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Article Transformation of Vanadium-Bearing Titanomagnetite Concentrate in Additive-Free Roasting and Alkaline-Pressure Leaching for Extracting Vanadium (V)

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Abstract: With a view to satisfying the requirements of environmental protest and efficient usage of resources, a novel process for efficiently extracting vanadium (V), titanium (Ti), and iron (Fe) from vanadium-bearing titanomagnetite concentrate was developed. In the new process, vanadium is pre-extracted by additive-free roasting under the air atmosphere and alkaline leaching technologies. In this paper, transformation of vanadium-bearing titanomagnetite concentrate in the roasting is investigated based on thermodynamic analyses and experimental discussion. Thermodynamic analyses show that oxidation of V(III) into V(V) would happen in the roasting experiment over the range of 327–1327 °C and vanadium-iron spinel phase (FeV₂O₄) can be oxidized more easily than magnetite (Fe₃O₄) when the temperature is higher than 861 °C. Experimental results show that some compounds (V₂O₅, Fe₂Al₄Si₅O₁₈, and Fe₂SiO₄) with low melting temperature were obtained by solid reactions at low temperature and melted as a binding phase at elevated temperature. Liquids were generated due to some chemical reactions or phase transformation reaction (Fe₂V₂O₄(s) \rightarrow $Fe_2O_3(s)$ + liquid) at elevated temperature. Main phases of Fe_2O_3 and Fe_2TiO_5 are connected and sintered with the binding phases of the compounds with low melting temperature or the mixtures with low liquidus temperature. In addition, higher roasting temperature leads to higher vanadium leaching efficiency over the range of 800–1200 °C. However, over-burning would happen at 1250 °C, some of vanadium oxide was wrapped by silicate network, and the conversion of V(III) into V(V) was prevented from occurring. Therefore, the vanadium leaching efficiency decreased from 59.1% $(T_{\rm roa.} = 1200 \,^{\circ}{\rm C})$ to 57% $(T_{\rm roa.} = 1250 \,^{\circ}{\rm C})$.

Keywords: vanadium-bearing titanomagnetite concentrate; additive-free roasting; vanadium extraction; transformation mechanism; silicate network

1. Introduction

Vanadium-bearing titanomagnetite is a very important mineral resource of vanadium, titanium and iron. Currently, the major process for smelting vanadium-bearing titanomagnetite involves firstly extracting iron and then extracting vanadium of slag by sodium salt roasting and water leaching technologies [1–8], which causes serious environmental pollution (especially hazardous gases, such as HCl, SO₂, or Cl₂) and low recovery ratio of vanadium (total recovery ratio < 45%) and titanium (total recovery ratio < 10%) [8]. In addition, soluble vanadium (V(IV) and V(V)) substances are toxic substances and vanadium-rich resources are a potential toxic solid because deleterious health effects induced by inorganic vanadium compounds have been reported [9,10]. Therefore, more attention has been drawn to comprehensive and efficient extraction of valuable elements (V, Ti, and Fe) from titanomagnetite deposits with a new environmentally-friendly method.

Regarding the extraction of vanadium from vanadium-bearing resources (such as vanadium-bearing titanomagnetite, vanadium-rich slag, stone coal) many efforts have been made by researchers [11–27]. A calcium roasting method followed by acid or alkaline leaching was an alternative process to extract vanadium with the purpose of avoiding harmful gas generation (such as HCl, SO₂, or Cl₂), but it always results in low quality vanadium products (V₂O₅ 94% < 98% of high quality) and high acid leaching [11]. Direct acid leaching method without roasting attracted more attention as it has no exhaust gas generation, but it also has the problems of low leaching efficiency (74%) of vanadium and usage of excess leaching agent [12].

