaviour of the system since the situation would merely be an extension of the 1:1 case, where excess iron was rejected as α-Fe_2O_3. However an increase in the Ti-Fe ratio must eventually affect the equilibrium conditions in favour of sodium titanates at high

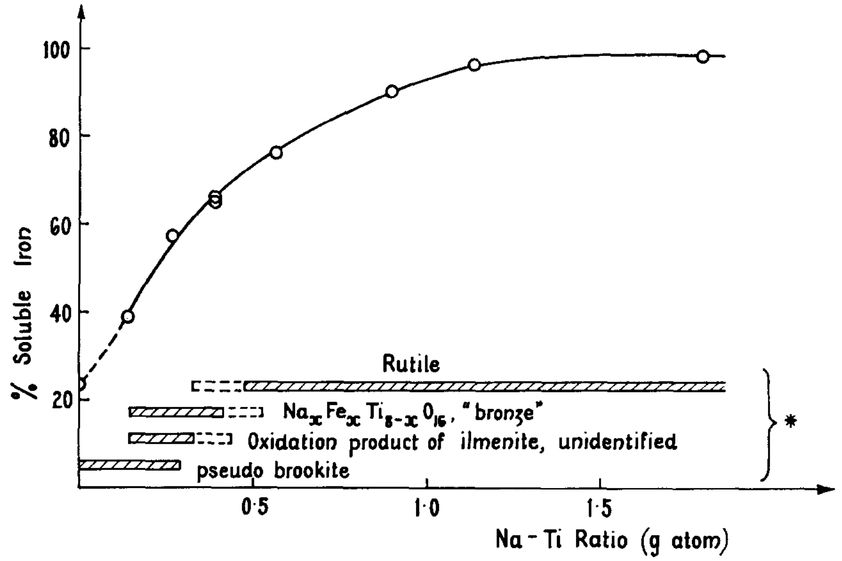

FIG. 3. HCl-soluble iron in Na-Fe-Ti oxide system. *Residues insoluble after leaching in 20% HCl. Dashed extensions show conditions where phases are occasionally detected.

alkali additions, and of the bronze-type phase at low alkali additions.

Selected concentrates which had Ti-Fe ratios close to 1.3:1 behaved very similarly to the ilmenite with a Ti-Fe ratio of 1:1. Mixtures having higher Ti-Fe ratios, up to 2.7:1, were synthesized by blending appropriate amounts of rutile with the ilmenite used in the main experiments. These were roasted with sodium carbonate for 4 h and the products were examined in the usual way. For Na-Ti ratios in the range 0.9:1–1.3:1, and the Ti:Fe ratio in excess of 1.5:1, $NaFeTiO_4$ together with $Na_2Ti_3O_7$, and minor amounts of other sodium titanates, were formed. No free rutile or α-Fe_2O_3 was observed. When the Na-Ti ratio was in the range 0.25:1–0.33:1 the sodium titanium bronze-type phase and α-Fe_2O_3 were invariably formed. However, when the Ti-Fe ratio exceeded 1.7:1, equilibrium seemed not to be attained at 860°C within the 4-h roasting period; α-Fe_2O_3, TiO_2 and $Na_2Ti_6O_{13}$ were each present in the product whereas further interaction to form more of the bronze-type phase would have been expected.

During the course of the present work three recent papers by Safiullin and Belyaev dealing with the roasting of mixtures of sodium carbonate with "modified" or "altered"† chromium-containing ilmenites became available (*10*), (*11*), and (*12*). The Ti-Fe atom ratios in the concentrates they examined varied from 2.2:1–2.4:1, and the X-ray data recorded showed that the concentrates were essentially rutile in structure. In the light of the present work it seems evident that the comments made by these authors concerning the formation of sodium titanates and ferrites, the acid-solubility of products formed at a given sodium carbonate-ilmenite ratio, as well as the behaviour of the chromium impurity, are relevant only to high TiO_2-ilmenite systems. Judging from the XRD data quoted, the phase identified by Safiullin and Belyaev at high sodium levels as $Na_2O.Fe_2O_3.3TiO_2$ (*11*) appears to be $Na_xFe_xTi_{2-x}O_4$, $0.75 < x < 0.9$ (*3*), and the unidentified phase with maxima reported at 2.48, 2.69, and 4.54 Å to be $NaFeTiO_4$ (*4*).

