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Exploration of Rhenium Volcanogenic Deposit and Technology Development

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A B S T R A C T

Rhenium is widely used in manufacturing industry and metallurgy. Today the consumption of rhenium is high, but there are very few deposits in the world where it is mined. Thus, the aim of the study is to identify areas of distribution of rhenium on Kudryavy volcano, located on the islands of the Kuril ridge (Russia). In this connection, during the field period, we took samples of a volcanic massif weighing 70 kg, and also studied the geothermal fields with a pyrometer. Laboratory research included the study of composition of samples by the method of inductively coupled plasma mass spectrometry and spectrometric analysis. The article defines the zones of distribution of rhenium mineralization, presents the results of measurements of the temperature of geothermal fields and the elemental composition of technological samples. The geology, development technology is described, the analysis of the destruction of rocks, determined by the acoustic method, the specific resistance of breakdown during electrothermal loosening is given. The parameters of the tubular shovel conveyor at which the productivity of 88 m^3/h is achieved. The results obtained will make it possible to identify promising geothermal fields, determine the development technology, and contribute to the study of volcanic deposits.

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1. INTRODUCTION

By 2019, rhenium production outside the Russian Federation increased by 9 % compared with 2013. This happened mainly due to a significant increase in the output of rhenium in the USA, which is the largest producer and consumer of this rare metal in the world. In 2019 the United States produced approximately 72 % of all rhenium. From 2013 to 2019, the production in this country almost doubled and amounted to 23120 kg per year, and consumption reached 25140 kg per year (Figure 1) [1, 2]. The demand for this metal in the world is very high with limited mineral resources [3-13].

Taking into account the plans of some companies to expand their capacity, it can be assumed that if there is such demand for this metal, the production of rhenium in salts at US steel mills may increase by about 3–4 tons per year in the coming years [12-23].

There are few rhenium deposits in the world that can meet the demand for this metal. One of these deposits is the Kudryavy volcano, located in Russia. This is a volcanic type deposit that can give the world the valuable metal rhenium.

Volcanic deposits can serve as a source of metals such as Zn, Cu, Au, Mo, Ni, Co, Ir, Mn, Re [1-6].

A review of studies of volcanogenic deposits carried out by the world's leading scientists proved that they can be a source of minerals. These studies give a definition to such deposits, provide a diagram of a modern sulfide deposit located in the Pacific Ocean, a classification of metals, their geographical distribution, an assessment of the amount of metals, examples of large-tonnage volcanogenic massifs of sulfide deposits in the world, and describe the principle of the formation of such deposits [1-23]. Despite this, the distribution of rhenium in the geothermal fields of volcanic deposits has not yet been studied, moreover technologies for their development have not been presented.

Further research in this area related to the study of volcanogenic deposits is a solution to a major problem

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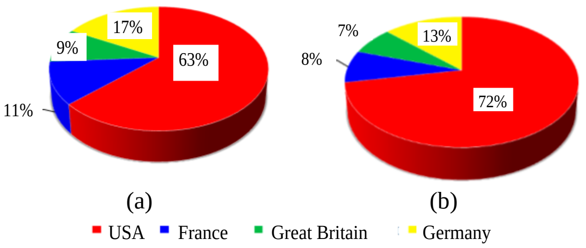

Figure 1. The share of foreign countries in rhenium production a. 2013; b. 2019

associated with an increase in efficiency of using mineral resources.

In this regard, this study is a relevant and timely direction of development for the purposes of providing rare elements to various industries.

The novelity of this research work is to establish the identification of patterns of rare elements accumulation in rocks located in high temperature zones, the dependence of the coefficient of rare element accumulation on the geothermal fields.

The limits of volcano crater rocks destruction by the seismic wave velocity were determined, which shows the possibility of using mechanical loosening. The dependence of the actual amount of material on the bucket capacity of excavation and loading equipment are defined at bucket fill factor Kn=0.4, 0.5, 0.6, as well as tubular scoop conveyor main parameters on the productivity of the mining complex and the density of the mineral was determined, which makes it possible to increase the efficiency of the complex and the profitability of the development.

The objective of the research is to identify areas of distribution of rhenium on Kudryavy volcano, as well as to describe the technology development and efficient transportation of rocks in difficult climatic conditions and at high temperatures.

The main results of the study passed semi-industrial tests and proved to be effective.

2. MATERIALS AND METHODS

The following tasks were solved in the course of research:

-Study of the material composition of rocks.

-Identification of geothermal fields with the highest temperature.

-Determination of main parameters of the technology for volcanogenic deposit development and rocks transportation.

The tasks were solved in two stages: field and laboratory.

During the field period, volcanic massif samples 70 kg each were taken from the geothermal site comprising Rhenievoye field, Angidridovoye field, Treschina field, Field 605, and Kupol field for further laboratory and technological study. The sampling place was a gas flow outlet on the flattened surface of a domal up warping in the Kudryavy Volcano vent.

The depth of sampling using bulk method varied from the daylight surface up to 0.5 m. The transfer to the «hot» zone of the gas jet discharge explained the sampling depth taken with a temperature exceeding 700˚C, which was measured using an external thermocouple. Samples were taken from a conical excavation with wall cutback up to 10 meters and narrowing to the depth. The sample comprised all observed rock differences without selecting preferable ones. The sampling area length was up to 400 meters in each geothermal field; samples were taken in 20 meters on average (Figure 2).

Temperature parameters of geothermal fields were measured using AKIP-9307 manual high-temperature pyrometer with measuring values up to plus 1000˚C. Measurements were made under minimal fumarole activity on the open surface site. Measurement results were recorded on the topographic surface.

Topographic survey of the vent relief was scaled 1:1000 with relief sectioning by horizontal intervals in each 1 meter using tacheometric procedure from survey control points by Sokia SET 630R electronic tacheometer. Topographic survey accuracy was checked by inspecting field data and comparing sketches and photographs. Field data was verified in terms of registration and completion of logs. The operating procedure was checked as well as tolerances for survey justification and the topographic survey procedure.

Then, laboratory tests were carried out for the samples taken, which were both coarse aggregates sizing more than 100 mm and fine-dispersed component (ash).

Taking into account the non-uniform grain-size distribution of samples, a set of preparative procedures was carried out comprising multistage crushing of the

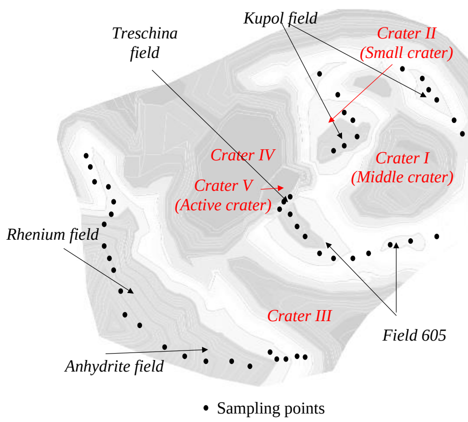

Figure 2. Sampling layout

initial material to fineness -1 mm with preliminary and control sieving. Figure 3 illustrates the preparation flowchart for the samples to be studied.

