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On the Subject of Losses of Rare Elements in Acid Processing Eudialite Concentrate

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Abstract

The causes and ways of reducing losses of zirconium and other rare elements with silica residues upon acid treatment of eudialite concentrate, *i.e.* a raw source of zirconium, hafnium, and rare earth elements of the middle and yttrium groups, were explored. Metals distribution was examined during acid treatment with 2 mass % solutions of nitric and sulphuric acids in the presence of sulphocationite. It was found that decomposition of eudialite, the main Zr-containing mineral, proceeded entirely. Herewith, losses of zirconium and other rare elements with silica residues formed during nitric acid and sulphuric acid processing of eudialite concentrate are mainly related to their ingress to silica gels. Rare elements are present therein as hydrated silica-based polymers that are bridge-coupled by hydroxyl (olation) or oxygen (oxyolation). As demonstrated, zirconium and other elements may be additionally derived by acid treatment. Their losses with silica residues may be reduced during eudialite concentrate decomposition in the presence of sulphocationite with sol production in the initial stage.

Keywords: eudialite concentrate, acid processing, rare elements, loss mechanisms

INTRODUCTION

Manufacture of zirconium products is based on the use of zirconium and to a lesser extent, baddeleyite concentrates. Alongside with that, eudialite ores containing rare earth elements (REE) elements and niobium in significant amounts in addition to zirconium and hafnium are of great interest. Rare earth elements of eudialite are enriched in yttrium and lanthanides of the moderate and severe groups.

There are eudialite deposits in the Kola Peninsula (Khibiny and Lovozero tundras), in Tuva, Greenland (Ilimaussaq), Australia, Canada, and Madagascar. In 1985, an eudialite deposit was discovered in the State of New Mexico (USA) [1].

A pilot batch of eudialite concentrate, using which a significant amount of research was carried out on the development of various technologies for its processing, was produced according to the technology developed by the Lovozero Mining and Processing Plant, KSC RAS in 2000.

Acid methods of decomposition are used in the main research trends. With technologically acceptable consumption of mineral acids, the extraction of zirconium into a solution, as a rule, does not exceed 75 % [2–10].

A better extraction of zirconium was reached during leaching with concentrated (2–

12 mol/L) solutions of nitric (with consumption multiply exceeding the stoichiometrically required [2]) or sulphuric acid (the concentration of about 50 mass % [11]), and also in introducing significant amounts of a fluoride ion into the solution [12]. Thus, there was either excluded silica gel production (large volumes of an acid solution ensured silica dissolution, and in case of concentrated H_2SO_4, it has a low degree of hydration) or zirconium was bound into a firm water-soluble fluoride complex due to the introduced fluoride ion.

The literature gives different suggestions regarding the causes of insufficient extraction of zirconium into leaching solutions.

The authors of [13] link this with the uneven distribution of titanium and niobium in the eudialite structure, the elevated content of which complicates mineral decomposition. They explain decomposition efficiency increase during introducing a fluoride ion by crystal lattice destruction due to binding titanium, niobium, and tantalum into fluoride complexes and their transition into a solution. In the author's opinion, eudialite concentrate with TiO_2 content of 1.9 mass % was decomposed by HCl on 65–70 %, and with 1.1 mass % of TiO_2 – by 95–97 % [13].

It was suggested that the silica in eudialite is contained in three forms, such as acid-soluble, insoluble in acids but soluble in alkali hydroxide solutions and as silicon-zirconium complexes insoluble either in acids or alkalis. The latter and determine zirconium losses during acid decomposition [14].

According to the author's opinion [15], one of the causes of insufficient extraction of eudialite concentrate may be blocking of rake products of eudialite by hydrated silica layer preventing acid diffusion and entering acid-resisting zirconium minerals, i.e. wadeite $(K,Na)_2ZrSi_3O_9$) and modified eudialite, into the silica residue. They are generated resulting from hydrothermal changes of general eudialite. It is stated that altered eudialite is not disclosed by sulphuric acid and hydrochloric acid even upon harsh treatment conditions but opens by hydrofluoric acid or during sintering with alkalis or lime, as "zirconium in altered eudialite is covered with dense silica layers, completely impermeable to acids" [15].

The goal of the present work was to investigate causes and search for ways to reduce zirconium and other rare elements losses in acid treatment of eudialite concentrate.

