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Thermodynamic analysis for separation of vanadium and chromium in V(IV)−Cr(III)−H_2O system

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Abstract: To recycle vanadium and chromium from the V−Cr-bearing reducing slag, the thermodynamics of separating V(IV) and Cr(III) at 298 K was summarized in the form of potential−pH diagram and activity−pH diagram. The potential−pH diagrams of V−Mn−H_2O and Cr−Mn−H_2O systems show that the electrode potential of MnO_2/Mn^{2+} is higher than that of VO_2^+/VO^{2+} but lower than that of $Cr_2O_7^{2-}/Cr^{3+}$, which proves that it is feasible to selectively oxidize low valent vanadium using MnO_2. The activity−pH diagrams of V(V)−H_2O and Cr(III)−H_2O systems show that the precipitation pH of V(V) is far lower than that of Cr(III), and therefore V(V) and Cr(III) can be separated through precipitation method. Based on the thermodynamic analysis, the flowsheet of recovery of vanadium and chromium from the V−Cr-bearing reducing slag is designed.

Key words: V−Cr−H_2O system; vanadium; chromium; selective oxidation; selective precipitation

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1 Introduction

Vanadium and chromium are important industrial elements and strategic metals. Due to the similar nature, vanadium and chromium are often in the form of symbiosis existing in minerals. In China, vanadium-bearing titanomagnetite is a typical representative of this kind of ore [1,2]. After reduction smelting in blast furnace and selective oxidation in converter, vanadium and chromium in vanadium-bearing titanomagnetite are separated in the form of slag, which is commonly referred to as vanadium slag [3]. Owing to the high value as well as high content of vanadium, vanadium slag is only used as the raw material for extraction vanadium. After recovery of vanadium from the vanadium slag, large amounts of wastewater containing Cr(VI) and V(V) was produced. The forms of vanadium (V) and Cr(VI) in aqueous are particularly toxic [4,5], and therefore they are strictly controlled to discharge. In Panzhihua Iron and Steel Company, the wastewater is treated by reduction with sodium pyrosulfite, followed by neutralization to form a V−Cr-bearing reducing slag [6]. In which, vanadium mainly occurs as V(IV) (>85%) and the other occurs as V(III). Chromium exists in the form of Cr(III). The content of vanadium and chromium varies between 5%−10% V and 10%−20% Cr, respectively.

Several oxidation alkaline leaching processes have been tested to recover vanadium from the V−Cr-bearing reducing slag, such as direct leaching using NaOH+H_2O_2 [7], NaOH leaching under electric field strengthening [8] and roasting followed by NaOH leaching [9].The leaching of vanadium in these methods is high in all cases, but chromium cannot be extracted. So far, the V−Cr-bearing reducing slag has not been treated effectively, resulting in a waste of vanadium and chromium resources as well as environmental pollution. Fortunately, when the V−Cr-bearing reducing slag was leached by sulfuric acid, more than 90% of vanadium and 97% of chromium were leached, and the pH of leach solution was in the range of 0−1.0 [10]. The precipitation pH of V(IV) is close to that of Cr(III), so they cannot be separated through precipitation method [11].

To separate and extract vanadium and chromium from the solution, several methods including solvent extraction [12−14] and ion exchange [15,16] have been proposed. These methods all can effectively separate vanadium and chromium, but they are only used for V(V) and Cr(VI), and the separation of V(IV) and Cr(III) as well as V(III) and Cr(III) has rarely been reported.

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The standard oxidation and reduction potentials of VO_2^+/VO^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ are 1.00 V and 1.33 V, respectively [11]. As can be seen, in theory the V(IV) in leach solution can be selectively oxidized to V(V) by a specific oxidant. Fortunately, it was found that the standard oxidation and reduction potential of MnO_2/Mn^{2+} is 1.208 V [11], that is to say, V(IV) in leach solution may be selectively oxidized by manganese dioxide under a certain condition. But very little work on the thermodynamic analysis of the V−Mn−Cr−H_2O systems has been published.

