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Effects of different alkalis on the behaviour of vanadium loss in the pretreatment of vanadium-bearing acid leaching solution

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ABSTRACT: This study examined the effect of different pretreating agents on vanadium loss from vanadium-bearing shale. Acid leaching solutions with added $Ca(OH)_2$, $CaCO_3$, NaOH, Na_2CO_3, and ammonia solution were evaluated. The pH of the acid leaching solution was adjusted to 2.0 to reduce vanadium loss and allow efficient removal of impurities, providing a high vanadium extraction efficiency. $Ca(OH)_2$ was the most effective neutralizer and its use resulted in a vanadium loss rate was as low as 4%. SEM-EDS analysis indicates that a major cause of vanadium loss is entrapment and absorption by precipitates. The low vanadium loss rate using $Ca(OH)_2$ as a neutralizer appears to be due to the smooth and flat surface of the precipitate, which limits vanadium entrainment. When the pH was adjusted with $CaCO_3$, the crystal structure of the precipitate was incomplete. In addition, $CaSO_4$ and iron phosphate particles interact, promoting entrainment and absorption of vanadium. Similarly, flocculent iron phosphate was generated when the pH was adjusted with NaOH, Na_2CO_3, or ammonia, resulting in a crystal with a rough surface that easily entrained vanadium.

KEYWORDS: vanadium, acid leaching solution, pH adjustment, alkali

INTRODUCTION

Vanadium is a vital rare element that is widely used in high-tech fields, including the production of redox batteries and aerospace[1], due to its special physical and chemical properties[2,3]. In China, the major source of vanadium is vanadium-bearing shale[4–6]. High salt roasting-water leaching, blank roasting-acid leaching, blank roasting-alkali leaching, and direct acid leaching[7–9] have been used to recover vanadium from vanadium-bearing shale. Among these processes, roasting-H_2SO_4 leaching has received considerable attention for extraction of vanadium-bearing shale due to its highest recovery rate[10]. However, impurities, such as Fe, P, and other elements, can be leached along with vanadium in the acid leaching process. This results in a complex, low pH mixture with the vanadium-containing extract contaminated with high concentrations of impurities. These conditions prevent efficient vanadium separation and concentration[11–13].

At present, the main methods for vanadium separation and concentration are solvent extraction[14–16] and ion exchange[17,18]. The solvent extraction method, with various extracting reagents, has gradually been the primary methods due to its high efficiency with no requirement for complex equipment[19]. Among the reagents used for vanadium extraction, the acid extractant D2EHPA (Bis(2-ethylhexyl) phosphate) provides advantages of acid system adaptability and easy stripping[20–22]. The appropriate pH range for solvent extraction of vanadium is 1.5–2.5; however, the acidity of the acid leaching solution is often excessive, requiring pretreated to allow subsequent steps in the extraction process[23,24]. Some methods for the disposal of acid leaching solution have also been developed, these include ion exchange, solvent extraction, and

Table 1 Chemical composition of acid leaching solutions (g/l).

Element	V	Fe	Na	Ca	Al	P	S	Si
Conc.	3.10	1.66	1.91	1.11	3.81	1.25	29.1	1.48

alkali neutralization[25–27]. Although ion exchange and solvent extraction can purify the acid leaching solution, the pH of treated solution does not meet the requirements for the next step in the extraction process[28]. Hence neutralization with alkali is a popular and necessary process to adjust the pH of acid leaching solution before subsequent extraction[29,30]. Currently, NaOH is used to adjust pH; however, this results in considerable vanadium loss and introduces many impurities.

In this study, $Ca(OH)_2$, $CaCO_3$, NaOH, Na_2CO_3, and ammonia were used to adjust the pH of vanadium-bearing shale acid leaching solution. The mechanisms of vanadium loss and the introduction of impurities during precipitation under different alkalis condition were investigated by XRD and SEM-EDS. Furthermore, the vanadium loss rate, removal rate of impurity ions, and vanadium extraction efficiency were evaluated to select the appropriate alkali and pH for the pretreatment process.