EXPERIMENTAL

According to X-ray phase and crystal-optical analysis data, eudialite concentrate is presented by the following main minerals: eudialite ($Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$), loparite $(Ce,Na,Ca)_2(Ti,Nb,Ta)_2O_6$), nepheline ($(Na,K)AlSiO_4$), lamprophyllite ($Na_2(Sr,Ba)_2Ti_3(SiO_4)_4(OH,F)$), albite ($NaAlSi_3O_8$), and aegirine ($NaFe^{3+}Si_2O_6$). The chemical formulas of the minerals are borrowed from [16].

As demonstrated by analysis of the chemical composition of the main monomineral fractions of eudialite concentrate, zirconium is quantitatively bound only with eudialite and its content in other minerals may be disregarded. A significant part of REE and niobium are included in loparite composition.

Samples of eudialite concentrate (hereafter concentrate), the composition of which is given

TABLE 1

Content of main components and major impurities in concentrate

Oxide	Content, mass %	Oxide	Content, mass %	Oxide	Content, mass %	Oxide	Content, mass %
Na_2O	12.96	Fe_2O_3	3.95	Y_2O_3	0.437	Tb_2O_3	0.013
K_2O	0.98	MnO	1.96	La_2O_3	0.262	Dy_2O_3	0.074
MgO	0.09	ZrO_2	9.32	Ce_2O_3	0.499	Ho_2O_3	0.015
CaO	3.95	HfO_2	0.25	Pr_2O_3	0.058	Er_2O_3	0.046
SrO	2.02	Nb_2O_5	0.61	Nd_2O_3	0.237	Tm_2O_3	0.006
Al_2O_3	3.69	Ta_2O_5	0.03	Sm_2O_3	0.067	Yb_2O_3	0.040
TiO_2	2.06	ThO_2	0.010	Eu_2O_3	0.020	Lu_2O_3	0.005
SiO_2	41.83	UO_2	0.009	Gd_2O_3	0.071	ΣTr_2O_3	1.85

in Table 1, were treated with 2 mass % solutions of HNO_3 or H_2SO_4 at 80 °C for 4 h in the presence of KU-2-8 ChS sulphocationite in the H^+-form.

Sulphocationite consumption was 70% of the stoichiometrically required for sorption of concentrate cations; HNO_3 – 30 %, H_2SO_4 – 39 % of the stoichiometrically necessary for their leaching. An increase in sorbent consumption to 100 % of the stoichiometrically required increased extraction of alkaline and alkaline earth elements but did not affect that of rare ones. As H_2SO_4 dissociation degree in the second stage is about 50 %, the concentration of hydrogen ions in both solutions at the beginning of the process is almost the same. Although pulp acidity gradually decreased in concentrate decomposition, when using sulphocationite in the H^+-form, it remained acceptable, as sorption of cations proceeds efficiently and hydrogen cations are released from sorbent into the solution during sorption. The sorbent was separated on mesh filter, the pulp obtained by centrifugation was divided for the remainder of undecomposed or partially decomposed minerals, silica gel, and solution.

Components content in the resulting products was determined by inductively coupled plasma mass spectrometry (ELAN 9000 DRC-e mass spectrometer, Perkin Elmer, USA). Solid products were previously completely dissolved in concentrated acids under autoclave conditions. The total measurement error did not exceed 10–14 rel. % and the difference between parallel measurements results was 5–7 rel. %.

Judging by the total extraction of zirconium in the sorbent and the mother liquor, eudialite decomposition efficiency during nitrogen and sulfuric acid treatment are almost the same (77.25 and 76.28 %, respectively). Losses of zirconium with the residue of non-decomposed minerals driven by incomplete decomposition of eudialite during nitrogen and sulphuric acid treatment were 11.3 and 6.6 %, respectively. Optimization of process modes or residues return to the repeated acid treatment allows eliminating these losses.

TABLE 2

Extraction of concentrate components into silica gels, rel. %

Medium	Na	K	Mg	Ca	Sr	Al	Ti	Si
HNO_3	9.3	12.7	2.47	6.35	6.76	3.71	9.4	42.4
H_2SO_4	9.5	4.1	3.37	6.44	1.50	4.52	18.5	46.0
Medium	Mn	Fe	Zr	Hf	Nb	ΣTr	Th	U
HNO_3	4.38	10.1	11.5	14.0	35.4	3.96	7.45	4.77
H_2SO_4	4.04	11.8	18.5	36.6	16.7	4.28	11.4	4.77

Extraction of REE from the concentrate reached 87 % in both cases, *i.e.* eudialite opening was almost complete since unleached REE (11–12 mass % of the total amount of REE in the concentrate) is a part of the non-decomposable in the used modes of treatment of loparite.