Based on the abovementioned background, a novel process for extracting vanadium, titanium, and iron from vanadium-bearing titanomagnetite concentrate was developed. The proposed new process involves three parts: (1) pre-extracting vanadium from vanadium-bearing resources by additive-free roasting under the air atmosphere and alkaline-pressure leaching technologies; (2) reducing the vanadium-free pellets after roasting for producing direct reduction iron (DRI); (3) separating the DRI from titano-rich slag, which can be used as the alternative of raw material for the production of titanium oxide or titanium smelting process. The advantages of this process are that it is possible to utilize vanadium-bearing resources rationally and recover vanadium, iron, and titanium efficiently; moreover, it is a simple, relatively fast, semi-continuous, easy to scale-up, and environmental-friendly process because it has no additive usage compared with the traditional process. Thus, it is beneficial to achieving sustainable development. This paper focuses on discussing the transformation of vanadium-bearing titanomagnetite concentrate in the roasting process.

2. Thermodynamic Criteria for Roasting

Usually, V as the form of V(III) solutes into iron oxide in the form of isomorphism instead of Fe(III) in Fe₃O₄ because the radius of V(III) is close to the radius of Fe(III) ($R_{V(III)} = 0.65 \text{ Å} \approx R_{Fe(III)} = 0.67 \text{ Å}$), vanadium in the ore or slag is therefore considered as the form of vanadium-iron spinel (FeV₂O₄ or FeO·V₂O₃) [28,29]. Furthermore, it is noted that the suboxide of vanadium (V(III), V(IV)) is hardly soluble into acid, neutral or alkaline solutions [30], therefore, it is required to change the suboxide (V(III), V(IV)) into V(V), which is soluble in alkaline solutions, in order to extract vanadium from the ore. Therefore, the reactions in the roasting, which are essential to vanadium extraction, are discussed from thermodynamic viewpoints.

While discussing the thermodynamic properties of the Fe-Ti-V-O system at elevated temperatures, it is essential to consider the existence of complex oxides, such as $FeTi_xO_y$, and FeV_xO_y . The Gibbs energy changes of the following reactions are not large compared to those of the redox reactions in the related systems as shown in Figure 1 [31].

$$FeO (s) + TiO_2 (s) = FeTiO_3 (s)$$

$$\Delta G^{\circ}_r = -10.987 \text{ kJ/mol at } 1100 \text{ K}$$
(1)

FeO (s) + V₂O₃ (s) = FeV₂O₄ (s)

$$\Delta G^{\circ}_{r} = -13.204 \text{ kJ/mol at } 1100 \text{ K}$$
(2)

Furthermore, when the activity of FeO_x decreases due to the formation of complex oxides, the activity of TiO₂ and V₂O₃ decreases by almost the same magnitude. In order to facilitate a simple discussion, FeTi_xO_y and FeV_xO_y are therefore considered to be the mixtures of TiO_x + FeO_x and VO_x + FeO_x respectively and vice versa. In Figure 1, Fe₂TiO₅ (Fe₂O₃·TiO₂) and Fe₂V₂O₈ (Fe₂O₃·V₂O₅) are considered to be the mixtures of TiO₂ + Fe₂O₃ and V₂O₅ + Fe₂O₃ respectively.

Figure 1 shows the relationship between standard Gibbs free energy of some Reactions (3)–(8) [31,32] listed below and temperature. As shown in Figure 1, ΔG° of oxidation Reactions (3)–(8) [31,32] over

the range of 327–1327 °C (600–1600 K) are lower than zero and the oxidation reactions are spontaneous from left to right. When the temperature is higher than 861 °C ($T_{\text{Cross}} = 1134$ K, the temperature at black cross point in Figure 1), vanadium-iron spinel phase (FeV₂O₄) can be oxidized more easily than magnetite (Fe₃O₄) from the view of thermodynamic analysis. Thus, the experiment temperature is set at 800 °C or higher in this study in order to ensure all the suboxide of vanadium (mainly V₂O₃) can be oxidized into V₂O₅, which can be dissolved easier than V₂O₃ into alkaline solution.

