

# Dephosphorization of Vanadate Leaching Solution by Chloride-Free Dephosphorizing Agent

Jinglei Zhang, Yanli Ren, Changlin Liu, Jianming Li, and Jinyang Zhang

**Abstract**— $\text{CaCl}_2$  was generally used as dephosphorizing agent during the sodiumization-vanadium extraction process. However, a large number of chloride ions were brought into wastewater from vanadium precipitation, which increased the corrosion of the evaporation-concentration equipments of wastewater treatment. Then, the chloride-free dephosphorizing agent (CFDA) was developed, and the dephosphorizing effect was compared with that of  $\text{CaCl}_2$ . The results showed that, with the chloride-free dephosphorizing agent, the dephosphorizing ratio  $\geq 99\%$ , clarification time of 120 min, vanadium loss  $\leq 3.5\%$ , and vanadate leaching solution dephosphorized by the CFDA could meet the demand of high density vanadium precipitation.

**Index Terms**—Chloride-free dephosphorizing agent, dephosphorization, vanadate leaching solution, vanadium precipitation.

## I. INTRODUCTION

At present, sodiumization-vanadium extraction is widely applied to vanadium production in most factories of the world, which is sodium salt oxidation roasting-water leaching-acidic ammonium salt precipitation of vanadate leaching solution [1]. The vanadate leaching solution after water leaching has to be dephosphorized before acidic ammonium salt precipitation. During the vanadium production process, ammonium polyvanadate (APV, for short) and wastewater were obtained. APV was roasted to prepare  $\text{V}_2\text{O}_5$  or  $\text{V}_2\text{O}_3$  [2], and the wastewater was treated by reduction-precipitation and evaporation-concentration to realize zero discharge of wastewater.

$\text{CaCl}_2$ , generally used as dephosphorizing agent during the sodiumization-vanadium extraction process [3], led to the entrance of chloride ions into the wastewater from vanadium precipitation [4]. The enrichment of chloride ions would give rise to the corrosion of wastewater treatment equipments during the evaporation-concentration [5], which influenced the continuous production of vanadium (see Fig. 1). Then development of chloride-free dephosphorizing agent (CFDA) would avoid the occurrence of this problem. The common chloride-free dephosphorizing agents contained  $\text{MgSO}_4$  series and  $\text{Al}_2(\text{SO}_4)_3$  series [6], but utilization of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  series would bring other metallic ions into wastewater, which made the wastewater treatment more difficult. Then, our laboratory developed the chloride-free dephosphorizing agent (CFDA), with  $\text{CaSO}_4$  series, which could avoid the

entrance of other metallic ions into wastewater. In this paper, the dephosphorizing effect of CFDA on vanadate leaching solution was investigated, and influences of CFDA on acidic ammonium salt precipitation and wastewater treatment were examined.



Fig. 1. Corrosion of the equipments during vanadium production

## II. MATERIALS AND METHODS

### A. Materials

*p*-toluenesulfonic acid, calcium carbonate, calcium oxide and polyacrylamide, which were all industrial grade, were used to prepare the chloride-free dephosphorizing agent.

### B. Methods

#### 1) Preparation of chloride-free dephosphorizing agent

Calcium oxide was the main raw material, and  $\text{CaSO}_4$  series dephosphorizing agent was prepared using chelation-dispersion principle, in which  $\text{Ca}^{2+}$  concentration was 14.4 g/L.

#### 2) Dephosphorization of vanadate leaching solution

The vanadate leaching solution obtained after water leaching was at 80-85 °C [7]. The chloride-free dephosphorizing agent or  $\text{CaCl}_2$  solution was added into the vanadate leaching solution, and then the solution was mixed at 80-85 °C, with reaction time of 20 min, clarification time of 2 h. Then the dephosphorizing effects were investigated.

#### 3) High density vanadium precipitation

The qualified vanadate leaching solution after dephosphorization was heated and adjusted pH, and then ammonium salt was added. The pH of mixture was adjusted, the mixture was boiled and standing for clarification, and then sediment and supernatant were obtained. The sediment was ammonium polyvanadate (APV), and the supernatant was wastewater from vanadium precipitation. When the

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vanadium content in the vanadate leaching solution was over 20 g/L, high density vanadium precipitation was called.