MATERIALS AND METHODS

Vanadium-bearing shale was supplied by Ping-fan Mining Co. Ltd., Zaoyang, China. The acid leaching solution from vanadium-bearing shale was prepared by heating vanadium-bearing shale at 850 °C for 1.5 h followed by leaching with 5% (wt) CaF_2 and 15% (v/v) H_2SO_4 solution (L/S= 1.5:1) at 98 °C for 2 h. The chemical composition of the acid leaching solution is shown in Table 1 and the initial pH was 0.33. Na_2SO_3 was used to reduce the vanadium(V) and iron(III) to vanadium(IV) and iron(II). Analytical grade $Ca(OH)_2$, $CaCO_3$, NaOH, Na_2CO_3, and $NH_3 \cdot H_2O$ were obtained from Shanghai Rare-Earth Chemical Co., Ltd., China. The extracting solution was composed of 5% (v/v) TBP (tributyl phosphate), 20% (v/v) P204 (Bis(2-ethylhexyl) phosphate D2EHPA), and 75% (v/v) sulfonated kerosene. P204 and TBP were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All other reagents used were of analytical grade.

The vanadium concentration in solution was measured indirectly using iron ammonium sulphate titration, with the iron concentration determined colorimetrically using 1,10-phenanthroline. The concentrations of other ions in the solution were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 4300DV, Perkin-Elmer, USA). The mineralogical composition of the neutralizing filtered residue was identified by XRD spectra pattern, recorded with a D/-MAX 2500PC X-ray powder diffractometer (Rigaku, Japan) at room temperature. Microscopic observation and elemental analysis (SEM with EDS) were conducted using a JEOL JSM-6610 scanning electronic microscope (JEOL, Japan) equipped with a BRUKER QUANTAX 200-30 energy dispersive spectrometer (BRUKER, Germany). The pH of the solution was measured with a pHS-3C digital pH meter (Shanghai Rex Instruments Factory, China).

The pH adjustment experiments were carried out using a magnetic stirrer. In each pH adjustment experiment, 100 ml acid leaching solution was reduced with Na_2SO_3 for 30 min. The pH of the solutions was then adjusted with $Ca(OH)_2$, $CaCO_3$, NaOH, Na_2CO_3, or $NH_3 \cdot H_2O$. After pH adjustment, the solutions were filtered and washed for a selected duration, preparing the feed solution for solvent extraction. The solvent extraction was performed by magnetically stirred with the organic and aqueous phases at a 1:2 ratio, for 8 min at 25 °C in a water bath. Phase separation was achieved by gravity using separatory funnels. After phase separation, the ion concentrations in the raffinate were determined with the concentration of ions in organic phase deduced from mass-balance calculations. The distribution ratio (D) and extraction efficiency (E) were calculated by $D = C_{org}/C_{aq}$ and $E = D/[D + (V_{aq}/V_{org})] \times 100\%$, respectively, where C_{org} is the concentration of vanadium presented in the organic phase, C_{aq} is the content of vanadium in the raffinate, and V_{aq} and V_{org} are the volumes of aqueous and organic phases used in the extraction, respectively.

RESULTS AND DISCUSSION

Effects of pH on ion precipitation

To determine the optimal pH in the neutralization process, the effect of pH on vanadium loss and removal of impurity ions was investigated. $Ca(OH)_2$, $CaCO_3$, NaOH, Na_2CO_3, and $NH_3 \cdot H_2O$ were used as alkali neutralizers to adjust the pH of acid leaching solution from 1.4–2.4. The results shown in Fig. 1 indicate that the solution pH is a factor that substantially influences the vanadium loss rate and impurity ion removal efficiency. The vanadium loss rate and impurity ion (Fe, Al, P, S) removal efficiency increases as pH increases; however, the