In this study, the potential−pH diagrams of V−Mn−H_2O and Cr−Mn−H_2O systems as well as the activity−pH diagrams of V(V)−H_2O and Cr(III)−H_2O systems are presented. Based on the thermodynamic analysis, the process of recovery of vanadium and chromium from V−Cr-bearing reducing slag was designed.

2 Thermodynamic data and equations

All the thermodynamic data cited in the study are calculated from the assessed reviews in Refs. [17−22], in which published standard Gibbs energies of formation for the various species and phases considered are given in Table 1. The equations and thermodynamic calculation involved in the diagrams are described in Tables 2−4. In the following diagrams, the solid lines

Table 1 Standard Gibbs energies of formation of species at 298 K

Species	Oxidation degree	State	$\Delta G_f/(kJ\cdot mol^{-1})$
V^{2+}	2	aq	−218
VO	2	s	−404.2
V^{3+}	3	aq	−251.3
V_2O_3	3	s	−1139
VO^{2+}	4	aq	−446.4
V_2O_4	4	s	−1318.6
$HV_2O_5^-$	4	aq	−1508.96
VO_2^+	5	aq	−587
V_2O_5	5	s	−1419.4
$H_2V_{10}O_{28}^{4-}$	5	aq	−7729
$HV_{10}O_{28}^{5-}$	5	aq	−7708
$HV_2O_7^{3-}$	5	aq	−1792
$V_4O_{12}^{4-}$	5	aq	−3202
HVO_4^{2-}	5	aq	−974.9
VO_4^{3-}	5	aq	−899.1
Mn	0	s	0
MnO	2	s	−377.3
Mn^{2+}	2	aq	−227.5
$HMnO^{2-}$	2	aq	−505.6
Mn_3O_4	2.67	s	−1279.7
Mn_2O_3	3	s	−887.8
Mn^{3+}	3	aq	−82.0
MnO_2	4	s	−464.6
MnO_4^{2-}	6	aq	−503.5
MnO_4^-	7	aq	−449.1
Cr	0	s	0
Cr^{2+}	2	aq	−164.9
Cr^{3+}	3	aq	−206.3
$Cr(OH)_3$	3	s	−846.5
CrO_2^-	3	aq	−524.2
Cr_2O_3	3	aq	−1057.6
CrO_4^{2-}	6	aq	−727.5
$Cr_2O_7^{2-}$	6	aq	−1300.6

