

## $\varphi$ -pH diagram of V–Ti–H<sub>2</sub>O system during pressure acid leaching of converter slag containing vanadium and titanium

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**Abstract:** To analyze the thermodynamic characteristics of leaching process of converter slag,  $\varphi$ -pH diagram of V–Ti–H<sub>2</sub>O system at oxygen partial pressure of 0.5 MPa, ionic mass concentration of 0.1 mol/kg and temperatures ranging from 60 to 200 °C was obtained by recently published critically assessed standard Gibbs energies and activity coefficients of various species. When pH<2, stable regions of V<sup>3+</sup>, VO<sup>2+</sup> and VO<sub>2</sub><sup>+</sup> exist in the stable region of TiO<sub>2</sub>. The pH values of stable regions of vanadium and titanium decrease and redox potentials become more positive with the temperature increasing. Vanadium and titanium could be separated by one-step leaching based on thermodynamics. The experiment results of pressure acid leaching of converter slag show that leaching rates of vanadium and titanium are 96.87% and 8.76% respectively, at 140 °C of temperature, 0.5 MPa of oxygen partial pressure, 0.055–0.075 mm of particle size, 15:1 of liquid to solid ratio, 120 min of leaching time, 500 r/min of stirring speed and 200 g/L of initial acid concentration. Vanadium and titanium could be selectively separated in the pressure acid leaching process, and the experiment result is in agreement with thermodynamic calculation result.

**Key words:**  $\varphi$ -pH diagram; V–Ti–H<sub>2</sub>O system; pressure acid leaching; converter slag; vanadium; titanium

## 1 Introduction

Vanadium is an important product which is used almost exclusively in ferrous and non-ferrous alloys due to its physical properties such as high hardness, large tensile strength, and good fatigue resistance. The vanadium ends up normally in the converter steel slag containing 3%–10% vanadium, which is the world's principal raw material for vanadium production [1–2].

Vanadium-bearing converter slag is treated by several methods, such as sodium salt roasting-low acidity leaching [3] or water leaching [4], oxidizing roasting-alkaline leaching [5] or low acidity leaching [6], calcium salt roasting-acidity leaching [7] or alkaline leaching [8]. Traditional roasting-leaching process has two main disadvantages: low recovering rate of vanadium and severe impact on the environment [9–10]. Pressure acid leaching process, which cancels the roasting step, is used to extract vanadium from converter slag in an environmental and economical way.

Thermodynamic diagrams provide a rapid and reliable method for visual assessment of equilibrium behavior and reaction feasibility [11].  $\varphi$ -pH diagram of V–H<sub>2</sub>O system is mainly reported at atmospheric pressure and normal temperature (25 °C, 0.1 MPa) at present [12]. At the mean time,  $\varphi$ -pH diagram of Ti–H<sub>2</sub>O system has been reported at elevated temperature [13], but it is a single system and V–Ti–H<sub>2</sub>O system described for pressure leaching process of converter slag has never been covered. Variation tendency of stable regions of dissolved ionics of vanadium and titanium has the originally thermodynamic guidance on experiment process.

## 2 Thermodynamics

### 2.1 Method

A brief method for construction of  $\varphi$ -pH diagram, which could be constructed from the stoichiometry of reactions and free energy data for the species involved. Either the van't Hoff isotherm or Nernst equation was

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utilized for the determination of the equilibrium lines of reactions.

The calculation required to obtain the  $\varphi$ -pH diagram was based upon the general equilibrium equations for an aqueous system containing vanadium and titanium. The basic equation of reactions was shown as formula (1),  $\varphi_T$  and pH for this equation could be calculated as formulas (2) and (3):



$$\varphi_T = \varphi_T^\Theta - 2.303(RTn/ZF)pH - 2.303[RT/(ZF)]\lg[\alpha_{B_a}^b / \alpha_{A_b}^a] \quad (2)$$

$$pH = pH^\Theta - 1/n \ln \alpha_{B_a}^b / \alpha_{A_b}^a \quad (3)$$

Values of  $\varphi_T^\Theta$  were determined according to Nernst equation,  $\varphi$ -pH diagram was obtained based on formulas (2) and (3) sequentially, and free energy data of high temperature were required by formula (4) [14]. Values of  $A$ ,  $D$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$  and free energy at 298 K could be required from Refs. [12–13, 15].

$$\Delta G_T^\Theta = \Delta G_{298}^\Theta + \alpha \Delta S_{298}^\Theta - \beta + \gamma Z \quad (4)$$

$$\alpha = (T - 298) \times \left[ 0.00224 \times \left( T - \frac{T - 298}{\ln(T/298)} \right) - 1 \right]$$

$$\beta = \left[ T - \frac{(T - 298)}{\ln(T/298)} \right] \times (T - 298) \times A$$

$$\gamma = \left[ T - \frac{(T - 298)}{\ln(T/298)} \right] \times (T - 298) \times D$$

Average activity coefficients of electrolyte changed with temperature variation. According to Ref. [16], Debye–Hückel equation, as formula (5), was used to estimate average activity coefficient at high temperature, where  $\gamma_\pm$  is average activity coefficient of electrolyte in the solution (calculated by the form of mass concentration),  $I$  is ionic strength which could be calculated as formula (6),  $A_T$  is a constant which changed with temperature increasing (see Table 1),  $z_+$  and  $z_-$  are number of positive and negative ion, respectively.

