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### Distribution and Geochemistry of Contaminated Subsurface Waters in Fissured Volcanogenic Bed Rocks of the Lake Karachai Area, Chelyabinsk, Southern Urals

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## DISTRIBUTION AND GEOCHEMISTRY OF CONTAMINATED SUBSURFACE WATERS IN FISSURED VOLCANOGENIC BED ROCKS OF THE LAKE KARACHAI AREA, CHELYABINSK, SOUTHERN URALS

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## ABSTRACT

The present investigation is devoted to the study of the distribution and geochemistry of contaminated subsurface waters, beneath the site of temporary storage of liquid radioactive waste known as Lake Karachai. For this purpose a method of hydrogeochemical logging (HGCL) together with standard hydrogeochemical and geophysical methods of uncased hole logging were used. The distribution of sodium nitrate brine plumes in the subsurface was determined by the physical and physico-chemical properties of these brines and by the petrochemical composition of enclosing rocks and the structural setting of the flow paths. The latter is represented by fractures and large faults in the bedrock of volcanogenic and volcanogenic-sedimentary rocks of intermediate-to-basic composition. The volcanogenic rocks are overlain in some places by a thin cover of unconsolidated sediments, i.e., by loams and relatively impermeable silts. Contaminated waters flow in accordance with the eluvium bottom relief towards local areas of natural (Mishelyak and Techa rivers) and artificial (Novogornenskii water intake) discharge of subsurface waters. The large Mishelyak fault, southwest of Lake Karachai and under fluvial sediments of the Mishelyak, is assumed to significantly influence the flow pattern of contaminated waters, diverting them from an intake of drinking water.

Alkaline waters (pH 11.2), flowing from the ash impoundment of the Argoyashskaya heating and power plant, were detected *in situ* by measurements using HGCL. Technogenic waters flow from the sources of contamination towards the drinking water intake in stratiform water-bearing horizons with dense sodium nitrate brines in the lower horizons, and lighter alkaline demineralized waters in the uppermost horizons. The application of geochemical technologies for the restoration of the subsurface water quality is considered theoretically.

## INTRODUCTION

Radiochemical enterprises of the Amalgamated Industry (AI) "Mayak" and associated industries are situated on the eastern slope of the Urals, Russia, in the region between Middle and Southern areas of this mountainous-fold belt. These industrial facilities are sources of surface environmental contamination. Between 1949 and the present, several water reservoirs containing liquid radioactive waste (RAW) of low and intermediate level were constructed to contain discharges from AI. Basins of the local Kyzyltash, Tatysh, and Karachai lakes and artificial reservoirs on the Techa river (reservoirs 3, 4, 10, and 11), as well as an artificial reservoir 17 (Fig. 1) were used as impoundments of the liquid RAW [Drozhko et al., 1993]. Of these impoundments, Lake Karachai (reservoir 9, or R-9), poses the greatest threat to the environment.

Waters from Lake Karachai, which are contaminated with stable and radioactive isotopes, percolate into the groundwater system. Rocks enclosing the system are represented by fissured volcanogenic and volcanogenic-sedimentary rocks, in some places overlain in the by clay weathering products up to a meter thick and thin deluvial, proluvial, and alluvial sediments not exceeding 10–15 m in thickness. The contaminated waters flow both southerly and northerly from the lake following the general regional flow of the subsurface waters in this area. *The southern branch of the flow (Fig. 2) is a serious hazard, because it is directed towards a water intake supplying the population of Novogornyi city with drinking water.*

The distribution of contaminated water in the water-bearing horizon is determined by a system of observation wells. They have been installed and monitored by AI "Mayak" and the Production State Association (PSA) "Gidrospetsgeologiya" for over 30 years (Drozhko et al., 1993).

