Vanadium Extraction Opportunities in Alumina Production and Vanadium Complex Study in Organic Phase

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Abstract

One of the steady vanadium extraction sources is by-products of alumina production. The object of study is circulating solution of alumina production, containing 280 g/dm^3 Na_2O and 0.40-0.57 g/dm^3 V_2O_5. Vanadium compounds can be extracted from alumina solution by crystalization. It was determined that the fluorine admixture has a considerable influence on crystallization of vanadium compounds. The presence of fluorine admixture decreases the vanadium dissolubility due to the formation of $Na_7(VO_4)_2F{\cdot}19H_2O$.

The physical-chemical analysis of crystallization products showed that the increase of extraction rate for vanadium was due to not only formation of salt containing fluorine, but also because of phosphorus crystallization on its surface. And this fluorine crystallization, in its turn, is the additional source for vanadium crystallization. The vanadic compound is identified as $Na_7(VO_4,PO_4)_2F{\cdot}19H_2O$.

Extraction of vanadium (V) from pulp using tributylphosphate (TBP) as extragent enables us to increase the effectiveness of the vanadium extraction and to decrease the amount of wastewater in technological process. Pulp is produced by introducing hydrochloric acid into vanadium by-product.

In practice, vanadium is extracted by tributylphosphate from hydrochloric acid solutions.

Hydrochloric acid solutions formed in the process of extraction from the pulp are intermediate between solid phase (insoluble part of vanadium product and compounds of impurities) and organic phase.

The study presents the findings of physical-chemical analysis of vanadium organic complex extracted by tributylphosphate. Such a complex, with high likelihood, has the form of $[H_3O^+{\cdot}nH_2O{\cdot}mTBP][VO_2Cl_2{\cdot}pTBP{\cdot}hH_2O]^-$.

Introduction

One of the key approaches of scientific-technical progress in mineral processing is an extraction of all useful mineral components. In the first place, this approach is referred to polymetallic ores processing containing wide range of rare and non-ferrous metals.

In this case, hydrometallurgical processes (in particular liquid extraction process) acquire the most important meaning in polymetallic ores processing. However, there are some factors that restrict use of extraction in industry, for example, the limit choice of effective extragents and not enough data of chemistry and of mechanism of extraction.

It is known that vanadium is mainly got by integrated iron-ore processing. However, important scientific and technological tasks are the search of new sources of raw materials for useful metal and the development of environmental concerned technologies for its extraction, with using effective organic compounds.

Experimental

The object of study is circulating solution of alumina production, containing 280 g/dm^3 Na_2O and 0.40-0.57 g/dm^3 V_2O_5. Vanadium crystallization from alumina solution was carried out by introducing the seeding in the form of concentrate received on the previous stage. We received optimal conditions of vanadium concentrate extraction: a cooling rate of solution (6-8°C per hour), an amount of seeding (15-30 g/dm^3), a temperature of seeding process (35°C), a rate of solution stirring (100-150 stirrings per min.).

Extraction with 100% TBP has been used as one of possible methods of processing of vanadium concentrate. While stirring the hydrochloric acid was

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added up to the concentration of 3 mole/dm^3 in the intermediate solution. Then we added the tributylphosphate in the proportion 5:1 (V-org.: solid). Three phases are formed after the extraction process: the solid product, the extract and aqua phase.

We have done physical-chemical investigations of vanadium concentrate, obtained from industrial solutions, and vanadium organic complex extracted by TBP. Chemical, UV, IR, NMR spectroscopy and conductometric methods of analysis have been used in this investigation.

Results

Crystallization process

The addition of seeding influences importantly the size of crystals of picked out product, as well as raises the concentrate extraction.

It was determined that the fluorine admixture has a considerable influence on crystallization of vanadium compounds. And the presence of fluorine admixture decreases the vanadium dissolubility due to the formation of $Na_7(VO_4)_2F{\cdot}19H_2O$.

The study presents the following analysis. The physical-chemical analysis of crystallization products showed that the increase of extraction rate for vanadium was due to not only formation of salt containing fluorine, but also because of phosphorus crystallization on its surface. And this fluorine crystallization, in its turn, is the additional source for vanadium crystallization.

Extraction process

The results of vanadium concentrate studies by phase and chemical composition showed that the main phase is the sodium aluminate. And also there are phosphate, carbonate, sodium fluoride in the concentrate. The vanadic compound is identified as $Na_7(VO_4,PO_4)_2F{\cdot}19H_2O$ [1].