$$\lg \gamma_{\pm m(T)} = \lg \gamma_{\pm m(25)} - |z_+ z_-| \frac{\sqrt{I}}{1 + \sqrt{I}} (A_T - A_{25}) \quad (5)$$

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (6)$$

**Table 1**  $A_T$  values at different temperatures

T/K	298	333	373	423	473	573
$A_T$	0.511	0.545	0.595	0.689	0.809	1.983

In this work, Davids equation was used to calculate the average activity coefficient of electrolyte at 25 °C, shown as formula (7). This equation, with average error

of 1.6%, is the widely used method [17].

$$\lg \gamma_\pm = -0.50 |z_+ z_-| \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30I \right) \quad (7)$$

## 2.2 $\varphi$ -pH diagram of V–H<sub>2</sub>O system

According to the thermodynamic data in Refs. [12–13, 15],  $G_T^\Theta$  of substance in V–H<sub>2</sub>O system could be calculated as formula (3) at 25, 60, 100, 150 and 200 °C, then  $\Delta G_T^\Theta$  of different reactions could be obtained according to  $\Delta G_T^\Theta = \sum G_{T,p}^\Theta - \sum G_{T,R}^\Theta$ . Values of  $\varphi^\Theta$  and pH<sup>Θ</sup> at different temperatures are listed in Tables 2–3. The activity coefficients of substance in V–H<sub>2</sub>O system at different temperatures are listed in Table 4.

$$\Delta G^\Theta = -ZF\varphi^\Theta \quad (8)$$

$$pH^\Theta = -\frac{\Delta G^\Theta}{2.303nRT} \quad (9)$$

Due to the different types of reaction in V–H<sub>2</sub>O system, the expressions of  $\varphi$  and pH were calculated by formula (2) or (3) and then  $\varphi$ -pH diagram of V–H<sub>2</sub>O system (Fig. 1) was realized at oxygen partial pressure of 0.5 MPa, ionic mass concentration of 0.1 mol/kg, and temperatures of 60, 100, 150 and 200 °C.

Vanadium exists as oxides in the stable region of water. V<sup>3+</sup>, VO<sup>2+</sup> and VO<sub>2</sub><sup>+</sup> exist in the acid solution of pH<2, HVO<sub>4</sub><sup>2-</sup>, HV<sub>2</sub>O<sub>5</sub><sup>-</sup> and VO<sub>4</sub><sup>3-</sup> exist in the alkaline solution of pH>8. The stable regions approved the feasibility of acid/alkali leaching of converter slag.

Thermodynamics of pressure acid leaching of converter slag were studied, the variation condition of soluble vanadium ionic at the acid situation was the main object of investigation.  $\varphi^\Theta$  of V<sup>3+</sup>, which is -0.211 V at 60 °C, becomes more negative with increasing temperature to -0.062 1 V at 200 °C. pH<sup>Θ</sup> values of stable regions of V<sup>3+</sup>, VO<sup>2+</sup> and VO<sub>2</sub><sup>+</sup> composed of reactions 19, 20 and 22 decrease from 1.64, 1.615 and -1.030 to 0.198, 0.283 and -1.606, respectively. Based on thermodynamic principle, increasing temperature is adverse for the leaching process, redox potentials and initial acid concentration need to be much higher. Consequently, it is possibly due to the kinetic control, the experiment needs to proceed at high temperature to ensure a rapidly leaching speed.

## 2.3 $\varphi$ -pH diagram of Ti–H<sub>2</sub>O system

The method of drawing  $\varphi$ -pH diagram of Ti–H<sub>2</sub>O system was the same as V–H<sub>2</sub>O system. Values of  $\varphi^\Theta$  and pH<sup>Θ</sup> of Ti–H<sub>2</sub>O system at different temperatures are shown in Tables 5–6, and activity coefficients are listed in Table 7.  $\varphi$ -pH diagram of Ti–H<sub>2</sub>O system (Fig.2) were obtained at oxygen partial pressure of 0.5 MPa, ionic mass concentration of 0.1 mol/kg, and temperatures of 60, 100, 150 and 200 °C.