Table 2 Reactions and thermodynamic equations for V−H_2O systems

No.	Chemical reaction	Thermodynamic formulation (298 K)
1	$VO+2H^++2e\leftrightarrow V+H_2O$	$\varphi=-0.866-0.05916pH$
2	$VO+2H^+\leftrightarrow V^{2+}+H_2O$	$\lg a(V^{2+})=8.929-2pH$
3	$V_2O_3+6H^+\leftrightarrow 2V^{3+}+3H_2O$	$\lg a(V^{3+})=6.580-3pH$
4	$V_2O_4+4H^+\leftrightarrow 2VO^{2+}+2H_2O$	$\lg a(VO^{2+})=4.253-2pH$
5	$HV_2O_5^-+H^+\leftrightarrow V_2O_4+H_2O$	$\lg a(HV_2O_5^-)=pH-8.201$
6	$V_2O_5+2H^+\leftrightarrow 2VO_2{}^++H_2O$	$\lg a(VO_2^+)=-pH-0.720$
7	$H_2V_{10}O_{28}^{4-}+4H^+\leftrightarrow 5V_2O_5+3H_2O$	$\lg a(H_2V_{10}O_{28}^{4-})=4pH-13.931$
8	$HV_{10}O_{28}^{5-}+H^+\leftrightarrow H_2V_{10}O_{28}^{4-}$	$\lg(a(H_2V_{10}O_{28}^{4-})/a(HV_{10}O_{28}^{5-}))=3.678-pH$
9	$5V_4O_{12}^{4-}+10H^+\leftrightarrow 2HV_{10}O_{28}^{5-}+4H_2O$	$2\lg a(HV_{10}O_{28}^{6-})-5\lg a(V_4O_{12}^{4-})=62.132-10pH$
10	$2HV_2O_7^{3-}+2H^+\leftrightarrow V_4O_{12}^{4-}+2H_2O$	$\lg a(V_4O_{12}^{4-})-2\lg a(HV_2O_7^{3-})=16.177-2pH$
11	$2HVO_4^{2-}+H^+\leftrightarrow HV_2O_7^{3-}+H_2O$	$\lg a(HV_2O_7^{3-})-2\lg a(HVO_4^{2-})=13.904-pH$
12	$VO_4^{3-}+H^+\leftrightarrow HVO_4^{2-}$	$\lg(a(HVO_4^{2-})/a(VO_4^{3-}))=13.277-pH$
13	$V^{2+}+2e\leftrightarrow V$	$\varphi=-1.130+0.02958\lg a(V^{2+})$
14	$V^{3+}+e\leftrightarrow V^{2+}$	$\varphi=-0.345+0.05916\lg(a(V^{3+})/a(V^{2+}))$
15	$V_2O_3+6H^++2e\leftrightarrow 2V^{2+}+3H_2O$	$\varphi=0.044-0.17748pH-0.05916\lg a(V^{2+})$
16	$V_2O_3+2H^++2e\leftrightarrow 2VO+H_2O$	$\varphi=-0.484-0.05916pH$
17	$VO^{2+}+2H^++e\leftrightarrow V^{3+}+H_2O$	$\varphi=0.436-0.11832pH+0.05916\lg(a(VO^{2+})/a(V^{3+}))$
18	$VO^{2+}+H_2O+2e\leftrightarrow V_2O_3+2H^+$	$\varphi=0.047+0.05916pH+0.05916\lg a(VO^{2+})$
19	$V_2O_4+2H^++2e\leftrightarrow V_2O_3+H_2O$	$\varphi=0.298-0.05916pH$
20	$HV_2O_5^-+3H^++2e\leftrightarrow V_2O_3+H_2O$	$\varphi=0.541-0.08874pH+0.02958\lg a(HV_2O_5^-)$
21	$V_2O_5+6H^++2e\leftrightarrow 2VO^{2+}+3H_2O$	$\varphi=0.958-0.17748pH-0.05916\lg a(VO^{2+})$
22	$H_2V_{10}O_{28}^{4-}+14H^++10e\leftrightarrow 5V_2O_4+8H_2O$	$\varphi=0.789-0.082824pH+0.005916\lg a(H_2V_{10}O_{28}^{4-})$
23	$H_2V_{10}O_{28}^{4-}+34H^++10e\leftrightarrow 10VO^{2+}+18H_2O$	$\varphi=1.041-0.201144pH+0.005916\lg a(H_2V_{10}O_{28}^{4-})-0.05916\lg a(VO^{2+})$
