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Solvent Extraction of Sc(III) by D2EHPA/TBP from the Leaching Solution of Vanadium Slag

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Received: 28 April 2020; Accepted: 11 June 2020; Published: 14 June 2020



Abstract: The solvent extraction of scandium by the mixture of di-(2-ethylhexyl) phosphate (D2EHPA) and tri-n-butyl phosphate (TBP) has been investigated in the acidic leaching solution of vanadium slag. Thermodynamic analysis of the species distribution diagrams on the Sc-S-H₂O system showed that scandium mainly exists as Sc³⁺ and Sc(SO₄)⁺, and sulfur mainly exists as HSO₄⁻ in the actual leaching solution of vanadium slag (pH = -0.75). The extraction process was studied to optimize various parameters such as the extractant concentration, dosage of TBP, phase ratio, and stirring speed. The results indicated that 83.64% of scandium and less than 2% of co-extracted elements were extracted under optimal conditions. Then, over 95% of the co-extracted elements and less than 1.1% of scandium were scrubbed from the loaded organic phase by 4.0 mol/L of HCl. Finally, 87.20% of scandium was stripped with 2 mol/L of NaOH and 1 mol/L of NaCl at a stripping O/A of 1:1.

Keywords: scandium; vanadium slag; waste acid; separation; solvent extraction

1. Introduction

Scandium, as a valuable by-product, has been mainly recovered from waste liquors, residues and tailings in the production process of other metals such as titanium, rare earths, aluminium, uranium, and tungsten [1]. Among them, titanium white waste acid is an important secondary metallurgical resource containing scandium. In the production of titanium dioxide by a sulphuric acid process, 5–8 tons of waste sulfuric acid containing 19%~23% of sulfuric acid will be produced per ton of titanium dioxide. In addition, waste acid also contains a large number of valuable metals such as iron, titanium, and trace scandium [2–4]. At present, neutralization and concentration methods have been widely used to treat waste acid in China and other countries. These processes generally possess the following problems: (1) the cost of processing is high, and (2) it is difficult to effectively utilize the acid resources and recover the valuable components (especially scandium) in waste acid [5,6]. Therefore, the recovery and comprehensive utilization of acid resources and valuable metal scandium in waste acid are particularly important.

In China, most of their vanadium is obtained by the H₂SO₄ acidic leaching process from converter vanadium slag. However, a large amount of CaO in converter slag increases the acid consumption, thus greatly increasing the cost [7–15].

Based on these, a novel method was proposed: titanium white waste acid was utilized in an acidic treatment process of converter vanadium slag [16–18]. Firstly, as the leaching agent, waste acid can greatly reduce the acid cost in the leaching process of vanadium slag and effectively utilize the waste acid resources. Moreover, it can realize the comprehensive recovery of valuable metals in the two resources. In particular, scandium in waste acid dissolves into the leaching solution. However, due to

the strong acidity of the leaching solution and the high concentration of impurity metals, the extraction of trace Sc becomes difficult.

At present, the recovery technology of scandium in solution mainly includes solvent extraction, ion exchange, ionic liquid, and membrane technology. Among these methods, solvent extraction and ion exchange are the most studied methods. In China, the extraction of scandium from titanium dioxide waste acid mainly adopts solvent extraction, and the main extractants are acid extractant (D2EHPA, EHEHPA, Cyanex272, Cyanex 302 and Cyanex 301) and neutral extractant (TBP, P350, Cyanex 923 and Cyanex 925) [1,19–21]. The di-(2-ethylhexyl) phosphate (D2EHPA) extraction method has been widely studied to extract trace scandium from the solution. The technology is matured and has been applied in industry, such as the extraction of scandium from titanium dioxide waste acid and red mud leaching solution.