$$4Fe_{3}O_{4}(s) + O_{2}(g) = 6Fe_{2}O_{3}(s)$$
(3)

$$V_2O_3(s) + O_2(g) = V_2O_5(s), T < 943$$
 K (4)

$$V_2O_3(s) + O_2(g) = V_2O_5(l), T > 943 K$$
 (5)

$$2/3FeV_2O_4(s) + 2/3FeO(s) + O_2 = 2/3Fe_2V_2O_8(s), T < 1113 K$$
(6)

$$2/3\text{FeV}_2\text{O}_4(s) + 2/3\text{FeO}(s) + \text{O}_2 = 2/3\text{Fe}_2\text{O}_3(s) + 2/3\text{V}_2\text{O}_5(l), T > 1113 \text{ K}$$
 (7)

$$2FeTiO_3(s) + 2FeO(s) + O_2(g) = 2Fe_2TiO_5(s)$$
 (8)



Figure 1. Standard Gibbs free energy diagram of some reactions. Reproduced with permission from [31], Copyright © 1995 VCH Verlagsgesellschaft mbH.

3. Materials and Methods

3.1. Raw Materials

Vanadium-bearing titanomaginetite concentrate used as the raw material in this study is provided from a steel factory of China and its composition by X-ray fluorescence spectrometry analysis (XRF, Rigaku ZSX Primus II) is shown in Table 1. As shown in Table 1, contents of vanadium and calcium in the ore are low. Low CaO is beneficial to the leaching of vanadium because calcium vanadate (xCaO·V₂O₅, x = 1, 2, 3) would be generated via the reaction of CaO with V₂O₅ and it is water-insoluble [30,33] which leads to a reduction in vanadium extraction.

Composition	Fe ₂ O ₃	TiO ₂	Al_2O_3	SiO ₂	MgO	CaO	V_2O_5	MnO	Sum
Content (%)	72.55	12.68	4.66	3.82	3.26	0.96	0.75	0.64	99.51

* Contents of Fe and V in the ore are determined as Fe_2O_3 and V_2O_5 respectively by XRF analysis. Contents of V, TFe, and FeO are 0.414%, 57.39%, and 33.76% respectively by chemical analysis. Sodium hydrate (\geq 96.0%, AR) was used as leaching agent in this study.

3.2. Experimental

Vanadium-bearing titanomagnetite concentrate from the factory cannot be used directly because it is damp. As a result, the ore needs to be dried for a few hours. In a typical experiment, the ground ore $(-74 \ \mu\text{m})$ without free water was subjected to oxidative roasting in air (partial pressure of oxygen is 0.021 MPa (0.21 atm)) without additives in a muffle furnace over the range of 800–1250 °C for 2 h. After roasting, the ore was cooled in the atmosphere and ground into the target particle size ($-74 \ \mu\text{m}$) for leaching or related analyses. The leaching conditions are 250 °C for 4 h in a sealed reactor with high pressure (1.3 MPa) and stirring of 300 r/min, 3:1 of the ratio of liquor to solid, and 100 g/L NaOH as leaching agent. After leaching, the residues are separated from leach liquor with suction device and cleaned with distilled water for three times. Finally, the residues are weighed and subjected to analysis.

Related analyses used in this study are chemical analysis, X-ray fluorescence spectrometry analysis (XRF, Rigaku ZSX Primus II, Rigaku Corporation, Tokyo, Japan), X-ray diffraction (XRD, PANalytical X Pertpro, PANalytical B.V., Almelo, The Netherlands), scanning electron microscopy-energy dispersive spectroscopy analysis (SEM-EDS, Shimadzu SSX-550, Shimadzu Corporation, Tokyo Japan), and thermal gravimetry-differential scanning calorimetry analysis (TG-DSC, Netzsch STA449 F3, Netzsch Group, Selb, Germany).

4. Results and Discussion

4.1. Mineral Analysis

As shown in Figure 2, the phases in the ore are magnetite (Fe_3O_4) and ilmenite ($FeO\cdot TiO_2$), which agrees with the analysis in Table 2. Other compositions cannot be found in the XRD pattern due to their low contents. Figure 3a shows that there are three different regions (point 1: white region, point 2: light grey region, and point 3: grey region). It is found that the compositions by EDS analyses in the ore are iron and titanium oxides (points 1 and 2 in Figure 3a) as shown in Figure 3b,c, vanadium oxides associated with iron and titanium oxides (point 1 in Figure 3a) as shown in Figure 3a, and magnesium, aluminum, and silicon oxides (point 3 in Figure 3a) as shown in Figure 3d. The EDS results agree with XRF analysis in Table 2 and XRD analysis in Figure 2.