24	$HV_{10}O_{28}^{5-}+15H^++10e\leftrightarrow 5V_2O_4+8H_2O$	$\varphi=0.811-0.08874pH+0.005916\lg a(HV_{10}O_{28}^{5-})$
25	$V_4O_{12}^{4-}+8H^++4e\leftrightarrow 2V_2O_4+4H_2O$	$\varphi=0.995-0.11832pH+0.01479\lg a(V_4O_{12}^{4-})$
26	$V_4O_{12}^{4-}+6H^++4e\leftrightarrow HV_2O_5^-+2H_2O$	$\varphi=0.752-0.08874pH+0.01479\lg a(V_4O_{12}^{4-})-0.02958\lg a(HV_2O_5^-)$
27	$HV_2O_7^{3-}+4H^++2e\leftrightarrow HV_2O_5^-+2H_2O$	$\varphi=0.991-0.11832pH+0.02958\lg(a(HV_2O_7^{3-})/a(HV_2O_5^-))$
28	$2HVO_4^{2-}+5H^++2e\leftrightarrow HV_2O_5^-+3H_2O$	$\varphi=1.403-0.1479pH+0.05916\lg a(HVO_4^{2-})-0.02958\lg a(HV_2O_5^-)$
29	$2VO_4^{3-}+7H^++2e\leftrightarrow HV_2O_5^-+3H_2O$	$\varphi=2.188-0.20706pH+0.05916\lg a(VO_4^{3-})-0.02958\lg a(HV_2O_5^-)$
30	$2VO_4^{3-}+10H^++4e\leftrightarrow V_2O_3+5H_2O$	$\varphi=1.3647-0.1479pH+0.02958\lg a(VO_4^{3-})$
31	$VO_2^++2H^++e\leftrightarrow VO^{2+}+H_2O$	$\varphi=1.001-0.11832pH+0.05916\lg(a(VO_2^+)/a(VO^{2+}))$
32	$H_2VO_4^-+2H^+\leftrightarrow VO_2^++2H_2O$	$\lg a(VO_2^+)-\lg a(H_2VO_4^-)=7.086-2pH$
33	$HVO_4^{2-}+H^+\leftrightarrow H_2VO_4^-$	$\lg(a(H_2VO_4^-)/a(HVO_4^{2-}))=8.057-pH$
34	$V_2O_5+2H_2O\leftrightarrow H_3V_2O_7^-+H^+$	$\lg a(H_3V_2O_7^-)=-4.74+pH$
35	$H_3V_2O_7^-+H_2O\leftrightarrow 2H_2VO_4^-+2H^+$	$2\lg a(H_2VO_4^-)-\lg a(H_3V_2O_7^-)=-7.38+pH$
36	$2VO_2^++3H_2O\leftrightarrow H_3V_2O_7^-+3H^+$	$0.666\lg a(VO_2^+)-0.333\lg a(H_3V_2O_7^-)=-pH+1.03$
37	$V_{10}O_{28}^{6-}+H^+\leftrightarrow HV_{10}O_{28}^{5-}$	$\lg a(HV_{10}O_{28}^{5-})-\lg a(V_{10}O_{28}^{6-})=5.78-pH$
38	$5V_4O_{12}^{4-}+8H^+\leftrightarrow 2V_{10}O_{28}^{6-}+4H_2O$	$2\lg a(V_{10}O_{28}^{6-})-5\lg a(V_4O_{12}^{4-})=50.57-8pH$
39	$2VO_4^{3-}+2H^+\leftrightarrow V_2O_7^{4-}+4H_2O$	$\lg a(V_2O_7^{4-})-2\lg a(VO_4^{3-})=27.847-2pH$
40	$HV_2O_7^{3-}+H_2O+H^+\leftrightarrow 2H_2VO_4^-$	$\lg a(HV_2O_7^{3-})-2\lg a(H_2VO_4^-)=pH-2.211$
41	$V_2O_7^{4-}+H^+\leftrightarrow HV_2O_7^{3-}$	$\lg a(HV_2O_7^{3-})-\lg a(V_2O_7^{4-})=12.612-pH$
42	$V_2O_7^{4-}+H_2O\leftrightarrow 2HVO_4^{2-}$	$2\lg a(HVO_4^{2-})-\lg a(V_2O_7^{4-})=-1.292$
43	$V_4O_{12}^{4-}+4H_2O\leftrightarrow 4H_2VO_4^-$	$4\lg a(H_2VO_4^-)-\lg a(V_4O_{12}^{4-})=-3.36$