However, the research of extracting scandium by D2EHPA in this paper is different from the previous research, which has special significance. The differences and significances lie in the fact that the solution used in this study is the leaching solution of vanadium slag by using titanium dioxide waste acid, which belongs to the specific solution produced under the new method. Its main characteristics are high acidity, low content of scandium, high content of iron (mainly trivalent iron) and many kinds of impurity elements, which are different from previous studies and industrial applications. This investigation is a new research. Furthermore, from the view of the reaction mechanism, the previous studies mainly used D2EHPA to separate scandium from a spot of divalent iron (Fe^{2+}), but seldom studied the extraction and separation effect of scandium and trivalent iron (Fe^{3+}). However, the content of Fe in this stock solution is high and it mainly exists in the form of trivalent iron, which is a new challenge and research direction for the extraction and separation of scandium by D2EHPA. In addition, in the previous research, the pH value of the treated feed solution by D2EHPA for extracting scandium is generally 1~2, while the acidity of the leaching solution treated in this paper is stronger, and the pH value is -0.75 . In conclusion, the research in this paper is not only a new exploration for the extraction of scandium from the new feed solution system, but is also of great significance for the treatment and utilization of vanadium slag and titanium white waste acid [22–33].

Therefore, the present work aims to extract Sc using D2EHPA and tri-*n*-butyl phosphate (TBP) from the acidic solution, which was produced by leaching converter slag with titanium white waste acid. The behaviours of valuable metals in the solvent extraction were studied systematically.

2. Experimental Section

2.1. Materials and Instruments

The commercial grade D2EHPA, TBP and sulphonated-kerosene supplied by Kopper Chemical Industry Co., Ltd. (Shanghai, China) were used in the study. The TBP was used as the third phase modifier and sulphonated-kerosene as the diluent. The extractant D2EHPA was used without any further purification. The other chemicals (hydrochloric acid, sodium hydroxide and sodium chloride) used were of analytical grade. The mass concentration of elements in the pressure acidic leaching solution of converter slag by titanium white waste acid was 18.78 g/L V, 9.16 g/L Fe^{2+} , 49.9 g/L Fe^{3+} , 0.008 g/L Sc, 12.30 g/L Mn, 0.41 g/L Ti, 0.88 g/L Al, 2.55 g/L Mg, and 1.90 g/L Cr. Meanwhile, the pH of the acidic leaching solution was -0.75 .

The concentrations of Sc, V, Fe, Mn, Ti, Al, Mg, and Cr in the aqueous solutions were determined by inductively coupled plasma emission spectrometry (ICP). Concentrations of metal ions were determined in triplicate with an uncertainty of less than 5%. The pH values of the aqueous solution were measured by a pH-meter (ORION-230A, made from ORION company in Beverly, MA, USA) with a minimum accuracy of 0.01.

2.2. General Experimental Procedure

The extraction, scrubbing and stripping experiments were conducted at 298 K in a thermostatic water bath equipped with electromagnetic stirring. Some volume of the aqueous solution and organic phase was stirred mechanically to ensure the same level of chemical reaction. After equilibration, the aqueous solution and organic phase were separated in a separating funnel, and their corresponding volumes were accurately measured. The concentrations of Sc, V, Fe, Mn, Ti, Al, Mg, and Cr in the loaded organic phases were calculated by the principle of mass balance.

The extraction efficiency of E and the scrubbing and stripping efficiency of S are defined as follows:

$$E = \frac{[M]_{\text{org}} \cdot V_{\text{org}}}{[M]_{\text{aq}} \cdot V_{\text{aq}}} \times 100\% \quad (1)$$

$$S = \frac{[M]_{\text{aq,a}} \cdot V_{\text{aq}}}{[M]_{\text{org,t}} \cdot V_{\text{org}}} \times 100\% \quad (2)$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases, $[M]_{\text{aq,a}}$ is the equilibrium concentration of metal ions in the scrubbed or stripped solution and $[M]_{\text{org,t}}$ is the initial concentration of metal ions in the organic phase, respectively.

In the solvent extraction process, the reaction time was 5 min. Moreover, the investigation factors and the corresponding parameter range are the D2EHPA concentration (1~15%), TBP addition (0~8%), O/A phase ratio (1:1~1:20) and stirring speed (300~1300 r/min), respectively.