At the same time, as demonstrated in Table 2, a significant part of zirconium, hafnium, niobium, and some other elements falls into silica gels derived from both nitrogen and sulphuric acid decomposition of the concentrate. Thus, not only the acidity of solutions (close to the content of free hydrogen ions) but also the acid type affects the efficiency of their leaching.

Assuming that dispersion solutions contained in silica gels correspond to mother liquors, wherein silica gels were formed, there was computed the fraction of components associated with dispersive solutions (Table 3). The amount of these solutions was determined according to a decrease in mass loss during drying silica gel at 80 °C.

From the data in Table 3 it follows that most of the components (with the exception of Na), including Zr, are directly bound to hydrated silica.

TABLE 3

Fraction of components associated with dispersion solution in silica gels, rel. %

Medium	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	ΣTr_2O_3	TiO_2
HNO_3	73.2	7.05	4.1	12.3	11.9	1.7	0.6	8.1
H_2SO_4	51.6	21.9	2.2	6.2	22.8	4.5	1.3	6.9
Medium	ZrO_2	HfO_2	Nb_2O_5	Ta_2O_5	MnO	Fe_2O_3	ThO_2	UO_2
HNO_3	4.8	7.1	7.5	6.0	15.4	0.34	0.18	2.9
H_2SO_4	19.0	7.2	14.5	6.2	8.8	2.1	0.6	5.0

An opportunity for extraction of rare elements by acid leaching silica gel produced by nitrogen and sulphuric acid transformation of eudialite concentrate was investigated. Table 4 gives the data on metal oxides content in products dried at 80 °C to constant mass.

For leaching, there was used the acid, in the medium of which silica gels were produced. The cost of the sorbent (550–600 %) and acids (260–300 %) was much higher than the stoichiometrically required. After stirring the mixture heated to 80 °C for 4 h, there were separated the sorbent, the solution and the silica gel and the last two products were analysed. The degree of the transition of components to the sulphocationite was determined according to the difference of masses in the initial silica gels and their amount in the resulting silica gels and solutions (Tables 5 and 6). Table 7 gives distribution coefficients (K_d) computed according to the equation:

$$K_d = m_{sor}V_{sol}/m_{sol}V_{sor}$$

where m_{sor} and m_{sol} are component masses in equilibrium sorbent and in solution, respectively; V_{sol} and V_{sor} are the volume of the solution and the sorbent, respectively.

It can be seen (see Tables 5–7) that extraction of zirconium like most components (excluding sodium and titanium) from the silica gel produced during sulphuric acid conversion is less than that in case of nitric acid transformation. Decreased extractions of calcium and strontium may be associated with lower sulphate solubility of these elements in sulphuric acid medium. The concentrations of rare elements in mother liquors are low, and K_d values

TABLE 4

Metal oxides content in silica gels dried at 80 °C, mass %

Medium	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	ΣTr_2O_3	TiO_2	SiO_2
HNO_3	3.15	0.52	0.075	0.78	0.42	0.42	0.23	0.60	55.1
H_2SO_4	2.99	0.16	0.095	0.73	0.39	0.48	0.23	1.01	55.3
Medium	Fe_2O_3	ZrO_2	HfO_2	Nb_2O_5	Ta_2O_5	MnO	ThO_2	UO_2	
HNO_3	1.24	3.32	0.11	0.67	0.044	0.27	0.0024	0.0013	
H_2SO_4	1.33	4.48	0.13	0.64	0.046	0.23	0.0034	0.0012	

TABLE 5

Extraction of components into sorbent and mother liquors during acid treatment of silica gels produced by sorption conversion of eudialite concentrate, rel. %