Table 3 Reactions and thermodynamic equations for Cr−H_2O systems

No.	Chemical reaction	Thermodynamic formulation (298 K)
44	$Cr(OH)_3+3H^+\leftrightarrow Cr^{3+}+3H_2O$	$pH=4.15-(1/3)\lg a(Cr^{3+})$
45	$CrO_2^-+H^++H_2O\leftrightarrow Cr(OH)_3$	$pH=14.9+\lg a(CrO_2^-)$
46	$2CrO_4^{2-}+2H^+\leftrightarrow Cr_2O_7^{2-}+H_2O$	$pH=7.25-0.5\lg a(Cr_2O_7^{2-})+\lg a(CrO_4^{2-})$
47	$Cr^{3+}+e\leftrightarrow Cr^{2+}$	$\varphi=-0.429-0.0591\lg(a(Cr^{2+})/a(Cr^{3+}))$
48	$Cr(OH)_3+3H^++e\leftrightarrow Cr^{2+}+3H_2O$	$\varphi=0.3078-0.0591\lg a(Cr^{2+})-0.1773pH$
49	$CrO_4^{2-}+4H^++3e\leftrightarrow CrO_2^-+2H_2O$	$\varphi=0.936-0.0197\lg(a(CrO_2^-)/a(CrO_4^{2-}))-0.0788pH$
50	$CrO_4^{2-}+5H^++3e\leftrightarrow Cr(OH)_3+H_2O$	$\varphi=1.23+0.0197\lg a(CrO_4^{2-})-0.0985pH$
51	$Cr_2O_7^{2-}+8H^++6e\leftrightarrow 2Cr(OH)_3+H_2O$	$\varphi=1.087+0.00985\lg a(Cr_2O_7^{2-})-0.0788pH$
52	$Cr_2O_7^{2-}+14H^++6e\leftrightarrow 2Cr^{3+}+7H_2O$	$\varphi=1.33+0.00985\lg a(CrO_7^{2-})-0.0197\lg a(Cr^{3+})-0.1379pH$

Table 4 Reactions and thermodynamic equations for Mn−H_2O systems

No.	Chemical reaction	Thermodynamic equations (298 K)
53	$MnO+2H^+\leftrightarrow Mn^{2+}+H_2O$	$pH=7.65-0.5\lg a(Mn^{2+})$
54	$Mn^{2+}+2e\leftrightarrow Mn$	$\varphi=-1.1795+0.0295\lg a(Mn^{2+})$
55	$MnO+2H^++2e\leftrightarrow Mn+H_2O$	$\varphi=-0.727-0.0591pH$
56	$Mn_3O_4+2H^++2e\leftrightarrow 3MnO+H_2O$	$\varphi=0.462-0.0591pH$
57	$Mn_3O_4+8H^++2e\leftrightarrow 3Mn^{2+}+4H_2O$	$\varphi=1.8205-0.2364pH-0.08865\lg a(Mn^{2+})$
58	$Mn_2O_3+6H^++2e\leftrightarrow 2Mn^{2+}+3H_2O$	$\varphi=1.4434-0.1773pH-0.0591\lg a(Mn^{2+})$
59	$3Mn_2O_3+2H^++2e\leftrightarrow 2Mn_3O_4+H_2O$	$\varphi=0.6893-0.0591pH$
60	$MnO_2+4H^++2e\leftrightarrow Mn^{2+}+2H_2O$	$\varphi=1.2290-0.1182pH-0.0295\lg a(Mn^{2+})$
61	$2MnO_2+2H^++2e\leftrightarrow Mn_2O_3+H_2O$	$\varphi=1.0145-0.0591pH$
62	$MnO_4^-+4H^++3e\leftrightarrow MnO_2+2H_2O$	$\varphi=1.6924-0.0788pH+0.0197\lg a(MnO_4^-)$

stand for V−H_2O and Cr−H_2O systems, and the dotted lines represent Mn−H_2O systems. Every line in all the diagrams indicates that a species exists in equilibrium with the adjacent ion or solid species at the particular specified activity.

3 Results and discussion

3.1 Potential−pH diagram for V−Mn−H_2O systems

In sulfuric acid leach solution of the V−Cr-bearing reducing slag, the concentration of vanadium was 4.0−8.0 g/L, and therefore the activity of dissolved vanadium of 0.1 was chosen for calculation. The potential−pH diagram for the vanadium−manganese−water systems with the activity of dissolved manganese of 0.1 is shown in Fig. 1.