As a result, samples with uniform grain-size distribution were prepared.

An element composition of process samples was studied using mass spectrometry with inductively coupled plasma (ICP-MS) and NSAM (Analytical Method Scientific Council) industry procedure No. 179-X "Rhenium Measurement in Rocks and Sulphide Ores by Photometric Method (2015), Russian Federation."

The following operating conditions applied for Agilent-7500 ICP-MS: plasma temperature 8000 to 10000˚C; carrier gas flow rate 0.8 to 1.3 L/min; plasma-supporting gas flow rate 15 L/min; high-frequency signal power 700 to 1600 W; signal integration time 0.1 s.

To calibrate the mass spectrometer and perform the assay, laser ablation was carried out for two zones in the sample. The results obtained in such a way were compared with certified element contents (Ag, As, Au, Br, Ba, Be, Bi, Ca, Cd, Ce, Cl, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, La, Li, Lu, Mg, Mn, Mo,

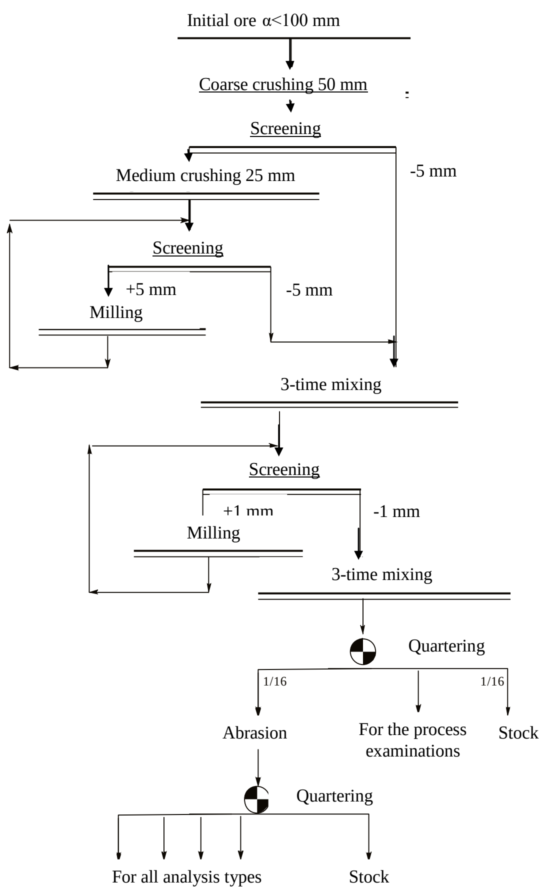

Figure 3. Preparation flowchart for the samples to be studied

Nb, Nd, Ni, Pd, Pb, Pr, Pt, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Zn, Zr). There were no systematic deviations; data variability did not exceed procedural error limits.

The samples featured high contents of molybdenite, titanium, iron and manganese that distorted the rhenium values measured using ICP-MS. Matrix effect affected the procedure accuracy. To minimize the matrix impact, it is necessary to dilute the samples in high proportion, but it was impossible to avoid the molybdenite impact completely. Rhenium separation from the matrix by isotope dilution is the most common procedure to minimize the matrix impact. Isotope dilution has several limitations: first of all, the element to be measured should have at least two isotopes; secondly, those isotopes should be free from spectral interferences. Despite the progress in ICP-MS technology over the last decades, high costs of equipment limit this procedure for routine assays.

To measure the rhenium contents, we used NSAM No. №179-X, which is based on spectrophotometric analysis and is relatively affordable, accessible and reliable ensuring the measurement of rhenium concentration within 10^{-2} % wt. to 10^{-5} wt% [24,25,26]. The applied procedure is standardized and certified. This method is fast and easy when executing [27]. It comprises the preparation of a rhenium (VII) solution, reducing it to rhenium (IV) with a tin (II) chloride solution, them converting it into a complex compound, sorbent separation from the solution, diffuse reflectance measurement at 510 nm, and calculation of rhenium (IV) contents using a calibration curve. Silica modified chemically with N-(1,3,4-thiodiazole -2-thiol)-N'-propylurea groups was used as a sorbent.

To establish calibration parameters of rhenium measurement, a reference solution (state standard reference sample) No. 100043-2 was used. Solutions with lower concentrations were prepared by dissolving aliquots of the reference solution. The used procedure had the following metrological characteristics specified in Table 1.

Quality indicators of NSAM No. 179-X procedure (Table 1) satisfied metrological requirements, and the results obtained were reliable.

Application and efficiency of the volcanic massif mechanical loosening were examined by seismoacoustic method based on the study of propagation of elastic vibrations in the massif.

The speed of elastic wave propagation sufficiently correlates with the massif strength and jointing and may serve as a generalized indicator that considers the change of these factors.

Elastic wave propagation speed increases with the rock strength increase and decreases with jointing increase.

TABLE 1. Quality indicators of NSAM No. 179-X rhenium measurement procedure (weight fraction, %)

Rhenium content, % wt.	Repeatability		Intra-laboratory precision		±Δ	Reproducibility		Uncertainty value		
	S_r	r	$S_{I(TO)}$	$R_{I(TO)}$		S_R	R	N	U_c, % wt.	U
0.05	0.0009	0.0025	0.0011	0.0030	0.0018	0.0014	0.0040	0,0140	0,007	0,014
0.10	0.0012	0.0033	0.0014	0.0040	0.0024	0.0019	0.0050	0,0323	0,0034	0,0068
0.50	0.0060	0.0170	0.0070	0.0200	0.0120	0.0110	0.0300	0,0600	0,0034	0,0068

Note: S_r, $S_{I(TO)}$, S_R are standard deviation of repeatability, intra-laboratory precision and reproducibility; r, $R_{I(TO)}$, R are repeatability, precision and reproducibility limits; ±Δ are the limits of the range for the analytical result error at confidence factor P=0.95, N is relative standard uncertainty, U_c is total standard uncertainty, U is extended uncertainty of analytical results.

To exclude the impact caused by the properties of the rocks forming the massif on the seismic wave propagation speed, the ratio was used between velocities of longitudinal waves with the same type defined by measuring at large 30 m bases and at bases approx. 10 cm in monolithic areas of the same massif. Measurements were carried out using a high-frequency mic survey in the first case and by ultrasonic method in the second one. The velocities obtained were designated as $V_{high\ frequency} = V_{ultrasonic}$, correspondingly; their ratio will define the acoustic jointing indicator, i.e. $R = V_{high\ frequency} / V_{ultrasonic}$. $V_{high\ frequency}$ may serve as an indicator taking into account the structural characteristics of the rocks to be loosened. Assessment of the massif by two parameters, R and $V_{ultrasonic}$, considers the most comprehensively the interaction between the ability to loosen and physical-technical parameters of the massif.

