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Acid Leaching Of Vanadium From Black Shales Of Big Karatau.

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ABSTRACT

The purpose of the real work was studying of process of an acid leaching of vanadium and other valuable components from black shales of Big Karatau of the Republic of Kazakhstan. The maintenance of principal components in ore of 0,8% V_2O_5, 67,7% of SiO_2, 3,1% of Al_2O_3, 0,3% of Mo, 0,2% of U_3O_8 and 0,05% of rare-earth metals. The main part of vanadium is in the lowest rates of oxidation of V^{2+} and V^{3+}. The offered two-stage leaching allows to extract vanadium for 95%. At the first stage of atmospheric leaching (fineness of ore -53% of 0,063 mm, temperature 70 ^{0}C, acid-70 g/l, time-2 hour, the solid/liquid ratio was maintained at 1/3) extraction of vanadium makes 40%. After autoclave leaching (temperature 140-160 ^{0}C, sulfuric acid 120-140 of kg/t, time-2 hour, solid/liquid =1/0,9) the common extraction of vanadium reaches 95%. Also processed in these parameters totally extraction made of two stages uranium of 98%, a molybdenum of 75%, rare-earth metals of 65%.

Keywords: black shale, vanadium, two-stage leaching

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INTRODUCTION

Black shales, also called carbonaceous stone, are one of the most larger natural sources of vanadium. Keeping of vanadium in them by 60 – 100 times is exceeded by Clark of crust [1]. Black shale ores of Big Karatau are large and perspective in Kazakhstan [2,3] where the content of vanadium V_2O_5 -0,8-1,2%. The useful components except vanadium, are a molybdenum of 0,3%, uranium of 0,2-0,5% and rare-earth metals (R.E.M.) with the content of 0,05-0,15%.

The basis of breed of black shales content short-grained quartz, sulfides and micas, there are organic matters and carbonates [4]. Persistence of ores is caused by two factors: low solubility of minerals concentrators of the useful components and extremely shallow amount of their selections (ultradispersion) therefore mechanical methods (gravitation, flotation) did not possible to receive the enriched concentrates [5].

Attempts of development of theoretical bases and creation of way of complex extraction of vanadium, uranium, molybdenum and R.E.M from the black shale ores were repeatedly made. Some of developments are listed below.

Researches [6-9] on pyro-hydrometallurgical way of processing of vanadium-bearing fields the black shale ores confirmed possibility of extraction of vanadium from the black shale ores with method of oxidizing roasting with sodium additives with the subsequent water or acid lixiviation of residue, in finally hydrolytic deposition of vanadium.

In work is studied [6] process of roasting of ore with additive mix Na_2CO_3-$CuSO_4$. Process is conducted 2,5 hours at 760 ^{0}C, after residue leach H_2SO_4 of 2%. Common extraction of vanadium makes 85%.

The flow diagram of processing of vanadic ores of Karatau offered in work [9] includes the following main operations: subdivision to fraction +10-50 mm; melting of granulouse lumpy ore together with phosphorites in electric furnaces. Receive iron-phosphorus -vanadium alloy, refine ferrophosphorus and receive slag with the maintenance of 10-25% of V_2O_5.

In works [10-13] the technology at which complex processing of vanadic shales of Big Karatau is carried out is offered. It includes the following main operations: heap leaching by solution of sulfuric acid, a sorption of uranium and vanadium on anion-exchange resins, with the subsequent division into stages of desorption of uranium and vanadium, deposition of uranium slag and polyvanadates. At the same time low extent of extraction of vanadium at leacing stage is observed, completeness of separation from phosphorus is not reached, the received pentoxide of vanadium has the high content of phosphorus.

For processing of vanadium-bearing materials often use process of the low-temperature sulfidation for the purpose of transfer of vanadium to the highest rates of oxidation which are easily giving in to leaching [5]. For obstinate black shale ores is investigated way of extraction of vanadium by the low-temperature sulfidation with the subsequent heap leaching. Extent of extraction of metal made 52%. Along with vanadium in solution valuable components such as are taken: uranium of 75%, molybdenum of 50% and rare earths of 38% [14-17].

In work [18] extraction of vanadium from black shales the activated leaching is offered. It is shown what, when using ore fineness of 45 microns, temperatures of process of 90 °C, time of a leaching of 120 min., concentration of sulfuric acid 100g/l with addition of CaF_2 60 of kg/t is reached extraction of 80%.

Authors of work [19] investigated a possibility of extraction of vanadium from black shales by sulfuric acid with addition of etching acid. Parameters: time of reaction of 6 h, concentration of sulfuric acid of 87,5 g/l, concentration of etching acid of 15 g/l, concentration of sodium hipochlorite in 1 g/l (added later time of reaction of 3 h), temperature of a leaching of 95 °C. Under these conditions extraction of vanadium makes 86%.