**Table 2**  $\phi^0$  of reactions in V–H<sub>2</sub>O system at high temperature (V)

No.	Reaction	25 °C	60 °C	100 °C	150 °C	200 °C
1	$V^{2+} + 2e = V$	-1.175	-1.140	-1.106	-1.073	-1.050
2	$VO + 2H^+ + 2e = V + H_2O$	-0.865	-0.848	-0.834	-0.823	-0.826
3	$V^{3+} + e = V^{2+}$	-0.256	-0.211	-0.164	-0.111	-0.0621
4	$V_2O_3 + 6H^+ + 2e = 2V^{2+} + 3H_2O$	0.134	0.114	0.0868	0.0495	-0.00636
5	$V_2O_3 + 2H^+ + 2e = 2VO + H_2O$	-0.486	-0.471	-0.458	-0.450	-0.454
6	$VO^{2+} + 2H^+ + e = V^{3+} + H_2O$	0.438	0.431	0.418	0.393	0.349
7	$V_2O_4 + 2H^+ + 2e = V_2O_3 + H_2O$	0.301	0.319	0.335	0.347	0.346
8	$2VO^{2+} + H_2O + 2e = V_2O_3 + 2H^+$	0.0477	0.106	0.167	0.233	0.293
9	$HV_2O_5^- + 3H^+ + 2e = V_2O_3 + 2H_2O$	0.542	0.597	0.655	0.723	0.777
10	$2VO_4^{3-} + 10H^+ + 4e = V_2O_3 + 6H_2O$	1.366	1.451	1.559	1.704	1.850
11	$V_2O_5 + 6H^+ + 2e = 2VO^{2+} + 3H_2O$	0.958	0.932	0.898	0.850	0.782
12	$VO_2^+ + 2H^+ + e = VO^{2+} + H_2O$	1.002	1.000	0.992	0.972	0.933
13	$V_2O_5 + 2H^+ + 2e = V_2O_4 + H_2O$	0.704	0.718	0.729	0.736	0.729
14	$2HVO_4^{2-} + 6H^+ + 2e = V_2O_4 + 4H_2O$	1.644	1.747	1.878	2.067	2.267
15	$2HVO_4^{2-} + 5H^+ + 2e = HV_2O_5^- + 3H_2O$	1.405	1.470	1.558	1.691	1.836
16	$2VO_4^{3-} + 7H^+ + 2e = HV_2O_5^- + 3H_2O$	2.190	2.308	2.461	2.683	2.921
17	$2HVO_4^{2-} + 8H^+ + 4e = V_2O_3 + 5H_2O$	0.973	1.033	1.107	1.207	1.307
A	$O_2 + 4H^+ + 4e = 2H_2O$	1.228	1.229	1.225	1.211	1.186
B	$2H^+ + 2e = H_2$	0	0.0296	0.0578	0.0848	0.0980

**Table 3** pH<sup>0</sup> of reactions in V–H<sub>2</sub>O system at high temperature

No.	Reaction	25 °C	60 °C	100 °C	150 °C	200 °C
18	$VO + 2H^+ = V^{2+} + H_2O$	5.243	4.422	3.682	2.975	2.387
19	$V_2O_3 + 6H^+ = 2V^{3+} + 3H_2O$	2.200	1.640	1.131	0.636	0.198
20	$V_2O_4 + 4H^+ = 2VO^{2+} + 2H_2O$	2.145	1.615	1.136	0.680	0.283
21	$HV_2O_5^- + H^+ = V_2O_4 + H_2O$	8.139	8.410	8.664	8.961	9.179
22	$V_2O_5 + 2H^+ = 2VO_2^+ + H_2O$	-0.733	-1.030	-1.272	-1.459	-1.606
23	$2HVO_4^{2-} + 4H^+ = V_2O_5 + 3H_2O$	7.949	7.789	7.762	7.930	8.194
24	$VO_4^{3-} + H^+ = HVO_4^{2-}$	13.272	12.692	12.207	11.821	11.552

**Table 4** Activity coefficients of substance in V–H<sub>2</sub>O system at high temperature

Ionic	Ionic strength	25 °C	60 °C	100 °C	150 °C	200 °C
$V^{2+}$	0.4	0.292	0.258	0.216	0.155	0.101
$V^{3+}$	0.75	0.192	0.154	0.112	0.0612	0.0283
$VO^{2+}$	0.4	0.292	0.258	0.216	0.155	0.101
$HV_2O_5^-$	0.1	0.785	0.770	0.749	0.711	0.666
$VO_2^+$	0.15	0.583	0.558	0.524	0.464	0.398
$VO_3^-$	0.1	0.785	0.770	0.749	0.711	0.666
$H_3V_2O_7^-$	0.1	0.785	0.770	0.749	0.711	0.666
$HV_2O_7^{3-}$	0.6	0.412	0.372	0.320	0.241	0.168
$HVO_4^{2-}$	0.3	0.545	0.515	0.475	0.407	0.335
$VO_4^{3-}$	0.6	0.412	0.372	0.320	0.241	0.168