The organization of vanadium extraction from pulp, received by introducing hydrochloric acid into the vanadium concentrate, can improve the effectiveness of technology for metal production in comparison with existing methods and can significantly decrease the wastewater volume. To improve the effectiveness of the technology of metal production, we offer to use available and cheap reagent- tributylphosphate (TBP), which in the extraction process from pulp factually extracts vanadium from hydrochloric acids solution. It is an intermediate unit between solid (the dissolved part of the concentrate and the admixture of compounds) and organic phases.

The chemical analysis of saturated organic phase shows that molar ratio of vanadium and chlorine is close to 1:3.

UV and IR spectroscopy measurements

The ultra-violet spectra (UV-spectra) of vanadium ions in organic phase are described by the absorption band with the max wavelength 226 nm ($\varepsilon = 2.7{\cdot}10^{-3}$ g·atom^{-1}·cm^{-1}). According to comparison of received and literature results, it is possible to suppose that vanadium in organic phase has the form of dioxide vanadium VO_2^+ [2].

When increasing vanadium concentration in extracts, the band of valence vibrations P=O in the infrared (IR) spectrums move to low frequency range due to formation of donor-acceptor bond of vanadium and TBP.

It is necessary to note that the observable widening of coordination group band P=O… is the result of formation of hydrogen bonds (solvates of hydroxonium, for example, $[H_3O^+{\cdot}3TBP]$, and TBP hydrosolvates- HCl- $[H_3O^+{\cdot}nH_2O{\cdot}mTBP]Cl^-$).

In range of 3000-3600 cm^{-1}, there are a wide band (with maximum about 3400 cm^{-1}) and emission band with the maximum 3250 cm^{-1}, which is related to the valence vibration of OH water group compounds. The presence of these bands can indicate on possibility for extraction of hydrocomplexes.

NMR^{51}V spectroscopy measurements

We also determined NMR^{51}V spectra for balance organic phase, containing vanadium. Only one narrow signal with the chemical shift 368 million shares is observed, intensity of which depends on vanadium concentration in the organic phase. Therefore, the intensity of this signal depends upon composition of aqueous phase.

To explain the received data, we made NMR^{51}V spectra of vanadium oxotrichloride solution in TBP and aqueous solution of sodium vanadium.

NMR^{51}V spectrum of sodium vanadium in water has a single narrow signal with chemical shift of 576 million shares, including complex $[(VO_3)_n{\cdot}\,mH_2O]^{n-}$ [3].

Adding hydrochloric acid to system causes the widening and shifting the signal into weak field, re-

sulting in formation of vanadium complexes containing in an intrinsic orb chlorine atoms, for example, $[VO_2Cl_x \cdot nH_2O]^{x-1}$.

At temperature down to – 10°C separate signals, conforming to different complex forms, were not observed. This indicates quick intermolecular exchange between complex vanadium forms.

In vanadium oxitrichloride spectra in TBP, at – 10°C, three signals were observed (Fig.1) with the chemical shift – 40, 90 and 380 million shares, which correspond to $[VOCl_4 \cdot TBP]^-$, $[VOCl_3 \cdot 2TBP]^o$ and $[VOCl_2 \cdot 3TBP]^+$ [4].

The signal $[VOCl_2 \cdot 3TBP]^+$, according to the chemical shift, is close to the signal of extractable vanadium compound. However, UV-spectra indicate VO_2^+ form vanadium in vanadium extracts. Replacement of chlorine atom by oxygen atom in $[VOCl_2 \cdot 3TBP]^+$ leads to the formation of neutral complex $[VO_2Cl \cdot 3TBP]^o$, the signal of which enters the stronger field than $[VOCl_2 \cdot 3TBP]^+$.

However, this signal in the spectrum is absent. This fact allows us to exclude $[VO_2Cl \cdot 3TBP]^o$ from the range of possible extractable vanadium forms.

The adding of water into vanadium oxitrichloride solution in TBP leads to the appearance of a signal with chemical shift of 364 million shares, which can be referred to a complex $[VO_2Cl_x \cdot nL]^{x-1}$ (where L-molecular of water or TBP).

Properties of vanadium complex

Besides, to evaluate the conditions for extractable vanadium complex, we have determined viscosity, density and electric conductivity of organic phase contained vanadium

Rectilinear dependence of molar electro-conductivity of extracts (l) on vanadium concentration (Fig. 2) indicates considerable ionization of vanadium compounds in TBP.

