Center of Earth Sciences, Metallurgy and Benefication

RHENIUM OF KAZAKHSTAN
(Review of Technologies for Rhenium Recovery from Mineral Raw Materials in Kazakhstan)

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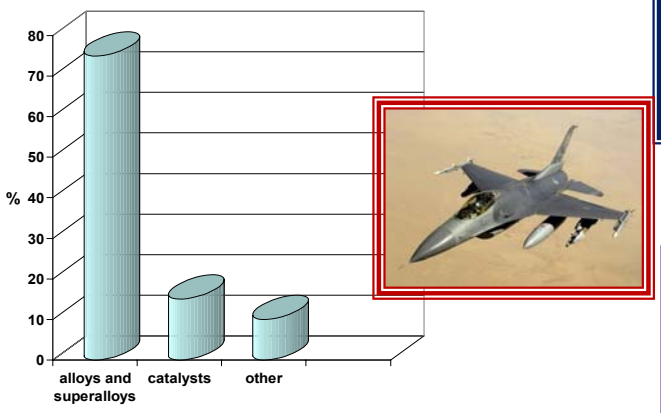
Kazakhstan

Major Mineral Resources of Kazakhstan

	Known reserves	Global Ranking
Chromium	350 mln tones	1
Lead	14.8 mln tones	1
Zink	34 mln tones	1
Uranium	900 000 tones	2
Copper	40 mln tones	4
Rhenium	250 tones	4
Oil	2.7 bln tones	7
Iron	17 bln tones	7
Gold	1 900 tones	9
Natural Gas	1.830 bln m^3	15

Aplications of rhenium

The main consumers of rhenium are petrochemistry, aviation, space (Re are used in the aerospace industry for production of high pressure and high temperature single crystal turbine blades). According to analysts, the world may face a significant lack of rhenium in the market. Therefore actual is the involvement of the scope of its production of new sources of raw materials and by-products of metallurgical industry.



Three types of deposits where rhenium presented were identified in Kazakhstan:

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•Copper-molybdenum deposits with high rhenium concentrations in molybdenite (300 to 3000 g/t),

•Rhenium containing cupriferous sandstones (concentration of rhenium 1-3 g/t). The main rhenium mineral in this ore is zhezkazganite ($CuReS_4$).

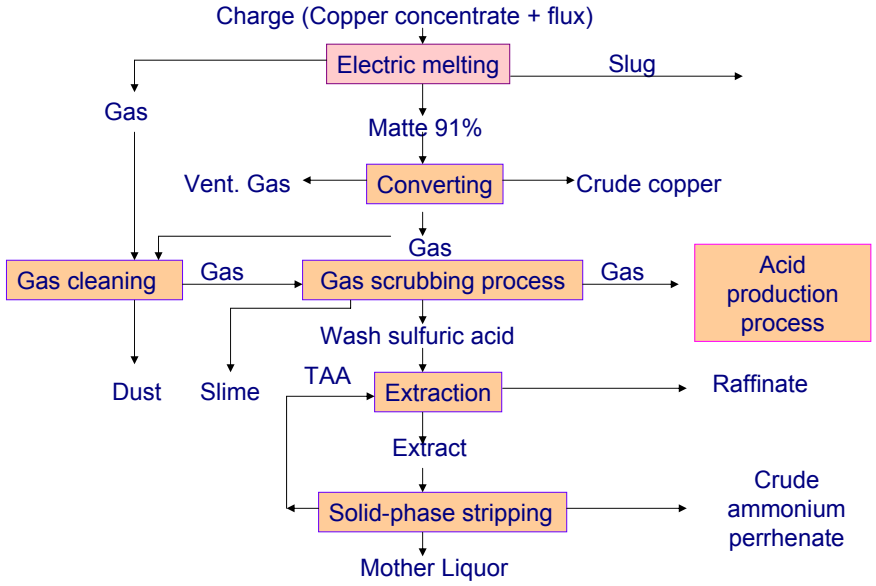
•Uranium ores (concentration of rhenium 0.7-1 g/t)

The main source of rhenium in Kazakhstan is Zhezkazgan sulphide copper ore deposit.