Practically all observation wells have the following design: in the upper part, unconsolidated sediments are cased with cemented steel casing (primarily for the first 5–15 m; rarely to a depth of 45 m); in the lower part the stable, yet fissured bedrock is penetrated without casing to a depth of 50–120 m and, in one well, to 400 m. With such a design, the uncased intervals of the wells are accessible for direct, highly detailed measurements of major parameters of the plume of contaminated water. But, until 1992, this unique opportunity was not exploited during routine hydrogeochemical observations. Two main sampling methods for observation wells were, and are still used:

1. In the distribution area of radioactive waters with contents of  $^{90}\text{Sr} > 10^{-7}$  Curie/l the interval sampling [Spravochnoe Rukovodstvo Gidrogeologa, 1967] is carried out using a

sampler designed by E. Simonov.\* Samples, as a rule, are taken from three intervals: 15–25, 40–50, and 80–100 m. With such a method of fissure water sampling there is a probability that the most contaminated intervals of the subsurface water flow might be missed. This drawback can be mitigated by increasing the number of sampling intervals, but leads an unworkable increase in the number of chemical and radiochemical measurements and analyses.

2. In recent years, the front of the contaminated water plume and natural waters ahead of the front in the zone of expected discharge are sampled through short-term airlift pumping of the observation wells. Drawbacks of this method are obvious and include the dilution of technogenic solutions with pure waters and distortion of *in situ* physicochemical conditions.

In 1992–1993, we designed, constructed, and used a hydrogeochemical probe for the hydrogeochemical logging of the observation wells. The incentive for developing this probe was to evaluate the extreme ecological threat of reservoir 9 and extraordinarily complicated pattern of subsurface flow of the contaminated waters associated with the structure of the host rock and other factors.

## **HYDROGEOCHEMICAL PROBE**

The hydrogeochemical probe and its set of service units is considered to be an information-gathering system. It includes the probe, which incorporates a signal processor, and a portable personal computer (Fig. 3). The system contains eight channels for measurement of temperature (T), hydrostatic pressure (P), specific electric conductivity (E), concentration of dissolved oxygen (O<sub>2</sub>), hydrogen index (pH), redox potential (Eh), and two potentiometric channels for measuring activities of different ions (NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, etc.), with the help of specific ion electrodes.

The technical specifications of the information-gathering system are given in Table 1. Not all observation wells in the investigated region are accessible for hydrogeochemical logging investigations, because of the large external diameter of the probe (65 mm). We conducted measurements in about 20 out of 70 wells.

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\*The sampler consists of a short pipe with enlarged ends and two metal pear shaped closures for each end. The lower closure is run into the well with a cable to the sampling depth. Then the pipe is dropped down with the cable passing through the pipe. The top closure follows the pipe. The sampler containing the sample is then recovered. The sampler is a flow-through type and does not seal hermetically exsolving gases may freely escape the sampler during its recovery.

During hydrogeochemical logging, the outputs from the probe sensors are transformed into a unified signal, consisting of a sequence of rectangular pulses with repetitive frequency modulation, which transmitted from the probe through three-core cable to the onboard signal processor, where the signal is transformed into digital binary code and then is input to the computer through a standard RS-232 interface. The sensors are generally interrogated every two seconds, but the frequency depends on the velocity at which the probe is inserted or withdrawn from the well. The resulting information is input into the computer in order to represent each 10–50 cm interval of the well. During data aquisition, the operator is able to observe the variation of measured parameters with depth in real time. The logging results are displayed on a computer as either tables or graphs. The hydrogeochemical probe, as it will be shown below, is an excellent instrument for investigation of uncased wells.

## **HYDRAULIC PROPERTIES AND COMPOSITION OF ROCKS ENCLOSING THE CONTAMINATED WATER**

Contaminated waters move from their surface sources in conformity with the structure of the subsurface medium, i.e., according to the distribution of porosity and the fissured state of unconsolidated material or bed rocks. During flow, their chemical composition is changed through reactions with the enclosing rocks. Without knowledge of the rock-water interactions, it impossible to describe the processes affecting the composition and distribution of contaminated water in the subsurface. In order to assess this problem comprehensively, the authors collected all the necessary information on the geotectonics, structural geology, geomorphology, and petrology from papers by Y.D. Filonenko, B.I. Omel'yanenko, N.N. Tarasov, A.V. Petrov, V.V. Poluektov, V.I. Myskin, V.S. Yudintsev, and B.S. Nikonov [Velichkin et al., 1992, 1993; Omel'yanenko et al., 1993]. Information of relevance to the problem at hand, is summarized in the following paragraphs.