Works of authors [20], on a leaching of black slates under pressure are known. Its essence consists in a two-stage counter-current leaching with an oxidizer additive. As an oxidizer use iron sulfate. At the first stage of an autoclave leaching it is reached extraction of 77%, and for the second higher than 90%, After office of Fe^{3+} and corrections of value pH solutions extract vanadium. A vanadium exit after extraction and a reextraction makes 98%. Then receive polyvanadate of an ammonium and burn it at temperature of 550 °C within 3 h with obtaining high purity of V_2O_5. The common extraction of vanadium at all stages of process made about 85%.

All above, technologies do not allow to receive high extent of extraction of all valuable components and are characterized by low efficiency of process: the considerable consumption of reagents, batch processes demanding larger expenses of time.

For efficient extraction of vanadium and the accompanying components from black shales process of the two-stage opening the black shale ores is investigated. The first stage – atmospheric, the second – an autoclave leaching.

EXPERIMENTAL

As a starting material for carrying out experiments used test of black shale of Big Karatau. Test of black shales represented the homogeneous black dry powder fineness ~ 53,2% - 0,063 mm with the content of vanadium V_2O_5 - 0,8%; C ~ 18%, SiO_2 – 67,7%. Chemical and distribution of sizes of the studied ore is presented in tables 1 and 2.

Table 1: Chemical content of black shales

Composition, %							
V_2O_5	**U_3O_8**	**MoO_3**	**REM**	**SiO_2**	**Al_2O_3**	**C**	**$Fe_{общ}$**
0,8	0,2	0,3	0,05	67,6	3,1	18,0	1,91
CaO	**P_2O_5**	**K**	**S**	**Na**	**MgO**	**BaO**	-
2,8	0,71	0,47	1,4	0,09	2,2	0,86	-

Table 2: Distribution of sizes

Size, mm	**Total, %**
+0,2	4,8
-0,2+0,1	34,0
-0,10+0,063	8,0
-0,063	53,2
	100,0

Researches were carried out in two steps.

Researches on determination of parameters of an atmospheric leaching

Experiments were made under atmospheric pressure in a glass reactor with a mechanical agitation and electric heating. The pulp was prepared by mixture mass of weighed of test of shale and solution of sulfuric acid. Pulp volume during experience was supported on fixed level. After the termination the pulp was filtered on a Buchner filter at ambient temperature, washed out of slag on the filter water to a neutral reaction (pH 6-7) and dried on air (105 ^{0}C) up to the constant weight. An exit of the dry washed of residue fall intoed to the mass of initial shale.

Conditions of carrying out experiences: mass of sample-50 гр, a ratio solid to liqiud S/L=1/3, we use chemically pure sulfuric acid. Defined parameters, this time effect (0,5; 1,0; 2,0; 3,0; 4,0; 5,0 hours) and temperatures (25; 50; 75; 85 ^{0}C). Also investigated an acid consumption (50; 70; 100 g/l) on process of an atmospheric leaching. After identification of parameters of leaching of the first stage кек we process under pressure.

Researches on determination of parameters of an autoclave lixiviation

Laboratory experiments were made in the laboratory autoclave with a capacity of 2 dm^3, the equipped high-speed two-stage mechanical agitator with adjustable range of speeds and the electric heater. Constructional material - stainless steel.

The pulp was prepared by mixture of simple of the residue processed at atmospheric conditions and sulfuric acid. The optimum ratio of S/L made 1:0,9 which allows to receive a pulp of necessary mobility and high density to 65% solid suitable for extraction of valuable components [17]. Then the pulp was placed in the ftoroplast of glass densely installed in the autoclave case. The agitator (ω=700 rpm) was included after potting of the autoclave, and then turned on the heater. The common pressure in the autoclave made ~ 6,0-14,5 atm. (0,6-1,5 MPas). Upon termination of experience, switched-off the heater, an agitator, cooled a pulp and after dumping of residual pressure unloaded the autoclave. The pulp was filtered further by repulped of 3% sulfuric acid a ratio S/L=1/1 for calculation of the complete extraction in solution of extracted metals, time treatment is made 0,5 h at 50 ^{0}C. After receiving repulped mass, residue washed out on the filter water to neutral reaction (pH 6-7) and dried on air (105 ^{0}C) up to the constant weight.

Vanadium, uranium, molybdenum, R.E.M. and other impurity in a solid phase of a pulp of a residue determined by chemical decomposition of test and the subsequent definition by method of an atomic absorption spectrometry. In a liquid phase of a pulp vanadium, molybdenum, uranium, R.E.M. and other impurity determined by the method of an atomic absorption spectrometry and method of a nuclear and issue spectrometry connected with inductively bound plasma. Content of sulfuric acid was determined by potentiometric titration with NaOH in presence of the indicator of methylorange.

