

# Extraction And Selective Purification of Gallium (III), Vanadium (IV) from Aluminum (III) Contained Acid Sulphate Solutions Using D2ehfa

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**Abstract:-** Di (2-ethylhexyl) phosphoric acid (abbreviated as D2EHPA, commercially as P204), an available reagent, has been used in this work to investigate the extraction of gallium (III) and vanadium (IV) from sulfuric acid solution by the presence of various other metals, such as aluminium (III). The different parameters affecting the extraction of gallium (III) and vanadium (IV) under equilibrium conditions were separately investigated to obtain the extraction characteristics of D2EHPA. The distribution ratio of gallium and vanadium increased with increasing equilibrium pH of the aqueous phase, the concentration of the extractants and temperature. Gallium (III) and vanadium (IV) were predominantly extracted at low pH and were completely separated from aluminum at pH = 2.0 with D2EHPA.

**Keywords:-** Red Mud, Gallium (III), Vanadium (IV), Aluminum (III), Liquid Extraction, Degree Of Extraction, Distribution Coefficient.

## I. INTRODUCTION

The extraction of alumina from aluminum-containing raw materials (bauxite, alunite, nepheline) by the Bayer method is accompanied by the formation of large-tonnage waste in the form of red mud (RM). So when processing 1 ton of alunite ore, 0.5-0.6 ton of waste (sludge) is formed. Sludge, in terms of its chemical and mineralogical composition, is a complex technogenic formation, the processing and disposal of which is very difficult. In bauxite sludge, about 1% of alumina, iron, some amount of rare and rare earth metals, such as titanium (20-120 kg / g), yttrium (60-150 g), are lost [1].

The important components of alunite sludge are gallium and vanadium, the demand for which is growing all over the world, which necessitates the implementation of their production.

At present, a significant number of technological schemes have been proposed that allow for both complex and partial processing of sludge to obtain individual liquid products from its components [2-4]. However, insufficient attention has been paid to the extraction of the most valuable

components from the sludge, such as gallium, vanadium and residual aluminum.

Due to their low content, it is difficult to directly extract gallium and vanadium from the sludge than the main components such as iron, aluminum and titanium.

Methods have been developed for the extraction of gallium and vanadium from bauxite sludge based on dissolution in mineral acids [5,8] or in alkaline solutions [7].

The extraction of Ga and rare earth elements from bauxite residues by selective acid leaching (6.0 M HCl) was investigated by Ujaczki et al [5,6]. After acid extraction from the gallium solution, liquid-liquid extraction was purified using di-2-ethylhexyl) phosphoric acid dissolved in kerosene. However, such a sludge treatment to recover gallium is not economical, since a large amount of acid is consumed at such a low content. A total of 29.0% gallium was extracted from the HCl containing solution into the organic solvent phase (D2EHPA in kerosene).

Red mud obtained from bauxite at one of the Turkish aluminum processing plants [7] contained 0.0055% Ga<sub>2</sub>O<sub>3</sub> and 0.026% V<sub>2</sub>O<sub>5</sub>. These valuable components were leached with alkali in an autoclave at a temperature of about 300°C. The gallium leaching efficiency was -58%. The degree of conversion of vanadium into the precipitate was 94.2-96.9%. The authors of work [8], after acid leaching of bauxite, obtained red mud containing,%: 0.0033 Ga and 0.034 V. After acid leaching of the sludge with hydrochloric acid, the solution was processed by ion exchange technology with a fivefold increase in the gallium concentration.

In our previous studies, a new approach was developed for the extraction of gallium and vanadium from sludge of alunite production [9]. The obtained results showed that sulfatization of red mud with sulfuric acid under appropriate conditions (mass ratio of KSh-a and sulfuric acid (1:1), temperature of sulfatizing roasting is 620°C and duration of roasting (1 hour), 85% of aluminum can be converted into a water-soluble form., 90-93% gallium and vanadium As a result of leaching of the sulfated mass with water, oxides of iron and silicon remain in the residue, and sulfates of aluminum, gallium and vanadium pass into solution.