Product	Medium	Na	K	Mg	Ca	Sr	Al	Ti	Si
Sorbent	HNO_3	59.6	70.0	48.3	67.9	70.3	56.7	57.3	–
«	H_2SO_4	63.2	47.1	51.4	53.7	58.4	52.2	70.5	–
Solution	HNO_3	24.0	12.4	3.13	0.84	0.73	0.77	2.13	7.40
«	H_2SO_4	15.0	5.21	0.22	4.29	1.42	0.27	1.53	5.32
Residue	HNO_3	16.4	17.6	48.6	31.3	28.97	42.5	40.6	92.6
«	H_2SO_4	21.8	47.7	48.4	42.0	40.18	47.5	28.0	94.7
Product	Среда	Mn	Fe	Zr	Hf	Nb	ΣTr	Th	U
Sorbent	HNO_3	67.3	56.2	49.8	37.2	27.4	56.6	55.2	57.2
«	H_2SO_4	52.4	48.8	47.7	33.5	4.29	44.4	58.3	49.0
Solution	HNO_3	0.82	0.01	0.80	1.60	1.95	0.24	0.09	0.56
«	H_2SO_4	0.42	0.01	0.63	3.32	2.62	1.14	2.00	1.00
Residue	HNO_3	31.9	43.8	49.4	61.2	70.6	43.2	44.7	42.2
«	H_2SO_4	47.2	51.2	51.7	63.2	93.1	54.5	39.7	50.0

TABLE 6

Components content (per oxides) in mother liquors of sorption conversion of silica gels, mg/L

Medium	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	MnO
HNO_3	65.51	5.6	0.204	0.57	0.270	0.28	1.11	0.19
H_2SO_4	46.45	0.01	0.022	3.25	0.128	0.14	1.74	0.10
Medium	Fe_2O_3	Nb_2O_5	Ta_2O_5	ZrO_2	HfO_2	ΣTr_2O_3	ThO_2	UO_2
HNO_3	0.01	1.12	0.15	2.32	0.15	0.05	0.00016	0.00040
H_2SO_4	0.011	1.72	0.20	29.1	0.46	0.27	0.0060	0.0014

for most cations are large, which indicates their high sorption efficiency. Hence, insufficient extraction of rare elements from silica gel is due to the complexity of their leaching from polymers of silicon hydroxides and polyvalent rare elements.

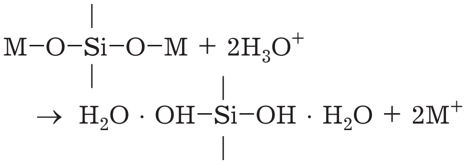
The mechanism of retention of zirconium and other elements by silica gel can be explained as follows. In the eudialite molecule, 22 oxygen atoms form of O–Si–O–Si–O and O–Si–O–M bonds (M is metal cation). The total number of bonds is 44. Given that OH^- and Cl^--groups are coupled with one of the cations, it follows from the eudialite formula that the number of second-type bonds varies from 13 to 16 (29.5–36.4 % of the total silicon-oxygen bonds).

As demonstrated by investigating the kinetics of leaching eudialite with 3 mass % H_2SO_4 solution at 20–100 °C, leaching sodium and zirconium increase with time, while the silicon concentration first rises equally with the concentration of these elements, and then decreases in the future remains constant [17]. Thus, the main part of eudialite in silica does not pass into the solution under these conditions.

For this reason, acid decomposition of eudialite mainly consists in the replacement of metal cations in eudialite crystals with hydroxide ones:

$$-Si-O-M + H_3O^+ \rightarrow -Si-OH \cdot H_2O + M^+$$

In some silicon atoms coordinated with two cations, two hydroxide cations are attached when cation leaching:



$$M-O-\underset{|}{\overset{|}{Si}}-O-M + 2H_3O^+ \rightarrow H_2O \cdot OH-\underset{|}{\overset{|}{Si}}-OH \cdot H_2O + 2M^+$$

During eliminating water molecules accompanied by generating “free” hydroxyl groups, silica gel is formed. Upon diffusion of hydronium cations in an eudialite grain and replacement of easily hydrolyzed zirconium by them, the formation of its hydroxocomplexes is probable. Polymerization of silicon and zirconium proceeds in silica-based gel and inter-bridged hydroxyl (olation) or oxygen (oxyolation) compounds, the leaching of Zr from which is complicated. In a similar way, cations of hafnium, niobium, tantalum, REE, *etc*. fall into silica gel.

One may assume that oxygen bonds are more stable than hydroxide ones during leaching. The ratio of the number of hydroxyl and oxygen bridges may vary in sulphuric and nitric acid media, therefore the efficiency of leaching zirconium from different genesis silica gels will also be different.