For definition optimum technological parameters of an autoclave leaching of test of black slates are carried out:

- Researches temperature effect in the range of 120-200 ^{0}C. Leaching leaching 3 hours, and consumption of acid made 140 kg/t of the mass of ore;
- Studying influence of duration of processing in the range of 1-3 hours, temperature 160 ^{0}C, concentration of sulfuric acid made 140 kg/t of the mass of ore;
- Variation researches on influence of a consumption of sulfuric acid, concentration from 120 - 200 kg/t of the mass of ore. Leaching time is 3 hours.

RESULTS AND DISCUSSIONS

According to researches, the two-stage method of processing of black shales yielded affirmative results. All valuable metals which are in composition of shales V, U, Mo and R.E.M. pass into solution with high extent of extraction.

First stage of leaching

At atmospheric conditions of leaching water-soluble forms of vanadium of rate of oxidation of V^{4+} and V^{5+} easily pass into solution. Process can be pass on the following reaction 1-2:

$$V_2O_5+H_2SO_4=VOSO_4+SO_2+H_2O \qquad (1)$$

$$VO_2+ H_2SO_4=VOSO_4+SO_2+H_2O \qquad (2)$$

Also at atmospheric conditions of leaching acid consuming carbonates collapse and the composition of organic matter changes.

Temperature effect on process of atmospheric leaching

The obtained data are shown in figure 5. Follows from the obtained data, despite changes of temperature, ore differs low extent of extraction of valuable components. Range of disolution of vanadium in solution of 9-40% at residual concentration of sulfuric acid in a liquid phase of pulp of 84-62 g/l. Recoverability of U, Mo and R.E.M. it is similar to vanadium.

Influences of time on process of atmospheric leaching

In figure 2 it is shown that during a time term from 0,5 to 3,0 h the noticeable increase of extraction of vanadium ~ 40% and other valuable components is provided. However, further increase of duration of process becomes over 3,0 h unefficient as the organic matters which are in ore have properties to include in themselves the dissolved metals. In the range of 2-3 watch extraction of vanadium comes to the direct platform.

Influences of consumption of sulfuric acid in process of atmospheric leaching

Follows from the obtained data of figure 3 that test of black shales, are badly opened in the studied strengths of acid. The satisfactory result was received at concentration of 70 g/l.

By results of experiences, optimum conditions of atmospheric leaching: the solvent concentration of 70 g/l, time-2 hour, temperature of process makes 70 ^{0}C. After such type of processing about 10% of the initial mass of ore are lost, chemical composition is presented in table 3.

Table 3: The composition of valuable components in slag after atmospheric processing, %

V_2O_5	U_3O_8	MoO_3	R.E.M.	Al	Fe	Mg
0,48	0,1	0,15	0,035	1,31	1,1	0,13
Si	**C**	**K**	**P**	**Ba**	**S**	**Cr**
33,3	15	0,49	0,08	0,3	0,3	0,02

Following the results of researches of extraction of vanadium makes 40%, other part of vanadium is the hardly opened lowest oxides of vanadium.