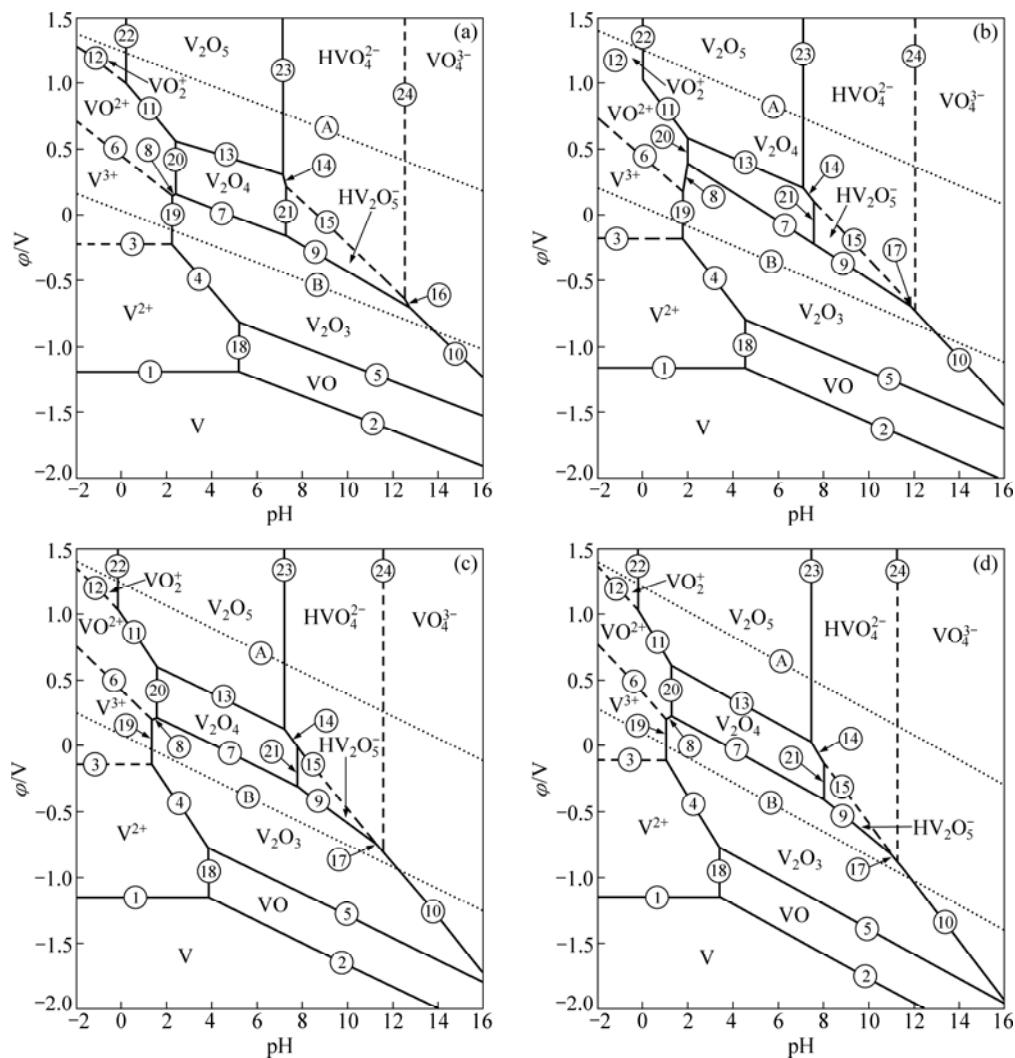


Fig. 1  $\phi$ -pH diagram of V-H<sub>2</sub>O system at different temperatures: (a) 60 °C; (b) 100 °C; (c) 150 °C; (d) 200 °C

Table 5  $\phi^\ominus$  of reactions of Ti-H<sub>2</sub>O system at high temperature (V)

No.	Reaction	25 °C	60 °C	100 °C	150 °C	200 °C
25	TiO+2H <sup>+</sup> +2e=Ti+H <sub>2</sub> O	-1.336	-1.347	-1.360	-1.374	-1.39
26	Ti <sub>2</sub> O <sub>3</sub> +2H <sup>+</sup> +2e=2TiO+H <sub>2</sub> O	-1.073	-1.086	-1.099	-1.116	-1.132
27	2TiO <sub>2</sub> +2H <sup>+</sup> +2e=Ti <sub>2</sub> O <sub>3</sub> +H <sub>2</sub> O	-0.557	-0.572	-0.588	-0.608	-0.624
28	Ti <sup>2+</sup> +2e= Ti	-1.628	-1.636	-1.644	-1.654	-1.658
29	Ti <sub>2</sub> O <sub>3</sub> +6H <sup>+</sup> +2e= 2Ti <sup>2+</sup> +3H <sub>2</sub> O	-0.489	-0.509	-0.531	-0.557	-0.591
30	TiO <sub>2</sub> +4H <sup>+</sup> +2e= Ti <sup>2+</sup> +2H <sub>2</sub> O	-0.523	-0.540	-0.559	-0.582	-0.608
31	TiO <sub>2</sub> +4H <sup>+</sup> +e= Ti <sup>3+</sup> +2H <sub>2</sub> O	-0.324	-0.361	-0.403	-0.454	-0.510
32	Ti <sup>3+</sup> +e= Ti <sup>2+</sup>	-0.357	-0.271	-0.172	-0.049	0.084
33	TiO <sup>2+</sup> +2H <sup>+</sup> +2e= Ti <sup>2+</sup> +H <sub>2</sub> O	-0.135	-0.0889	-0.0395	0.0173	0.0679
34	HTiO <sub>3</sub> <sup>-</sup> +5H <sup>+</sup> +2e =Ti <sup>2+</sup> +3H <sub>2</sub> O	0.362	0.350	0.340	0.334	0.325
35	TiO <sup>2+</sup> +2H <sup>+</sup> +e=Ti <sup>3+</sup> +H <sub>2</sub> O	0.198	0.295	0.394	0.496	0.567
A	O <sub>2</sub> +4H <sup>+</sup> +4e=2H <sub>2</sub> O	1.228	1.229	1.225	1.211	1.186
B	2H <sup>+</sup> +2e=H <sub>2</sub>	0	0.0296	0.0578	0.0848	0.0980

Table 6 pH<sup>⊖</sup> of reactions of Ti-H<sub>2</sub>O system at high temperature

No.	Reaction	25 °C	60 °C	100 °C	150 °C	200 °C
36	TiO+2H <sup>+</sup> = Ti <sup>2+</sup> +H <sub>2</sub> O	4.945	4.365	3.841	3.330	2.880
37	HTiO <sub>3</sub> <sup>-</sup> +H <sup>+</sup> =TiO <sub>2</sub> +H <sub>2</sub> O	29.938	26.968	24.318	21.812	19.885
38	HTiO <sub>3</sub> <sup>-</sup> +3H <sup>+</sup> =TiO <sup>2+</sup> +2H <sub>2</sub> O	5.601	4.432	3.423	2.516	1.829