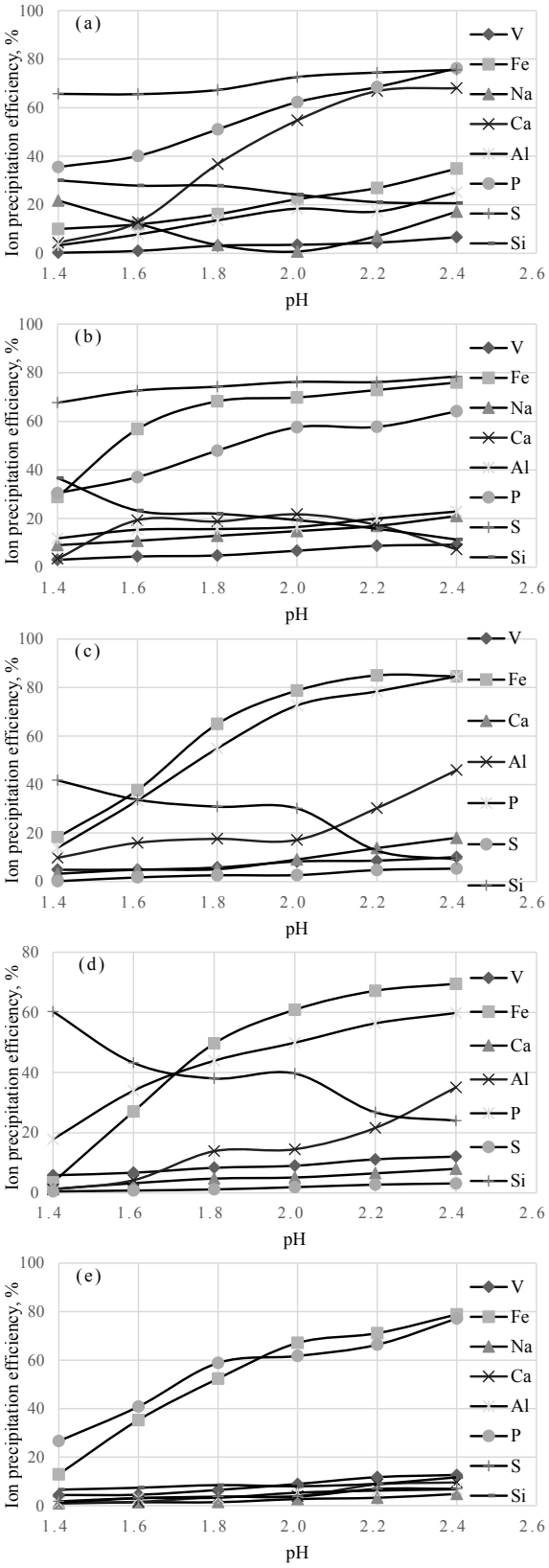

Fig. 1 Effect of pH on ion precipitation when adjusting pH with: (a) $Ca(OH)_2$, (b) $CaCO_3$, (c) NaOH, (d) Na_2CO_3, and (e) $NH_3 \cdot H_2O$.

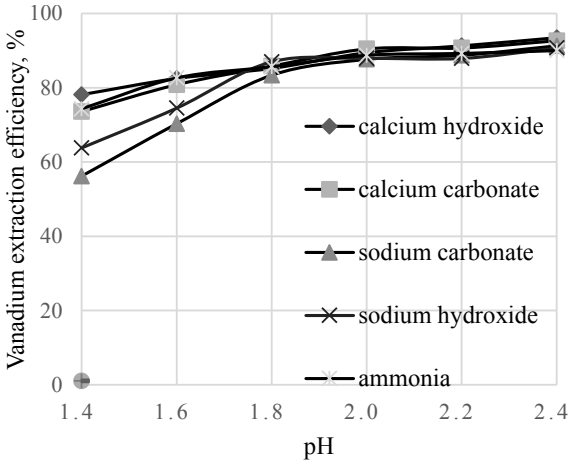

Fig. 2 Effect of pH on vanadium extraction using different alkali neutralizers.

removal efficiency of Si decreases as pH increases. The removal efficiency of Fe and P increases as pH increases. As shown in Fig. 1a,b, when pH was adjusted with $Ca(OH)_2$ and $CaCO_3$, the removal rate of S was enhanced 60%, this may be due to the generation of $CaSO_4$ from dissolved $Ca(OH)_2$ and $CaCO_3$. Possible chemical reactions are described in Table 4(1,2).

As shown in Fig. 1c,d, when the pH was adjusted with NaOH and Na_2CO_3, the removal efficiency of Si sharply decreases as pH increases from 2.0–2.2. When pH was adjusted with $NH_3 \cdot H_2O$, vanadium loss rate and impurity ion (Al, S, Na, Ca) removal efficiency increases as pH increases slightly, however, the removal efficiency of Fe and P increases as pH increases significantly (Fig. 1e).

Based on the experiments described above, we conclude that the removal efficiency of P and Fe increases significantly when pH increases, however, the vanadium loss rate also increases. Hence the optimal pH range was determined to be 1.8–2.2 to promote precipitation of less vanadium and more impurities.

Effects of pH on vanadium extraction

The effect of pH on vanadium extraction efficiency was also investigated. Solution extraction experiments were carried out under the following conditions: contact time, 8 min; temperature, 25 °C; and organic to aqueous phase ratio (O/A), 1:2. Under these conditions, the extraction efficiency of vanadium increases as pH increases (Fig. 2). When pH was greater than 2.0, the extraction of vanadium was almost constant even with further increases in

Table 2 The ion precipitation efficiency with pH adjusted to 2.0 (%).