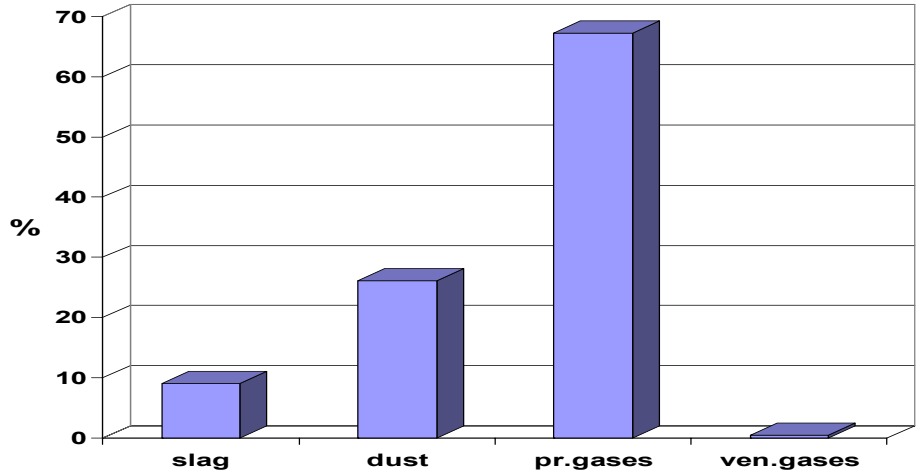
Main goals and objectives of our work are:

- To review the current and future situation with rhenium recovery in Kazakhstan.
- To investigate distribution of rhenium throughout a copper concentrate smelting process and develop the technology of rhenium recovery from by-products of the copper concentrates processing.
- To develop the technology of rhenium recovery from by-products of the lead concentrates processing.
- Determination of rhenium content in the uranium ores. Investigation of rhenium behaviour during the sorption of uranium in the existent technology.
- Carrying out of investigation on concentration of rhenium from technological solutions of various composition by methods of sorption and solvent extraction.
- Development of technology for recovery of rhenium from solutions of underground leaching of uranium ore

Flow sheet for processing of copper concentrates



Rhenium distribution among products of sulfide copper concentrates processing



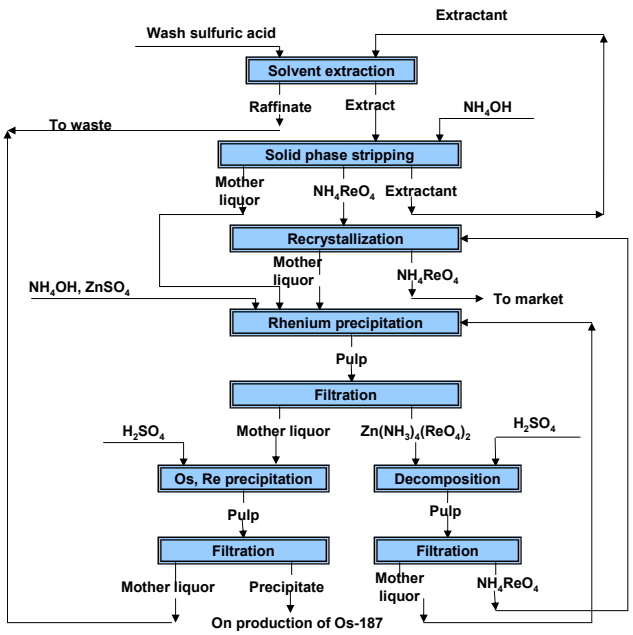
Process gases, %: electric furnace gas - 28, converter gas – 39, dust – 26, wash sulfuric acid – 63, slime – 4

The rhenium content varies:

- in the wash sulfuric acid from 100 to 250 mg/L,
- in the electrostatic dust: from 140 to 320 g/t,
- in the slime from 400 to 900 g/t.