As you can see, acid leaching is an effective method for extracting gallium and vanadium from aluminum-containing resources, but a large amount of impurity ions such as aluminum is also leached along with gallium and vanadium. Therefore, the separation and recovery of gallium and vanadium from leached sulfuric acid solutions is a key and necessary process for the recovery of these rare metals.

The aim of this work is to study the possibility of extracting and purifying gallium and vanadium from a solution containing aluminum (III). The possibility of separating Al (III) from gallium and vanadium in a sulfate medium by partial neutralization of the solution is being considered.

For the extraction of gallium and vanadium from acidic sulfate solutions, in which these metals are predominantly in the cationic form, cation exchange reagents are most often used. At present, such a reagent is often used rather strong, widely used in radiochemistry, analytical chemistry, and chemical technology D2EHPA (di 2-ethyl-hexyl phosphoric acid) [10].

D2EHPA was used to extract vanadium from sulfuric acid solutions, as well as to extract vanadium from coal with leaching [11]. We have previously studied the liquid extraction of gallium from model sulfuric acid media with a solution of D2EHPA in kerosene [12]. However, in most hydrometallurgical processes, metals are extracted in mixed solutions, i.e. high concentration gallium, vanadium and aluminum can be recovered together using acidic organophosphorus extractants.

In a sulfate environment, gallium, vanadium and aluminum can be recovered together with D2EHPA. In this work, special attention is paid to the extraction of gallium (III) and vanadium (IV) from the solution of sulfate leaching of red mud by extraction with D2EHPA at low pH.

## II. EXPERIMENTAL PART

Research objects. Reagents and solutions. The work used a sample of KSh after leaching alunite, composition, wt.%, Al<sub>2</sub>O<sub>3</sub>-4.53; SiO<sub>2</sub>-82.21; Fe<sub>2</sub>O<sub>3</sub>-8.60; TiO<sub>2</sub>-1.15; K<sub>2</sub>O-0.07; Na<sub>2</sub>O-0.23; SO<sub>3</sub>-0.15; V 0.099; Ga-0.005.

The RM sample of the specified composition is mixed with concentrated sulfuric acid at a mass ratio of 1:1, sulfatized at a temperature of 620°C, with a firing duration of 1 hour. In this case, aluminum, gallium and vanadium in the cinder exist in the sulfate form Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, VOSO<sub>4</sub>). As a result of leaching of the sulfated mass with water, iron oxide and silicon remain in the residue, aluminum, gallium and vanadium sulfates go into solution. After the circulating solution, the concentration of these elements reached Ga -0.0067 mol / l, V -0.04 mol / l, Al -0.193 mol / l.

Extraction experiments were carried out with model and technological solutions.

Model solutions of vanadium, gallium and aluminum were prepared from sulfate and chloride salts of chemically pure grade. the required pH value was adjusted by adding 1N NaOH and H<sub>2</sub>SO<sub>4</sub> solutions. The di-2-ethyl-hexylphosphoric acid used in the study was obtained commercially.

Aviation kerosene of grade "4" was used as a diluent, and for extraction, solutions of D2EHPA of various concentrations-0.15-0.6 M. vanadium and aluminum in the solution was carried out by the photolorimetric method, by measuring the optical density of the solutions on a KFK-3 photocalorimeter.

The pH values of aqueous solutions were monitored using an EV-74 universal ion meter. Extraction was carried out in separating funnels by contacting an aqueous solution of metals with an extractant solution at a ratio of organic and aqueous phases Vo: Vw = 1:1, contact time no less than 15 minutes, temperature -20 ± 1C. After phase separation, the aqueous layer was separated, and the equilibrium concentration of gallium, vanadium, and aluminum was determined therein.