In its structural setting, Lake Karachai and a plume of associated contaminated subsurface waters are located in the core of the Gornenskaya syncline, extending in a roughly N-S direction for more than 20 km. Its width varies from 7–8 km in the south to 5–6 km in the north. The syncline has the form of a brachiform fold with a gentle closure of the limbs. The core of the syncline is composed of volcanogenic Sergaidinian Silurian rocks ( $S_2$ – $D_1$  sr). At a distance of about 3 km from the lake, the western limb is cut by a fault which results in the Sergaidinian volcanic rocks coming into contact with rocks of a schist-amphibolite complex. The eastern limb of the syncline is composed by the Upper Zairian volcanogenic-sedimentary rocks ( $S_1$ – $S_2$ – $nz_2$ ). It dips westward at the angle of 50–70 degrees. Both complexes of volcanogenic and volcanogenic-sedimentary rocks are similar in their

petrographical composition, but they differ in the ratio of volcanoclastic and volcanogenic-sedimentary material.

Tuffaceous sandstones, tuffaceous aleurolites, siliceous tuffites, and schists (siliceous, carbonaceous-silicic, argillaceous, and carbonaceous-argillaceous) predominate in the lower complex. Rocks of the upper volcanogenic complex occupy the central part of the area. Tuffogenic associations (psammite, lithic-psammite tuffs), intercalated with layers of lavas and tuffaceous lavas of andesite-basalt porphyrites, predominate in this complex.

The rock forming minerals in the volcanogenic metamorphosed rocks are represented by augite, plagioclase, amphiboles, calcite, chlorites, and neogenic albite. The volcanogenic rocks were regionally metamorphosed to greenschist facies.

The volcanogenic rocks are irregularly faulted both longitudinally and laterally. The faults are represented predominately by linear schistose zones, located to the southwest and east of Lake Karachai (Fig. 2). The fault zones are comprised of irregular rock lenses, whose structure and mineral composition have been subjected to alteration during the formation of wide bands of subparallel fractures. The Mishelyakskii fault [Velichkin et al., 1993] was distinguished within a southwestern schistose zone with the help of various features, such as variations in relief, thicker eluvium, and the presence of intensive helium anomalies ( $4.4 \cdot 10^{-3}$  with the background values of  $(8.2-40) \cdot 10^{-5}$  ml/l). This area of the volcanogenic rocks is characterized by more intensive fracturing.

*The Mishelyakskii fault zone and accompanying dislocations may influence the flow of the contaminated subsurface water: (1) by directing the southern branch of plume in a southeasterly direction; (2) if the fault terminates and has a distinct closure at its southeastern end, it may act as a structural trap of the dense technogenic solutions; (3) in contrast to the second case, if the fault has considerable length and hydraulic interaction with other tectonic dislocations, and with permeable rocks of the sedimentary cover in the eastern part of the region, the southeastern zone may be considered as a deep conduit that transports contaminated waters for considerable distances. The last two cases will require further thorough investigations to clarify the provisional interpretations.*

The porosity of volcanic rocks occurring between large faults, was studied under both laboratory and field conditions by measuring the actual porosity of monolithic blocks by wetting the comminuted core samples, through macroscopic descriptions of the core and rock outcrops [Velichkin et al., 1992], and by telephotometry of the well walls, with subsequent computer processing [Glagolev et al., 1992]. According to these data, the voids are characterized by the following types of pores and fractures.