Figure 2. XRD pattern of vanadium-bearing titanomagnetite concentrate used in this study.

(b) Fe Point 1 40 30 Counts, Ti 10 v KeV (d) Mg (c) Point 2 Point 3 40 Fe 40 S . 30 30 Counts, Counts, 20 Ti Fe 100 10 Ti 14 12 KeV KeV

Figure 3. SEM micrograph and EDS of vanadium-bearing titanomagnetite concentrate: (**a**) SEM micrograph; (**b**) EDS of Point 1 in Figure 3a; (**c**) EDS of Point 2 in Figure 3a; (**d**) EDS of Point 3 in Figure 3a.

4.2. TG-DSC Analysis

The TG-DSC analysis for vanadium-bearing titanomagnetite was conducted in order to investigate the physicochemical behavior during the roasting process. Figure 4 is the TG-DSC analysis of vanadium-bearing titanomagnetite under the air atmosphere.



Figure 4. TG-DSC analysis of vanadium-bearing titanomagnetite concentrate.

There are two stages of weight loss (stage 1 and stage 4), one stage of no change in weight (stage 2), and one stage of weight increase (stage 3) as shown in Figure 4. Weight change in TG is -1.1% from room temperature to 140 °C. Corresponding to the stage 1 of TG, an endothermic peak in DSC appears

and is caused by the evaporation of absorbed water (mass loss) in the ore. From 140 °C to 320 °C (stage 2), escape of crystal water accompanying mass loss and endothermic process and the oxidation of some oxides accompanying mass increase and exothermic process happened. Therefore, TG-DSC shows no change in weight and endothermic process due to the coupling effect of evaporation of crystal water (mass loss) and the oxidation of some low valent oxides, such as the oxides of V(III), Fe(II), Mn(II), in the ore (mass increase). Weight change in TG is +2.2% at the stage 3 from 320 °C to 920 °C. There is an exothermic trough corresponding to the stage 3, which is caused by the oxidation of suboxide, such as Fe(II) or V(III), in the ore. Weight change in TG is -1.8% at the stage 4 from 920 °C to 1200 °C and there is an endothermic peak corresponding to the stage 4, which is considered as the contribution of the mineral melt, the evaporation of liquid, such as V₂O₅ with low melting temperature ($T_{\text{Met.}} = 670$ °C = 943 K [31]) and V₂O₅-Fe₂O₃ binary system (mol fraction of Fe₂O₃ < 0.5) with low liquidus temperature [32], and the decomposition of high valent manganese oxide (such as MnO₂) with the following Reaction (9) [31,34,35].

$$4MnO_{2} (s) = 2Mn_{2}O_{3} (s) + O_{2} (g)$$

$$T_{Dec.} = 460 \ ^{\circ}C, \ T_{Boi.} = 550 \ ^{\circ}C;$$

$$\Delta G^{\circ}{}_{r} = -74.028 \ \text{kJ/mol}, \ \Delta G^{\circ}{}_{r} = -75.890 \ \text{kJ/mol} \ \text{at } 1100 \ \text{K} \ (\text{Extrapolated data});$$

$$\Delta H^{\circ}{}_{r} = 149.026 \ \text{kJ/mol}, \ \Delta H^{\circ}{}_{r} = 166.00 \ \text{kJ/mol} \ \text{at } 1100 \ \text{K} \ (\text{Extrapolated data});$$
(9)

4.3. Vanadium Loss and Vanadium Leaching Efficiency

As the abovementioned analyses, roasting temperature is important for the interaction reactions among the compounds in the ore and transformation process in roasting is significant for the vanadium leaching efficiency in the subsequent leaching process. In order to clear the transformation of vanadium-bearing titanomagnetite concentrate in the roasting, the experimental conditions in this study are set at 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, or 1250 °C of roasting temperature respectively, 2 h of roasting time, $-74 \mu m$ of particle size, 250 °C of leaching temperature with high pressure of 1.3 MPa, 4 h of leaching time, 3:1 of the ratio of liquor to solid, and 100 g/L NaOH as leaching agent.