As can be seen, at low pH V(V) forms a pervanadyl cation VO_2^+ and V(IV) exists in the form of VO^{2+}. Moreover, V(III) and V(II) dissolve in aqueous solution of low pH to form V^{3+} and V^{2+}, respectively. Compared with vanadium, only one kind of Mn^{2+} formed at low potential and low pH. The position of MnO_2 is always above VO^{2+} and V^{3+}, which means that the electrode potential of MnO_2 is higher than that of VO^{2+} and V^{3+}, i.e., MnO_2 can oxidize VO^{2+} and V^{3+} into VO_2^+ in a specified condition. The oxidation reaction of VO^{2+} and V^{3+} by MnO_2 can be expressed as follows:

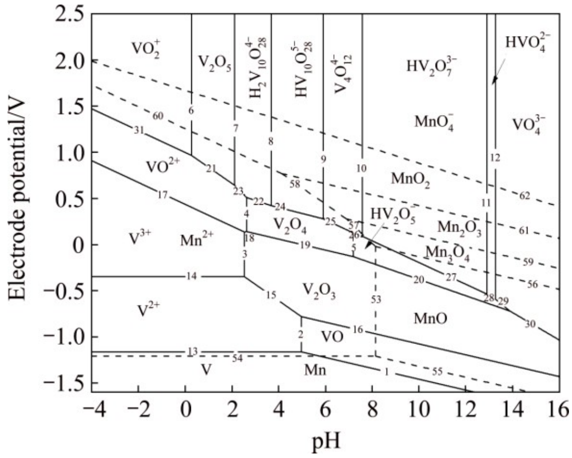

Fig. 1 Potential−pH diagram for V−Mn−H_2O systems at 298 K

$$MnO_2+2VO^{2+}=Mn^{2+}+2VO_2^+ \quad (1)$$

$$MnO_2+V^{3+}=Mn^{2+}+VO_2^+ \quad (2)$$

3.2 Potential−pH diagram for Cr−Mn−H_2O systems

In sulfuric acid leach solution of V−Cr-bearing reducing slag, the concentration of chromium was 15−30 g/L, and therefore the activities of dissolved chromium of 0.1 and 1 were chosen for calculation, respectively. The potential−pH diagrams for the Cr−Mn−H_2O systems at 298 K with an activity of dissolved manganese of 0.1 are shown in Fig. 2.

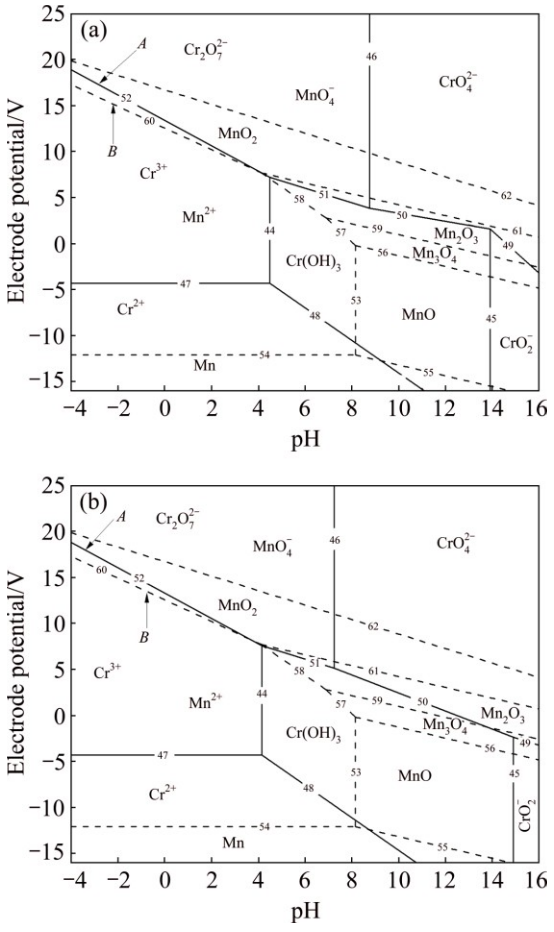

Fig. 2 Potential−pH diagrams for Cr−Mn−H_2O systems at 298 K with different activities of dissolved chromium: (a) 0.1; (b) 1