3. Results and Discussion

3.1. Thermodynamic Analysis and Discussions

3.1.1. Thermodynamic Data and Equilibrium Calculation

The existence forms of the ions in the Sc-S-H₂O solution are HSO_4^- , SO_4^{2-} , Sc^{3+} , $\text{Sc}(\text{OH})_2^+$, $\text{Sc}(\text{OH})_3$, $\text{Sc}(\text{OH})_4^-$, $\text{Sc}(\text{OH})_5^{2-}$, $\text{Sc}(\text{SO}_4)^+$, and $\text{Sc}(\text{SO}_4)_2^-$. The relevant thermodynamic data of chemical reactions are listed in Table 1.

Table 1. Equilibrium reactions and thermodynamic constant of the Sc-S-H₂O system at 298 K.

No.	Equilibrium Reaction	lgK [34]
1	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2.00
2	$\text{Sc}^{3+} + \text{OH}^- = \text{Sc}(\text{OH})_2^+$	2.40
3	$\text{Sc}^{3+} + 4\text{OH}^- = \text{Sc}(\text{OH})_4^-$	3.28
4	$\text{Sc}^{3+} + 5\text{OH}^- = \text{Sc}(\text{OH})_5^{2-}$	3.13
5	$\text{Sc}^{3+} + \text{SO}_4^{2-} = \text{Sc}(\text{SO}_4)^+$	0.62
6	$\text{Sc}^{3+} + 2\text{SO}_4^{2-} = \text{Sc}(\text{SO}_4)_2^-$	0.94
7	$\text{Sc}^{3+} + 3\text{OH}^- = \text{Sc}(\text{OH})_3$	7.33

According to the data listed in Table 1, thermodynamic analysis was conducted. In the calculation, the concentration was used instead of the activity [35–37]. The mathematical relationships of these species can be expressed as follows:

$$[\text{SO}_4^{2-}][\text{H}^+] = 10^2[\text{HSO}_4^-] \quad (3)$$

$$[\text{Sc}(\text{OH})_2^+] = 10^{2.4}[\text{Sc}^{3+}][\text{OH}^-]^2 \quad (4)$$

$$[\text{Sc}(\text{OH})_4^-] = 10^{3.28}[\text{Sc}^{3+}][\text{OH}^-]^4 \quad (5)$$

$$[\text{Sc}(\text{OH})_5^{2-}] = 10^{3.13}[\text{Sc}^{3+}][\text{OH}^-]^5 \quad (6)$$

$$[\text{Sc}(\text{SO}_4)^+] = 10^{0.62}[\text{Sc}^{3+}][\text{SO}_4^{2-}] \quad (7)$$

$$[\text{Sc}(\text{SO}_4)_2^-] = 10^{0.94}[\text{Sc}^{3+}][\text{SO}_4^{2-}]^2 \quad (8)$$

$$[\text{Sc}(\text{OH})_3] = 10^{7.33}[\text{Sc}^{3+}][\text{OH}^-]^3 \quad (9)$$

The total concentrations of Sc and S are expressed in Equation (10) and Equation (11), respectively. In the Sc-S-H₂O solution:

$$[\text{Sc}]_{\text{T(Sc-S-H}_2\text{O)}} = [\text{Sc}^{3+}] + [\text{Sc}(\text{OH})^{2+}] + [\text{Sc}(\text{OH})_4^-] + [\text{Sc}(\text{OH})_5^{2-}] + [\text{Sc}(\text{SO}_4)^+] + [\text{Sc}(\text{SO}_4)_2^-] \quad (10)$$

$$[\text{S}]_{\text{T(Sc-S-H}_2\text{O)}} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{Sc}(\text{SO}_4)^+] + 2[\text{Sc}(\text{SO}_4)_2^-] \quad (11)$$

Based on the above nine equations, thermodynamic study of the Sc-S-H₂O system was conducted to determine the solution state of scandium species in the acidic leaching solution [38–45].

3.1.2. Concentration Distribution of Ions Containing Scandium and Sulfur in the Sc-S-H₂O System

Thermodynamic equilibrium diagrams of the Sc-S-H₂O system are shown in Figures 1 and 2. The mole fraction of scandium and sulfur ions with different pH values when $[\text{Sc}^{3+}] = 0.001 \text{ mol/L}$ and $[\text{S}^{6+}] = 4 \text{ mol/L}$ is shown in Figure 1.