Vanadium compounds will evaporate at elevated temperature and this will cause a loss of vanadium, mass change -1.8%, as shown in Figure 4 and reduce the recovery ratio of vanadium. Therefore, vanadium loss defined as Formula (10) is related to roasting temperature.

$$\eta = (1 - \frac{m_2 \beta}{m_1 \alpha}) \times 100\% \tag{10}$$

where η —vanadium loss, %; m_1 —mass of the sample before roasting, g; m_2 —mass of the sample after roasting, g; α —vanadium content in the sample before roasting, %; β —vanadium content in the sample after roasting, %.

The detail data on masses and vanadium contents of the samples before and after roasting for calculating vanadium loss are shown in Table 2. Figure 5 shows the relationship of vanadium loss with roasting temperature. As shown in Figure 5, vanadium loss is not high and lower than 20% in general. Vanadium loss increases with the increase of temperature because the evaporation of vanadium compounds at elevated temperature is high. The trend of increase of vanadium loss is obvious when roasting temperature is higher than 1000 °C, which is in agreement with the TG-DSC analysis. Therefore, roasting of the ore is necessary and low roasting temperature is required for reducing vanadium loss to satisfy the high demand.

Leaching efficiency was introduced as an index for evaluating the roasting and leaching processes and defined as Formula (11), which indicates that higher conversion ratio of V(III) into V(V) leads to higher vanadium leaching efficiency and vice versa when leaching conditions are same.

$$\gamma = \left(1 - \frac{m_4 \varphi}{m_3 \psi}\right) \times 100\% \tag{11}$$

where γ —vanadium leaching efficiency, %; m_3 —mass of sample before leaching, g; m_4 —mass of residue after leaching, g; ψ —vanadium content in the sample before leaching, %; φ —vanadium content of residue after leaching, %.



Figure 5. Effect of roasting temperature on vanadium loss.

Table 2. Masses and vanadium contents of the samples before and after roasting and vanadium loss. Roasting time: 2 h, particle size: -74μ m of particle size, atmosphere: air.

$T_{\rm roa.}$ (°C)	<i>m</i> ₁ (g)	α (%)	<i>m</i> ₂ (g)	β (%)	η (%)
800	75.14	0.414	75.89	0.398	2.9
900	75.36	0.414	76.88	0.387	4.6
1000	75.10	0.414	75.89	0.378	7.7
1100	75.21	0.414	74.18	0.367	12.6
1200	75.16	0.414	73.16	0.353	17.0
1250	75.25	0.414	72.17	0.339	21.5

The detail data on masses and vanadium contents of the samples before and after leaching for calculating vanadium leaching efficiency are shown in Table 3. Figure 6 shows the relationship of vanadium leaching efficiency with roasting temperature. As shown in Figure 6, vanadium leaching efficiency increases with the increase of temperature, when roasting temperature is lower than 1200 °C. This indicates that conversion ratio of V(III) into V(V) increases with the increase of temperature when the roasting temperature is lower than 1200 °C. The vanadium leaching efficiency is 59.1% at 1200 °C for 2 h under the air atmosphere (particle size: -74μ m) and it indicates that the novel process is feasible. However, the vanadium leaching efficiency decreases when the roasting temperature is above 1200 °C. The reason for the reduction in leaching efficiency at 1250 °C of roasting temperature will be discussed by XRD and SEM-EDS analyses at subsequent discussion on transformation of vanadium-bearing titanomagnetite in roasting.

Table 3. Masses and vanadium contents of the samples before and after leaching and vanadium leaching efficiency. Leaching temperature: 250 °C, pressure: 1.3 MPa, leaching time: 4 h, the ratio of liquor to solid: 3:1, leaching agent: 100 g/L NaOH.