The distribution coefficient (D) was calculated as the ratio of the concentration of metals in the organic and aqueous phases

$$D = \frac{M_{\text{org.}}}{M_{\text{wat.}}}$$

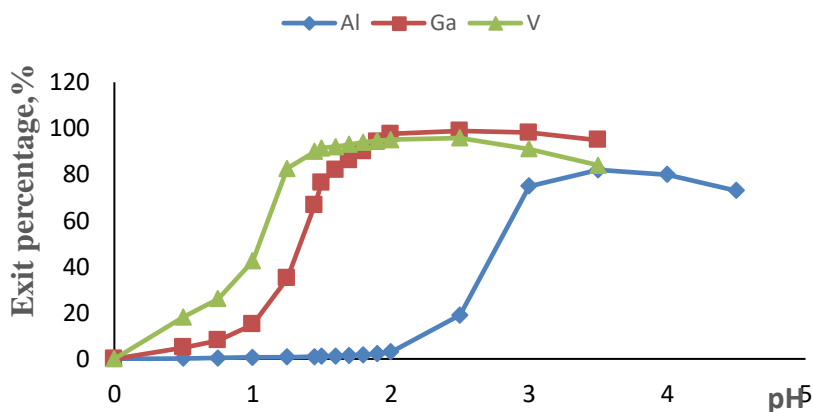
and the separation coefficient (β) was calculated according to the distribution coefficient of Ga, V and Al

$$\beta_{\text{Ga/V}} = \frac{D_{\text{Ga}}}{D_{\text{V}}} \quad \text{or} \quad \beta_{\text{Ga/Al}} = \frac{D_{\text{Ga}}}{D_{\text{Al}}}$$

In the course of the analysis, the metal distribution coefficient (D), the percentage of the organic phase (ε,%) and the separation coefficient (β) were calculated. The determination of Ga, V and Al in the solution was carried out by the photolorimetric method by measuring the optical density of solutions on a KFK-3 photometer, and to ensure the accuracy of the results, additional measurements were carried out on a Bruker S2 Picofox spectrometer (Germany).

## III. RESULTS AND DISCUSSION

**Extraction of Ga (III), V (IV), Al (III) depending on the equilibrium pH.** The effect of the equilibrium pH of the solution on the outcome of gallium, vanadium, and aluminum was studied under the following conditions: the equilibrium time was 15 min, in the ratio Vo: Vw = 1: 1, the initial concentration of the organic phase was 0.3 M solution of D2EHPA in kerosene. The research results are shown in Figure 1.

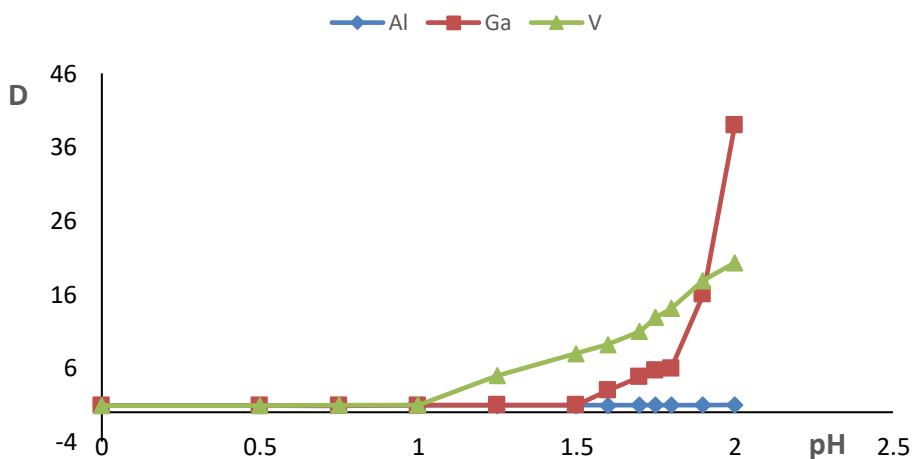


**Fig. 1.** Dependence of the extraction of Ga (III), V (IV) and Al (III) on the equilibrium pH of the solution  $V_o: V_w = 1: 1$ ,  $t = 20^\circ\text{C}$ ,  $\tau = 15 \text{ min}$ ,  $C_{D2EHPA} = 0.3\text{M}$  (kerosene solution),  $C_{(Ga(III))} = 0.007 \text{ mol / l}$ ,  $C_{(V(IV))} = 0.04 \text{ mol / l}$ ,  $C_{Al} = 0.193 \text{ mol / l}$ .