Roasting with Potassium Salts

One or more of the K-Fe-Ti oxide phases listed in Table III were formed during roasting ilmenite with varying proportions of potassium carbonate or nitrate for 1–4 h at 860°C. Surplus iron was again rejected as HCl-soluble α-Fe_2O_3, and at K-Ti ratios above 1.5:1 simple titanates were observed. When the initial K-Ti ratio was below that required for conversion of all the ilmenite to the phase of lowest potassium content, $K_xFe_xTi_{8-x}O_{16}$, the products of roasting also contained the unidentified ilmenite oxidation product described in the sodium-ilmenite section. The failure to detect a stoichiometric phase analogous to $NaFeTiO_4$ agrees with the studies of

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† No further information was given concerning these concentrates, but other publications quoted by the Russian authors reveal that the word thus translated appears to be a term in general use when referring to weathered ilmenite containing leucoxene or rutile.

TABLE III

PHASES IDENTIFIED IN THE PRODUCTS OF ROASTING ILMENITE WITH POTASSIUM NITRATE

Initial K-Ti Atom Ratio	Phase				Solubility in 71% H_2SO_4[a]
	Formula of Phase	x (Composition Range)	Structure	References	
< 0.5:1	$K_xFe_xTi_{8-x}O_{16}$	1.3[b]	Isomorphous with α-MnO_2, or hollandite	(*6*), (*14*)	Soluble after two hours
0.19:1–2:1	$K_xFe_xTi_{2-x}O_4$	0.76[b]	Rearrangement of $Rb_xMn_xTi_{2-x}O_4$ structure (*13*)	(*14*)	Immediately soluble
0.6:1	$K_xFe_xTi_{1-x}O_2$	0.67–1	α-$KFeO_2$-type, with deficiency of potassium	(*14*)	Immediately soluble

[a] Refluxed for 2 h, see test.

[b] Maximum value for x established in this work.

Mumme and Reid (*14*) which indicated that such a phase does not exist in the K-Fe-Ti system.

The ternary K-Fe-Ti oxide phases formed at this temperature were readily interconverted by the addition of appropriate amounts of alkali or ilmenite and reroasting, and the formation of any given phase was dominated by the alkali-titanium ratio, provided sufficient iron was present. The reversibility of the system is shown graphically in Fig. 4(a) and (b). At equilibrium the phases present in the final product were independant of the number of reagent additions and roasting stages, depending only on the terminal K-Ti ratio.

It has already been observed by Bayer and Hoffman (*7*) that the Na_xTiO_2-type structure assumed by $Na_xFe_xTi_{8-x}O_{16}$ has no counterpart in the K-Fe-Ti system; instead the potassium phase, $K_xFe_xTi_{8-x}O_{16}$, has a hollandite-type structure. The results of the present work, and those of Mumme and Reid (*14*) are in agreement with this observation. Bayer and Hoffman have reported that $K_xFe_xTi_{8-x}O_{16}$ was the only phase present at overall compositions corresponding to $K_{1.78}Fe_{1.78}Ti_{6.22}O_{16}$ (*7*) and $K_2Fe_2Ti_6O_{16}$ (*6*) ($x = 1.78$ and 2.0, respectively). In the present investigation however, as shown in Fig. 4(a), a second phase was invariably detected when the K-Ti ratio exceeded 0.19:1 ($x = 1.3$), the ratio corresponding to maximum formation of the hollandite-type structure. Parallel experiments using low-chromium ilmenite† gave similar results. The ratio of 0.19:1 suggests $x = 1.3$ as the upper limit of stability of $K_xFe_xTi_{8-x}O_{16}$, in agreement with other studies (*15*) in which it was found that the upper limit of stability of the hollandites $Cs_xM_xTi_{8-x}O_{16}$ with M = Sc or Fe corresponded to x being about 1.4.