Alkali	Element							
	V	Fe	Na	Ca	Al	P	S	Si
$Ca(OH)_2$	3.5	54.8	22.3	0.8	18.4	62.3	72.6	27.8
$CaCO_3$	6.8	69.8	14.8	21.8	16.6	57.6	76.2	19.4
NaOH	8.3	78.7	–	7.1	17.2	72.6	2.7	30.2
Na_2CO_3	9.0	60.7	–	6.5	22.5	50.9	1.9	39.7
$NH_3 \cdot H_2O$	8.9	67.1	2.7	3.9	5.3	61.7	3.8	8.0

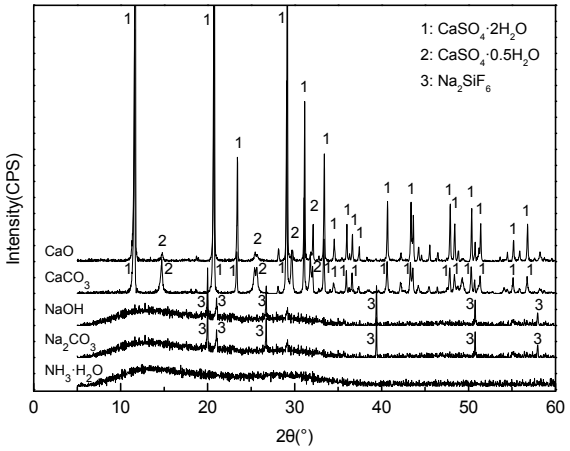

Fig. 3 XRD pattern of precipitate when pH was adjusted with alkalis.

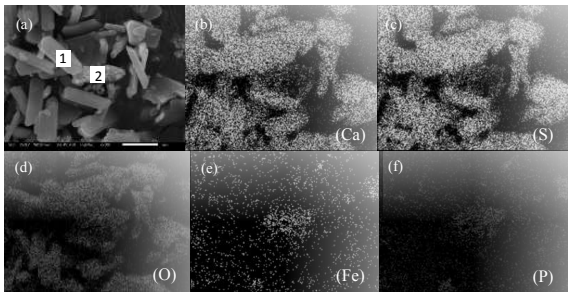

Fig. 4 (a) SEM image of precipitate when pH was adjusted with $Ca(OH)_2$, EDS elemental distribution: (b) Ca; (c) S; (d) O; (e) Fe; (f) P.

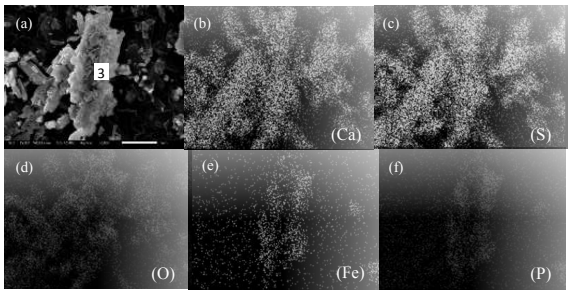

Fig. 5 (a) SEM image of precipitate when pH was adjusted with $CaCO_3$, EDS elemental distribution: (b) Ca; (c) S; (d) O; (e) Fe; (f) P.

pH. Hence the optimal pH for acid leaching solution was 2.0.

Comparison of different alkali neutralizers

Alkali neutralizers, to adjust the pH of the acid leaching solution, were investigated with regard to vanadium loss rate and impurity ion removal efficiency. The lowest vanadium loss rate, 4%, and efficient removal of other impurity ions was achieved with $Ca(OH)_2$ used to adjust pH (Table 2). When the pH was adjusted with $Ca(OH)_2$ and $CaCO_3$, the number of calcium ions generated was relatively small. However, using NaOH and Na_2CO_3 as alkali neutralizers, a large amount of Na ions was produced. The use of $NH_3 \cdot H_2O$ resulted in the generation of ammonia nitrogen wastewater, which is difficult to treat. Considering the above factors, the best alkali neutralizer for the neutralization process was determined to be $Ca(OH)_2$.