It can be clearly seen that ions containing scandium in the Sc-S-H₂O system were mainly Sc^{3+} , $\text{Sc}(\text{SO}_4)^+$, $\text{Sc}(\text{OH})_3$, and $\text{Sc}(\text{OH})_5^{2-}$. At pH = −2.0, scandium in the acidic solution was 85.70% of Sc^{3+} and 14.24% of $\text{Sc}(\text{SO}_4)^+$. As the pH value increased, scandium existed mainly in the form of $\text{Sc}(\text{SO}_4)^+$, and the maximum mole fraction can reach 96.65% at pH = 1.0. When the pH value increased to 2.0~5.0, $\text{Sc}(\text{SO}_4)^+$ transformed into $\text{Sc}(\text{OH})_3$, and the maximum mole fraction could reach 99.98% at pH = 3.0. At pH = 6.0~14.0, $\text{Sc}(\text{OH})_3$ transformed into $\text{Sc}(\text{OH})_5^{2-}$, and the maximum mole fraction could reach 99.91%.

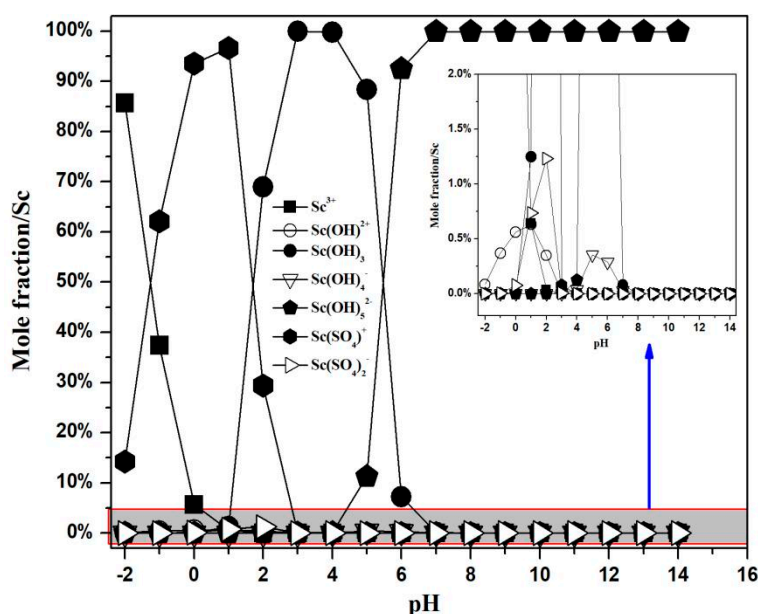


Figure 1. Mole fraction diagram of ions containing scandium in the Sc-S-H₂O system at 298 K with various pH values ($[\text{Sc}^{3+}] = 0.001 \text{ M}$ and $[\text{S}^{6+}] = 4 \text{ M}$).

As seen in Figure 2, HSO_4^- and SO_4^{2-} are the main existing forms of sulfur in the Sc-S-H₂O system. At pH = −2.0~2.0, sulfur was mainly HSO_4^- , with its maximum mole fraction reaching 99.99%. As the pH value increased, the anion HSO_4^- gradually disappeared. At pH = 4~14, almost 100% of sulfur in the solution was in the form of SO_4^{2-} . Moreover, the mole fraction of $\text{Sc}(\text{SO}_4)^+$ and $\text{Sc}(\text{SO}_4)_2^-$ was almost zero in the whole pH range of 0~14.

Based on the above thermodynamic analysis, in the actual leaching solution of vanadium slag by titanium white waste acid (pH = -0.75), the main existing forms of Sc were the cations of Sc³⁺ and Sc(SO₄)⁺. Moreover, the main existing form of S was HSO₄⁻.