The second phase, $K_xFe_xTi_{2-x}O_4$, observed beyond the point of maximum formation of the potassium hollandite-type phase has been shown by Reid et al. (*14*) to have a layer structure containing less than the stoichiometric amount of potassium, x having a narrow range of permissible values somewhere between 0.6 and 0.8. In the present work, the K-Ti ratio for maximum incidence of this phase appears to be at 0.63:1, suggesting that the maximum value for x in $K_xFe_xTi_{2-x}O_4$ is 0.77, in agreement with the limits reported above. Since equilibrium conditions for formation of this phase were difficult to establish at 860°C, the above value of 0.77 was derived by averaging the behaviour over a series of five 1-h roasts at each composition [Fig. 4(c)].

The phase exhibiting the XRD pattern characteristic of potassium ferrite has been shown (*14*) to be a potassium-deficient α-$KFeO_2$-type phase. It is readily hydrolyzed and in this investigation was first detected in the potassium-ilmenite system at an alkali-titanium ratio of 0.6:1, which is considerably lower than that required for the formation of the corresponding sodium-deficient α-$NaFeO_2$-type phase.

Acid Solubility of Roast Products. Little has been published concerning these K-Fe-Ti oxide phases, and no information was available regarding their behaviour in acid media. During the present work it was found that samples composed of α-Fe_2O_3 and the phase of lowest alkali content, $K_xFe_xTi_{8-x}O_{16}$,

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† Composition: 50.5% TiO_2, 25.4% FeO, 21.7% Fe_2O_3, 0.14% Cr_2O_3, 1.41% MnO, 0.69% MgO, Ti:Fe = 1.02:1.