#### 4) Computational methods of vanadium recovery

The vanadium recovery was calculated as follow:

$$R=1-(C_1 \times V_1 / C_2 \times V_2)$$

R: vanadium recovery, %;

C<sub>1</sub>: vanadium content in the supernatant, g/L;

V<sub>1</sub>: volume of the supernatant, L;

C<sub>2</sub>: vanadium content in the vanadate leaching solution, g/L;

V<sub>2</sub>: volume of the vanadate leaching solution, L.

#### 5) Wastewater treatment by fractional crystallization

The wastewater from vanadium precipitation was treated by reduction-precipitation to remove vanadium and chromium, and then by evaporation-concentration to get anhydrous sodium sulfate and high-concentration ammonium sulfate solution (ammonium-rich solution). The ammonium sulfate was reused to vanadium precipitation. The anhydrous sodium sulfate was used to prepare sodium sulfide.

### III. RESULTS AND DISCUSSIONS

#### A. Dephosphorizing Effect of Chloride-Free Dephosphorizing Agent

The chloride-free dephosphorizing agent was prepared in which the Ca<sup>2+</sup> concentration was 14.4 g/L, which was colorless transparent liquid (see Fig. 2). Different volumes of CFDA were added into the vanadate leaching solution, and the dephosphorizing effects were showed in Table I.

TABLE I: EFFECT OF CFDA ADDITION VOLUME ON DEPHOSPHORIZATION OF VANADATE LEACHING SOLUTION

CFDA (mL/L)	Floc Occurrence (min)	Clarification Time (h)
30	65	> 3
36	40	2.5
40	20	2
44	10	< 2

CFDA (mL/L)	Sediment	Sedimentation Rate
30	smaller amount	slow
36	small amount	slightly fast
40	large amount	fast
44	larger amount	very fast



Fig. 2. Chloride-free dephosphorizing agent

The demands of dephosphorizing agent should be that the clarification time is not too long and the sediment is not too large amount. Table I showed that 40 mL CFDA per 1 L vanadate leaching solution was optimal, when the clarification time was not too long, and the sediment amount was just the right amount.

Forty milliliter CFDA was added into one liter vanadate leaching solution, and then the dephosphorizing effect was compared with that of CaCl<sub>2</sub> (Table II).

TABLE II: DEPHOSPHORIZING EFFECT BETWEEN CFDA AND CaCl<sub>2</sub>

Dephosphorizing Agent	Vanadate Leaching Solution		Clarification Time (min)
	TV(g/L)*	TP(g/L)*	
CaCl <sub>2</sub>	28.84	0.021	120
CFDA	28.84	0.021	120

Dephosphorizing Agent	Supernatant		Vanadium Loss (%)
	TV(g/L)*	TP(g/L)*	
CaCl <sub>2</sub>	27.35	<0.01	5.17
CFDA	27.88	<0.01	3.31

TV\*: total vanadium concentration;

TP\*: total phosphorus concentration.

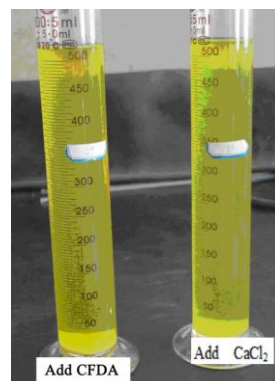


Fig. 3. Dephosphorization by CFDA and CaCl<sub>2</sub>

In the same clarification time, the dephosphorizing effect was very close whether using CFDA or CaCl<sub>2</sub> (Fig. 3). It was also found that the dephosphorizing effect of CFDA was more stable than that of CaCl<sub>2</sub>. Table II showed that the vanadium loss using CFDA (3.31%) was lower than that of CaCl<sub>2</sub> (5.17%).