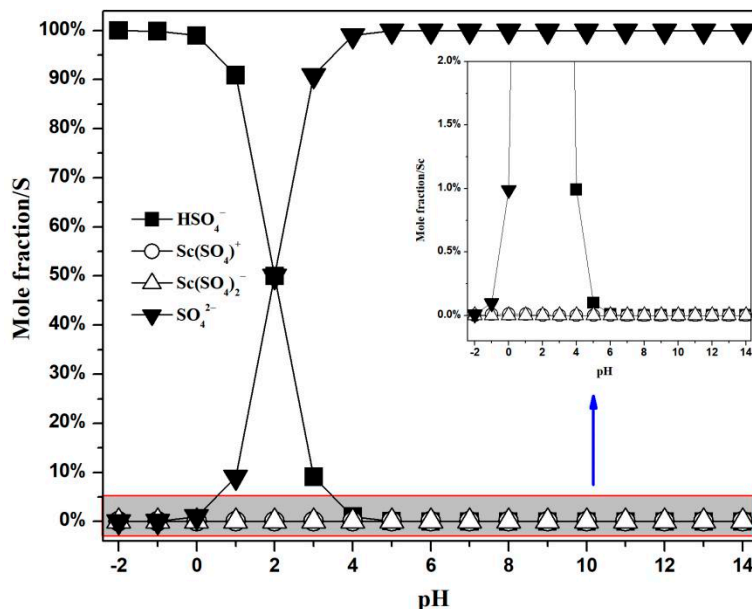


Figure 2. Mole fraction diagram of ions containing sulfur in the Sc-S-H₂O system at 298 K with various pH values ([Sc³⁺] = 0.001 M and [S⁶⁺] = 4 M).

3.2. Solvent Extraction of Sc(III) by Using D2EHPA and TBP

3.2.1. Effect of Extractant D2EHPA Concentration on the Sc Extraction

Experimental results of single-stage extractions at different D2EHPA concentrations are shown in Figure 3.

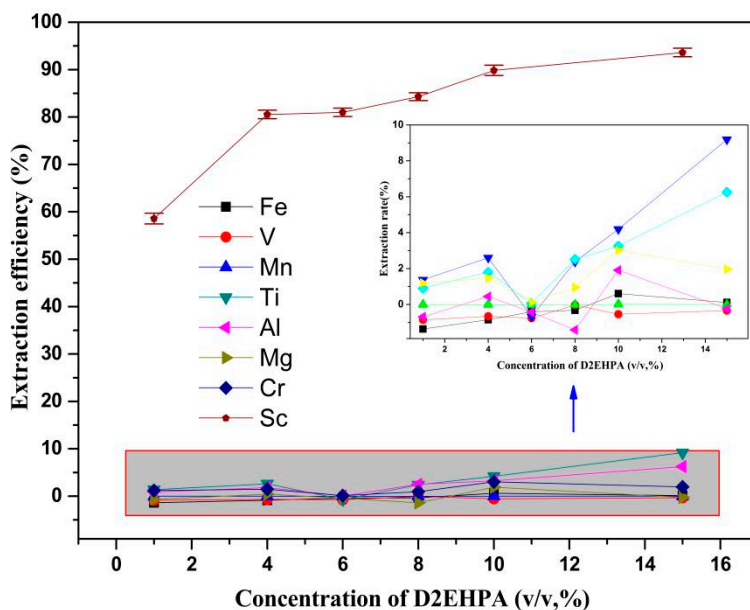
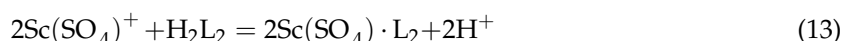
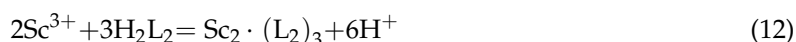


Figure 3. Effect of the di-(2-ethylhexyl) phosphate (D2EHPA) concentration on the Sc extraction (2% of tri-n-butyl phosphate (TBP), O/A = 1:10, pH = -0.75 and 5 min at 298 K).

The results show that the extraction efficiency of scandium significantly increases with increasing extractant concentration, compared with the extraction efficiency of other metals. When the concentration of D2EHPA increased from 1% to 15%, the extraction efficiency of Sc gradually increased from 57.31% to 93.48%. According to the thermodynamic analysis and discussions in Section 3.1, scandium, as shown in Figure 1, mainly exists in the cation form of Sc^{3+} and $\text{Sc}(\text{SO}_4)^+$ at $\text{pH} = -0.75$, while D2EHPA, as an acid extractant, is generally in the form of H_2L_2 in this acid condition. Therefore, the extraction mechanism is mainly carried out in the form of a cation exchange. The chemical reaction equations are as follows:



Meanwhile, the extraction efficiency of Fe, V, Mn, Mg and Cr was basically less than 1%. The finding shows that D2EHPA has a better extractive selectivity for Sc than for other metals. That is to say, for the D2EHPA and TBP solvent extraction system, although the concentration of scandium is low, its selectivity is far greater than other impurity ions. Therefore, scandium will be extracted preferentially.