XRD and SEM-EDS analysis

pH adjustment with $Ca(OH)_2$ and $CaCO_3$

XRD and SEM-EDS were used to analyse precipitates generated after adjusting pH to 2.0 to determine the mechanism of vanadium loss. When $Ca(OH)_2$ and $CaCO_3$ were used to adjust pH, the major components of the precipitate were $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 0.5H_2O$ (Fig. 3). The SEM-EDS electronic images from precipitates formed when adjusting the pH with $Ca(OH)_2$ indicates the presence of prismatic gypsum crystals with surfaces that are smooth and flat, limiting the potential for vanadium to be entrained (Fig. 4). The type of crystal structure formed with $Ca(OH)_2$ likely contributes to the lowest vanadium loss rate with this alkali neutralizer. In contrast, the precipitate formed when adjusting pH with $CaCO_3$ (Fig. 5) exhibits many small gypsum particles stuck together. This crystal structure could more easily intercalate vanadium consistent with the increased loss rate when the pH was adjusted with $Ca(OH)_2$.

The EDS elemental distribution reveals that the contribution of O, P, and Fe was limited, suggesting that the Fe, P, and O might exist in the form of iron phosphate. However, the content of iron phosphate is too low to account for the EDS result, as there is no peak for iron phosphate in the XRD pattern. The result of the EDS spot analysis (Table 3) indicates

Table 3 EDS spot analysis (labeled boxes 1–6) of precipitates based on Figs. 4–8 (wt%).

Element	V	Fe	P	O	K	Na	Ca	F	Si	S	Al
1	–	0.69	–	64.44	–	–	18.30	–	–	16.57	–
2	0.57	12.65	7.54	61.60	1.50	–	7.71	–	–	8.39	–
3	0.37	8.88	4.43	46.46	–	–	20.15	–	–	19.10	0.61
4	0.47	22.27	14.43	46.83	0.96	4.52	–	10.26	0.27	–	–
5	1.02	28.81	19.15	45.57	1.49	3.72	0.24	–	–	–	–
6	0.61	17.57	11.42	69.90	0.50	–	–	–	–	–	–

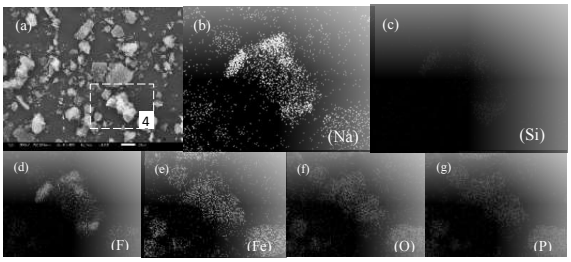

Fig. 6 (a) SEM image of precipitate when pH was adjusted with NaOH, EDS elemental distribution: (b) Na; (c) Si; (d) F; (e) Fe; (f) O; (g) P.

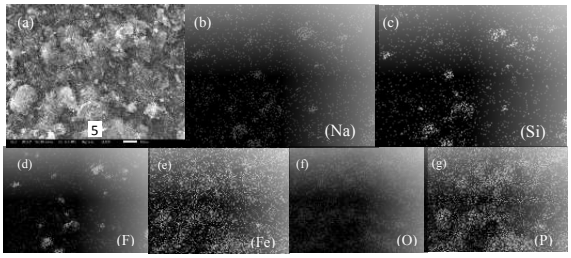

Fig. 7 (a) SEM image of precipitate when pH was adjusted with Na_2CO_3, EDS elemental distribution: (b) Na; (c) Si; (d) F; (e) Fe; (f) O; (g) P.

that the surface of $CaSO_4$ crystals does not contain vanadium. However, adherence of small iron phosphate particles to the $CaSO_4$ surface can promote the absorption of vanadium, resulting in vanadium loss (vanadium content of 0.57% and 0.37%).

pH adjustment with NaOH and Na_2CO_3

The major component of precipitate when pH was adjusted with NaOH was Na_2SiF_6 (Fig. 3). When dissolved NaOH and Na_2CO_3 released Na^+, which reacted with SiF_6^{2-} in the acid leaching solution generating Na_2SiF_6 [31]. However, the large number of dispersion peaks in the XRD pattern indicates poor crystallization of sodium fluorosilicate. Possible chemical reaction equations are shown in

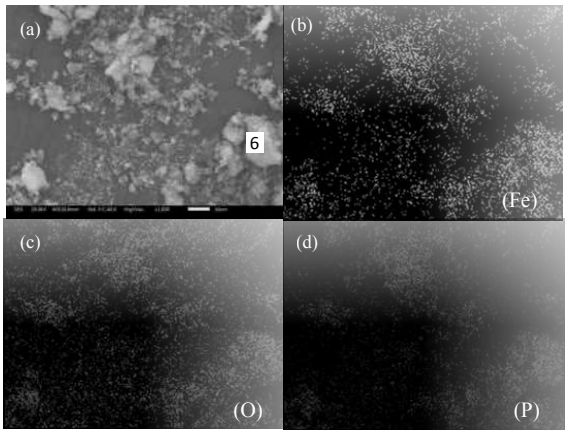

Fig. 8 (a) SEM image of precipitate when pH was adjusted with $NH_3 \cdot H_2O$, EDS elemental distribution: (b) Fe; (c) O; (d) P.