At the present time wash sulfuric acid is the only source of its industrial production in Kazakhstan. There is another valuable element, an stable isotope of osmium 187, in the wash sulfuric acid and slime. Its content is 0.3-0.8 mg/L and 50-90 g/t, respectively.

Technological flowsheet for recovery of rhenium and osmium from wash sulfuric acid



Overall recovery of rhenium to commercial ammonium perrhenate from the solution according to the technology is 98,05 %.

The rhenium recoveries for each stage in the process are:

- extraction - 99,5%;
- solid phase stripping – 99,36%, of which 89,1% in crude ammonium perrhenate and 10,26% in mother liquor;
- dissolution of the pulp with formation of crude ammonium perrhenate – 92,27%;
- re-crystallization of crude ammonium perrhenate into commercial salt – 99,99%;
- precipitation of complex salt - $Zn(NH_3)_4(ReO_4)_2$ from mother liquor of solid phase rhenium re-extraction, mother liquor from pulp dissolution and wash solution – 88,7%;
- decomposition of complex rhenium salt during separation of rhenium (solution) and zinc (precipitate) – 99,3%;
- evaporation of rhenium containing solution after the decomposition and crystallization of crude ammonium perrhenate – 89,40 %.

Rhenium and Osmium Recovery from Dusts and Slimes

Composition, % of lead slime generated by copper production: Pb 65.7, Os 0.011, Re 0.15, Ag 0.012.

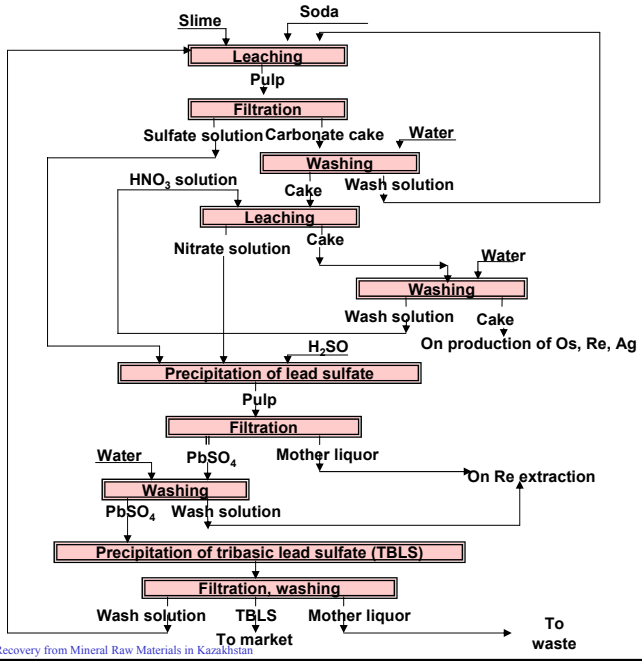
Composition, % of dusts generated at the copper smelters: Pb 44.5, S 11.7, Cu 6.2, Zn 5.7, F 1.2, As 1.1, Bi 0.04, Re 0.017, Ag 0.016.

During the slime processed by two consecutive operations the following components are extracted in the solution, %: 97,3 Pb, 93,4 Re, 90,5 Cu, 98,1 Zn, 99,7 Cd, 95 Se. Osmium and silver remain in the cake.

