ANOMALIES IN GAS-HYDROGEOCHEMICAL INDICATORS OF MUD VOLCANOES IN CONNECTION WITH SEISMIC ACTIVITY: ON THE BASIS OF MUD VOLCANOES DATA IN SHAMAKHI-GOBUSTAN (AZERBAIJAN) AND SAKHALIN ISLAND (RUSSIA)

**Abstract:** The paper is devoted to the results of studies on mud volcanoes of the Shamakhi-Gobustan region (Azerbaijan) and Sakhalin Island (Russia) in the aspect of intensifying their activities related to seismicity in adjacent areas. Monitorings in Azerbaijan and Sakhalin Island were carried out at different periods and were based on measuring temperatures and flow rates of active mud volcanoes. In addition, some distribution regularities of gas-hydrogeochemical indicators were established in connection with seismicity, based on monitoring of the chemical composition of gas and water ejected during the daily activity of the mud volcanoes. Depending on the magnitude of the seismic event in the periods before and after seismic activity some anomalous changes were recorded in the composition of fluids (for gases: CO₂, CH₄, N₂, He and for waters: B, SO₄, Cl) carried to the Earth's surface by mud volcanoes for both study objects. Earthquakes with a large magnitude affect the temperature regime in the microforms of mud volcanoes too. During the activation of mud volcano, the channel ejects fluids from ultra-depth opens wider, which leads to an increase in the flow of gases from deep sources, in which the predominant components are CO₂ (in Shamakhi-Gobustan) and CH₄ (on Sakhalin Island).
Key words: mud volcanism, fluids, monitoring, seismicity, Shamakhi-Gobustan, Sakhalin Island, gryphon activity.

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Introduction and Background

Mud volcanoes give necessary information about the depths of the Earth, as well as complex geological and geochemical processes occurring on inaccessible depths for exploratory wells. [1; 7; 8; 11; 31; 32]. In recent years, various aspects of mud volcanism: the conditions for the formation of mud volcanoes, the tectonic features of mud volcanic areas, the geochemistry of rocks and fluids, the connection with the hydrocarbon systems of large depths and etc. have been studying in detail [30].

Regions of a complex tectonic structure are distinguished by active seismogeodynamic properties. The strong and weak tremors that occur in these regions have a certain influence on the activity of mud volcanoes. In addition, shortly before seismic events some abnormal gas-hydrogeochemical changes are observed in the composition of mud volcanic fluids. In connection with this, in recent years the issue of studying the connection of mud volcanism with seismicity is topical.

Opinions of scientists on the connection of mud volcanism with seismicity were formed in the 19 th century. Ideas were also expressed about the paragenetic connection of seismic events with the activity of mud volcanoes in Azerbaijan [2; 5; 6; 9; 12; 15; 24; 43; 45-47; 51], as well as the Sakhalin island [10].

Some monitoring studies were carried out in the mud volcanoes (Demirchi, Madrara, Gyzmeydan and others) of the Shamakhi-Gobustan seismic active region. The monitoring was related to study the gas and element compositions, as well as temperatures of the fluids on 14 mud volcanoes. The conducted researches covered various periods of activity of mud volcanoes and seismic events. The main tasks of the studies were to investigate the variations in the daily activity of volcanoes, the effect of seismic events on volcanic activity, as well as prediction of earthquakes. Also, carrying out these studies has a significant role on the analysis of both the current database and new results of monitorings for comparative interpretation of similar studies conducted in Russia, and clarification of the reasons for the relationship between mud volcanism and seismic activity. It was carried out the same monitoring in the Yuzhno-Sakhalinsk mud volcano by the Institute of Marine Geology and Geophysics of the Far Eastern Branch of the Russian Academy of Sciences [14; 19; 20; 23; 29].

Shamakhi-Gobustan region (Azerbaijan)

The region occupies a significant part of the southeastern immersion of the Greater Caucasus and is characterized by the widest spread of mud volcanoes with a total number of 120 [25; 48-50]. The sizes of mud volcanoes in the northern part of the region are small (Gyzmeydan, Demirchi, Madrara, Gushchu and etc.). The largest and most active mud volcanoes are located in the southeastern part of the region, with altitudes up to 400 m.

Mesozoic Cenozoic and Quaternary formations take part in the geological structure of the region [26; 33-35; 44]. Deposits of the Cretaceous and Paleogene are replaced by the Pliocene formations to the south [3; 4].