Laboratory research included the study of composition of samples, technological tests of new equipment for the transportation of rocks at various angles of inclination from 0° to 180°, according to the description of Russian patent RU No. 170400, as well as an electrothermal method of selected samples destruction using aluminum cathodes, IOM 100/25 high-voltage transformer (single-phase oil test transformer with a frequency of 50 Hz) with a rated power of 25 kVA, and IOM 100/100 transformer with a rated power of 100 kVA.

3. RESULTS

3. 1. Geological Structure of Kudryavy Volcano

Kudryavy Volcano is 986 m high and its base diameter is about 5 km. It is superimposed on an ancient, heavily reworked volcano structure. Including the Sredney volcano. All rocks of the volcano are subdivided into three strata of different ages. The lower thickness consists of numerous blocky lava flows of andesite-basalt and andesite composition, exposed at the periphery of the volcano and separated from each other by breccia crusts. The extruded sheet occurred mainly in the western direction; to the east, the spread of lavas was limited by the buildings of the rhyolite dome and Sredney volcano. The surface of the lava flows is overgrown with elfin, alder, birch, especially at elevations less than 350 m. After the formation of this stratum, the Kudryavy Volcano, apparently, was in a state of relative rest. Slope breccias with interlayers of tuffs and organic matter formed on the southern and northern slopes.

The section of the sediments overlying the lavas of the lower strata described by us is in a dry ravine between the extrusive body and the lava flow of the last eruption on the northern slope of the Kudryavy Volcano.

On the lavas of the southern slope of Kudryavy volcano, there is a lens composed of interbedded loam with peat bogs. In total, there are 5 interlayers of peat bogs with the thickness of 3-4 cm. The age of the second peat bog on top is 4450 ± 100 years. Thus, the age of the lower complex of Kudryavy Volcano is possibly over 5000 years old.

The middle stratum is composed of highly oxidized viscous lavas and an andesitic extrusive dome. The distribution of this stratum is limited by the near-crater part of the volcano. It is described in more detail in the description of the peak Kudryavy Volcano.

The upper thickness includes 7 flows of olivine-bearing bipyroxene basaltic andesite and andesite, traced towards the northwest, west and south of the peak. Its lavas are separated from the middle strata by a section that includes lacustrine-swamp deposits and pumice. It is the most fully sketched in (from top to bottom) on the northern slope of the Menshoy Brat Volcano. It follows that the marking pumice horizon has an age of <700 ± 40 years, and the upper age limit of the sequence is limited by the dating of uncarbonized elfin wood (170 ± 40 years), underlying the largest flow of block lavas of the upper sequence.

At the top of the Kudryay Volcano, according to geological and morphological features, elements of four craters and an explosion funnel are distinguished, they are differing in age, structure and mode of fumarolic activity (Figure 2).

Crater I is a middle crater (230 m in diameter) and the most ancient (it forms the lower stratum), is represented by a somma fragment in the center of the somma of Kudryay volcano. Spatially it limits all high-temperature sites of the Kudryay Volcano. Its somma is composed of interbedded basaltic and andesite lavas and agglomerates strongly altered by solfatary-fumarolic activity. The rest of the crater was destroyed by later eruptions.

Crater II is superimposed on the first one and is located in the eastern part of the volcano. In its outlines, it is close to a regular circle (130 m in diameter along the upper edge of the somma), it is open to the east. The somma is formed by viscous andesite lavas (middle stratum) with inclusions and veins of cordierite glass. Andesite extrusion (Kupol field) is located inside the crater, occupying more than half of the crater area. It is associated with 3 fumarole sites with high-temperature gases, which received their own names (in brackets: area in square m; average / maximum t ° C): «Treshina field» (322; 528/750), «Kupol field» (980; 620/920) and «Field 605» (396; 586/784) - confined to the upper edge of the somma

The lowered parts of the relief are filled with crater-lacustrine deposits, the formation of which is due to erosion (to a significant extent is the wind) of the surrounding hills and temporary flows associated with melting snow and heavy rainfall. The depression to the west of the extrusion dome is quite hot (52 ºC at a depth of 5 cm). With a deepening of 1.5 m, the temperature rises up to 96 ºC and is accompanied by intense release of sulfurous gases. Possibly, sandy-argillaceous deposits are the barrier to gas jets and form the cover that prevents the dispersion of volcanic gases and directs their movement to the «Rhenium field site». In other depressions during pits driving (up to 2 m), the temperature rise was not recorded. These depressions are likely traces of large explosion craters that formed around the Kupol field, similar to the crater in October 1999, but later filled with tephra and sediments of temporary streams.

Crater III is 80 m in diameter. It is located to the west of the first one and is superimposed on the somma of Crater I of the Kudryavy volcano. Its formation is associated with weak eruptive activity and the intrusion of a small stock-like body of andesites, now completely processed by high-temperature gas jets. The somma of Crater III is also practically not preserved, and its position is reconstructed fragmentarily. In its western part there are two fumarole sites (in brackets: area in m^2; average / maximum t ºC): «Rhenium field» (1048; 481/020); «Anhydrite field» (140; 280/360).

Crater IV spatially limits the distribution of low-temperature fumaroles and has the shape of an ellipsewhich is open to the north. The last three lava flows erupted from it towards the northern, southern and southwestern directions (upper strata), and andesite-basaltic slags were thrown out, overlapping all formations of the volcano. Curly, several isolated areas with fumaroles are also distinguished here, the gases of which have temperatures predominantly of 98-120 ºC (up to 21.0 ºC) and intensively deposit sulfur. However, in some areas, the gas temperature exceeds the melting point of sulfur.

Crater V was formed as a result of the eruption on October 7-8, 1999, which began as a phreatic [30, 31]. Later, Znamensky et al. [28] informed about lava observed at the bottom of the crater in the second half of October. Crater V is an explosion funnel with a depth of 15 to 40 m, an upper circumference is about 15 m in diameter and almost sheer walls. The funnel cut off a part of the Crater II ridge and exposed a part of the exocontact of the Kupol field extrusion. At its bottom, an eruption of gases from a hole in red-hot (to a red glow) rocks was observed. Although all high-temperature fumarole sites are located within a radius of 200 m from this funnel, its explosion did not affect the mode of their degassing to a visually noticeable degree, while the extinct fumarole of the dacite dome was activated.

3. 2. Geothermal Fields of Kudryavy Volcano and Rare Metal Mineralization

Scientists' research proves the accumulation of minerals in areas of high temperatures of the volcanogenic massif [32,33,34]. Such a phenomenon was identified in the geothermal fields Kudryavy volcano too.