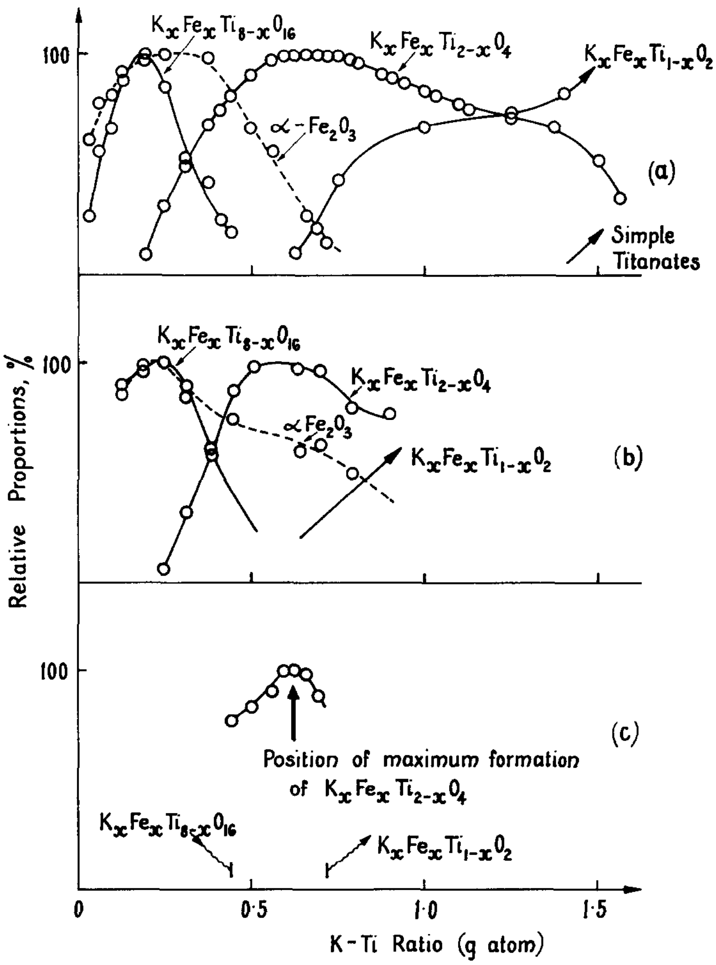

FIG. 4. Regions of occurrence of tertiary titanates from the roasting of ilmenite with potassium nitrate. (a) Phases formed on successive additions of KNO_3 to the same sample of ilmenite, reroasting for 1 h after each addition. (b) Phases formed on successive additions of ilmenite to an initial sample of KNO_3, reroasting for 1 h after each addition. (c) $K_xFe_xTi_{2-x}O_4$, formed on successive additions of KNO_3 to the same sample of ilmenite, reroasting for five 1-h periods after each addition.

were more than 90% soluble after refluxing for 2 h in 71% H_2SO_4, and samples of the other two K-Fe-Ti oxide phases were rapidly soluble once reflux was established.

The solubility of these phases in more dilute acids was also examined. After a 6-h leach with a twofold excess of boiling 25% H_2SO_4, 50% of the titania content of the hollandite-type phase, and approximately 40% of the free α-Fe_2O_3 associated with this phase were soluble. Complete decomposition of the phase $K_xFe_xTi_{2-x}O_4$ was effected by a single 2-h leach with a slight excess of acid; none of the original K-Fe-Ti oxide phase could be detected, the residues containing only anatase and α-Fe_2O_3. After a 6-h leach with a twofold excess of 25% H_2SO_4 about 70% of the titania content of the $K_xFe_xTi_{2-x}O_4$, and about 52% of the original free α-Fe_2O_3 were soluble.

Iron could be dissolved in refluxing 20% HCl from all phases observed in the ilmenite-potassium nitrate system, leaving residues rich in TiO_2, so that even for low initial K-Ti ratios the proportion of soluble iron in samples was fairly high (Fig. 5). Leaching with this reagent therefore merely demonstrated the presence or absence of ilmenite oxidation products. This behaviour contrasts with that observed in the ilmenite-sodium carbonate system, where the sodium titanium bronze-type phase was unaffected by boiling 20% HCl (Fig. 3).

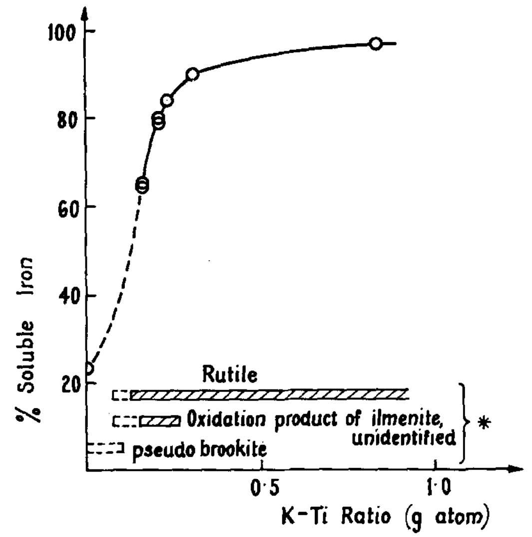

FIG. 5. HCl-soluble iron in K-Fe-Ti oxide system. *Residues insoluble after leaching in 20 % HCl. Dashed extensions show conditions where phases are occasionally detected.