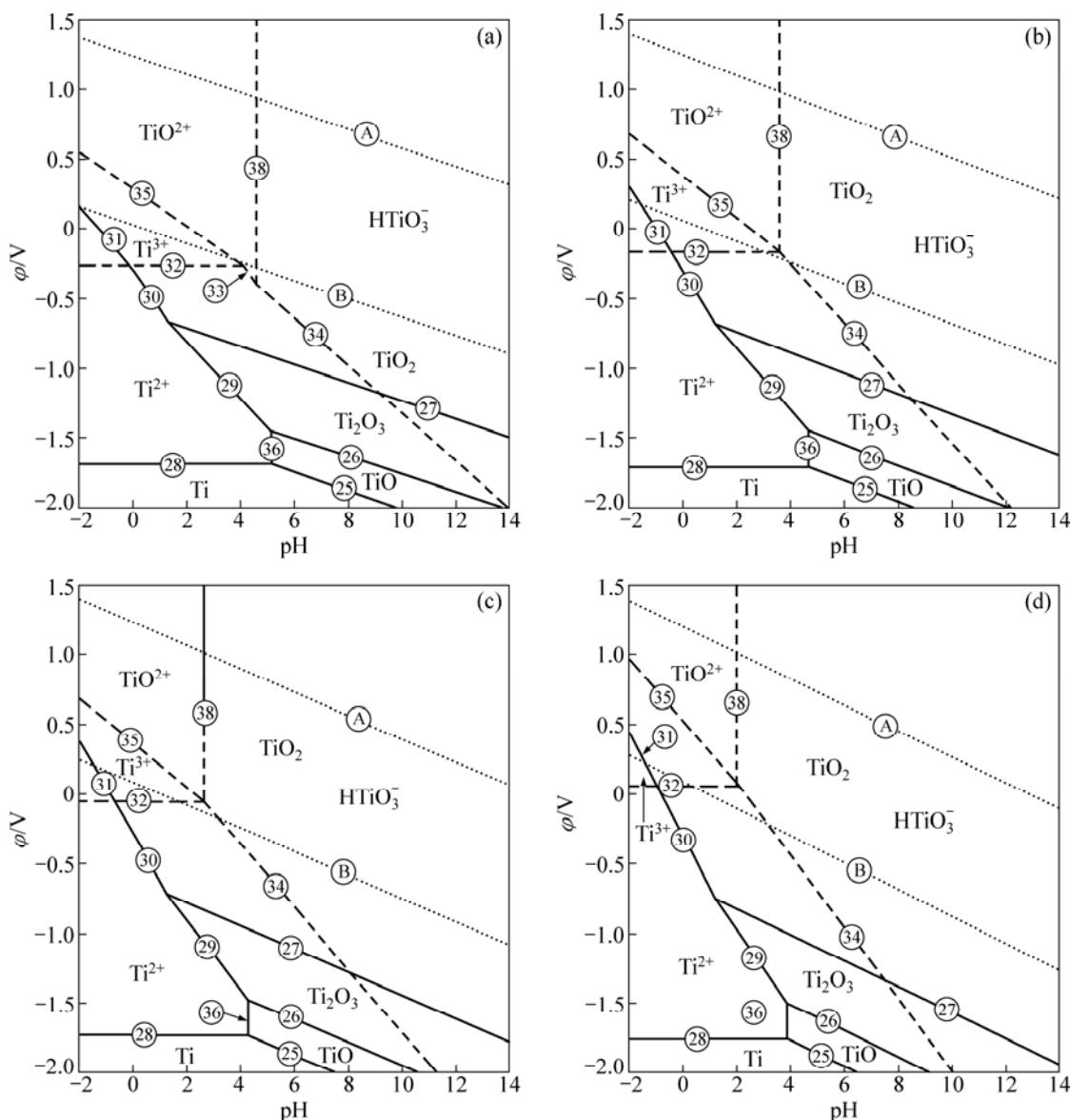
**Table 7** Activity coefficients for substances in Ti–H<sub>2</sub>O system at high temperature

Ionic	Ionic strength	Activity coefficient				
		25 °C	60 °C	100 °C	150 °C	200 °C
Ti <sup>2+</sup>	0.4	0.2918	0.2585	0.2163	0.1546	0.1008
Ti <sup>3+</sup>	1.5	0.4994	0.3856	0.2636	0.1290	0.05178
TiO <sup>2+</sup>	0.4	0.2918	0.2585	0.2163	0.1546	0.1008
HTiO <sub>3</sub> <sup>−</sup>	0.1	0.7850	0.7704	0.7494	0.7114	0.6657

Based on Fig.2, reactions occurring by dissoluble titanium oxides are expressed as solid line, and by soluble titanium ionics are dotted line respectively. Stable regions of TiO<sup>2+</sup> and HTiO<sub>3</sub><sup>−</sup> (formed by dotted line) exist in the stable region of water when only soluble titanium ionics exist in the solution. This is hydrolysis reaction of titanium, which can proceed at low acid

concentration and high temperature, due to the fact that pH values become less positive from 4.432 at 60 °C to 1.829 at 200 °C.