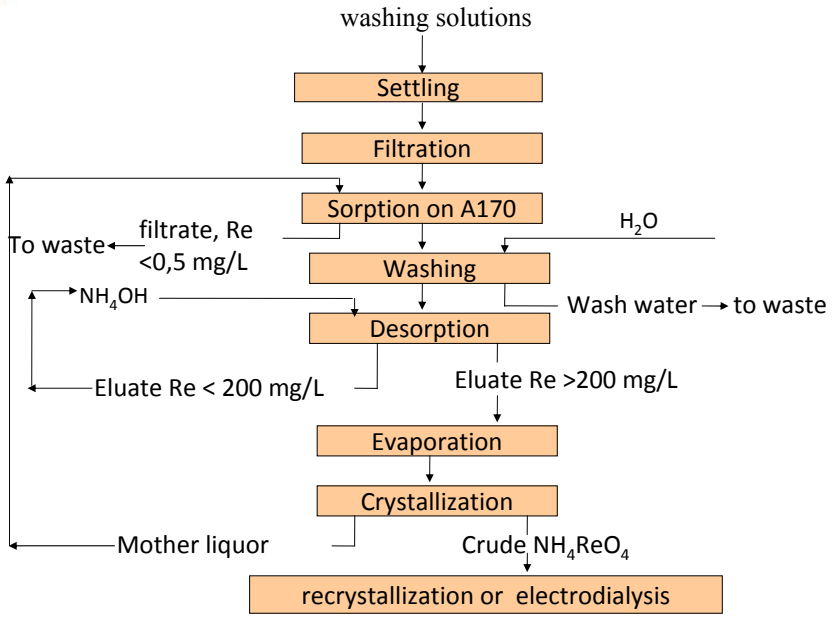
The cake yield from the slime weight can vary from 3.53 to 14.56%.

Os and Ag are concentrated in the cakes. Thus, the osmium content increases up to 22 times, silver – up to 26.

Technological flowsheet for processing of lead slime with production of rhenium, TBLS and Os-Re-Ag- containing concentrate



Flow sheet for recovery of rhenium from washing solutions of BGMK



Technological parameters

- Rhenium concentration in wash sulfuric acid - 13 mg/L, sulfuric acid - 60,5 g/L

Sorption

- full dynamic exchange capacity (FDEC) – 30 kg/m^3, anionite A170,
- specific volumes of solution passed through column before breakthrough of rhenium 95 % – 3000,
- specific volumes of solution passed through column before breakthrough of rhenium 3 % - 560,
- speed of solutions passing through column – 4-6 specific volumes /h,
- recovery on the stage of sorption – 97 %.

Desorption

- speed of eluent passing through column – 0,5 – 1,0 specific volumes /h,
- temperature – 40 ^{0}C,
- ammonia concentration– 3 M,
- 96 % of rhenium is recovered into 4 specific volume of eluent,
- average rhenium concentration in united effluent fractions – 5,4 g/L

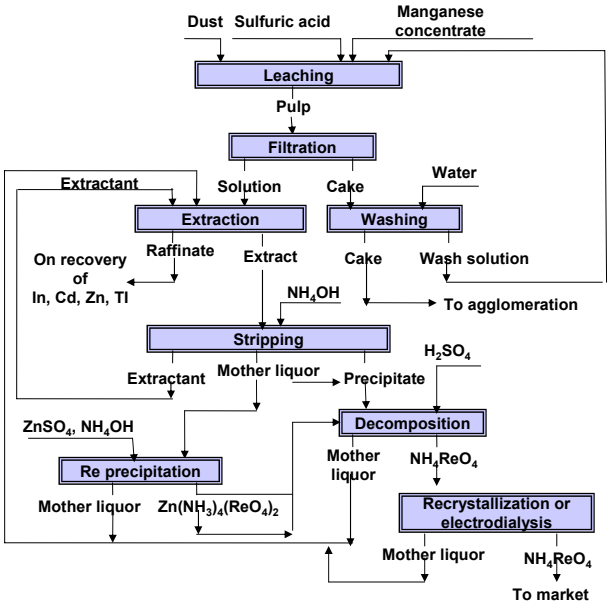
The dusts of copper production are sent to a lead factory, where they are processed together with the lead concentrates and circulating plant materials. The charge is oxidatively roasted into sinters with their further reduction smelting into crude lead in the shaft furnaces. During this process dusts containing,% (wt.): 66.02 Pb; 0.58 Zn; 0.09 Re; 6.15 Cd; 0.10 Se; 0.042 Te; 0.23 Tl; 0.0015 In; 0.56 Fe; 0.72 Cu; 5.37 Cl; 0.814 As; 0.024 Hg; 8.90 S are formed.

The method of dust leaching by solutions of sulfuric acid in a mix with the manganese concentrates produced in Kazakhstan is proposed for dust processing.