The Central Gobustan zone is composed mainly of Paleogene-Miocene sediments. The thickness of these sediments reach of 2.5-4.5 km [22; 36-42]. Mud volcanoes of this zone are characterized mainly by small size and weak eruptive activity (Fig. 1) [52; 53].
Sakhalin Island (Russia)

The Island is part of the Asia-Pacific transition zone from continent to the ocean and is an area of intense seismic tectonic activity [18]. Sakhalin is characterized by a wide distribution of powerful marine Paleogene and Neogene deposits, large concentrations of fossil stone and brown coals associated with continental strata, and widely manifested fields of oil and gas. Sedimentary and volcanogenic-sedimentary formations of the Mesozoic and Cenozoic were recorded in the geological structure of the island [13].

The island is divided by a system of deep faults intersecting it in the longitudinal direction, through which a gas-fluid transfer takes place. Their intensity is also regulated by seismic activity. Sakhalin is a unique testing object for gas hydrogeochemical research. Here, 4 areas of mud volcanism and volcanoes are confined to a major regional fault of the Central Sakhalin upthrow-shift (Fig. 2).
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| ISRA (India)   | 1.344  | SIS (USA)      | 0.912  |
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| ICV (Poland)   | 6.630  | PIF (India)    | 1.940  |
| IBI (India)    | 4.260  |                |        |

![Figure 2 - Location map of mud volcanoes in Sakhalin region [44].](image)

On the island there are two large volcanoes - Yuzhno-Sakhalinsk and Pugachevskaya group of mud volcanoes. The first is located 18 km north-west of the city of Yuzhno-Sakhalinsk, the Pugachev group - 60 km from the city of Makarov between the village Pugachevo and Vostochniy. On the island there are also three mud volcanoes named Vostochniy, Lesnoye and Dagi. They are related in their activity closer to small mud manifestations [16; 17].

Method and theory

The regime monitoring observations were conducted daily in the volcanoes of Shamakhi-Gobustan region. Flow measurement and analysis of chemical compositions of gas and water for each mud volcano were carried out on two or more gryphons. The data were compared with the earthquakes recorded in the region.

On the Sakhalin Island, similar observations were conducted in different gryphons, characterized by varying degrees of activity. The air temperature, the surface of the mud field, the water-mud mixture and the rate of free gases were measured. Measurements were carried out three times a day - in the morning at 9, in the afternoon at 12 and in the evening at 18 o'clock.

The temperature of the water mud mixture in gryphons were measured with a digital thermometer (Ebro TFX 410).

Gas chromatography was used to analyze the chemical composition of gas samples.

Results and discussion

In the gas samples of Demirchi mud volcano were established an abnormal values (4.05 and 4.75%) for CO₂. It was associated with the earthquakes occurred on July 1 and August 3 of the same year. Shortly before the earthquake that occurred in August, for a gas sample of Gyzmeydan mud volcano was recorded the increasing of He to 0.01%. Anomalous were established in the amount of sulfates (0.41 mg/l) on the mud volcano Madrasa a few days before the earthquake on August 10. Earthquake preceded increasing boron content in waters mud volcano Ayranteken (137 mg/l), and detection of mercury mud volcano Demirchi (0.013 mg/l). The anomalous changes in the chemical composition of fluids of mud volcanoes during the earthquake preparation period is shown in table.
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| ICV (Poland)     | 6.630         |
| PIIF (India)     | 1.940         |

Changing the gas-hydrochemical composition of mud volcanoes connection with seismicity

| Mud volcano     | Analysis time | Components       | Date of earthquake |
|-----------------|---------------|------------------|--------------------|
| Demirchi        | 26.06.1984    | 4.05 % (average 2 %) | CO₂                | 01.07.1984 |
|                 | 30.07.1984    | 4.75 % (average 2 %) | CO₂                | 10.08.1985 |
|                 |               | 0.013 mg/l       | Hg                 |
| Ayrantoken      | 06.08.1985    | 137 mg/l (average 20 mg/l) | B | 10.08.1985 |
| Dashgil         | 06.08.1985    | 110 mg/l (average 38-76 mg/l) | B | - |
| Madrasa         | 24.08.1985    | 0.4 mg/l (average 0.24 mg/l) | SO₄ | 28.08.1985 |
| Gyzmeydan       | 24.06.1985    | 0.01 %            | He                 | 10.08.1985 |
|                 | 12.07.1985    | 0.02 %            |                    | |
|                 | 27.07.1985    | 433 mg/l (average 350 mg/l) | B | 01.08.1985 |

It is assumed that, in contrast to calm mood of mud volcano, during activation, the outlet channel of mud volcano opens somewhat wider, so it results with a flow of gases from deep sources, in which the predominant component is CO₂ (Shamakhi-Gobustan region) and CH₄ (Sakhalin Island) (Fig. 3).