However, the extraction efficiency of Ti and Al exceeded 1% when the D2EHPA concentration was more than 8%. In addition, an increase in the D2EHPA concentration causes the increase in organic phase viscosity, which plays a negative role in phase separation [46]. Therefore, 8% (v/v) of D2EHPA was sufficient for the quantitative extraction of scandium and the separation of other metals.

3.2.2. Effect of Modifier TBP Addition on the Sc Extraction

As a phase modifier, TBP is usually added during the solvent extraction process to prevent the appearance of the third phase. The effect of the modifier TBP concentration on the separation of scandium from other metals is shown in Figure 4.

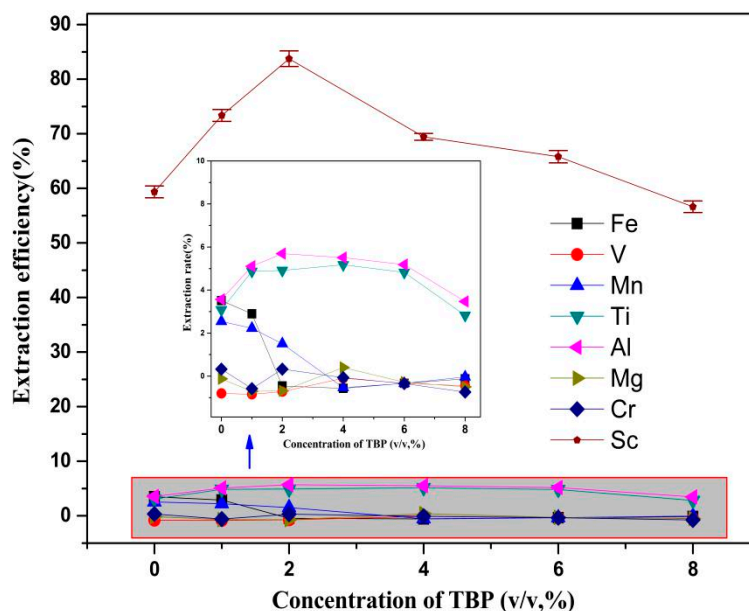


Figure 4. Effect of the modifier TBP concentration on the Sc extraction (8% of extractant D2EHPA, $\text{pH} = -0.75$, O/A = 1:10, and 5 min at 298 K).

As can be seen in Figure 4, TBP had a great effect on the Sc extraction. The extraction efficiency of Sc gradually increased from 59.83% to 84.38% by the varying modifier TBP concentration of 0%~2%, and then decreased to 55.97% when the TBP concentration was 8%. The excessive TBP had a negative impact on the extraction of Sc because TBP is not only a phase modifier but also a neutral extractant, which can combine with D2EHPA to form a neutral molecule. The formation of this neutral molecule

can cause a decrease in the effective concentration of D2EHPA in the solvent, which results in a decrease in the Sc(III) extraction [47,48].

Moreover, TBP had little effect on the extraction of other metals. The extraction efficiencies of Fe, V, Mn, Mg and Cr were less than 1%, and those of Ti and Al were 2%~5% for the whole concentration range studied. Hence, 2% (v/v) of TBP was selected as the optimum experimental condition.

3.2.3. Effect of the O/A Phase Ratio on the Sc Extraction

Extraction experiments were conducted at a different phase ratio (O/A). As can be seen from Figure 5, the extraction efficiency of scandium decreased with the decrease in the phase ratio (O/A). When the phase ratio decreased from 1:1 to 1:10, scandium's extraction efficiency decreased from 92.27% to 84.16%. Further decreasing the phase ratio to 1:15 and 1:20, the extraction efficiency of scandium dramatically decreased to 53.74% and 47.01%. Moreover, the extraction efficiency of Fe, V, Mn, Mg, and Cr in the studied O/A range remained below 2%, and those of Ti and Al were 5%~10% when the phase ratio decreased from 1:1 to 1:5. Therefore, the optimal phase ratio (O/A) was determined to be 1:10.