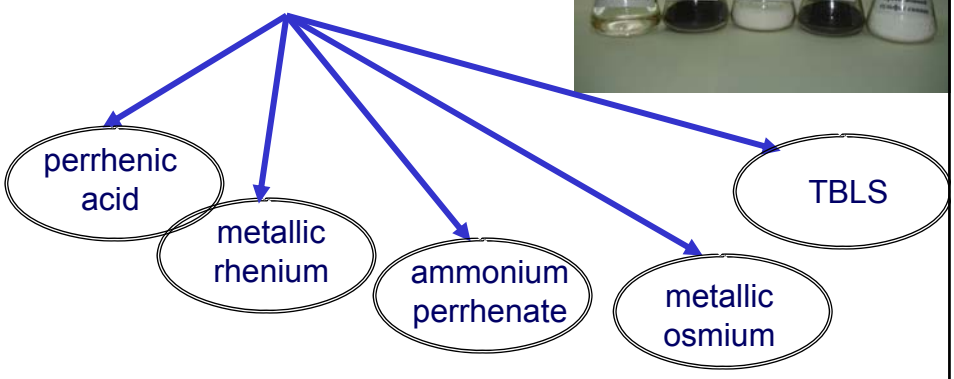
The optimum conditions of processing the dusts were determined: concentration of H_2SO_4 – 1 mol/L; consumption of concentrate – 15 % of the weight of agglodust, duration – 1 hour, S:L=1:3, temperature – 80 0C. At that the degree of recovery is 91% for rhenium, 88% - cadmium and 92% - zinc.

The solutions of processing the dusts contain, g/L: 0.1-0.25 rhenium, 20-30 cadmium, 30-35 manganese, 80-100 zinc, 18 - 20 chlorine, 0.03 iron, 0.005 – 0.006 arsenic and 0.12 – 0.2 thallium, pH=4.

Technological flowsheet for recovery of rhenium from dust of lead plant



Main commercial Re, lead and Os products



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Rhenium content in uranium ores of Tien Shan side province

Province	Content	
	Uranium, % (weight)	Rhenium, g/t
Central-Kyzylkumsky (Northern Bukinaj, Southern Bukinaj, Beshcac, Ketmentchi, Sabyrsaj)	0.01-0.1	0.5-2
Syr-Darya (Northern Karamurun, Southern Karamurun)	0.01-0.1	0.02-1
Chu-Sarysujskaya (Uvanas, Kanzhugan, Mynkuduk, Moyinkum)	0.03-0.05	0.1-0.5

The main stages of UL solutions processing:

- sorption,
- washing of saturated anionite,
- additional saturation of anionite,
- desorption,
- denitration,
- anionite regeneration,
- uranium compound precipitation

Underground leaching solutions along with uranium contain rhenium and other valuable elements, including (g/L): 0.035- 0.100 U, 0.32 - 1.45 Fe, 0.28 -1.21 Al, 0.40 - 0.43 Ca, 0.22 - 0.53 Mg, 0.07 - 1.54 Si02, 0.22 - 1.28 Cl, 8.7 -16.0 SO42-, 0.20 - 1.72 NO3-, 0.28 - 0.60 Re (mg/L) , and pH 2.03 - 2.10

The behavior of rhenium in the technology of uranium recovery from UL solutions

- rhenium concentration in the solutions incoming on sorption varies from 0.56 to 0.88 mg/L,

- rhenium is partially sorbed together with uranium, both at sorption operation, and at operation of additional saturation. Content of rhenium in additional-saturated anionite is practically constant - 840 g/t,

- rhenium is partially eluated together with uranium. This is confirmed by the presence of rhenium in the poor and rich eluates and also on anionites. The average content of rhenium in them is 2.5 and 3 mg/L, and 840 g/t, respectively,

- presence of rhenium in eluent (2.5 – 8.75 mg/L) is caused by the use for its preparation of denitration operation filtrates(1.12 - 7 mg/L),

- presence of rhenium in the solution-precipitant (4 – 5.6 mg/L) is caused by its presence in rich eluates (2 – 7.6 mg/L), of which uranium is precipitated, as well as mother liquors are returned for preparation of solution-precipitant.