$T_{\rm roa.}$ (°C)	<i>m</i> ₃ (g)	ψ (%)	<i>m</i> ₄ (g)	φ (%)	γ (%)
800	150	0.395	147.803	0.272	32.1
900	150	0.387	147.207	0.249	36.9
1000	150	0.375	147.113	0.209	45.3
1100	150	0.361	146.562	0.186	49.7
1200	150	0.355	146.121	0.149	59.1
1250	150	0.337	146.891	0.148	57.0



Figure 6. Effect of roasting temperature on vanadium leaching efficiency.

4.4. Transformation Reactions Analyses in Roasting

In order to clear the transformation reactions, the samples before and after roasting were analyzed by XRD, as shown in Figure 7. Fe₂O₃ and Fe₂TiO₅ (Fe₂O₃·TiO₂) were detected in the samples after roasting, which is attributed that Fe₃O₄ and FeTiO₃ (FeO·TiO₂) were oxidized respectively in the atmosphere as shown by the Reactions (3) and (8) [31] in Figure 1. Figure 7 shows that there was a little Fe₃O₄ in the sample due to its inadequate oxidation at 800 °C (Figure 7b), but all of Fe(II) were oxidized into Fe(III) (Fe₂O₃) at 1000 °C or higher temperature (Figure 7c–e). Furthermore, it is found that there was no vanadium oxide in Figure 7 because the amounts of vanadium oxides, usually considered as the form of FeO·V₂O₃, in the ores are small (<0.8%). However, the oxidizations of V₂O₃ (Reaction (12) [31]) and FeO·V₂O₃ (Reaction (13) [31]) is easier than that of Fe₃O₄ (Reaction (14) [31]) based on thermodynamic analysis (shown in Figure 1 and listed below) when the roasting temperature is higher than 1134 K, so oxidization of V₂O₃ would happen during the roasting experiment if there were Fe₂O₃ in the ore, i.e., Reactions (12) and (13) [31] would happen in the roasting, although the related compounds (V₂O₅) were not found in Figure 7.

$$V_2O_3 (s) + O_2 (g) = V_2O_5 (l)$$

 $\Delta G^{\circ}_r = -137.521 \text{ kJ/mol } O_2 \text{ at } 1300 \text{ K}$
(12)

$$2/3\text{FeO} \cdot \text{V}_2\text{O}_3 \text{ (s)} + 2/3\text{FeO} \text{ (s)} + \text{O}_2 \text{ (g)} = 2/3\text{Fe}_2\text{O}_3 \text{ (s)} + 2/3\text{V}_2\text{O}_5 \text{ (l)}$$

$$\Delta G^\circ_r = -156.521 \text{ kJ/mol O}_2 \text{ at } 1300 \text{ K}$$
(13)

$$4Fe_3O_4 (s) + O_2 (g) = 6Fe_2O_3 (s)$$

$$\Delta G^{\circ}_r = -108.968 \text{ kJ/mol } O_2 \text{ at } 1300 \text{ K}$$
(14)

The samples before and after roasting were subjected to SEM-EDS analysis. Figure 8 shows microphotographs of the samples before and after experiments at different roasting temperatures. As shown in Figure 8a,b, there were no obvious changes for the samples before and after experiments at 800 °C. However, some solids react at low temperature, according to Reactions (3)–(8) [31,32] as evident from Figure 1, and crystal bridges, which can connect the neighboring particles with different compositions together, are generated between the solid compositions at lower temperature. Melting on the surface of particles happened when roasting temperature is higher than 1000 °C (Figure 8c,d), which is endothermic and agrees with the results of TG-DSC (Figure 4). Figure 8d shows that melting of the ore particle was more obvious and ore particles become bigger at 1200 °C than those in Figure 8c at 1000 °C. The melting on the surface is considered that compounds with low melting temperature, such as vanadium pentaoxide (V₂O₅, $T_{Mel.} = 670$ °C [31,32]), iron cordierite (Fe₂Al₄Si₅O₁₈, $T_{Mel.} = 1083$ °C [32]) and fayalite (Fe₂SiO₄, $T_{Mel.} = 1205$ °C [32]), were generated at low temperature as shown by Reactions (15) [31], (16) [31,32], (18) [32], and (19) [31] respectively and melt