Figure 3 - Conceptual model for mud volcanoes.

The monitoring was conducted on the Yuzhno-Sakhalinsk mud volcano prior to the Takoiskoe swarm of earthquakes that lasted from late July to mid-September [10]. The strongest earthquake (M = 5.2) in this period was on September 1 earthquake. Its hypocenter was located in the fault zone of Central Sakhalin, at a depth of 2-14 km. The distance between the hypocenter and volcano is about 10-30 km. On July 13-23, in the gryphon of the mud volcano was observed an increase in temperature to 3-4 °C and in the gas production rate by 2-3 times, the amount of Ba, Ca, Fe, Mn carried away from the gryphon of the mud with respect to Al. On August 17, significant changes were observed on the crater field of the mud volcano, in particular, the formation of a dome with a diameter of 30 and a height of 2 meters. And at the end of December, a powerful eruption of the Yuzhno-Sakhalin mud volcano was recorded.

After Gornozavodsk (August 18, 2006, M = 5.6) and Nevelsk (August 2, 2007, M = 6.1) earthquakes marked a sharp increase in gas production rate by 2-5 times compared with its average level before the earthquakes (Fig. 4) [29].
| Impact Factor: | ISRA (India) = 1.344 | SIS (USA) = 0.912 | ICV (Poland) = 6.630 |
|---------------|------------------|----------------|------------------|
| ISI (Dubai, UAE) = 0.829 | PIIH (Russia) = 0.207 | PIF (India) = 1.940 |
| GIF (Australia) = 0.564 | ESJ (KZ) = 4.102 | IB (India) = 4.260 |
| JIF = 1.500 | SJIF (Morocco) = 2.031 | |

Figure 4 - Change in the rate of free gas flow to the mud volcano Yuzhno-Sakhalinsk during the observation period of 2005, 2006 (Gornozavodsk earthquake) and the 2007 (Nevel earthquake) [29].

After the same earthquake (August 2 and 9) was observed a decrease in CO$_2$ and CH$_4$ increase in all studied gryphons. Concentrations of CH$_4$ were about 28.1%, and CO$_2$ was about 69% (Fig. 5). It has also been found that immediately after the earthquake (within one hour), the total concentration of hydrocarbon gases significantly increased [21; 27; 28]. Stabilization of the chemical composition occurred within 70 to 140 days.

Figure 5 - Chemical composition of free gases in gryphons for the observation period of 2007 with the date of the Nevel earthquake [29].

During the Nevel earthquake, a sharp increase in the N$_2$ content was observed, the minimum contents of which were found in the composition of the gas of all gryphons before the earthquake (Fig. 6) [21].
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| Journal            | Impact Factor |
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| JIF                | 1.500         |
| SIS (USA)          | 0.912         |
| PIF (India)        | 1.940         |
| GIF (Australia)    | 0.564         |
| SJIF (Morocco)     | 2.031         |
| ICV (Poland)       | 6.630         |
| PIF (India)        | 1.940         |
| IBI (India)        | 4.260         |

Figure 6 - The nitrogen content of free gases on the mud volcano Yuzhno-Sakhalinsk in the period of observations of 2007 [21].

Blue graph - for gryphon F, green graph - for gryphon G, red graph - for gryphon H, black line - date indicator of Nevelsky earthquake.

In 2006-2007, after the Gornozavodsk and Nevelsk earthquakes, anomalous changes were observed in most active gryphons (Fig. 7) [29].

Figure 7 - Temperature changes in gryphons of the mud volcano Yuzhno-Sakhalinsk in 2005, 2006 (the Gornozavodsk earthquake) and 2007 (Nevel earthquake) [29].

Conclusion

Anomalous changes in the composition of fluids ejected to the Earth's surface by the mud volcanoes of the Shamakhi-Gobustan region and Sakhalin Island in the periods before and after seismotectonic activity were established;

Depending on the strength of the seismic event, anomalous changes occur in the composition of fluids (in gases CO₂, CH₄, N₂, He, in waters B, SO₄, Cl);

In addition, earthquakes with a large magnitude affect the temperature regime of fluids in gryphons;

During activation, the outlet channel of mud volcano opens wider, so it results with a flow of gases from deep sources, in which the predominant component is CO₂ (Shamakhi-Gobustan region) and CH₄ (Sakhalin Island).
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