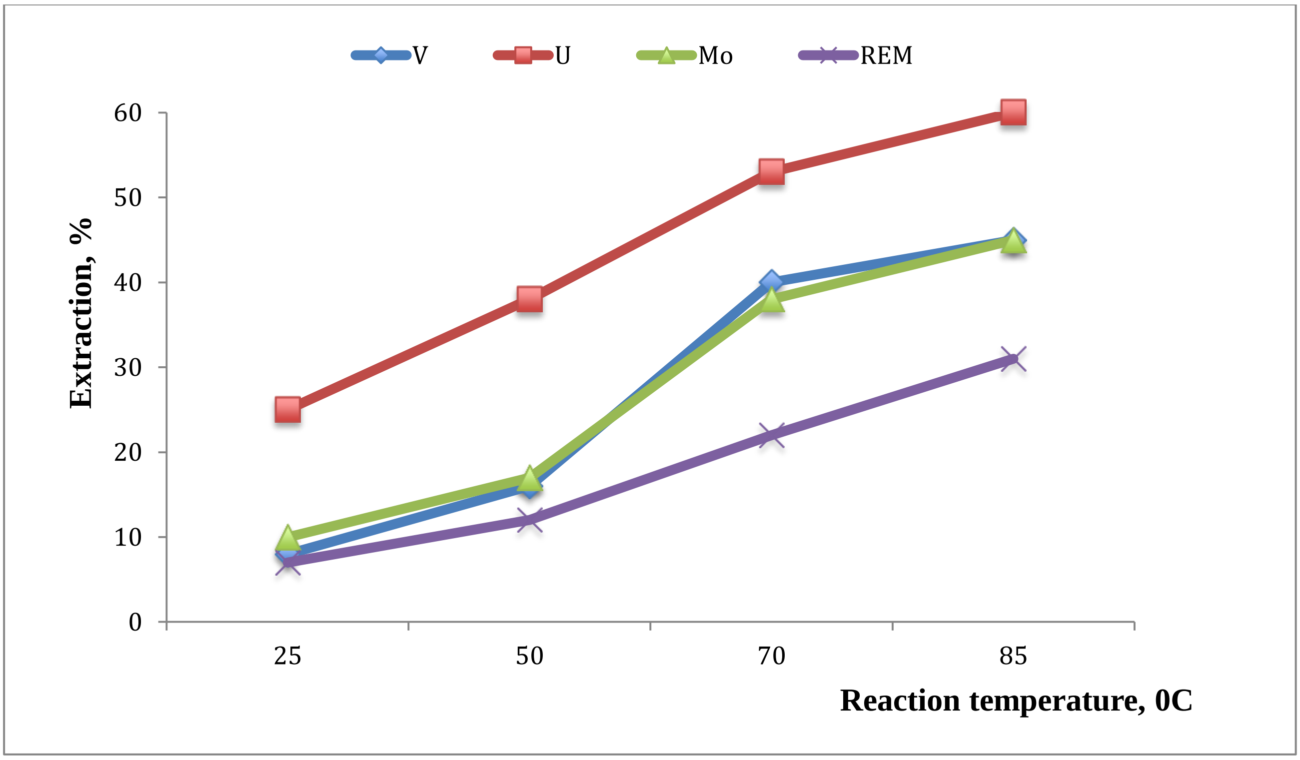

Figure 1. Temperature effect on process of atmospheric leaching

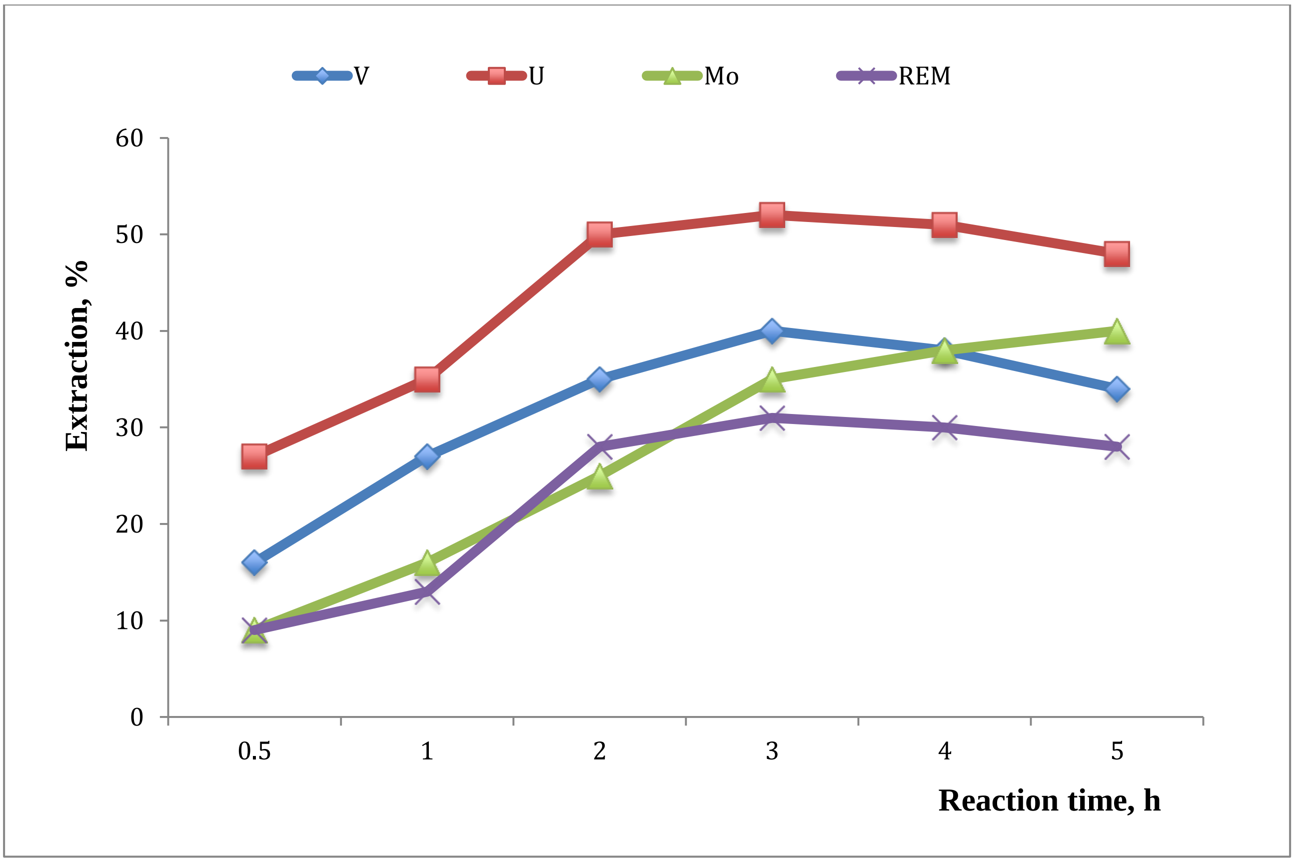