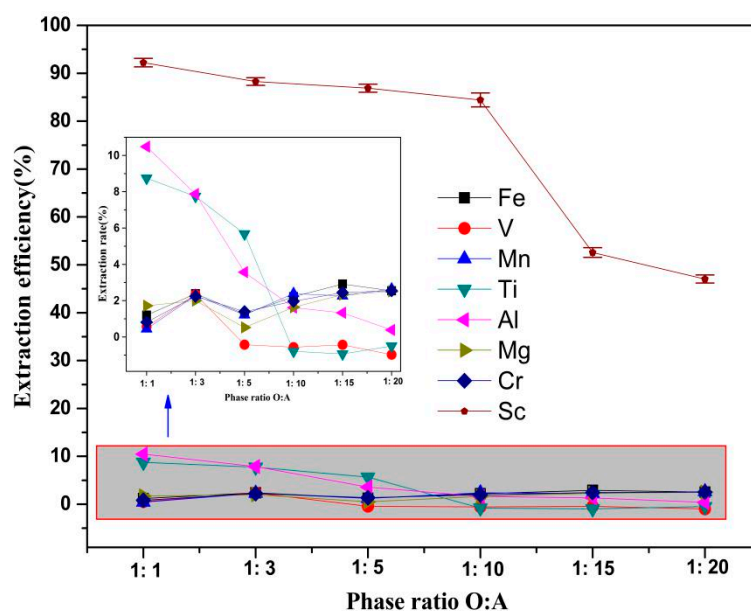


Figure 5. Effect of the O/A phase ratio on the Sc extraction (8% of D2EHPA, 2% of TBP, pH = −0.75, 5 min, at 298 K).

3.2.4. Effect of the Stirring Speed on the Sc Extraction

Solvent extraction of Sc was conducted at different stirring speeds.

As shown in Figure 6, when the stirring speed increased from 300 r/min to 1300 r/min, the extraction efficiency of Sc dramatically increased from 21.44% to 84.47%. Meanwhile, the extraction efficiencies of Fe, V, Mn, Mg, and Cr were very low and remained below 2% in the stirring speed range studied, and those of Ti and Al were 5%~8% when stirring speed increased from 900 r/min to 1300 r/min. Therefore, the optimal stirring speed was selected as 900 r/min.

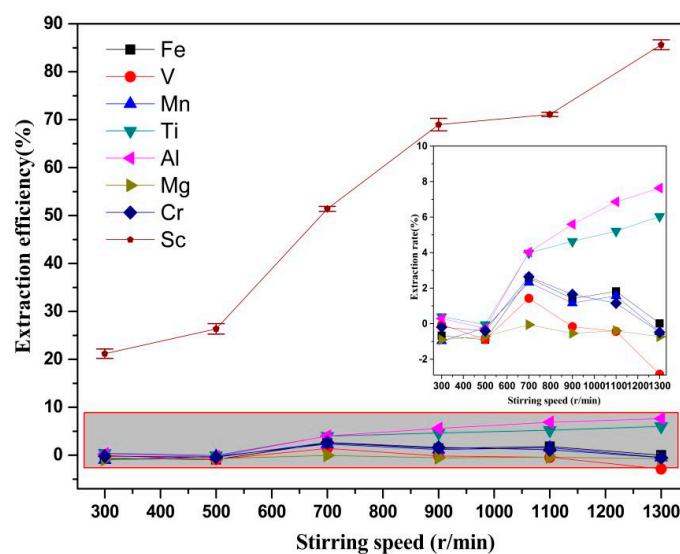


Figure 6. Effect of stirring speed on the Sc extraction (8% of D2EHPA, 2% of TBP, O/A 1:10, pH= −0.75, 5 min, at 298 K).