The study of geothermal fields was carried out along all profiles where samples were taken, which made it possible to identify the highest temperature of 900 ºC that was observed in the Kupol field.

The results of measurements are presented in the form of a diagram of volcano crater surface temperature distribution in Figure 4.

Fieldwork and analytical works showed that rare metal mineralization forms in high-temperature geothermal fields and is distributed over a total area of 7,600 m^2, which can exceed bulk earth values. The low-temperature region of the volcano is distinguished by little rare-metal mineralization. The nature and composition of accumulations are directly dependent on the temperature and structure of adjacent rocks. The most favorable rocks for such accumulations are porous slags, as well as fractured rocks and tectonic breccias, which attract and deposit minerals, which is confirmed by visual inspection during sampling.

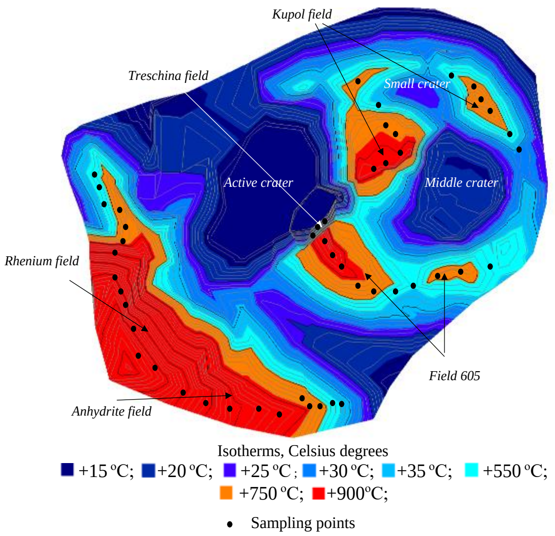

Figure 4. Diagrams of Kudryavy volcano crater surface temperature distribution (Russia)

The results of the analysis of the elemental composition of technological samples by the ICP-MS method (Table 2) showed that the samples are characterized by an increased content of molybdenum, titanium, iron and manganese, and a lower content of tungsten and zinc. Each sample was analyzed from two portions - quartered from abraded samples of 2 kg (6112 and 6115) and samples of 50 g taken by the standard method (6112-1 and 6115-1). Comparison of the obtained data confirms the uneven distribution of valuable components and the need for more thorough mixing of the material in the process of analytical research.

According to the results of the analysis of initial samples by method NSAM No. 179-X, the content of Re in them is as follows: in sample 6112 - 280.5-387.7 gpt, in sample 6115 - 10.43-25.72 gpt. (Table 3).

TABLE 2 Results of analysis of the elemental composition of technological samples by ICP-MS

Element	Content, ppm			
	Sample No.			
	6112	**6112-1**	**6115**	**6115-1**
Be	1.75	0.775	1.83	1.04
Ti	2366	3437	3721	3984
V	300	257	292	232
Cr	32.5	33.8	23.1	29.5
Mn	1840	1347	1341	1384
Fe	142134	63258	79633	79490
Co	32.0	15.8	21.8	25.4
Ni	25.2	14.4	15.1	20.2
Cu	308	296	549	171
Zn	760	80.3	1047	4.14
Ga	20.7	22.2	21.2	17.6
Rb	52.6	6.56	26.4	15.2
Sr	272	230	308	229
Y	22.7	21.9	23.1	20.1
Zr	44.3	53.6	53.7	49.9
Nb	0.988	0.642	0.916	0.694
Mo	15973	125	3299	206
Sn	49.6	3.83	9.47	2.12
Cs	3.93	0.155	1.56	0.189
Ba	93.9	122	206	150
La	3.39	3.96	4.20	3.86
Ce	9.76	10.7	11.5	10.6
Pr	1.56	1.67	1.81	1.61
Nd	8.25	7.78	9.02	7.74
Sm	2.64	2.71	2.72	2.36
Eu	0.684	0.621	0.823	0.759
Gd	2.86	2.94	3.20	3.03
Tb	0.590	0.570	0.626	0.553
Dy	3.92	3.68	3.97	3.45
Ho	0.885	0.872	0.889	0.793
Er	2.73	2.60	2.63	2.38
Tm	0.424	0.422	0.400	0.383
Yb	2.88	2.73	2.87	2.32
Lu	0.470	0.408	0.431	0.371
Hf	1.30	1.41	1.51	1.41
Ta	0.228	0.075	0.083	0.094
W	525	5.18	242	6.80
Th	0.605	0.598	0.515	0.756
U	0.510	0.359	0.411	0.338

Note: There were no systematic deviations; data variability did not exceed the procedural error limits.

TABLE 3 Determination of the content of Re in the initial samples by method NSAM No. 179-X

Sample No.	Re content, gpt	S_r	±Δ	U
6112	387.7	0.0010	0.0018	0.012
6112-1	280.5	0.0013	0.0023	0.0073
6115	25.72	0.0008	0.0016	0.0074
6115-1	10.43	0.0015	0.0025	0.0068

Some of the studied elements can be differentiated by geothermal field depending on the temperature (Figure 5).

Thus, it can be seen from the Figure 5 that the maximum Re concentrations (up to 300 g per ton) were found in the Rhenium field ores, and formed at 560 ºC. Three peaks are distinguished in the Re distribution. The main one (at 500-620 ºC) is provided with samples from the «Rhenium field», where rhenium disulfide itself makes the greatest contribution. Somewhat less (at 620-720 ºC) is due to samples from Crater II. Here Re is positively correlated with Zn (0.50), Cu (0.37), W (0.26), Ge and Mo (0.19). Rhenium disulfide was not detected in this temperature range, but there are single determinations of rhenium in molybdenite and sphalerite, and in the sublimates of quartz tubes, K-Re oxide was found, which is close in composition to $3KReO_4*ReO_3$. Although complete isomorphism in the Mo - Re series is assumed for the former, the absence of a significant correlation between these elements forces us to assume that sphalerite is also a Re concentrator in high-temperature ores. The third maximum stands out in samples at <400 ºC and is associated with Re impurities in Pb-Bi sulfosalts and pyrites.

Increasing concentrations of In (>1000 g per ton) is typical for samples deposited at 450-600 ºC, mainly at «Rhenium field». Positive correlations of In with Cd (0.70), Zn and Sn (>0.45) indicate the predominant deposition of native In minerals (sulfides and sulfo salts) in this temperature range, with the weak deposition of In halides in the low temperature range.