Titanium mainly exists as oxides in the converter, so a stable region of TiO<sub>2</sub> mainly exists in the stable region of water, and regions of ionics dissolved from oxides. For example, Ti<sup>3+</sup> and Ti<sup>2+</sup> are seldom in the region of water. The oxide is thermodynamically stable in almost any noncomplexing aqueous solution from strong acid to strong alkali. Stable region of TiO<sup>2−</sup> exists at pH<2, which is outside the pH range of this study. Thermodynamically, there are only a small amount of Ti<sup>3+</sup> in the leachate but most exist as TiO<sub>2</sub> in the slag during the pressure acid leaching process of converter slag. TiO<sup>2−</sup> would exist at a high acid concentration. Based on thermodynamic principle, titanium can be enriched in the residue as TiO<sub>2</sub>.



**Fig. 2**  $\varphi$ –pH diagram of Ti–H<sub>2</sub>O system at different temperatures: (a) 60 °C; (b) 100 °C; (c) 150 °C; (d) 200 °C

$\varphi^0$  of  $\text{Ti}^{3+}$  dissolved from  $\text{TiO}_2$  is  $-0.271\text{V}$  at  $60\text{ }^\circ\text{C}$  and becomes more positive with increasing temperature to  $0.084\text{ V}$  at  $200\text{ }^\circ\text{C}$ . The area of stable region of  $\text{Ti}^{3+}$ , which entered into stable region of water, enlarges gradually. Based on thermodynamics principle, increasing temperature, which tends to improve  $\text{TiO}_2$  dissolution at the same oxygen partial pressure and acid concentration, is adverse for selective separation of vanadium and titanium. At the same time, the reaction speed and leaching rate of titanium arise with the increasing temperature. Consequently, leaching temperature cannot be too high to keep titanium stable in the residue.

#### 2.4 $\varphi$ -pH diagram of V-Ti-H<sub>2</sub>O system

Due to the  $\varphi$ -pH expressions of V-H<sub>2</sub>O system and Ti-H<sub>2</sub>O system,  $\varphi$ -pH diagram of V-Ti-H<sub>2</sub>O system (Fig. 3) was obtained at the oxygen partial pressure of

0.5 MPa, ionic mass concentration of 0.1 mol/kg, and temperatures of 60, 100, 150 and 200  $^\circ\text{C}$ . The reactions 33, 34, 35 and 38, which were carried out by soluble titanium ionics (stable regions formed by dotted lines) were not contained in Fig. 3 because only titanium oxides exist in the converter slag, but not soluble titanium ionics.

Based on Fig. 3, the stable regions of  $\text{V}^{3+}$ ,  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  are practically contained in that of  $\text{TiO}_2$ , but few coincide with stable regions of  $\text{Ti}^{3+}$  and  $\text{TiO}^{2+}$  at pH<2. Coexistence of stable region shows that pressure acid leaching process could selectively separate vanadium from titanium based on thermodynamic principle.

Redox potentials of stable region of vanadium and titanium become more positive as well as pH values get more negative with temperature increasing from  $60\text{ }^\circ\text{C}$  to  $200\text{ }^\circ\text{C}$ . The acid concentration should be high enough to dissolve vanadium ionics from converter slag, but