The results showed that as the pH increased, the percentage of extraction of all three cations increased. Figure 1 shows that, despite the fact that D2EHPA effectively separates gallium and vanadium in the pH range 1.4–1.8, aluminum extraction occurs at  $\text{pH} > 2$ . A further increase in pH also increases the recovery of gallium and vanadium. If the equilibrium pH of the solution rises from 0.5 to 2.5, the yield of vanadium increases from 18.1 to 95.8%, such a yield of gallium (~ 98.2) occurs when the equilibrium pH of the solution is within 1.0-2.0. The low equilibrium pH value ( $\text{pH} 1.8$ ) allows the simultaneous separation of V and Ga from aluminum. The maximum extraction of aluminum (82%) occurs at  $\text{pH} = 2$ , and the equilibrium of the solution at  $\text{pH} = 4$ . An increase in pH to 4.5 reduces the extraction of Al (III) from 82 to 71%. At

$\text{pH} > 4$ , the aluminum solution becomes cloudy, and a third phase is formed during the extraction process. X-ray phase analysis of the third phase confirmed the presence of phases  $\text{Al}(\text{OH})_3$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  и  $\text{CaPO}_3(\text{OH})_2 \cdot \text{H}_2\text{O}$ . Therefore, it is not recommended to increase the pH above 4.0 when extracting gallium and vanadium from sulfate solution, since  $\text{Al}(\text{OH})_3$  is precipitated, also the gallium-vanadium extract is contaminated with aluminum.

The dependence of the equilibrium pH on the distribution coefficient in a sulfated solution of gallium (III), vanadium (IV) and aluminum can be seen from the graph (Fig. 2), all these metals are recovered in the pH range 1.0. - 2.0.



**Fig. 2.** Dependence of the distribution coefficient of gallium, vanadium and aluminum on the equilibrium pH of the solution ( $C_{D2EHPA} = 0.3\text{M}$ ,  $V_{(org.): V_{(wat.)}} = 1: 1$ ,  $t = 20^\circ \text{C}$ ,  $\tau = 10 \text{ min.}$ ,  $C_{Ga} = 0.0067 \text{ mol / l}$ ,  $C_v = 0.04 \text{ mol / l}$ ,  $C_{Al} = 0.193 \text{ mol / l}$ )

However, at  $\text{pH} = 2$ , their distribution coefficients differ sharply. Thus, the gallium ion ( $D \geq 41$ ) is most extracted from the equilibrium aqueous phase at  $\text{pH} 2.0$ . In this case, the pH maximum distribution coefficient of vanadium is  $D = 19.39$ . The distribution coefficient of aluminum is significantly lower than Ga and V, and does not exceed 0.32.

Table 1 shows the distribution coefficients of gallium, vanadium and aluminum depending on the equilibrium pH of the solution, as well as the results of the coefficients of separation of gallium and vanadium from aluminum. As can be seen from the table, the distribution and separation coefficients of these elements differ depending on the value of the equilibrium pH. So, at an extractant density of 0.3 M, an equilibrium pH of 2.3, which is 308.9 times for