Mo-bearing mineralization occurs in two areas of deposition. The first bearing, with Mo contents in most samples >1000 g per ton, represents the high-temperature areas of the Crater, and the second one, with Mo concentrations <800 g per ton, is represented mainly by samples from the Rhenium field. In both cases, the direct dependence of the Mo content on temperature is clearly manifested. High concentrations of molybdenum in the ores of Crater II are due to massive crystallization of molybdenite (at temperatures >620 ºC) and other Mo-containing minerals (ilsemanite, novellite, molybdite, etc.) at lower temperatures.

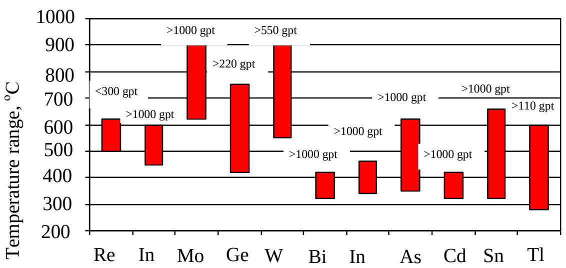

Figure 5. Temperature range of elements accumulation in rocks

The maximum Ge concentrations (100-220 g per ton) are characteristic of the Field 605 mineralization formed in the temperature range 420-750 ºC. Minerals of Ge have not yet been found, but not excluded. The high values of the correlation coefficients of Ge (at the critical value $r_{0.05}$ = 0.2732 for a selection of 51 samples) with Cu (0.68), Zn (0.60), Ag (0.38) are explained by its occurrence in sphalerites and sulfosalts, while with Mo (0.62) and W (0.45) are allowed to suggest an isomorphic incorporation of Ge into the minerals of tungsten and molybdenum. Although the latter are one of the important carriers of Re in ores, the correlation coefficient of Re and Ge is estimated to be insignificant (-0.02 at $r_{0.05}$= 0.2732) for volcano. Curly in general. However, in the most renaissance sites «Field 605» and «Rhenium field», the correlation of Re and Ge is estimated by the coefficients + 0.19 (at $r_{0.05}$ = 0.1954 for the sample of 69 samples) and + 0.26 (at $r_{0.05}$ = 0,1638 for the sample of 147 samples). Diagrams of correlations in ores Kudryavy volcono ones show the incorporation of Re into the Re-Ag-Cd-InCo-Ni association, and Ge - into the Zn-Ag-Ge-Ge-Ga-Cu-Mo-W association. These associations form mineralization in different temperature zones, but are linked through Ag. The fact of joint accumulation of Re and Ge in ores (at Re/Ge = 1.9) attracts attention as an unusual phenomenon, previously noted only in the conditions of the bituminous metalliferous formations of Mansfeld and Colorado [32]. It must be of special consideration in the conditions of the South Okhotsk region, where large deposits of germanium are known, and now Re-bearing objects have also been identified.

Concentrations of W (> 500 g per ton) are inherent in ores deposited at temperatures of > 550 ºC on all high-temperature areas. The intrinsic minerals W are represented by scheelite, povellite, stolcite, and tungstenite [34]; Hubnerite (Fe, Mn) WO_4 also sublimes in the tubes [34]. The positive correlation of W with Ge (0.45), Mo (0.26) and Re (0.19) indicates similar physicochemical conditions for the crystallization of minerals-carriers of these elements

In general, rare metal ores of high-temperature sites are characterized by low Cu concentrations, with the Zn/Cu ratio being one of the highest for the ores of the Kuril Islands. The maximum concentrations of Cu at high-temperature sites are inherent in the ores of Crater II, deposited at temperatures >550 ºC. No native Cu minerals were found here, and preparations of metallic copper «dissolve» in steam-gas jets with the removal of copper in the form of chlorides. The positive correlation of Cu with In, Ge, Sn, Re (0.30) and with Mo (0.45) indicates the possibility of the joint occurrence of these elements in the pyrites and pyrrhotites deposited at these temperatures. At the same time, in the sulfur-sulfide sublimates of Crater IV, copper forms its own minerals (chalcopyrite, covellite, bornite, chalcocite) or impurities in Fe sulfides (pyrrhotite, pyrite, marcasite).

The maximum concentrations of Zn (>1000 g per ton) are typical for ores of all high-temperature areas and are provided by the development of zinc sulfides (sphalerite, ZnCdIn-minerals, etc. [32]), less oxychlorides [34], There is a direct correlation between the Zn abundance and temperature.

The maximum concentrations of Pb (> 10 000 g per ton) are inherent in the Rhenium field ores. They are due to the development of intrinsic minerals, mainly Pb-Bi-Se sulfosalts, and in pipes, at relatively low temperatures, also chlorides [34], which is reflected by the negative correlation between Pb and temperature.

The maximum Bi concentrations (>1000 g per ton) are characteristic only for the Rhenium field and show an inverse dependence on temperature. Two peaks can be distinguished at 320-420 ºC and 500-650 C, indicating two temperature ranges and different modifications of the deposition of bismuth minerals: sulfide-sulfosaline and oxychloride.

The maximum As concentrations (>1000 g per ton) practically coincide with the Bi maximums in the Rhenium field ores deposited at temperatures of 340-460 ºC. Here, a positive correlation of As with Sb (0.40), T1 (0.38), Bi (0.21), indicating the probable dominance of Sb-As sulfosalts, the possible presence of lorandites and sulfates.

The maximum concentrations of Sb (30-100 g per ton) are also characteristic of the «Rhenium field» in the temperature range 350-620 ºC. Positive correlation coefficients of Sb with As, Bi, Sn, Ga (>0.20) and negative - with temperature evidence in favor of Sb deposition in low-temperature eulphosalts. Attention is drawn to the very high value of the As / Sb (s85) ratio in ores, probably exceeding As/Sb in most other volcanoes and ores of the Kuril islands.

The maximum Cd concentrations (>1000 g per ton) are typical mainly for the Rhenium field. As well as for Bi, two ranges of Cd concentration are clearly distinguished: at 320-420 ºC and at 500-650 ºC. This testifies to the presence of at least 2 mineral species - Cd concentrators. Of these, sphalerites, ZnCdIn sulfides, and greenockites are now known, and also chlorides in pipes [32].

The maximum concentrations of Sn (>1000 g per ton) are characteristic only for the Rhenium field in a wide temperature range (320-660 ºC). No intrinsic Sn minerals have been found, but both cassiterites and sulfostannates (at high temperatures) and chlorides (at lower temperatures) are assumed.

The content of Tl shows a good inverse dependence on temperature and maximum concentrations (> 110 g per ton) in the temperature range 280-600 ºC. The positive correlation of T1 with As (0.38) testifies in favor of the predominant occurrence of T1 in low-temperature lorandites together with As, Thallium chlorides were also found in the pipes. [32]

The general representation of the dependence of elements accumulation in rocks can be characterized by the accumulation coefficient normalized by the average composition in the earth's crust (Figure 6).