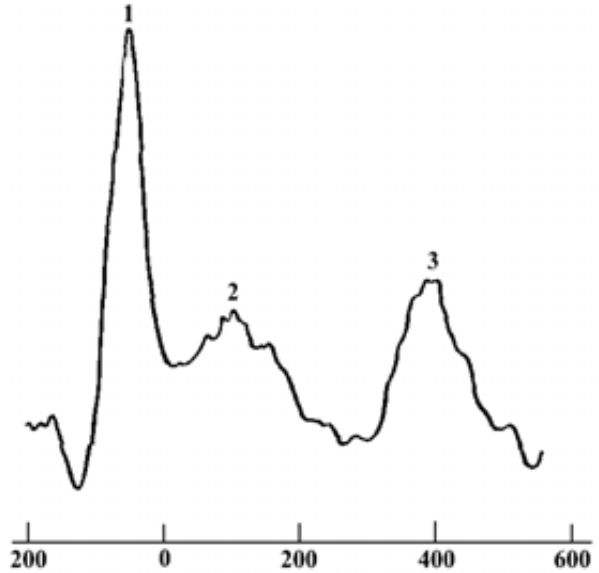

Fig. 1. Spectrum $NMR^{51}V$ of: 1- $[VOCl_4 \cdot L]^-$; 2- $[VOCl_3 \cdot 2L]^0$; 3- $[VOCl_2 \cdot 3L]^+$

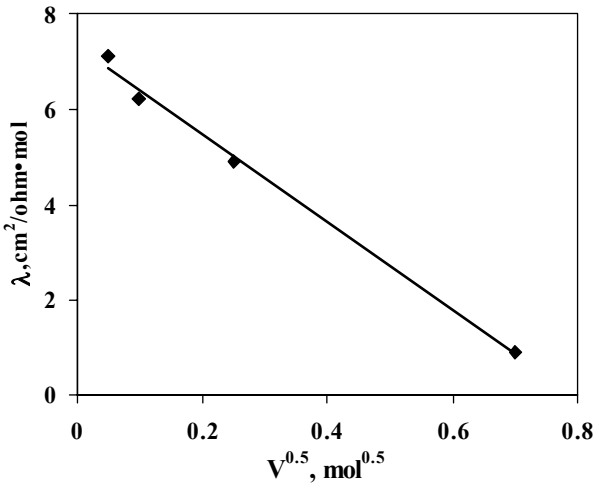

Fig. 2. Dependence of molar electro-conductivity of extractable vanadium compound from its concentrate in TBP.

Discussion

On the basis of our investigation data concerning the system HCl-H_2O-V(V)-TBP, received by different physical-chemical methods, we can come to the conclusion concerning the composition of extractable vanadium complex from pulp of vanadic concentrate. Such a complex, with high likelihood, has the form of $[H_3O^+ \cdot nH_2O \cdot mTBP][VO_2Cl_2 \cdot pTBP \cdot hH_2O]^-$.

The extraction reaction can be written in the following equations:

1) $VO_2^+{}_{(Aq)} + H_3O^+_{(Aq)} + 2Cl^-_{(Aq)} + (m+p)TBP_{(O)} + nH_2O_{(Aq)} \leftrightarrow [H_3O^+ \cdot nH_2O \cdot mTBP][VO_2Cl_2 \cdot pTBP]^-_{(O)}$

2) $HCl_{(Aq)} + TBP_{(O)} \leftrightarrow HCl \cdot TBP_{(O)}$

if $[HCL]_{(o)} \rightarrow 0$, the following balance is possible:

3) $VO_2^+{}_{(Aq)} + (n-1)H_2O_{(Aq)} + 3Cl^-_{(Aq)} + (m+p)TBP_{(O)} + 2H_3O^+_{(Aq)} \leftrightarrow [H_3O^+ \cdot nH_2O \cdot mTBP]\{H[VO_2Cl_3 \cdot pTBP]\}^-_{(O)}$

Conclusions

Using the physical-chemical methods of analy-

sis, the composition of vanadium salt was defined, which is received by crystallization from aluminate solution. And also, the structure of the extractable complexes of vanadium, received from the concentrate by tributylphosphate, was found. The received data can be recommended to use for accompanying vanadium extraction in alumina production.

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