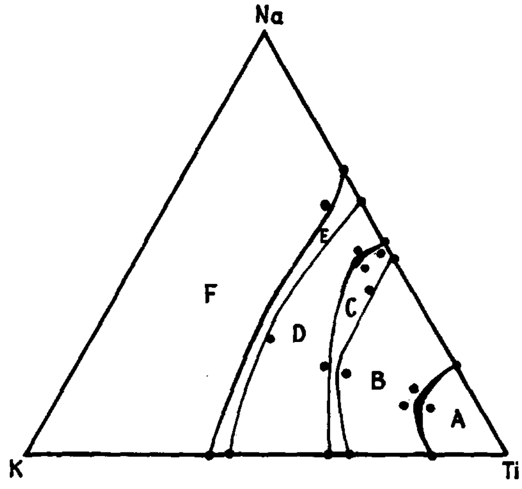

FIG. 6. Approximate fields of occurrence of tertiary titanates formed from ilmenite at 860°C (Fe-Ti ratio 1:1 in all samples): A. $Na_xFe_xTi_{8-x}O_{16}$ and/or $K_xFe_xTi_{8-x}O_{16}$ + α-Fe_2O_3; B. $Na_xFe_xTi_{8-x}O_{16}$ and/or $K_xFe_xTi_{8-x}O_{16}$ + α-Fe_2O_3 + $NaFeTiO_4$ and/or $K_xFe_xTi_{2-x}O_4$; C. $NaFeTiO_4$ and/or $K_xFe_xTi_{2-x}O_4$ + α-Fe_2O_3; D. $NaFeTiO_4$ and/or K_x Fe_x Ti_{2-x} O_4 + α-Fe_2 O_3 + Na_x Fe_x Ti_{1-x} O_2 and/or $K_xFe_xTi_{1-x}O_2$; E. Simple sodium and/or potassium titanates–$K_xFe_xTi_{1-x}O_2$; E. Simple sodium and/or potassium titanates + phases observed in D; F. $Na_xFe_xTi_{1-x}O_2$ and/or $K_xFe_xTi_{1-x}O_2$ + simple sodium and/or potassium titanates.

Roasting with Sodium and Potassium Salts

Roasting of ilmenite in the presence of both sodium and potassium salts produced only those phases previously obtained after roasting with either alkali alone. The relative proportions of each pair of comparable phases, viz., alkali-deficient α-$MFeO_2$, $M_xFe_xTi_{2-x}O_4$, or $M_xFe_xTi_{8-x}O_{16}$, were controlled largely by the total alkali-ilmenite ratio in the particular sample, the approximate fields of occurrence for these phases at 860°C being as shown in Fig. 6. The relative proportions of each of a particular pair of phases obtained at a given terminal K-Na-Ti ratio depended on the steps involved in reaching the final composition.

These K,Na-Fe-Ti systems were found to be readily interconverted by addition of the appropriate alkali or ilmenite, and reroasting. For instance, when a product obtained by roasting a sample of ilmenite with potassium nitrate (K-Ti ratio 0.16:1) for 1 h at 860°C was subsequently reroasted for 1-h periods after successive additions of sodium carbonate, the compositions of the products progressed as shown in Fig. 7. The traces of the sodium titanium bronze-type phase observed were probably due to incomplete attack of the ilmenite during the initial potassium roasting (cf., Fig. 5), since none was observed if the initial K-Ti ratio was raised to 0.24:1. $NaFeTiO_4$ and $K_xFe_xTi_{2-x}O_4$ were readily interconverted by reroasting after addition of suitable amounts of the appropriate alkali.

Roasting with Alkaline Earth Carbonates

No Ca,Mg-Fe-Ti phases were obtained after roasting ilmenite with either calcium or magnesium carbonates for 4 h at 860 °C; the over-all effect was merely to oxidise the ilmenite to pseudobrookite although, in agreement with the claims of a recent patent (*16*), the pseudobrookite formed in the presence of magnesium carbonate had an enhanced solubility in 71 % H_2SO_4. Roasting in the presence of these carbonates caused the proportion of HCl-soluble iron to fall slightly from an initial value of about 23 % to one of about 18 %.