1. Within the rock matrix, there are two types of micropores: plane-parallel systems of microfractures and linear oriented systems of pore-capillaries. Their dimensions range

from microns to tens of microns. The hydraulically interconnected pores to the depth of 80 m occupy 0.2–0.34% of the rock volume. At greater depths the actual porosity decreases, disappearing almost completely in some areas (this parameter was investigated to the depth of 1200 m).

2. There are two types of tectonic fractures associated with viscous-plastic and with brittle deformation of the volcanic bedrock. Longitudinal and lateral regular hydraulically interrelated fracturing of the first type is observed to a depth of 80 m. The fracture openings are of the order of millimeters, and their length ranges from centimeters to tens of centimeters. Open fractures that appeared during brittle deformation, are a few millimeters wide, and rarely a few centimeters wide. Their length ranges from meters to a few tens of meters. There are two subtypes of fractures—tear and shear. In the determining the overall porosity and permeability of the volcanogenic rocks the tear fractures play a primary role.
3. In the upper part of the bedrock to a depth of several tens of meters, there are voids where calcite has been leached from quartz-calcite and calcite veins. The voids occur below the subzone of weathering where rock disintegration has taken place, and also below the bottoms of the modern river valleys and lake basins. This suggests that deep circulation of contaminated waters could take place in the hypergenic permeable zones.

In general, the percentage of voids, determined by the telephotometry and well wall caliper logging data, is characterized as follows (Fig. 4): in the upper part of the volcanogenic rock section to a depth of 20 m it attains a maximum value of 2.8%; in the depth interval of 20–80 m it is 0.5–2.0%; and at depths greater than 80 m, it does not exceed 0.5%. The mean hydraulic conductivity calculated from the telephotometry results is 6.6 m/day in zone I (to the depth of 80 m). In zone II (80–210 m) its value is considerably lower –0.2 m/day [Glagolev et al., 1992].

The rock porosity diminishes but does not disappear with depth. At depths of 100–102, 515 m, and 832–843 m in the 1200 m deep hole, there are zones of intense schistosity in the volcanogenic rocks, that may serve as channels for deep circulation of contaminated waters. It is necessary to evaluate their permeability and determine the presence or absence of hydraulic connections between the sources of contamination and these zones.

The processes of weathering have played a significant role in affecting variations of mineral and chemical compositions of volcanogenic and volcanogenic-sedimentary rocks. In the relict weathering profile there are (from the top to the bottom) zones of disintegration, incipient clay alteration and clay alteration. The thickness of the weathered rock profile

varies widely from less than one meter to 80 meters. The thickness of the clay alteration zone ranges up to a maximum of 30 meters.

In studied sections of the weathering profile it is found that the natural alteration to newly formed clay minerals is proportionate to the intensity of hypogene alteration. In the zones of disintegration and incipient clay alteration, various mixed-layer clay predominates among the secondary minerals. In the zone of incipient clay alteration, the montmorillonite fraction increases and vermiculite and kaolinite appear. Kaolinite predominates in the upper part of the weathering profile in the zone of clay alteration. The general feature of mineral compositions in different weathering profiles is the development of significant mixed layer chlorite-vermiculite and vermiculite, which forms from the primary chlorite. Thus, the sorption and ion-exchange capacities of rocks increase naturally in the direction from the bottom to top in the weathering profile as illustrated in the following table.

The depth of occurrence eluvial bottoms shows a greater relief in absolute terms (from +250 to +175 m) than does the modern surface whose maximum relief is 35 m. The eluvial bottom may be arbitrarily accepted as the water-confining stratum of the water-bearing horizon in fissured rocks. The general slope of the arbitrary water-confining stratum and the presence of incised channels and troughs determines the morphology of the contaminated

Composition of newly formed minerals in the weathering profile. (After V.I. Myskin and B.S. Nikonorov)

Weathering Zone	Mineral composition of the clay fraction				
	Major	Secondary	Major	Secondary	
Clay	Vermiculite Kaolinite Kaolinite-montmorillonite **	Montmorillonite Kaolinite-montmorillonite Montmorillonite (sericite)***	Kaolinite Chlorite-montmorillonite		(Sericite)
Incipient clay alteration	Montmorillonite Vermiculite	Kaolinite-montmorillonite (Sericite)	Montmorillonite (Chlorite)	Kaolinite (Amphibole)	
Disintegration	None	None	(Chlorite) (Amphibole)	Metamorphosed sahistose (Sericite)	
Host rock	Andesite-basalt porphyrites			Metamorphosed schistose tuffs of basic xxxx	

\*Mineral composition of the clay fraction (<0.001 mm) by phase diffraction analysis.