#### B. Influence of CFDA on Vanadium Precipitation

High density vanadium precipitation was done in our laboratory. Five hundred milliliter vanadate leaching solution dephosphorized by CFDA and CaCl<sub>2</sub>, respectively, were taken to do vanadium precipitation [9]. The influence of CFDA and CaCl<sub>2</sub> on vanadium precipitation was showed in Table III.

The vanadate leaching solution dephosphorized by CaCl<sub>2</sub> or CFDA, respectively, was taken to do high density vanadium precipitation experiment, then the vanadium recovery (> 99.34 %) and the vanadium content in APV using CFDA were higher than that of CaCl<sub>2</sub>, Na<sub>2</sub>O and K<sub>2</sub>O contents in APV were lower than that of CaCl<sub>2</sub> (Table III). The shape of APV after vanadium precipitation was all

spherical using whether  $\text{CaCl}_2$  or CFDA (Fig. 4). The vanadate leaching solution dephosphorized by CFDA had no significant influence on vanadium precipitation, and APV after vanadium precipitation could be satisfied with the demand of later production.

TABLE III: EFFECT OF DIFFERENT DEPHOSPHORIZING AGENT ON VANADIUM PRECIPITATION

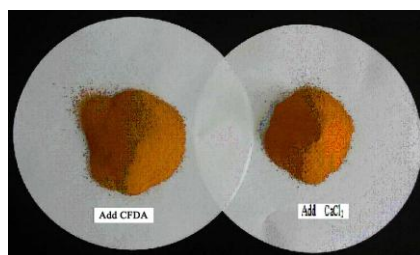
Agent	Vanadate Leaching Solution	Ammonium Addition Coefficient	Recovery (%)	Supernatant TV*(g/L)
$\text{CaCl}_2$	32	2.2	98.74	0.443
$\text{CaCl}_2$	29	2.2	98.68	0.424
$\text{CaCl}_2$	29	2	99.28	0.253
$\text{CaCl}_2$	26	2	99.57	0.194
CFDA	30	2	99.68	0.1
CFDA	30	2	99.34	0.199
CFDA	30	2.2	99.53	0.152
CFDA	30	2.2	99.34	0.252

Agent	APV* (%)					
	TV*	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	S	Si	TFe*
$\text{CaCl}_2$	50.09	0.071	0.21	0.123	0.041	<0.01
$\text{CaCl}_2$	50.46	0.09	0.12	0.109	0.053	0.013
$\text{CaCl}_2$	50.38	0.094	0.14	0.084	0.066	<0.01
$\text{CaCl}_2$	50.35	0.089	0.057	0.085	0.029	< 0.01
CFDA	50.47	0.12	0.056	0.164	0.031	0.031
CFDA	50.47	0.14	0.075	0.13	0.044	0.025
CFDA	50.56	0.11	0.048	0.162	0.03	0.035
CFDA	50.56	0.11	0.047	0.195	0.026	0.038

TV\*: total vanadium concentration;

APV\*: ammonium polyvanadate;

TFe\*: total ferrum.

Fig. 4. APV disposed by CFDA or  $\text{CaCl}_2$ 

### C. Influence of CFDA on Fractional Crystallization

The wastewater after vanadium precipitation was treated by fractional crystallization, and anhydrous sodium sulfate and ammonium-rich solution were obtained. Fifteen liter wastewater, in which vanadium and chromium had been removed, was treated by evaporation-concentration-fractional crystallization, and then sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was obtained (Table IV).

The anhydrous sodium sulfate after fractional crystallization met with the technical requirements of GB/T6009-2003, and the refining effect of ammonium-rich

liquid was good. The particles of anhydrous sodium sulfate after dephosphorized by CFDA were finer than by  $\text{CaCl}_2$ , and the moisture content was higher, which was the main reason why the anhydrous sodium sulfate purity decreased (see Table IV).