The elevated content of ZrO_2 in relation to SiO_2 in sulfuric acid conversion silica gel and its lower extraction during acid treatment is determined by the complication of its sorption by sulphocationite, which is confirmed by the high concentrations of both eudialite and silica in mother liquors from sulphuric acid treatment. The acidity of nitric and sulphuric acid solutions is almost the same, therefore, the low degree of sorption is determined by different

TABLE 7

Distribution coefficients (K_d) upon acid leaching from silica gels

Medium	Na	K	Mg	Ca	Sr	Al	Ti	Mn
HNO_3	6.21	14.1	38.6	202	241	184	67.2	205
H_2SO_4	10.5	1090	584	31.3	103	483	115	312
Medium	Fe	Nb	Zr	Hf	ΣTr	Th	U	
HNO_3	14050	35.1	156	58.1	590	1533	255	
H_2SO_4	12200	4.1	189	25.2	97.4	72.9	104	

compositions of complexes formed in weakly concentrated solutions.

Elevated extractions of zirconium into the nitric acid solution with an increase in the consumption and concentration of HNO_3 [2] is due to the fact that, with the higher volume of the solution, the amount of dissolved silica increases, as a result, the amount of silica gel formed decreases significantly.

The introduction of fluorine into the acid solution, which has a much greater affinity for zirconium and silicon than oxygen, contributes to the destruction of silica gel and an increase in extraction of zirconium into the solution:

$$[Si(OH) \cdot H_2O]^{3+} + 6F^- \rightarrow SiF_6^{2-} + H_2O + OH^-$$
$$[Si(OH)_2 \cdot 2H_2O]^{3+} + 6F^- \rightarrow SiF_6^{2-} + 2H_2O + 2OH^-$$
$$[Zr(OH) \cdot H_2O]^{3+} + 6F^- \rightarrow ZrF_6^{2-} + H_2O + OH^-$$
$$[Zr(OH)_2 \cdot 2H_2O]^{3+} + 6F^- \rightarrow ZrF_6^{2-} + 2H_2O + 2OH^-$$

In the acidic medium, fluoride complexes of zirconium are much more stable than those of silicon [18]:

$$[Zr(OH) \cdot H_2O]^{3+} + SiF_6^{2-} \rightarrow ZrF_6^{2-} + [Si(OH) \cdot H_2O]^{3+}$$
$$[Zr(OH)_2 \cdot 2H_2O]^{3+} + SiF_6^{2-} \rightarrow ZrF_6^{2-} + [Si(OH)_2 \cdot 2H_2O]^{3+}$$

This allows using fluosilicates as a source of fluorine [19].

It was found that the sorption conversion in the medium of 2 mass % of nitric acid with the introduction of inorganic microadditives in the amount of 0.1–0.25 mass. % of eudialite concentrate mass might yield, silica sol that passes into silica gel only after ageing for at least 3 h. Table 8 gives the composition of silica gel produced in sol decomposition.

As can be seen from the data of Tables 4 and 8, the gel released by sol decomposition contains twice less zirconium, in 14 – hafnium, in 31 – REE compared to the gel produced directly by decomposition of eudialite concentrate.

TABLE 8

Metal oxides content in silica gel dried at 80 °C obtained during decomposition of nitric acid sol

Oxide	Content, mass %	Oxide	Content, mass %
Na_2O	4.72	Fe_2O_3	0.02
K_2O	0.10	ZrO_2	1.78
MgO	0.037	HfO_2	0.0081
CaO	0.22	Nb_2O_5	0.53
SrO	0.026	Ta_2O_5	0.066
Al_2O_3	0.023	MnO	0.051
ΣTr_2O_3	0.0075	ThO_2	0.00001
TiO_2	0.116	UO_2	0.00006
SiO_2	57.3		

CONCLUSION

1. Significant losses of zirconium and other rare elements with silica residues formed during eudialite concentrate processing are determined by their ingress into the silica gels, where they are present as inter-bridged hydroxyl (olation) or oxygen (oxyolation) hydrated silica-based polymers.

2. Zirconium and other elements may be additionally extracted from silica gels by acid treatment under conditions similar to acid decomposition of eudialite concentrate.

3. Losses of zirconium and other rare elements with silica gels are reduced in the decomposition of eudialite concentrate with initial sol production.

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