\*\*Mixed layer minerals.

\*\*\*In brackets the relict minerals of the primary rock.

water in the horizontal plan and cross-section. The troughs, associated with tectonic fault zones, act as structural traps of the higher density technogenic solutions. The presence of a channel is the primary influence in directing contaminant flow. *One such channel, running from the Lake Karachai basin to the Mishelyak river and coinciding with an erosional incision (Fig. 5, 6, and 7) in the form of the northern branch of the Paleomyshelyak River, considerably influences the structure of the southern branch of contaminated water plume.*

A geomorphological analysis of the modern surface relief allowed us to reconstruct the history of the formation of Lake Karachai. According to the reconstruction, the eastern rim of the lake is a block, uplifted along a fault striking north-north-westerly. This led to the closure of a valley that existed here in the Late Miocene time. During the Pliocene-Quaternary stage, the valley was closed with the formation of the upland swamp and the accumulation of a thin 0.1–0.2 m layer of peat and silty sediments. *It is important to emphasize that the artificial lake area is considerably larger than that of the natural lake, because of the flooding of the southern and western banks, composed of thin (to 2 m) Aralian loams (Fig. 7) and in some places of slightly altered bedrock. The predominant infiltration of technogenic solutions into subsurface waters took place through those rocks during years of intensive precipitation.*

The slightly weathered porphyrites under the Lake Karachai basin are recognized to a depth of not more than 10 m. Numerous linear pockets of eluvial loams and weathered rocks, confined to the ancient fault zones (Fig. 6 and 7), are preserved over the whole region. In some wells the weathered rocks occur to depths of 80 m below the modern surface. Basins of the Kyzyl-Tash and Ulagach lakes and valleys of the Techa, Mishelyak, and Zyuzelga rivers are filled with Naurumian variegated clays with a thickness of not more than 10–15 m whereas on steep slopes they are represented by the Chagranian deluvium (loams). The sedimentary rock porosity has not been studied, and therefore, its hydraulic conductivity is not yet known.

## SOURCES OF SUBSURFACE WATER CONTAMINATION

There are two surface sources of the subsurface water contamination in the region under investigation. One of them consists of water from reservoirs containing liquid radioactive waste (Fig. 1), the other is represented by (fly-ash impoundments) of the Argoyashskaya (Fig. 2) coal-fired thermal power plant (TPP).

As was pointed out earlier, the greatest threat to the environment is represented by Lake Karachai, which contains concentrated waste of intermediate activity [Drozhko et al., 1993]. The surface area of the lake is 0.2 square km and the volume of water is 0.2 million cubic

meters. At present, its surface is covered with special ferroconcrete blocks and rocks from local quarries.

Radioactive solutions were discharged into the lake from 1951 to 1989, resulting in the accumulation of 5 million cubic meters of waste with a total radioactivity of 120 million curies. The waste effluents in the lake consist primarily of slightly alkaline sodium nitrate (pH 7.9–9.3) brine. The overall concentration of the sodium nitrate varied between 16 and 145 g/l during the period that the lake was used as a waste repository. The brine density varied from 1.006 to 1.095 g/cm<sup>3</sup>, in concordance with variations in salt concentration. The concentrations of the principal chemical constituents of the solution (in g/l) ranged from 11–78 for NO<sub>3</sub>, 0.6–20 for CH<sub>3</sub>COO (acetate), 0.9–14 for H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (oxalate, determined by the method of bichromate oxiditation), 0.12–1.3 for SC<sub>4</sub>, and 6–32 for Na. The concentrations of secondary components were (in mg/l) 20–350 for Cl, 13–196 for U, 8–80 for Ca, and 8–69 for Mg (Samsonova et al., 1994). Radionuclides with the highest migration capacity were determined in quantities of (in curies/l) <sup>90</sup>Sr, 4·10<sup>-3</sup>, and <sup>137</sup>Cs, 9·10<sup>-3</sup>, in the lake water and 0.3 and 1.4 (in curies/kg) in the bottom sediments respectively.