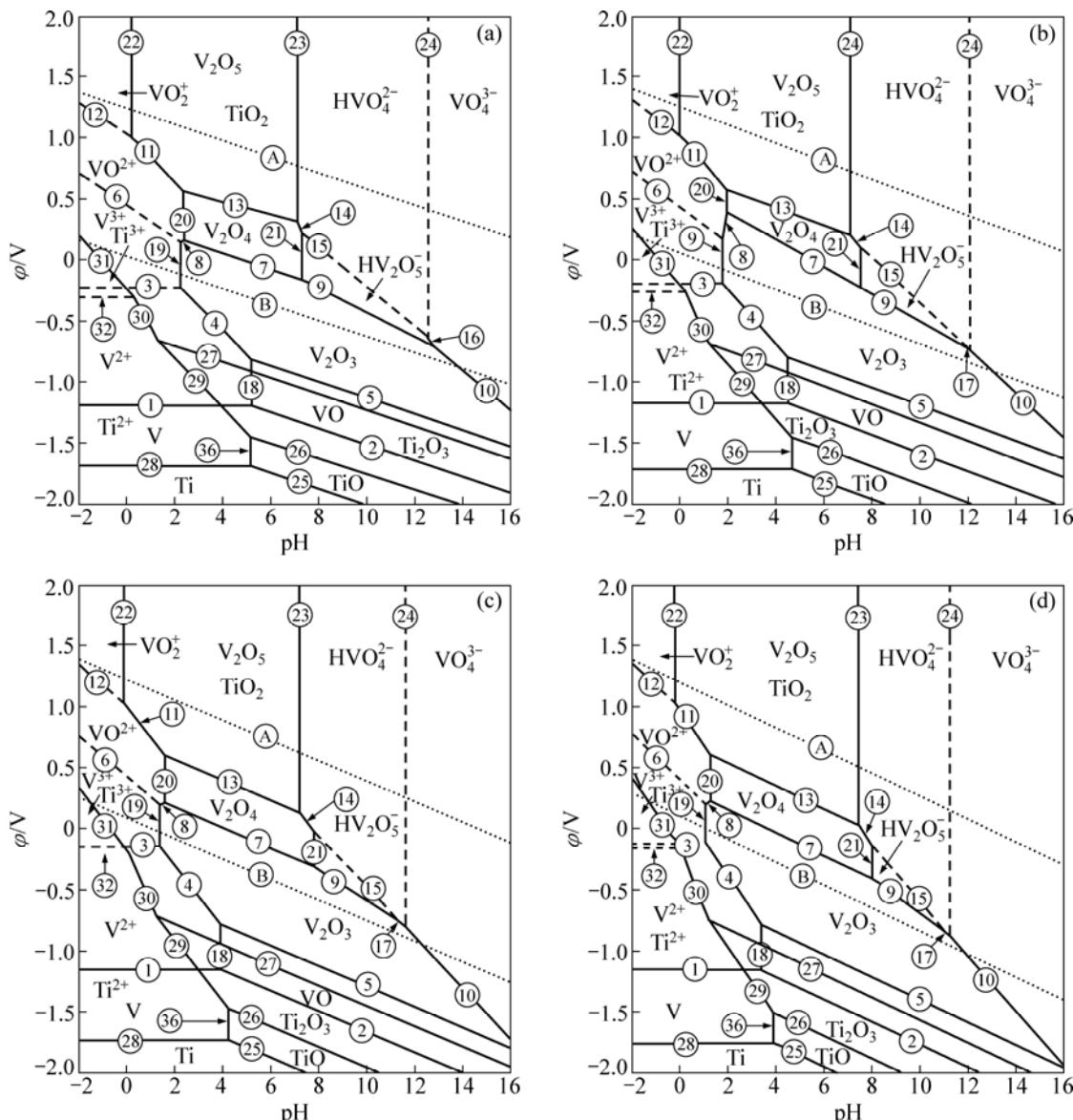


Fig. 3  $\varphi$ -pH diagram of V-Ti-H<sub>2</sub>O system at different temperatures: (a)  $60\text{ }^\circ\text{C}$ ; (b)  $100\text{ }^\circ\text{C}$ ; (c)  $150\text{ }^\circ\text{C}$ ; (d)  $200\text{ }^\circ\text{C}$

titanium would be easy to be dissolved at this condition as well. Some factors, such as acid concentration, oxygen partial pressure and temperature, which control the redox potentials and pH, are used to dissolve vanadium sufficiently and enrich titanium oxides in the residue during the pressure acid leaching process. Coexisting characteristics of stable region of vanadium and titanium would be stable with temperature increasing from 60 °C to 200 °C.

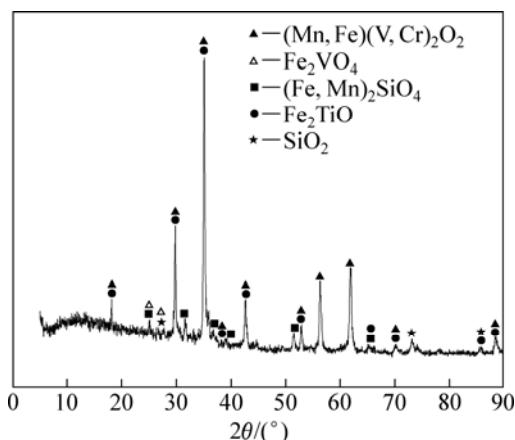
### 3 Experimental

#### 3.1 Materials

The converter slag containing vanadium and titanium was from Panzhihua of Sichuan province, China. Mineralogical and chemical analyses of the sample were carried out using X-ray diffractometer (XRD, model PW3040/60, Netherland) and X-ray fluorescence spectroscope (XRF, model ZSX100e, Japan). The XRD pattern of the mineral sample is shown in Fig.4. The XRD result reveals that the major phases in the slag are vanadium and ferrous spinel containing manganese and chromium, fayalite, titanium and ferrous spinel and quartz. Based on the XRD pattern, vanadium and titanium in the complex spinel phase exist in oxide forms. Table 8 presents the chemical compositions of the slag. Leaching agent was sulfuric acid solution which was diluted from 98% to a certain concentration range. The used gas was bottled oxygen for industry.

**Table 8** Main compositions of converter slag (mass fraction, %)

V	TiO <sub>2</sub>	TFe	SiO <sub>2</sub>	MnO	MgO	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO
8.07	10.71	36.33	15.43	7.72	5.47	3.23	2.58	2.38



**Fig. 4** XRD pattern of converter slag

#### 3.2 Equipments

Experiment equipments included autoclave (model

KCFD2-10), planetary high energy ball mill (model Pulverisette5), rotary-vane vacuum pump (model 2XZ-1) and vacuum drying oven (model ZK-82B).

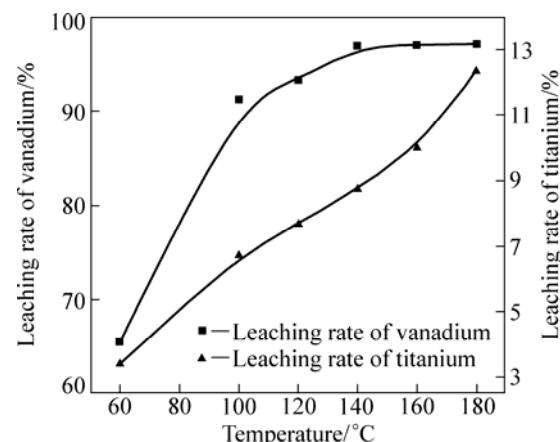
Inductively coupled plasma-atomic emission spectrometer (ICP, model Prodigy XP, America) was used to test the ionic concentration of vanadium and titanium in the leachate. X-ray fluorescence spectroscope (XRF, model ZSX100e, Japan) was used to analyze the elemental content of vanadium and titanium in the residue.