Potential sources of raw materials for recovery of rhenium in the uranium industry:

- UL solutions,
- uranium sorption filtrates,
- anionite after uranium elution,
- mother liquors from uranium precipitation.

Chemical composition of technological solutions

№	Concentration, g/dm^3												
	pH	U	Re	Fe^{3+}	Fe^{2+}	NO_3^-	SO_4^{2-}	Cl^-	Ca	Mg	Al	SiO_2	P
1*	2.03	0.061	0.0006	0.11	0.43	0.69	8.7	1.28	0.40	0.13	0.31	0.05	0.006
2**	2.10	0.001	0.0005	0.11	0.44	0.63	8.7	1.12	0.42	0.10	0.29	0.05	0.005
3***	0.6	0.005	0.0048			77.4	0.79	0.02				0.04	

Notes: 1* – UL solution, 2** –filtrate of sorption, 3*** – mother liquor from uranium precipitation

From filtrates of uranium sorption processing, rhenium was adsorbed on the A 920 and IRA 910 anionites of Ambersep DOW Chemical company. These anionites are currently applied in the uranium technology.

Experiments on sorption were carried out in dynamic conditions in columns with a fixed bed of anionites in chloride form. Solutions onto columns are fed with a speed of 5 specific volume/h. Each hundred volumes of filtrates were analyzed for rhenium content. It was established that rhenium is sorbed by both anionites.

Anionites A 920 and IRA 910 are saturated with Re when 4500 and 3600 specific volumes of solution, respectively, pass through columns. Rhenium full dynamic exchange capacity (FDEC) of these anionites is practically identical: 1 ton of dry A 920 anionite sorbs 3.62 kg of rhenium, and IRA 910 sorbs 3.52 kg.

Rhenium desorption from anionites A 920 and IRA 910 (the content, kg/t: 3.62 Re, 10,6 U in A 920; 3.52 Re, 7,22 U in IRA 910)

Specific volumes of eluent pass through	Concentration in eluate		Recovery from anionite, %	
	Re, mg/dm³	U, mg/dm³	Re	U
AnioniteA 920				
1	7.5	233.3	1.07	6.85
2	27.5	419.0	5.00	19.17
3	32.5	462.0	9.64	32.76
4	45.0	438.0	16.07	45.64
5	37.5	357.0	21.43	56.14
6	30.0	285.6	25.72	64.52
7	18.0	223.7	28.29	70.08
8	12.5	181.0	30.08	75.40
9	11.0	181.0	31.65	80.72
10	11.0	176.0	33.22	85.90
11	9.0	176.0	34. 51	90.26
Anionite IRA 910				
1	14.0	285.6	2.39	14.30
2	95.0	381.0	16.57	33.35
3	62.5	285.0	27.22	47.60
4	70.0	162.0	39.14	55.70
5	45.0	152.0	46.80	63.30
6	37.5	143.0	53.18	70.45
7	15.0	133.0	55.73	77.08
8	11.0	67.0	58.28	80.43
9	11.0	47.6	60.15	82.78
10	10.5	47.6	61.94	85.13
11	7.5	47.6	63.22	87.48