3.3. Scrubbing of Co-extracted Elements and Stripping of Sc

Although D2EHPA has a high selectivity of scandium, some impurity ions (Fe, V, Mn, Ti, Al, Mg and Cr) are inevitably extracted into the loaded organic phase during the extraction process. If they are not completely removed, they will be harmful to the stripping effect of Sc due to the formed hydroxide precipitation. Therefore, it is significant to remove impurity ions before stripping experiments by scrubbing the loaded organic phase.

The scrubbing process was conducted under the following conditions: O/A = 2:1, equilibrium time of 5 min, and 4 mol/L HCl (the optimal condition of the scrubbing process in the previous separation study of scandium and iron [49]).

As can be seen in Figure 7, the scrubbing efficiencies of Fe, Mn, Ti, Al, Mg, and Cr were all over 95% and the scrubbing efficiency of V was 89.86%. Conversely, the scrubbing rate of scandium was only 1.1% under the condition. Therefore, Sc can be effectively separated from co-extracted elements under these experimental conditions.

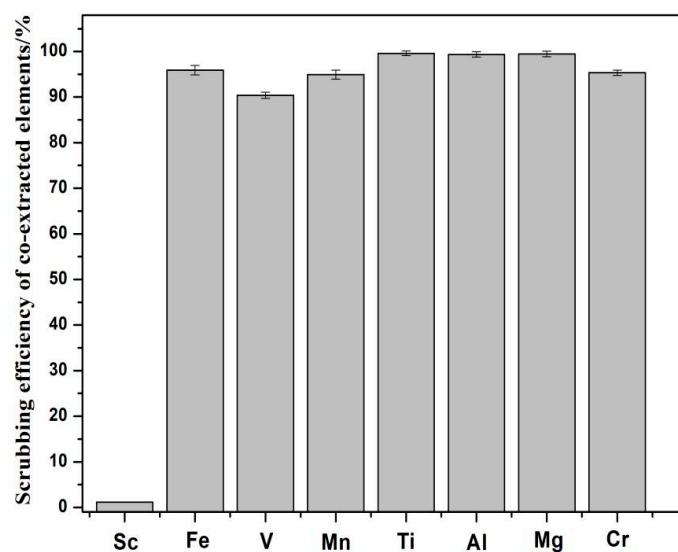


Figure 7. Scrubbing of co-extracted elements (O/A = 2:1 and 4 mol/L HCl for 5 min at 298 K).

After the scrubbing experiment of co-extracted elements, the stripping of Sc was carried out with 2 mol/L NaOH + 1 mol/L NaCl at O/A = 1:1 for 30 min at 313 K (the optimal condition of the stripping process in the previous separation study of scandium and iron [49]), and 87.20% of Sc can be effectively stripped. Therefore, Sc can be effectively extracted from pressure acidic leaching solution of converter slag.

4. Conclusions

Based on the results obtained in this study, the following conclusions were made:

(1) The thermodynamic analysis on the species distribution diagrams of Sc-S-H₂O systems was studied. In the actual leaching solution of vanadium slag by titanium white waste acid (pH = −0.75), the main existing forms of Sc were the cations of Sc³⁺ and Sc(SO₄)⁺, and the main existing form of S was HSO₄[−].

(2) The Sc extraction efficiency was 83.64% with less than 2% of co-extracted elements under optimal conditions. Deep separation of Sc and co-extracted elements can be realized in the extraction process. Firstly, over 95% of the co-extracted elements in the loaded organic phase were scrubbed with a 4 mol/L hydrochloric acid solution. Then, 87.20% of Sc was stripped with a 2 mol/L sodium hydroxide and 1 mol/L sodium chloride solution. These results are slightly lower than those which directly extract scandium from titanium dioxide waste acid (the extraction efficiency of scandium is about 95%, the total recovery efficiency is close to 85%).

Author Contributions: Writing—original draft, X.C.; writing—review and editing, T.-a.Z.; resources, W.Z.; writing—review and editing, G.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Fundamental Research Funds for the Central Universities (N182504018), the National Natural Science Foundation of China (Nos.51874078), the Fund of Liaoning S&T Project (20180551008).

Acknowledgments: The authors would like to thank Laboratory Center of Northeastern University for analysis.

Conflicts of Interest: The authors declare no conflict of interest.

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