Figure 2: Influences of time on process of atmospheric leaching

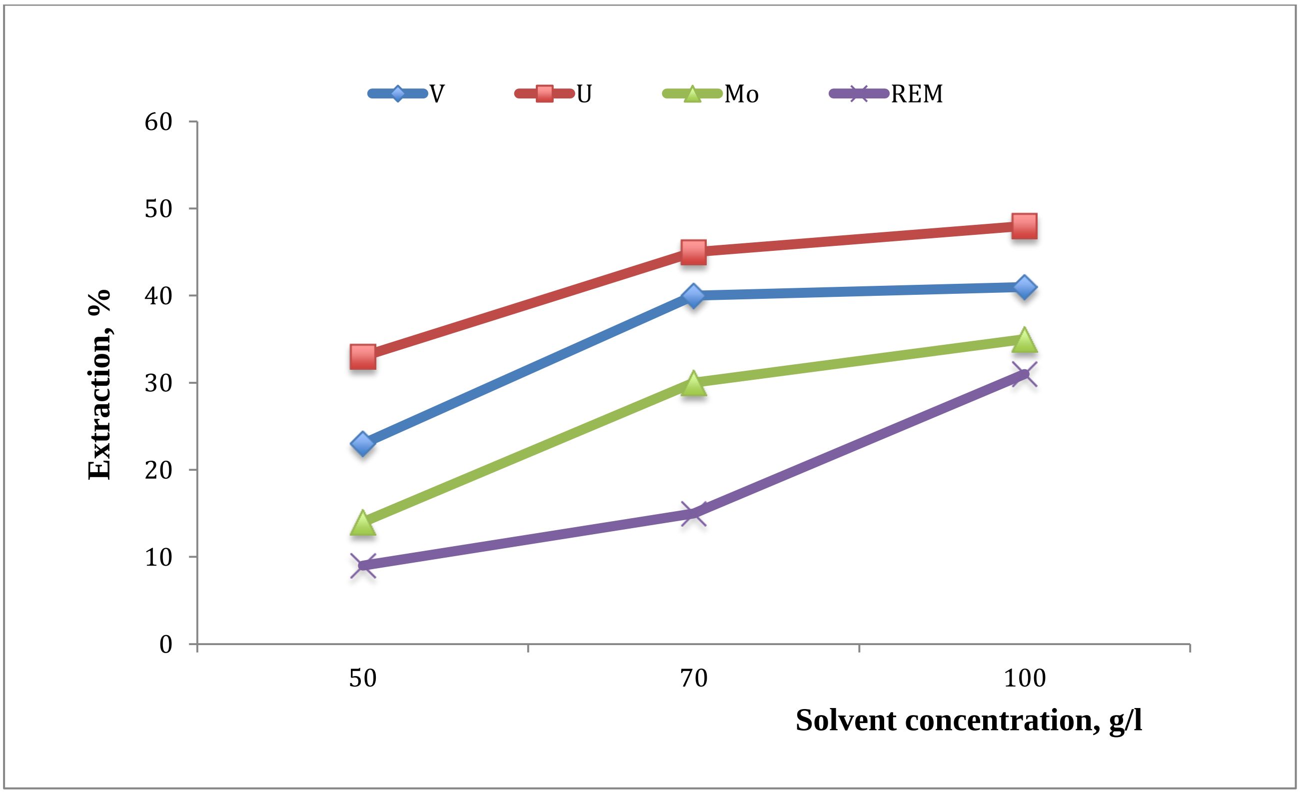

Figure 3: Influences of consumption of sulfuric acid in process of atmospheric leaching