From Figure 6 it follows that in ores (Kn) decrease in the sequence: >1000 for Bi, Re, Cd, Mo, In; 100/1000 for W, Sn, Ag; 10/100 for Tl, B, Zn, Ge, Au, Sb, Cl, Pb, F, Cu.

The above figures characterize only the general tendencies of the accumulation of elements in the ores of the Kudraуvy Volcano. According to individual analyzes of certain mineral types of ores, Kn may be 1-3 orders of magnitude higher. Attention is drawn to the fact that the largest Kn have elements with the smallest clarkes and possessing chalcophilic and siderophilic properties.

3. 3. Technology of Development of Volcanic Deposits (Kudryavy Volcano)

On the basis of the studied development technologies [35-39], a new development technology with further transportation of minerals has been created. This technology includes layer-by-layer mechanical loosening, and when areas that are not amenable to mechanical loosening appear, the electrothermal method of destruction is used to create a system of cracks. The ripper is mounted on a bucket of earthmoving equipment that digs up minerals and loads them onto a conveyor (Figure 7).

Based on the results of field tests carried out on the geothermal massifs of rocks of the Kudryavy volcano, a diagram of manual jackhammer efficiency plotted according by the velocity of seismic waves were developed (Figure 8).

Figure 8 shows that geothermal volcanic rock mass has different strengths even in rocks of the same type. This is explained by the different rate of fumarole activity (the higher the activity, the higher the porosity of the material) and the temperature zone in the geothermal field. Therefore, a low seismic velocity

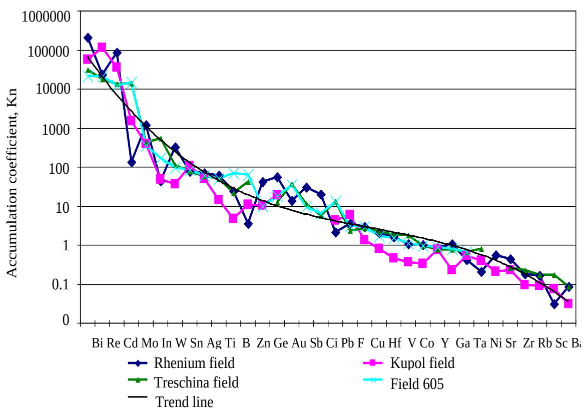

Figure 6. Coefficient of accumulation (Kn) of elements in the rocks of Kudryavy volcano

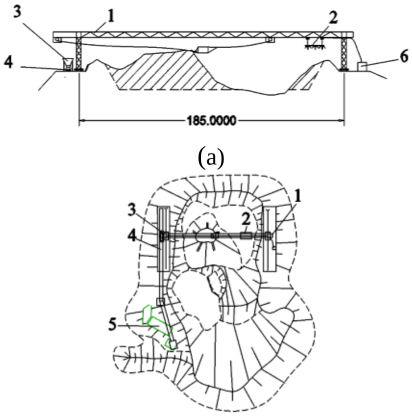

Figure 7. Principle scheme of Kudryavy volcano geothermal fields development using a modernized scraper a - transverse view; b - plan view; 1- modernized scraper with a suspended electrothermal installation; 2 - electrothermal installation; 3 - mobile bunker; 4 - conveyor; 5 - working platform with rock rehandling; 6 - power generator.

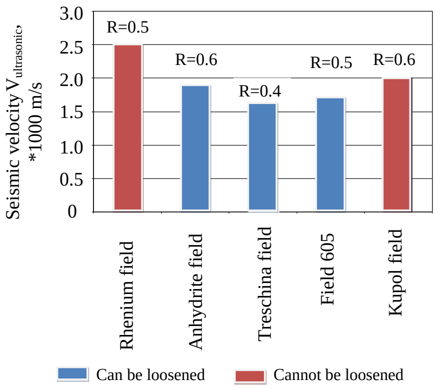

Figure 8. Diagram characterizing the destruction of rocks using an electric jackhammer, with a power of 1.75 kW and a mass of 16.5 kg, according to the speed of seismic waves

(up to Vultrasonic = 1800 m/s and an acoustic fracture index of R = 0.6) in ores of geothermal fields serves as an indicator of possible crushing using a mechanical ripper based on a ladle [44-47]. This crushing method may be ineffective in the Rhenium and Kupol fields due to solid inclusions.

These inclusions are well exposed to loosening by the electrothermal method [45–48]. It has been experimentally established that the specific resistance of breakdown in solid inclusions is 4.3-5.0 kOhm/cm when using a high-voltage transformer of the IOM 100/25 type (single-phase oil test transformer with a frequency of 50 Hz) with a rated power of 25 kVA, and with a transformer of the IOM 100/100 type, the specific breakdown resistance is 0.9 - 1 kOhm/cm.

As a result of a rupture, a system of cracks forms in the sample, which split it into several parts. If the sample is thick enough (more than 100 mm), then the general property of solid inclusions in which there is a breakdown is the complete regeneration of its dielectric properties after the voltage is removed. Subsequent exposure of the rock sample to the current does not cause the formation of a breakdown along the same trajectory, but is formed in a new region of the dielectric. This is due to the fact that as a result of melting and subsequent crystallization, a new substance is created, which has the more ordered structure and, as a result, lower conductivity. The breakdown channel in the crystalline state includes the air cavity surrounded by a tube of crystalline substance and the adjacent annealed part of the sample.

After loosening by a mechanical or electrothermal method, the rock is dug out using a bucket fixed with cables between two supports, which is driven by two winches. At the same time, an experiment carried out in laboratory conditions with selected samples revealed the filling factor of a ladle with a volume of up to 10 m^3 in the range of 40-60 % (Figure 9). Using of large buckets is not technologically easy.

Figure 9 shows that an increase in the lumpiness of extracted minerals can lead to a decrease in the productivity of mining equipment by reducing the actual amount of material in the bucket. This, in turn, leads to a decrease in productivity and all economic indicators.

To increase the productivity by minerals distinguished by increased lumpiness, it is necessary to perform additional loosening by the mechanical method. Then the maximum possible theoretical productivity of the mining complex can reach up to 1 million tons/year taking into account the actual amount of material in the bucket and the mode of occurrence.

The extracted material from the geothermal fields will be transported to the caldera, where the main production site with a tubular scoop conveyor is planned to be. It will allow you to overcome steep slopes,

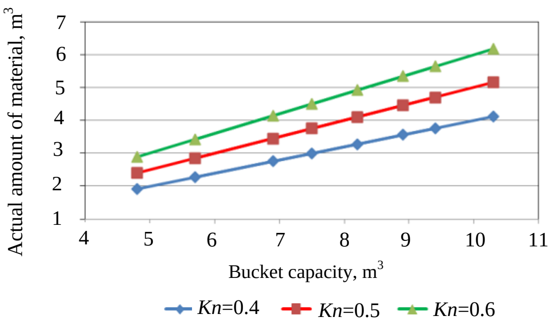

Figure 9. Dependence of the actual amount of material on the bucket capacity of excavation and loading equipment are defined at bucket fill factor *Kn*=0.4, 0.5, 0.6

preventing slipping, clogging, freezing and wetting of the transported material. Thanks to the cooling jacket located on the tubular body or the spiral heating element with thermal insulation coating, the device can operate in a wide temperature range from +50 to -60 ºC. The description of the new conveyor is given in the patent (RU No. 170400) (Figure 10).