at elevated temperature. In addition, liquids would be generated because some chemical reactions or phase transformation reaction happened at elevated temperature as shown by Reactions (17) [31,32] and (20) [32]. Furthermore, the addition of other components can decrease the liquidus temperature of mixtures to some extent. For example, the liquidus temperature of mixture of $(Fe_2SiO_4 + Al_2O_3)$ with a composition near to Fe_2SiO_4 is lower than 1205 °C, the melting temperature of Fe_2SiO_4 , based on the phase diagram analysis. Although there is no ΔG°_{r} data on Reaction (18) for justifying the reaction, FeO-SiO₂-Al₂O₃ ternary phase diagram [32] and Figure 9 both show that there is $Fe_2Al_4Si_5O_{18}$ in the system, which indicates that Reaction (18) [32] would happen in the roasting. Therefore, main phases of Fe₂O₃ and Fe₂TiO₅ were connected and sintered with crystal bridges and the binding phases of the compounds with low melting temperature. In fact, the generation of the compounds with low melting temperature is beneficial to the oxidation of V(III) into V(V) because vanadium oxide and oxygen transport easily in liquid. This is also the reason that high temperature roasting is in favor of the vanadium extraction, i.e., conversion ratio of V(III) into V(V) increases with the increase of temperature which finally leads to the increase of vanadium leaching efficiency as shown in Figure 6. Another reason why high temperature is beneficial to vanadium extraction is the decomposition of complex compounds at elevated temperature and recrystallization at low temperature, after breaking the structure of vanadium spinel.

$$V_2O_3(s) + O_2(g) = V_2O_5(s)$$

 $\Delta G^\circ_r = -178.176 \text{ kJ/mol } O_2 \text{ at } 900 \text{ K}$
(15)

$$2/3\text{FeV}_2\text{O}_4 (s) + 2/3\text{FeO} (s) + \text{O}_2 (g) = 2/3\text{Fe}_2\text{V}_2\text{O}_8 (s), T < 1113 \text{ K} (840 \,^\circ\text{C})$$

$$\Delta G^\circ_r = -215.877 \text{ kJ/mol O}_2 \text{ at } 900 \text{ K}, \Delta G^\circ_r = -184.979 \text{ kJ/mol O}_2 \text{ at } 1100 \text{ K}$$
(16)

$$2/3\text{FeV}_2\text{O}_4 (s) + 2/3\text{FeO} (s) + \text{O}_2 (g) = 2/3\text{Fe}_2\text{O}_3 (s) + 2/3\text{V}_2\text{O}_5 (l), T > 1113 \text{ K} (840 \ ^\circ\text{C})$$

$$\Delta G^\circ_r = -128.231 \text{ kJ/mol O}_2 \text{ at } 1300 \text{ K}$$
(17)

$$2\text{FeO}(s) + 5\text{SiO}_2(s) + 2\text{Al}_2\text{O}_3(s) = \text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}(l), T > 1356 \text{ K}(1083 \ ^\circ\text{C})$$
(18)

$$2\text{FeO}(s) + \text{SiO}_2(s) = \text{Fe}_2\text{SiO}_4(s)$$

$$\Delta G^\circ_r = -6.221 \text{ kJ/mol at 900 K}, \Delta G^\circ_r = -1.044 \text{ kJ/mol at 1100 K}$$
(19)

$$Fe_2V_2O_4 (s) \rightarrow Fe_2O_3 (s) + liquid (Fe_2O_3 + V_2O_5) at T_{Dec.} = 1113 \text{ K} (840 \,^{\circ}\text{C})$$
 (20)



Figure 7. XRD patterns of vanadium-bearing titanomagnetite concentrate before and after roasting (roasting time: 2 h; atmosphere: air): (**a**) Concentrate; (**b**) 800 °C; (**c**) 1000 °C; (**d**) 1200 °C; (**e**) 1250 °C.