Second stage of leaching

At an autoclave leaching in difference of earlier seen works we do not add oxidizers. According to our assumptions the mechanism of oxidation occurs at the expense of the reaction following 3-6:

$$FeO+ H_2SO_4 =FeSO_4+2H_2O \quad (3)$$

$$2FeSO_4+ 2H_2SO_4 = Fe_2(SO_4)_3+SO_2+2H_2O \quad (4)$$

$$Fe_2(SO_4)_3+2H_2O= 2[FeOHSO_4]+ H_2SO_4 \quad (5)$$

$$VO+2[FeOHSO_4]+ H_2SO_4=VOSO_4+2\ FeSO_4 +2H_2O \quad (6)$$

Also process of oxidation is possible at decomposition of sulfuric acid in sulphuric anhydride and water on reaction 7-9:

$$VO+ H_2SO_4= VOSO_4+SO_2+2H_2O \quad (7)$$

$$V_2O_3+H_2SO_4= 2VOSO_4+SO_2+3H_2O \quad (8)$$

$$SO_2+H_2O= H_2SO_3 \quad (9)$$

Temperature effect on process of of autoclave leaching

In figure 4 dependence extraction of V, U, Mo and R.E.M. in solution from temperature is shown. It is established that, high temperatures lead to increase of extraction of vanadium and other valuable components. In the range of temperatures 140 to 160 ^{0}C stable high extraction of vanadium at the level of 88-90% is observed, and at 180-200 ^{0}C concentration of metals decreases. At a temperature over 160 of ^{0}C sulfuric acid decays in a hydrogen sulfide which is the strongest reducer. It is confirmed also by residual concentration sulfuric acid in solution of 70-50 g/l. Apparently from the schedule of the dynamics of extraction of molybdenum and rare earths it is similar to vanadium. Extent of extraction of Mo at 160 ^{0}C reaches the maximum of 70%, and R.E.M.-42%. Uranus passes into solution practical completely, irrespective of process temperature, on graphics it is visible at 180-200 ^{0}C recession is noticed.

Temperature effect on process of autoclave leaching

By results follows (figure 5) that one hour of a lixiviation for V, U, Mo and R.E.M. does not provide the complete extraction of metals. Only at three to hour processing the full is reached practical of extraction of all metals interesting us. Two hour processing give almost identical data on extraction of vanadium, uranium and rare earths, except a molybdenum which extraction makes 50%.

Influences of consumption of sulfuric acid in process of autoclave leaching

The consumption of solvent is one of important components, providing extraction of valuable elements in solution. Dependence of extent of extraction on concentration of sulfuric acid is shown in figure 6. The maximal extraction made 95% at a consumption of acid of 200 kg/t. Hyperacidity increases the extraction of molybdenum to 84%. Satisfactory extraction of vanadium and uranium, a molybdenum, R.E.M. is reached at a consumption of sulfuric acid of 120-140 kg/t of the mass of ore as it is visible from the schedule, the curve comes to the primary line in these ranges. Further strengthening leads to slight body height of extraction of metals and increases residual acidity to solution. Uranium after all tests practical is completely extracted to 99%, extent of extraction of R.E.M. was made by 36-60%.