Influence of Hostarex A324 concentration on rhenium extraction

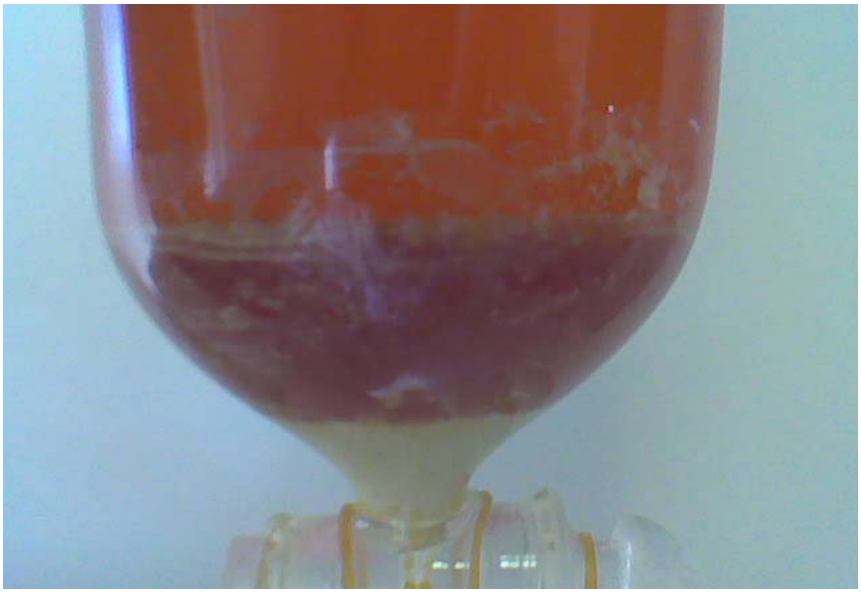
Initial solutions, g/L: 0.034 Re, 0.170 U, 58.0 NO-3, with pH=0.4

Concentration of Hostarex A324 in extractant, % (vol.)	Raffinate concentration, mg/dm³		Extract Re concentration, mg/dm³	Recovery of Re, %	Re distribution coefficient
	Re	U			
O:A=1:5					
1.0	29.0	168.0	25.0	14.0	0.9
2.5	24.3	166.0	48.5	28.5	1.9
5.0	20.4	169.0	68.0	40.0	3.3
10.0	13.6	168.0	102.0	60.0	7.5
15.0	8.2	166.0	129.0	76.0	15.7
20.0	2.7	162.0	156.5	92.1	16.0
25.0	1.0	170.0	165.0	97.1	165.0
40.0	0.2	175.0	169.0	99.4	845.0

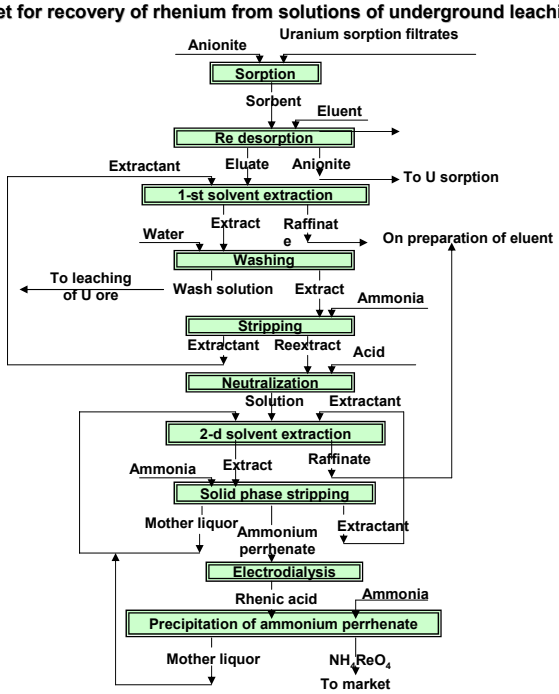
After first extraction and stripping the Concentration of Re in solution was in g/L: 2.97 Re, 175 NO3- and U was not found.

Secondary extraction is carried out in 4 steps at O:A =1:5 The concentration of rhenium in raffinate is 25 mg/L, in the extract – 14.7 g/L. Recovery into an extract is 99.0 %.

Solid phase stripping is conducted in one step by 8 mol/L solution of ammonia at O:A=10:1. During this process the pulp is divided into 3 phases: the lower is the salt of ammonium perrhenate, intermediate - mother liquor and the top is extractant. The salt of ammonium perrhenate is filtrated and washed from mother liquor. Marketable ammonium perrhenate is produced by recrystallization or by electrodialysis.