TABLE IV:  $\text{Na}_2\text{SO}_4$  AFTER USING DIFFERENT DEPHOSPHORIZING AGENT

Dephosphorizing Agent	$\text{Na}^+$ (%)	$\text{NH}_4^+$ (%)	$\text{SO}_4^{2-}$ (%)	$\text{Cl}^-$ (%)	Purity (%)
$\text{CaCl}_2$	29.60	1.14	68.57	0.24	95.1
CFDA	31.6	2.54	68.50	<0.11	91.3

### D. Influence of CFDA on Vanadium Precipitation by Ammonium-Rich Solution

The wastewater after dephosphorizing by CFDA or  $\text{CaCl}_2$  was treated by fractional crystallization, and the ammonium-rich solution was obtained. The ammonium-rich solution was reused to vanadium precipitation, and the effects of obtained ammonium-rich solution on high density vanadium precipitation were investigated. The results were showed in Table V.

The results showed that ammonium-rich solution obtained after dephosphorization by whether  $\text{CaCl}_2$  or CFDA were all satisfied with the demand of high density vanadium precipitation. Vanadium content in APV obtained which was treated by whether  $\text{CaCl}_2$  or CFDA was over 50 %. The impurity content ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) in APV treated by  $\text{CaCl}_2$  was lower than by CFDA.

TABLE V: VANADIUM PRECIPITATION BY DIFFERENT AMMONIUM-RICH SOLUTION DISPOSED BY CFDA OR  $\text{CaCl}_2$ 

Solution	Vanadate Leaching Solution	Ammonium Addition Coefficient	Recovery (%)	Supernatant TV (g/L)
A	30	2	98.95	0.177
B	30	2	99.61	0.113

Solution	APV (%)					
	TV*	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	S	Si	TFe*
A	50.45	0.13	0.06	0.136	0.038	0.024
B	50.51	0.147	0.075	0.152	0.074	< 0.010

Solution A: ammonium-rich solution obtained after dephosphorization by  $\text{CaCl}_2$ ; solution B: ammonium-rich solution obtained after dephosphorization by CFDA.

### E. Where do the CFDA Go during the Vanadium Production?

From process of dephosphorization, the chloride-free dephosphorizing agent was entered into the vanadium production steps. During the dephosphorization of vanadate leaching solution, cation in the CFDA ( $[\text{Ca}^{2+}]$ ) was separated from vanadate leaching solution in the form of calcium phosphate sediment or calcium vanadate sediment; trace of anion group was entered into APV during the vanadium precipitation process; residual anion group was flown to wastewater, and finally to anhydrous sodium sulfate and

ammonium-rich solution treated by fractional crystallization.

At present, calcination was applied to prepare  $V_2O_5$  or  $V_2O_3$  in most vanadium production factories. In the calcinations process, the temperature was maintained over 400 °C, when the anion from the CFDA in the APV would be decomposed into oxycarbide and water steam to the air. The anion group in the anhydrous sodium sulfate would be decomposed into oxycarbide and water steam during preparation from sodium sulfate to sodium sulfide; the anion group of the CFDA in the ammonium sulfate was recycled into the system.

Therefore, dephosphorization by this chloride-free dephosphorizing agent not only avoided chloride ion corrosion during evaporation-concentration of wastewater, but also no secondary pollution, for the CFDA was finally decomposed into oxycarbide and water steam.

#### IV. CONCLUSION

During the dephosphorization of the vanadate leaching solution, the dephosphorizing ratio and clarification time were close between CFDA and  $CaCl_2$ . The dephosphorizing effect of CFDA was more stable than that of  $CaCl_2$ , and the vanadium loss was lower than that of  $CaCl_2$ .

The vanadate leaching solution after dephosphorized by CFDA, could meet with the demand of high density vanadium precipitation, and the acquired APV could be satisfied with the demand of vanadium production whether appearance or purity.

The wastewater was then dealt with by fractional crystallization, and the fine particle size of anhydrous sodium sulfate was obtained. The moisture content of anhydrous sodium sulfate disposed by CFDA was a little higher than that disposed by  $CaCl_2$ , and this was the main reason why the purity of sodium sulfate decreased.

This chloride-free dephosphorizing agent was applied in the dephosphorization of vanadate leaching solution, which not only avoided the corrosion of equipments, but also no secondary pollution.

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