At the same time, the main parameters of the conveyor (Figure 11) depend on the productivity of the mining complex and the density of the mineral, which was determined empirically and amounted to 7.5 t/m^3 for rhenium and from 4.0 to 7.0 t/m^3 for the rest of the minerals.

The analysis of the results obtained (Figure 11) allows to determine optimal parameters at which the minimum energy consumption and wear rate are observed.

Therefore, if the mineral density of 6.0 t/m^3 prevails, the transportation capacity can reach 88 m^3/h at a speed of 2.0 m/s, the scoop filling capacity of 80 % and the diameter of the outer tubular body of 160 mm

The calculated coefficients and actual loads carried by the scoops are derived from the condition of rocks supply to the conveyor using a feeder or other means that ensure the normal loading of vehicles. Such an organization of cargo flows is accepted for tubular scoop conveyors based on the calculations under similar conditions. When designing taking into account the specified productivity and drive power, the size of scoops and other parameters of the conveyor shall be chosen considering the calculated resistance to scoops motion caused by loading conditions, as well as the load that may arise at the transportation route.

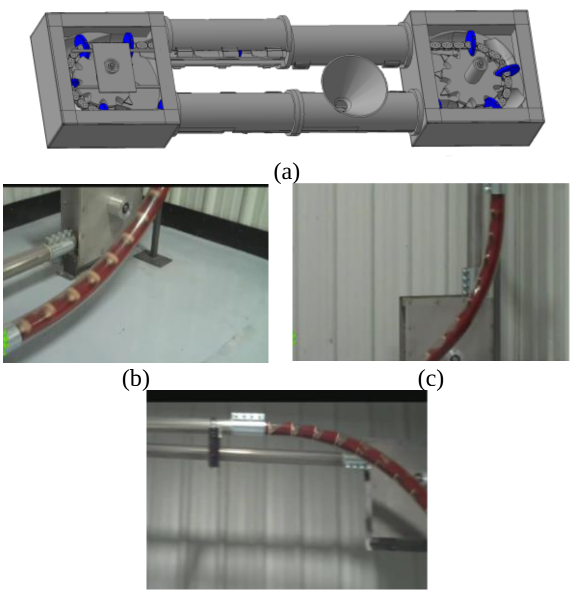

Figure 10. Tubular scoop conveyor (a) computer 3D model; (b) laboratory installation (transfer of the transported material from the horizontal section to the inclined one); (c) laboratory installation (the transported material overcomes the vertical section); (d) laboratory installation (transfer of the transported material from the vertical section to the horizontal one)

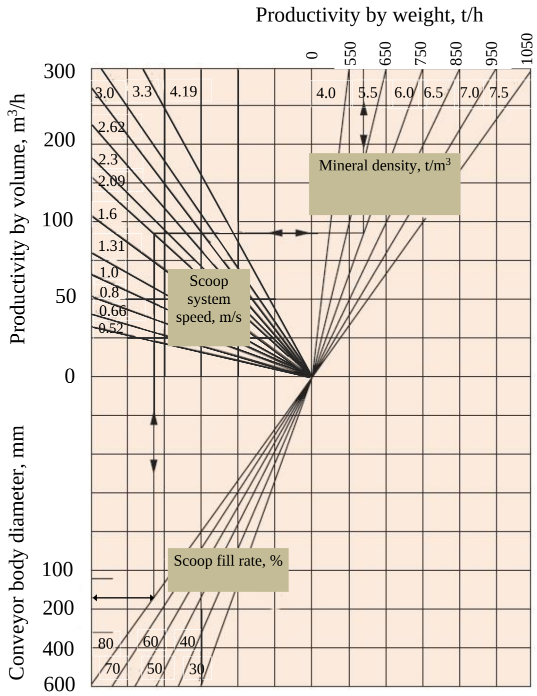

Figure 11. Dependence of the parameters of the tubular scoop conveyor on the productivity

4. DISCUSSION

Rhenium consumption increased by 9% in 2019 as compared with 2013. The USA is the major manufacturer of this metal with 72% of total production worldwide. At the same time, an increase in consumption will be about 3 to 4 tons annually over the coming years. Generally, this metal is very high in demand while its reserves are limited.

Rhenium volcanogenic deposit located in the Kudryavy Volcano vent (Kuril Islands) may become an additional source of this mineral, where areas of accumulation of large amounts of rhenium have been identified.

All rocks of the volcano are subdivided into three strata of different ages. The lower sequence consists of numerous blocky lava flows of andesite-basalt and andesite composition, exposed at the periphery of the volcano and separated from each other by breccia crusts. The outpouring of lava flows mainly in the western direction; to the east, the spread of lavas was limited by the buildings of the rhyolite dome and Sredny Volcano.

The middle stratum is composed of highly oxidized viscous lavas and an andesitic extrusive dome. The distribution of this stratum is limited by the near-crater part of the volcano.

The upper thickness includes 7 flows of olivine-bearing bipyroxene basaltic andesite and andesite, traced towards the northwest, west and south of the summit. Its lavas are separated from the middle strata by a section that includes lacustrine-swamp deposits and pumice. At the top of the Kydrayvy Volcano, according to geological and morphological features, elements of four craters and an explosion funnel are distinguished, they are differing in age, structure and mode of fumarolic activity.

As a result of the examination, 70 kg samples taken from each geothermal field in the Kudryavy Volcano vent have demonstrated rhenium content up to 387.7 g/t. Topographic survey and analytical study has shown that rare-metal mineralization was formed in high-temperature geothermal fields and covered a total area 7600 m^2, which could exceed the abundance ratio. At the same time, significant rhenium accumulation was revealed in geothermal fields within the temperature ranges of 500 ºC to 613 ºC. Rhenium is found on porous slag, jointed rocks and volcanic breccias.