As can be seen in Fig. 2, the most species of chromium exist in the form of ion expect $Cr(OH)_3$. It is obvious by comparison between Figs. 2(a) and (b) that the stability area of $Cr(OH)_3$ increases with the increase of chromium activity from 0.1 to 1. There is no obvious effect on the electrode potential of chromium with the increase of chromium activity. When the pH was less than about 4, the electrode potential of $Cr_2O_7^{2-}/Cr^{3+}$ (sold line *A*) was higher than that of MnO_2/Mn^{2+} (dotted line *B*), which means that MnO_2 cannot oxidize Cr^{3+}. Combined with Fig. 1 and Fig. 2, a conclusion can be made that MnO_2 can selectively oxidize low valent vanadium.

3.3 Activity−pH diagrams for V(V)−H_2O and Cr(III)−H_2O systems

To separate vanadium and chromium, the keys are to find the difference between them. In the sulfuric acid leach solution of V−Cr-bearing reducing slag, vanadium occurred as V(IV) and V(III), and chromium existed in the form of Cr(III). The precipitation pH of V(IV) is close to that of Cr(III), so they cannot be separated through precipitation method. Fortunately, there is a large difference between the precipitation pH of V(V) and Cr(III). It is well know that the precipitation of vanadium and chromium depends on not only the solution pH but also their concentration. Activity−pH diagrams for the V(V)−H_2O and Cr (III)−H_2O systems are represented in Fig. 3.

Figure 3 (a) shows that in aqueous solution the V(V) exists in the form of ions in addition to vanadium pentoxide. When the activity of vanadium is 0.1, the precipitation pH of vanadium pentoxide is about 0.3. It can also be seen from Fig. 3(a) that when the solution pH is about 1.8, the solubility of vanadium pentoxide is minimal, that is to say precipitating vanadium pentoxide, the solution pH should be controlled at about 1.8. As can be seen in Fig. 3(b), when the activity of chromium is 0.1, the precipitation pH of chromic hydroxide is about

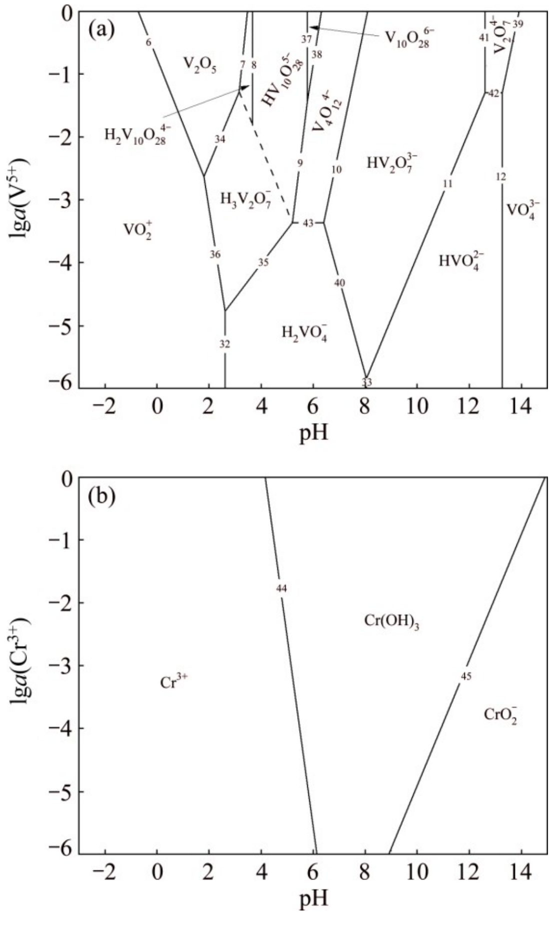

Fig. 3 Activity−pH diagrams at 298 K: (a) V(V)−H_2O system; (b) Cr (III)−H_2O system

4.4. It is indicated by comparison of Figs. 1, 2 and 3 that after V(IV) and V(III) in leach solution were selectively oxidized to V(V) by manganese dioxide, they would be easy to separate with Cr(III) by precipitation method.