Figure 8. Changes of concentrate appearances at different roasting temperatures: (**a**) Raw material; (**b**) Sample after roasting at 800 °C; (**c**) Sample after roasting at 1000 °C; (**d**) Sample after roasting at 1200 °C.



Figure 9. SEM micrograph and EDS of the roasted product at 1250 °C: (**a**) SEM micrograph; (**b**) EDS of Point 1 in Figure 9a; (**c**) EDS of Point 2 in Figure 9a; (**d**) EDS of Point 3 in Figure 9a.

It is noted that over high temperature (>1200 $^{\circ}$ C) can cause a decrease in the vanadium leaching efficiency as shown in Figure 6. This result can be explained using the SEM-EDS analysis of the roasted product at 1250 $^{\circ}$ C shown in Figure 9.

Figure 9a shows that sinter of the ore particle is significant and there are some of white aggregations on the surface of the ore particle, which is called as over-burning. Based on the analysis of EDS (Figure 9b), the white aggregations are the complex compounds of Fe, Ti, V, and O. The particle size is larger than the original size because high temperature would accelerate the melting, aggregation,

and sinter of silicate which causes some of the vanadium wrapped by molten silicate, called a silicate network, prevents the conversion of V(III) into V(V), and finally decreases the vanadium leaching efficiency. Figure 9c,d indicate that the complex compounds of Fe, Si, Mg, Al, and O are generated and it agrees with the Reaction (18) and FeO-SiO₂-Al₂O₃ ternary phase diagram [32].

The schematic diagrams of transformation behavior of the samples are shown in Figure 10. Figure 10a is the schematic diagram for Figure 8a in which the outline of the samples before roasting is straight and sharp. Figure 10b is for Figure 8b–d in which the crystal bridges obtained by the reactions among solid compounds and some of binding phases generated connect the neighboring particles and thus the outline become blunt. Figure 10c is the equivalent for Figure 9a.



Figure 10. The schematic diagrams of phase transformation behavior of the samples: (**a**) A particle before roasting; (**b**) A particle after roasting (800–1200 $^{\circ}$ C); (**c**) Aggregation and sinter of two particles after roasting (1250 $^{\circ}$ C).

Based on the abovementioned analyses, the proposed process by additive-free roasting-alkaline leaching is successful. The roasting of the ore is necessary for improving the leaching efficiency and roasting at 1200 °C for 2 h under the air atmosphere is appropriate to minimize vanadium loss and reduce energy consumption by 3.6% compared with roasting at 1250 °C for 2 h (based on laboratory conditions).

5. Conclusions

Transformation of vanadium-bearing titanomagnetite concentrate in the roasting (over the range of 800–1250 °C) was discussed based on thermodynamic analyses and experimental results. Some conclusions are achieved as follows.

- Thermodynamic analyses show that oxidation of V₂O₃ would happen in the roasting experiment over the range of 327–1327 °C and vanadium-iron spinel phase (FeV₂O₄) can be oxidized more easily than magnetite (Fe₃O₄) when the temperature is higher than 861 °C.
- The compounds (V₂O₅, Fe₂Al₄Si₅O₁₈, and Fe₂SiO₄) with low melting temperature were generated at low temperature and melted at elevated temperature; liquids were generated due to some chemical reactions or phase transformation reaction (Fe₂V₂O₄(s) → Fe₂O₃(s) + liquid) happened at elevated temperature; main phases of Fe₂O₃ and Fe₂TiO₅ are connected and sintered with the binding phases of the compounds with low melting temperature or the mixtures with low liquidus temperature.
- Higher roasting temperature is beneficial for improving the vanadium leaching efficiency. However, over-burning causes some vanadium oxide wrapped by silicate network and reductions in the vanadium leaching efficiency from 59.1% at $T_{roa.} = 1200 \degree C$ to 57% at $T_{roa.} = 1250 \degree C$ (250 °C of leaching temperature with high pressure of 1.3 MPa, 4 h of leaching time, 3:1 of the ratio of liquor to solid, and 100 g/L NaOH as leaching agent).

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