ICP-MS and NSAM No. 179-X procedures for the element composition measurement have demonstrated high accuracy and expanded uncertainty for assay results. However, ICP-MS method was limited when measuring rhenium in samples with high molybdenum contents. The matrix effect affected the procedure accuracy. Samples should be highly diluted, but it is not possible to avoid molybdenite impact completely to decrease the matrix impact. That’s why we used NSAM No. 179-X. The procedure accuracy was ±0.0018 % wt. to 0.0025 % wt.; expanded uncertainty of procedural results was 0.0068 % wt. to 0.012 % wt. It was achieved by preparing a rhenium (VII) solution, reducing it to rhenium (IV) with a tin (II) chloride solution, converting it into a complex compound, sorbent separation from the solution, diffuse reflectance measurement at 510 nm, and calculation of rhenium (IV) contents using a calibration curve. Silica modified chemically with N-(1,3,4-thiodiazole-2-thiol)-N'-propylurea groups was used as a sorbent.

The designed volcanogenic deposit exploration technology comprised massif crushing, excavation-loading works and transportation.

The geothermal massif of volcanic rocks features different strength even in the rocks of the same type. It is explained by the different rate of fumarole activity (the higher the activity, the higher the material porosity) and temperature zone in the geothermal field. Rock crushing by a mechanical ripper is possible at seismic speed of $V_{ultrasonic}$=1800 m/s and jointing acoustic indicator of R=0.6. This crushing method may be inefficient in Rhenievoye and Kupol fields due to solid inclusions. Taking into account the thermostatic condition for these areas, it is advisable to crush rocks using the electrothermal method at a specific resistance of breakdown path up to 1 kOhm/s, which makes the further mechanical loosening possible.

The studied material demonstrated a very low actual weight of the load in the bucket of the extraction and loading equipment during each digging cycle. The laboratory experiment carried out using the samples revealed a filling rate within the range of 40 % to 60 % of the bucket capacity up to 10 m^3 due to the large rock lumpiness.

Transportation of minerals by a tubular scoop conveyor at an average mineral density of 5.5 t/m^3 may ensure the productivity of 88 m^3/h at a speed of 2.0 m/s and overcome steep slopes and the elevation difference of 900 m between the mining area and the work area.

5. CONCLUSIONS

To sum it up, it is possible to conclude that an annual increase in global rhenium demand requires looking for new deposits. Kudryavy Volcano is a volcanogenic deposit where rhenium mineralization occurs in geothermal fields on a total area of 7200 m^2. Moreover, all rocks of the volcano are divided into three strata of different ages. The lower thickness consists of numerous blocky lava flows of andesite-basalt and andesite composition, exposed at the periphery of the volcano and separated from each other by breccia crusts. The outpouring of lava flows occurred mainly in the western direction; to the east, the spread of lavas was limited by the buildings of the rhyolite dome and Sredny Volcano.

The middle stratum is composed of highly oxidized viscous lavas and an andesitic extrusive dome. The distribution of this stratum is limited by the near-crater part of the volcano.

The upper thickness includes 7 flows of olivine-bearing bipyroxene basaltic andesite and andesite, traced towards the northwest, west and south of the peak. Its lavas are separated from the middle strata by a section that includes lacustrine-swamp deposits and pumice. At the top of the Kudryavy Volcano according to geological and morphological features, elements of four craters and an explosion funnel are distinguished, differing in age, structure and mode of fumarolic activity.

It was found that the maximum rhenium concentration was observed within the temperature range of 500ºC to 613ºC by comparing the results of studying the samples from the volcanic massif and temperature distribution on the geothermal field surface. Mineralization occurred on porous slag, jointed rocks and volcanic breccias.

Rhenium content was measured using a spectrometric procedure that allowed avoiding the impact of high molybdenum contents and attaining high measurement accuracy. The basic concept of such an analysis was to reduce rhenium from oxidation degree 7+ (perrhenate ions) to 4+ in an acidic medium with further sorbent separation from the solution. Silica modified chemically with N-(1,3,4-thiodiazole -2-thiol)-N'-propylurea groups was used as a sorbent.

Exploration of this deposit is complicated by high temperature in geothermal fields up to 900ºC, fumarole gas releases and different strength of rocks of the same type. It was explained by the different rates of fumarole activity (the higher the activity, the higher the material porosity) and temperature zone in the geothermal field. Considering these facts, the technology should comprise the following processes: mechanical loosening, additional loosening using an electrothermal device, excavation by a bucket, and transportation from elevation of 900 m to the working platform via a tubular scoop conveyor.

Acoustic measurement of the rock massif has shown the possibility to mechanically crush the massif at $V_{ultrasonic}$=1 800 m/s and acoustic jointing indicator of R=0.6. However, large temperature differences of geothermal fields Rhenievoye and Kupol formed solid inclusions that required electrothermal crushing with specific resistance of breakdown path of 1 kOhm/cm.

The tubular scoop conveyor productivity could attain 88 m^3/h at a speed of 2.0 m/s at the average density of the mined mineral of 5.5 t/m^3.

Finally, this examination has demonstrated that the geothermal fields of Kudryavy Volcano under study are prospective in terms of rhenium mineralization. The technology for ore mining and transportation to the work site allowed conducting industrial mining operations with acceptable risk.

An increase in the geothermal field temperature could result in a powerful eruption and loss of valuable elements. That is why exploitation of the deposit in Kudryavy Volcano is an urgent task for the near future.

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Persian Abstract

چکیده

از رنیوم به طور گسترده ای در صنعت تولید و متالورژی استفاده می شود. امروزه مصرف رنیوم زیاد است ، اما ذخایر بسیار کمی در جهان وجود دارد که در آن استخراج می شود. بنابراین ، هدف از این مطالعه شناسایی مناطق توزیع رنیوم در آتشفشان کودریاوی ، واقع در جزایر خط الراس Kuril (روسیه) است. در این ارتباط ، در طول دوره مزرعه ، ما نمونه هایی از یک توده آتشفشانی به وزن ۷۰ کیلوگرم را برداشتیم ، و همچنین زمینه های زمین گرمایی را با یک فشار سنج بررسی کردیم. تحقیقات آزمایشگاهی شامل مطالعه ترکیب نمونه ها با استفاده از روش طیف سنجی جرمی پلاسما و تجزیه و تحلیل طیف سنجی القایی بود. این مقاله مناطق توزیع کانی سازی رنیوم را تعریف می کند ، نتایج اندازه گیری درجه حرارت زمینه های زمین گرمایی و ترکیب اولیه نمونه های فن آوری را ارائه می دهد. زمین شناسی ، فن آوری توسعه شرح داده شده است ، تجزیه و تحلیل تخریب سنگ ها ، تعیین شده توسط روش صوتی ، مقاومت خاص در برابر شکست در هنگام شل شدن الکترو گرمایی داده شده است. پارامترهای نوار نقاله بیل لوله ای که در آن بهره وری ۸۸ متر مکعب در ساعت حاصل می شود. نتایج به دست آمده امکان شناسایی زمینه های زمین گرمایی امیدوار کننده ، تعیین فناوری توسعه و کمک به مطالعه ذخایر آتشفشانی را فراهم می کند.