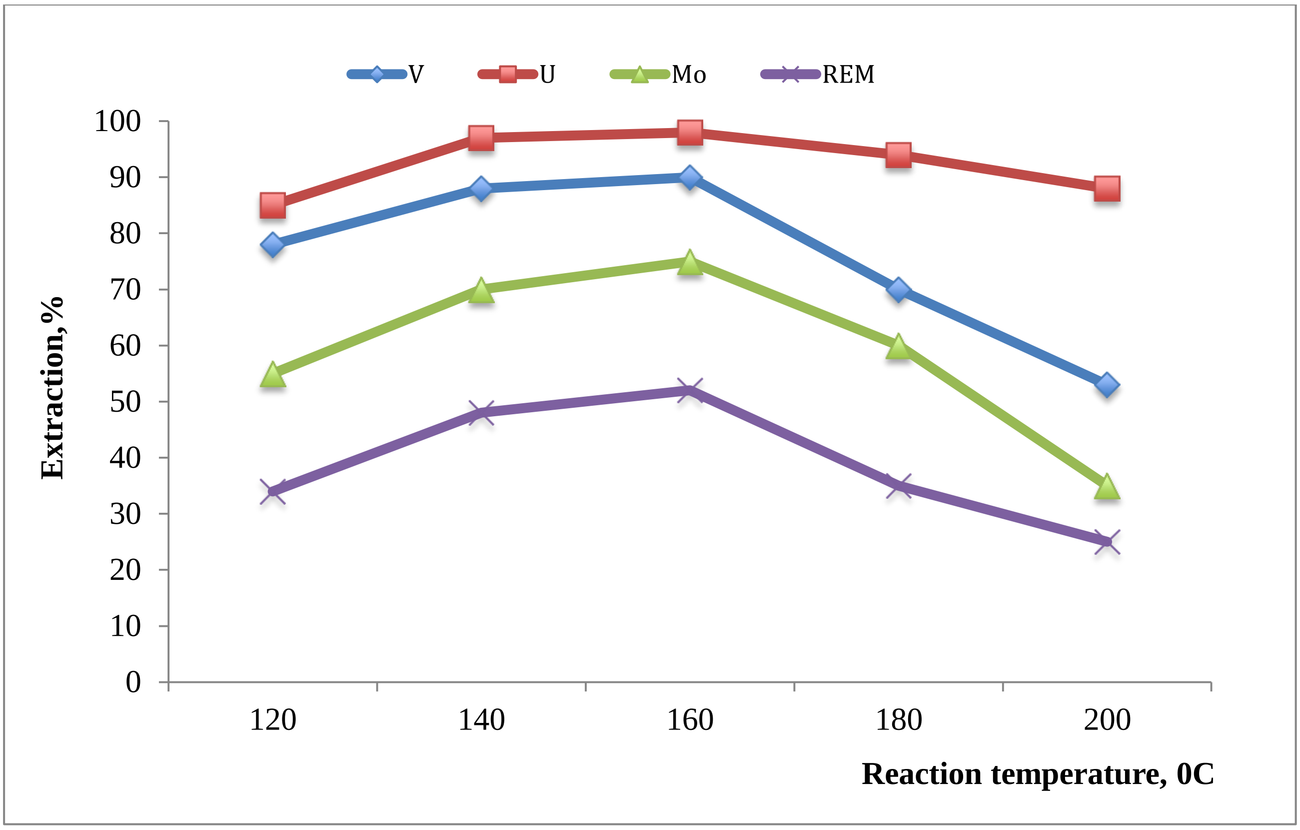

Figure 4: Temperature effect on process of autoclave leaching

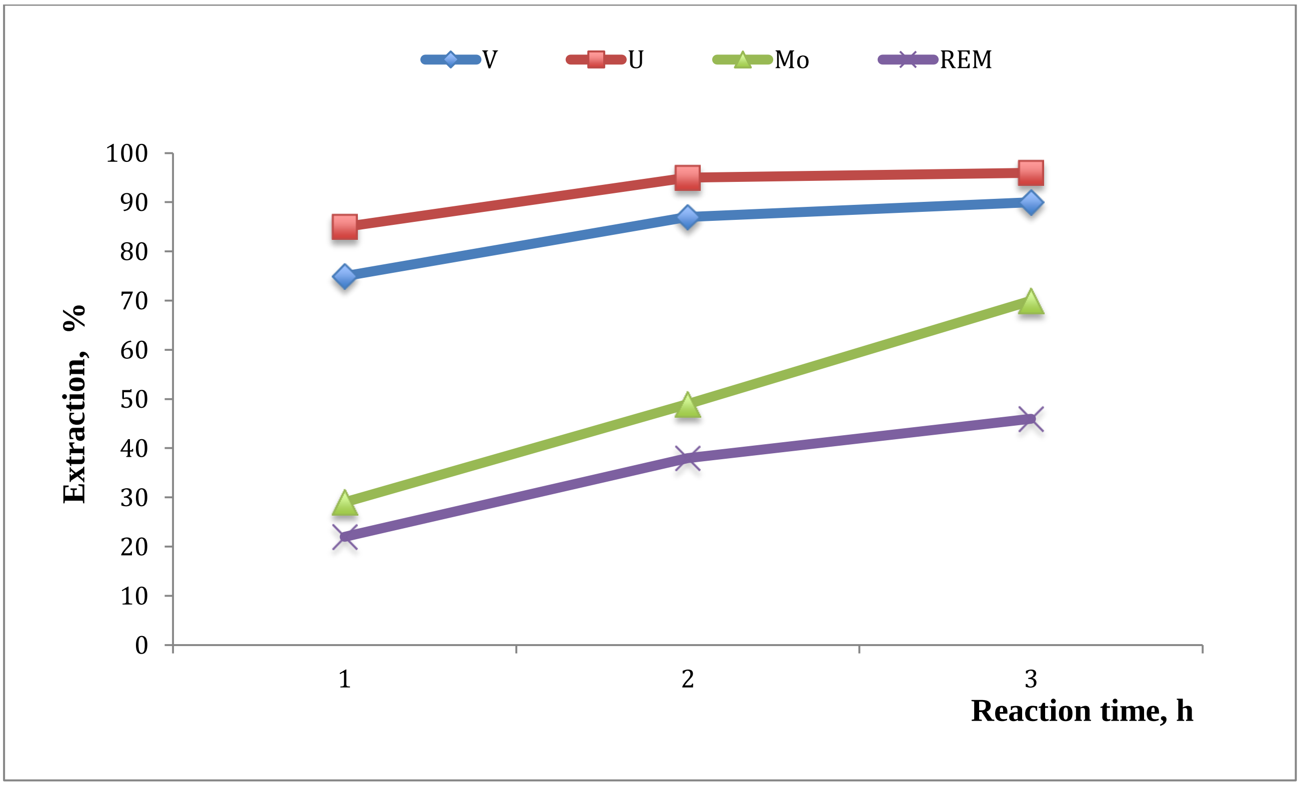

Figure 5: Influences of time on process of autoclave leaching

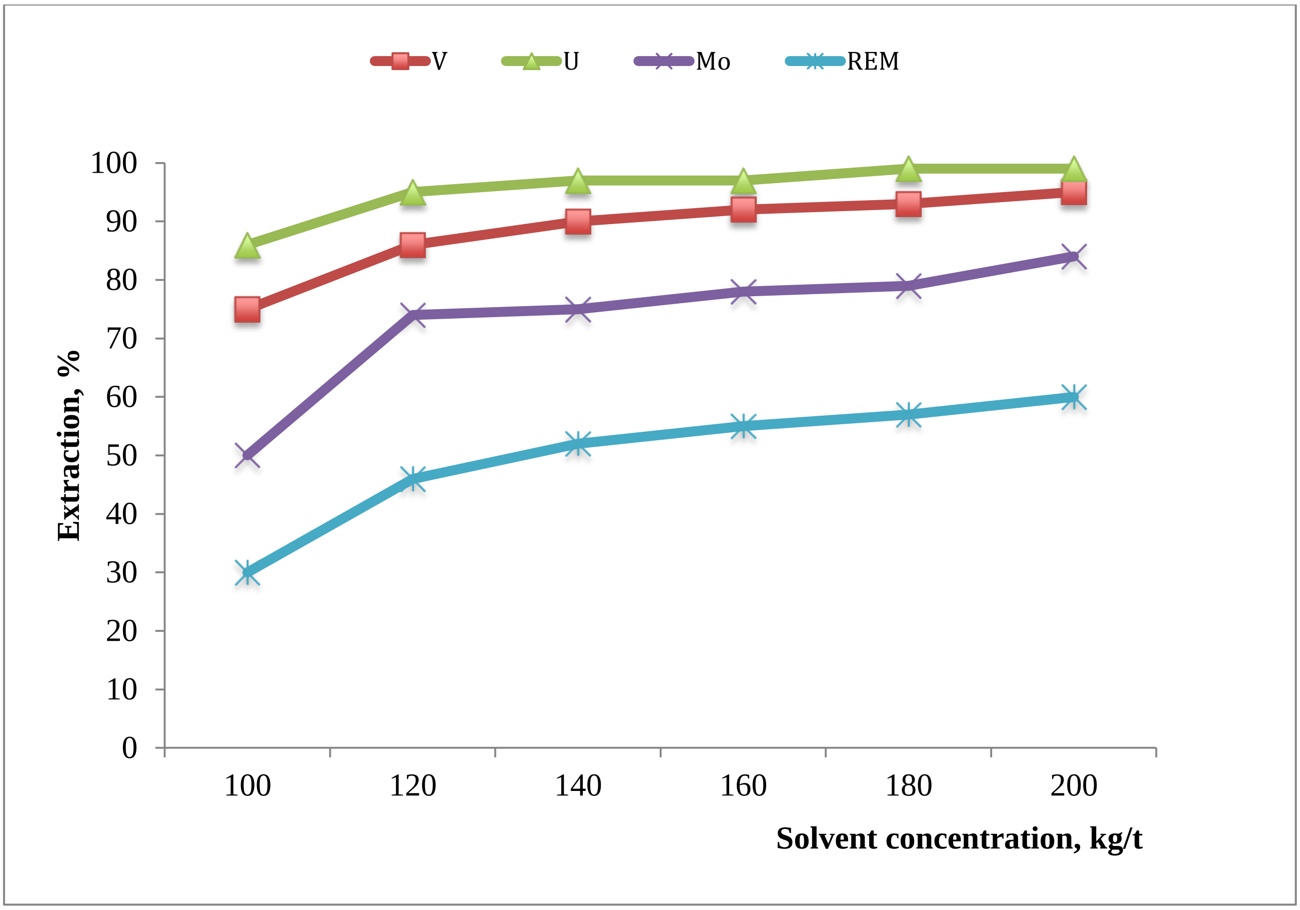

Figure 6: Influences of consumption of sulfuric acid in process of autoclave leaching

CONCLUSION

The offered two-stage leaching allows to extract vanadium for 95%. At the first stage of atmospheric leaching (fineness of ore -53% of 0,063 mm, temperature 70 ^{0}C, acid-70 g/l, time-2 hour, the solid/liquid ratio was maintained at 1/3) extraction of vanadium makes 40%. After autoclave leaching (temperature 140-160 ^{0}C, sulfuric acid 120-140 of kg/t, time-2 hour, solid/liquid =10,9) the common extraction of vanadium reaches 95%. Also processed in these parameters totally extraction made of two stages uranium 98%, a molybdenum of 75%, rare-earth metals of 65%.

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