3.4 Process design of recovery of vanadium and chromium from V−Cr-bearing reducing slag

Combined with the sulfuric acid leaching and thermodynamic analysis, the recovery flowsheet of vanadium and chromium from the V−Cr-bearing reducing slag is designed, as shown in Fig. 4, which includes the procedure of sulfuric acid leaching, selective oxidation of V(IV) and V(III), selective separating of V(V) and Cr(III) by precipitation method.

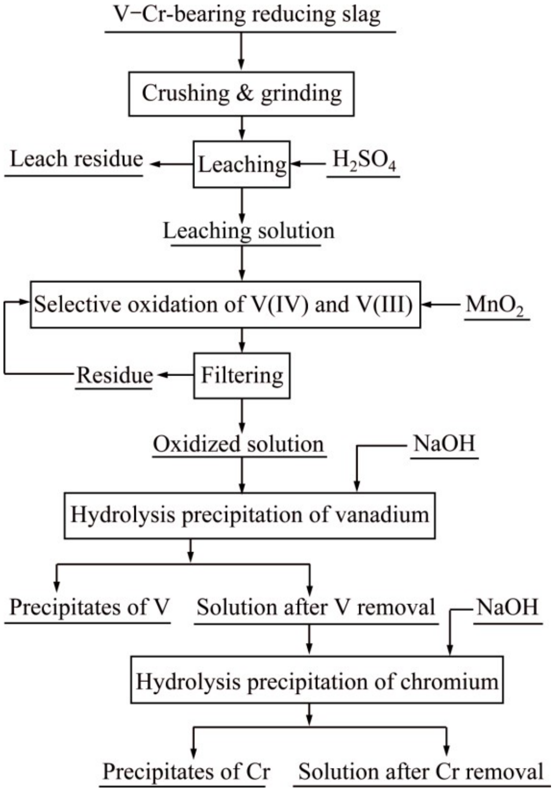

Fig. 4 Recovery flowsheet of vanadium and chromium from V−Cr-bearing reducing slag

4 Conclusions

1) The thermodynamics of V−Mn−H_2O and Cr−Mn−H_2O systems at 298 K is summarized in the form of potential−pH and activity−pH diagrams. The electrode potential of MnO_2/Mn^{2+} is higher than that of VO_2^+/VO^{2+}, while it is lower than that of $Cr_2O_7^{2-}/Cr^{3+}$, that is to say MnO_2 can selectively oxidize low valent vanadium.

2) When the activities of vanadium and chromium are both 0.1, the precipitation pH values of the vanadium pentoxide and chromic hydroxide are about 0.3 and 4.4, respectively, so in theory V(V) and Cr(III) can be separated through precipitation method.

3) Based on the thermomechanical analysis, the recovery flowsheet of vanadium and chromium from the V−Cr-bearing reducing slag is designed.

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V(IV)−Cr(III)−H_2O 体系钒铬分离的热力学分析

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摘 要：为了从钒铬还原渣中回收钒和铬，以电位−pH 和活度−pH 的形式总结 298 K 时 V(IV)和 Cr(III)分离的热力学。V−Mn−H_2O 体系和 Cr−Mn−H_2O 体系的电位−pH 图表明，MnO_2/Mn^{2+}的电极电位高于 VO_2^{+}/VO^{2+}的电极电位，但是低于 $Cr_2O_7^{2-}/Cr^{3+}$的电极电位，这表明采用 MnO_2 来选择性氧化低价钒是可行的。V(V)−H_2O 体系和 Cr(III)−H_2O 体系的活度−pH 图表明，V(V)开始沉淀时的 pH 远低于 Cr(III)开始沉淀时的 pH，因此可以采用沉淀析出法分离 V(V) 和 Cr(III)。通过热力学分析，设计了钒铬还原渣中分离回收钒和铬的技术路线。

关键词：V−Cr−H_2O 体系；钒；铬；选择性氧化；选择性析出

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