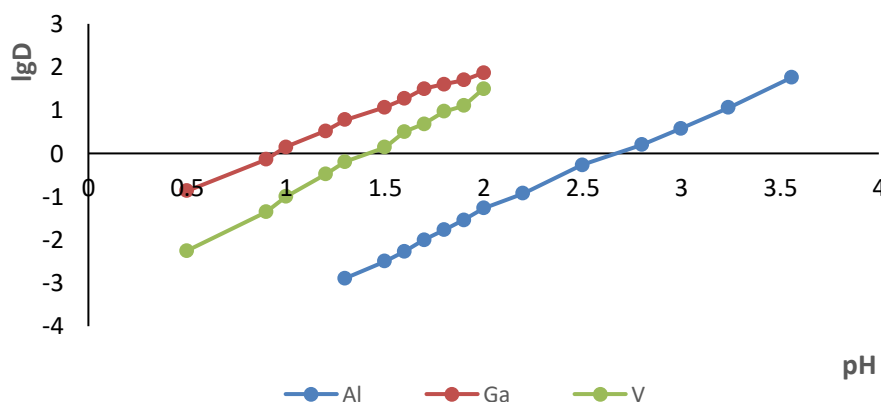
$D_{Ga}/D_{Al}$  and 43.96 times for  $D_V/D_{Al}$ , that is, gallium is released 308.9 times more than aluminum, and vanadium is

released 43.96 times more, than aluminum.

**Table 1.** Influence of the equilibrium pH of the solution on the distribution coefficient (D) and separation coefficient ( $\beta$ ) of aluminum.  $C_{Al}=0.193 \text{ mol/l}$  (5.211 g/l),  $C_{Ga}=6,7 \cdot 10^{-3} \text{ mol/l}$  (0.474 g/l),  $C_V=0.04 \text{ mol/l}$  (2.06 g/l)

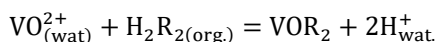
Equilibrium pH	$D_{Ga}$	$D_{Al}$	$D_V$	$\beta = \frac{D_{Ga}}{D_{Al}}$	$\beta = \frac{D_V}{D_{Al}}$
0,5	0,05	0,0101	0,208	4,95	20,59
0,75	0,07	0,011	0,369	6,36	33,54
1,0	0,11	0,012	0,736	9,16	61,33
1,25	0,6	0,038	4,75	15,78	125
1,50	2,8	0,060	9,50	46,6	158,3
1,70	5,09	0,090	14,0	56,55	188
1,80	6,35	0,10	16,0	63,5	160
1,90	16,13	0,22	18,0	73,32	81,81
2,00	40,21	0,32	19,34	125,6	60
2,2	173	0,56	24,62	308,9	43,96

In fig. 3 that the vanadium distribution coefficient increases linearly with an increase in the equilibrium pH of the solution. The slope of this line is 2.1 by 0.3 mol of the extractant. This indicates the release of 1 mol of vanadium in an aqueous medium up to 2 mol of  $H^+$ .

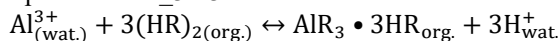


**Fig. 3.** Dependence of lgD on the equilibrium pH of the solution.  $C_{Ga(III) \text{ water}} = 0.007 \text{ mol/l}$ ;  $C_{V(IV) \text{ water}} = 0.04 \text{ mol/l}$ ;  $C_{Al(III) \text{ water}} = 0.193 \text{ mol/l}$ ;  $C_{D2EHPA} = 0.3 \text{ mol/l}$ ;  $V_{(org.): V_{(wat)}} = 1:1$ ;  $t = 20^\circ C$

The results are consistent with the conclusions of Sato T., Takeda T. [13], Xing-bin Li and others [14]. Thus, the reaction of the cation exchange  $VO^{2+}$  can be expressed as follows:



The slope of the calculated line for Al is 2.9. This indicates that the chemical formula of the extract corresponds to  $AR_3 \cdot 3HR$ .



Our research [12] confirmed that the extraction of gallium proceeds by the cation-exchange mechanism and the chemical formula of the extract obtained in the organic phase corresponds to  $AR_3 \cdot 3HR$ .

#### IV. CONCLUSIONS

As a result of studying the extraction of gallium, vanadium and aluminum ions from sulfate solutions, it was found that all three cations can be extracted with the extractant D2EHPA.

It was also found that gallium (IV), vanadium (IV) maximum is extracted at pH 1.4-1.8, and aluminum extraction occurs at  $pH > 2$  (maximum at  $pH = 3-4$ )

It was found that all three cations are extracted from acidic sulfate solutions by the cation exchange mechanism.

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