Table 4(3,4)

The results of SEM-EDS (Fig. 6 and Fig. 7) indicate that sodium fluorosilicate crystals are incomplete and covered with floccule. The precipitate surface structure allows for vanadium to be entrained at higher levels compared with $Ca(OH)_2$ and $CaCO_3$ as alkali neutralizers. Meanwhile, the floccule consists of O, P, and Fe suggesting the presence of iron phosphate. When the pH was adjusted with Na_2CO_3, the floccule surface was rougher, entraining more vanadium than when using NaOH. The result of EDS spot analysis shows the vanadium content was 0.47% and 1%, indicating that the iron phosphate entrained and absorbed vanadium, resulting in vanadium loss (Table 3).

pH adjustment with $NH_3 \cdot H_2O$

The XRD diffraction pattern of precipitate when pH was adjusted with $NH_3 \cdot H_2O$ was a dispersion peak, indicating that the residue was an amorphous material (Fig. 3). The results of SEM-EDS electronic image and elemental distribution (Fig. 8) reveal

Table 4 Δ°G(298K)/kj·mol^{-1} of reaction equations.

	Reaction equations	Δ°G(298K)
1.	$Ca(OH)_2 + 2H^+ + (SO_4)^{2-} = CaSO_4\downarrow + 2H_2O$	-156.8
2.	$CaCO_3 + 2H^+ + (SO_4)^{2-} = CaSO_4\downarrow + H_2O + CO_2\uparrow$	-84.2
3.	$2NaOH + 2H^+ + SiF_6^{2-} = Na_2SiF_6\downarrow + 2H_2O$	-272.5
4.	$Na_2CO_3 + 2H^+ + SiF_6^{2-} = Na_2SiF_6\downarrow + H_2O + CO_2\uparrow$	-140.9
5.	$H_3PO_4 + Fe^{3+} = FePO_4\downarrow + 3H^+$	-46.1
6.	$H_2PO_4^- + Fe^{3+} = FePO_4\downarrow + 2H^+$	-27.9

that floccule iron phosphate was formed. Fe can exist as the cation Fe^{3+} and P is often present as neutral H_3PO_4 and $H_2PO_4^-$. Possible chemical reactions with Fe^{3+}, H_3PO_4 and $H_2PO_4^{4-}$ were described in Table 4(5,6). The result of EDS spot analysis (Table 3) shows that the content of vanadium was 0.61 wt%, indicating that the iron phosphate entrained and absorbed vanadium resulting in vanadium loss.

Thermodynamics

The feasibility of the reactions described in these equations should be theoretically discussed using thermic analyses. The Δ°G (standard free energy change of reaction) can be calculated using the °G (T) (standard free energy) of the substances involved in the chemical reaction[32]. The functions describing the Δ°G (298K) for the reaction equations are shown in Table 4.

Table 4 shows that Δ°G (298K) was negative for all reaction equations. Hence all reactions above are spontaneous at 298K.

CONCLUSIONS

To obtain a low vanadium loss rate, high impurity ions removal rate and high vanadium extraction efficiency, the pH of acid leaching solution should be adjusted to 2.0 with $Ca(OH)_2$.

The mechanism of vanadium loss is that vanadium was entrained and absorbed by precipitate. When adjusting pH with $Ca(OH)_2$, the lowest vanadium loss rate is achieved because crystal structure was the most integrated compared with using other alkalis. When adjusting pH with $CaCO_3$, crystal structure was relatively integrated with tiny calcium sulphate particles stuck together, making it easier to entrain vanadium compared with $Ca(OH)_2$. Meanwhile, the tiny iron phosphate particles adhered to $CaSO_4$ surface would entrain and absorb vanadium and result in vanadium loss.

Compared with $Ca(OH)_2$, when NaOH and Na_2CO_3 were used to adjust pH, the structure of sodium fluorosilicate was incomplete, and the floccule iron phosphate was produced, which makes the surface rough and causes higher vanadium loss. When $NH_3 \cdot H_2O$ was used to adjust pH, amorphous flocculent materials were formed, making it easier to entrain vanadium than when adjusting pH with $Ca(OH)_2$.

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