#### 3.3 Methods

A sample of converter slag was added to a zirconium autoclave at the desired temperature and then oxygen was continuously aerated into the reactor to produce a certain pressure. The reaction time (after achieving the desired temperature), initial acid concentration, liquid to solid ratio, oxygen partial pressure, particle size and stirring speed were fixed, and desired temperature was varied. When the reaction completed, the cover of autoclave was removed. The slurry was separated by vacuum filtration, and the leachate and residue were analyzed for vanadium and titanium content to calculate leaching rate.

### 4 Results and discussion

Figure 5 illustrates the effect of temperature on leaching rate of vanadium and titanium ranging from 60 °C to 180 °C, at oxygen partial pressure of 0.5 MPa, particle size of 0.055–0.075 mm, liquid to solid ratio of 15:1, leaching time of 120 min, stirring speed of 500 r/min and initial acid concentration of 200 g/L. When the temperature increases from 60 to 140 °C, leaching rate of vanadium rises from 65.48% to 96.87%. However, leaching rate of vanadium gets 97.07% at the temperature of 180 °C, which is stable above 140 °C.



**Fig. 5** Effect of temperature on leaching rates of V and Ti

Leaching rate of titanium increases from 3.41% to 12.33% with the temperature increasing from 60 to 180 °C.

Leaching process is mainly controlled by the kinetics process of liquid-solid reaction according to the experiment results at different temperatures. Dissolved reaction speed is rapidly to promote the leaching process of vanadium and titanium with temperature increasing. From Fig. 5, leaching temperature cannot be above 140 °C, and leaching rates of vanadium and titanium are 96.87% and 8.76% at this temperature, respectively.

## 5 Conclusions

1) Based on  $\varphi$ -pH diagram of V-H<sub>2</sub>O system at different temperatures, the stable regions of V<sup>3+</sup>, VO<sup>2+</sup> and VO<sub>2</sub><sup>+</sup> are contained in the stable region of solution at pH<2, which provides the thermodynamic feasibility of pressure acid leaching of vanadium.

2) Titanium mainly exists as oxides in the converter, so the stable region of TiO<sub>2</sub> mainly exists in the stable region of solution according to  $\varphi$ -pH diagram of Ti-H<sub>2</sub>O system at different temperatures, which provides the thermodynamics principle of enrichment of titanium in the residue.

3) Based on  $\varphi$ -pH diagram of V-Ti-H<sub>2</sub>O system at different temperatures, the stable regions of V<sup>3+</sup>, VO<sup>2+</sup> and VO<sub>2</sub><sup>+</sup> are practically contained in stable region of TiO<sub>2</sub>. Redox potentials of stable region of vanadium and titanium become more positive as well as pH values get more negative with temperature increasing from 60 °C to 200 °C. Coexisting characteristics of stable regions, which would be stable with temperature increasing, provide a thermodynamic view that vanadium dissolves in the leachate as well as titanium oxides enrich in the residue during the pressure acid leaching of converter slag.

4) Leaching rate of vanadium and titanium are 96.87% and 8.76% at 140 °C, 0.5 MPa of oxygen partial pressure, 0.055–0.075 mm of particle size, 15:1 of liquid to solid ratio, 120 min of leaching time, 500 r/min of stirring speed and 200 g/L of initial acid concentration. Vanadium and titanium can be selectively separated in the pressure acid leaching process, and the experiment result is in agreement with that of thermodynamic calculation.

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# 含钒钛转炉渣氧压酸浸过程 $V-Ti-H_2O$ 系的电位-pH 图

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**摘要:** 为了分析含钒钛转炉渣氧压酸浸过程的热力学特点, 根据高温水溶液中计算标准摩尔吉布斯自由能和活度系数的经验公式, 通过计算得到了氧分压 0.5 MPa、对应离子的质量浓度 0.1 mol/kg、温度 60~200 °C 条件下  $V-Ti-H_2O$  系的电位-pH 图。在 pH<2 的酸性条件下, 可溶性  $V^{3+}$ ,  $VO^{2+}$ ,  $VO_2^+$  的稳定区几乎全部包含在  $TiO_2$  的稳定区范围内, 随着温度由 60 °C 升高到 200 °C, 钒、钛稳定共存区对应的氧化还原电位逐渐增大, pH 逐渐降低。钒、钛稳定区的共存特点从热力学角度为转炉渣采用氧压酸浸工艺通过一步酸浸将钒浸出的同时使钛富集在渣中提供了理论依据。含钒钛转炉渣的氧压酸浸实验结果表明, 在浸出温度 140 °C、氧分压 0.5 MPa、粒度 0.055~0.075 mm、液固比 15:1、浸出时间 120 min、搅拌速度 500 r/min、初酸浓度 200 g/L 的条件下, 钒的浸出率为 96.87%, 钛的浸出率为 8.76%。钒与钛通过氧压酸浸工艺能够得到有效分离, 实验结果与热力学计算结果一致。

**关键词:** 电位-pH 图;  $V-Ti-H_2O$  系; 氧压酸浸; 转炉渣; 钒; 钛

(Edited by LI Xiang-qun)