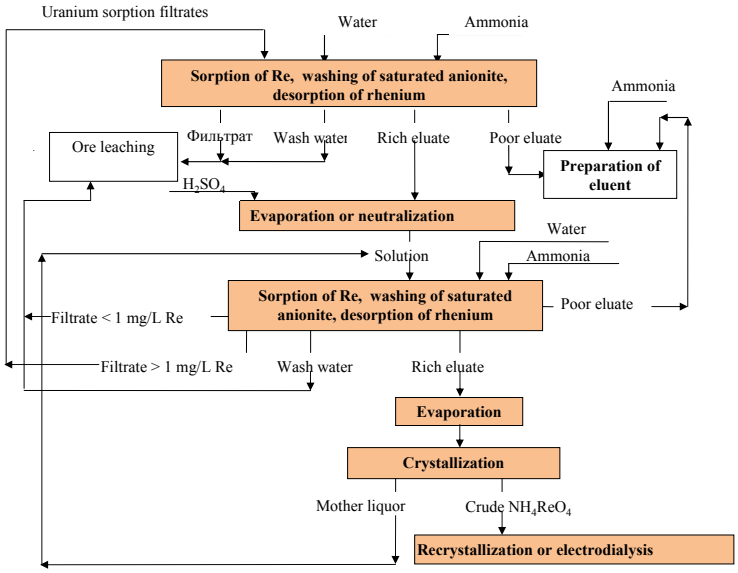
Technological flowsheet for recovery of rhenium from solutions of underground leaching of uranium ores



Main commercial rhenium products

- perrhenic acid
- metallic rhenium
- ammonium perrhenate

Flow sheet for recovery of rhenium recovery from uranium sorption filtrates



Technological parameters

Concentration in uranium sorption filtrates, mg/L: 0,48 Re, 2 U.

First stage sorption - desorption

- **Sorption:** speed of solutions passing through column – 6 – 10 sp.vol./h; specific volumes of solution passed through column before breakthrough of rhenium - 98 % - 6000 – 7000; full dynamic exchange capacity (FDEC) - 4 – 6 Re и 5 – 7 U kg/t of dry ionite, recovery – 70 %.
- **Desorption:** speed of eluent passing through column – 0,5 – 1 sp.vol./h; temperature – 50^{0}C, specific volumes of eluate passed through column– 30; average composition of eluates, directed on 2-d stage of concentration, g/L: 0.054 Re, 2,4 NO^-_3, 0.170 SO^{2-}_4

Second stage sorption - desorption

- **Сорбция:** speed of solutions passing through column – 4 sp.vol./h, specific volumes of solution passed through column before breakthrough of rhenium - 98 % - 2000 – 2200; full dynamic exchange capacity (FDEC) – 78 - 83 Re kg/t.

Desorption: speed of eluent passing through column – 0,5 – 1 sp.vol./h; temperature– 50 ^{0}C, specific volumes of eluate passed through column – 5 sp.vol./h; average concentration of rhenium in eluates, directed on evaporation - 4 g/L.

CONCLUSION

The main source of rhenium in Kazakhstan is Zhezkazgan sulphide copper ore deposit. The most part of rhenium at the processing of copper concentrate passes into the wash sulfuric acid. Technological flowsheets of rhenium recovery from various by-products of copper concentrate processing are proposed.

It is shown that dusts of oxidizing agglomerating roasting of lead charge are a real source for rhenium recovery in lead industry. The 91% of rhenium, 85.2% of cadmium, 92.3% of zinc and 90.7% of manganese are recovered into a solution during leaching of dusts by sulfuric acid solutions with use of a manganous concentrate as an oxidizer. For recovery of rhenium from these solutions solvent extraction technology is developed and introduced. Recovery of rhenium from the dusts into marketable products was 77%.

The results of studies on the development of technology for production ammonium perrhenate from solutions after underground leaching of uranium ores have been presented. The basic stages of rhenium recovery are sorption on anionites, and desorption with the subsequent concentrating by a method of solvent extraction. The technology of rhenium recovery from filtrates after uranium sorption has been proposed.

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