Roasting with Sodium and Calcium Carbonates

The nature and proportions of the phases produced from ilmenite using mixtures in which the Ca-Na ratio varied from 4.2:1–0.2:1 were sensibly the same as those obtained on omitting the calcium. XRD methods did not detect any Ca-Fe-Ti phases, and the lattice parameters of the sodium titanium bronze-type phases prepared either with or without calcium present were identical.

The apparent nonincorporation of divalent calcium ions into the bronze structure was supported by the fact that calcium addition had little effect on

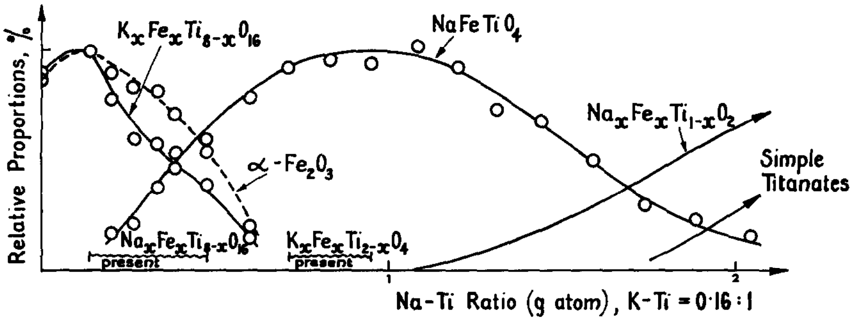

FIG. 7. Regions of occurrence of tertiary titanates formed on roasting ilmenite with sodium carbonate, in the presence of a constant proportion of potassium nitrate [K-Ti ratio 0.16:1].

the proportion of HCl-soluble iron present in roast products.

Roasting with Potassium Nitrate and Calcium Carbonate

When ilmenite was roasted with potassium nitrate such that the K-Ti ratio was below that required for complete formation of the potassium-hollandite phase, the addition of calcium carbonate prior to roasting increased the extent of formation of the hollandite-type phase. This effect was reflected in an increased intensity of the α-Fe_2O_3 peaks relative to those of the hollandite, and in an increase in the proportion of iron extracted by 20% HCl. The unidentified oxidation product of ilmenite previously seen at this K-Ti ratio in the absence of calcium could not be detected by XRD.

These observations suggest a possible incorporation of calcium ions into the hollandite lattice, a possibility supported by the existence of priderite (*17*), a naturally-occurring hollandite-type mineral which has been shown to contain barium ions, the K-Ba ratio averaging 2.5:1, and with an overall composition $(K,Ba)_{1.3}(Fe,Ti)_8O_{16}$. Entry of divalent ions into the lattice would be expected to cause a lowering of the Fe-Ti ratio in the hollandite lattice, and a consequent increase in rejection of α-Fe_2O_3, as was observed.

Conclusion

Natural ilmenite reacts readily with Na_2CO_3 or KNO_3, separately or in admixture, at 860°C under oxidizing conditions to give a well defined series of M-Fe-Ti oxide phases (M = Na or K) with rejection of excess iron as acid-soluble α-Fe_2O_3. This reactivity contrasts with the use of temperatures at or above 1000°C when preparing the same phases from their constituent oxides.

The phases formed in either Na, K, or mixed alkali systems are readily interconvertible at 860°C by addition of the appropriate reactant, but no mixed alkali compounds are formed. The M-Ti ratio needed for maximum formation of each phase is well-defined enabling the upper composition limit of each particular phase to be determined or confirmed.

All of the M-Fe-Ti oxide phases are decomposed by 71% H_2SO_4 and, with the notable exception of the sodium titanium bronze-type phase, are extensively attacked on refluxing with 20% HCl. Because of this, at low M-Ti ratios, i.e., where the sodium titanium bronze- and potassium hollandite-type phases predominate, leaching of iron by 20% HCl is more effective in the K-Ti system than in the Na-Ti system.

Under the experimental conditions, neither calcium- nor magnesium-titanium compounds appeared to form to any significant extent.

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