Subsurface water contamination from the second source is represented by two fly-ash impoundments of the Argayashskaya TPP referred to as A-1 and A-2 respectively, A-1 being the older of the two. The TPP has been in operation since 1953. Swampy areas near waste reservoir 9 are used for ash disposal. The ash is transported hydraulically to the disposal sites through pipes. As we managed to establish [Velichkin et al., 1992], extremely alkaline ground waters are formed in the area around the older fly-ash impoundment, A-1. Their alkalinity is caused by the relatively high concentration of alkaline-earth element (Ca and Mg) oxides in the ash.

## TECHNOLOGY OF HYDROGEOCHEMICAL INVESTIGATIONS

Hydrogeochemical investigations included the hydrogeochemical logging of wells and interval sampling of waters and the consecutive chemical analyses. Hydrogeochemical logging of wells was executed with the standard geophysical logging unit. Initially, we evaluated the influence of water agitation in the well due to insertion and withdrawal of the probe and estimated sensor response time under defined physico-chemical conditions.

The response time of the measurement part of the information-measurement system is in the same range as the two-second sensor interrogation interval, and therefore need not be taken into consideration. According to observations of measured parameter variations within fixed intervals of wells through gradually increasing time intervals, the only sensor which has a noticeable physico-chemical response time is the Eh sensor. Having tested glass and

platinum sensors, we found that the glass ones have the longest response time. To obtain actual values of the redox potential, it is necessary to run the Eh-logging in the discrete mode, keeping the probe for 0.5–2 minutes at each point to ensure stabilization of the Eh.

In wells with an internal diameter of 90–110 mm, the repeated runs in and out do not introduce significant distortions into the general appearance of the logs. Maximum shifts of intervals displaying maxima or minima were within the range of 1–2 m (and rarely as large as 5 m), and deviations relative to the first measured value did not exceed 25%.

The wells, in which the hydrogeochemical logging was executed, are shown in Fig. 2. Samples of subsurface waters and technogenic solutions from the observation wells were taken after hydrogeochemical logging. This allowed us to choose the most characteristic flow intervals for sampling in the investigated water-bearing horizon. The samples were taken with a non-circulating anticorrosive (polyethylene + titanium) sampler. To exclude the influence of atmospheric oxygen on the physico-chemical setting of water, the solution sample, after delivery to the surface, was stored in an air-tight plastic container.

Water samples were analyzed using the following methods: potentiometry—Na, NO<sub>3</sub>, NH<sub>4</sub>, F; volumetric titrimetry—sum of CO<sub>2</sub>, titrimetric alkalinity (in the form of HCO<sub>3</sub>), Cl, Ca, Mg; colorimetry—SO<sub>4</sub>, Si, NO<sub>2</sub>, P; flame photometry—K, Na, atomic absorption—Na, K, Cs, Ca, Mg, Sr, Ba, Fe, Mn; ion chromatography—acetate, Cl, F, NO<sub>3</sub>, NO<sub>2</sub>, SO<sub>4</sub>; bichromatic oxidation—sum of reducing agents, expressed in the form of oxalate. Some of the above-mentioned components and all others, given in the following tables, were determined by the instrumental neutron-activation and quantitative spectral analysis.

The results of pH, Eh, NO<sub>3</sub>, and Na measurements, obtained in the wells with the probe, are marked with the index “p” in the tables. Comparison of pH and NO<sub>3</sub> measurements *in situ* with the laboratory measurements allowed us to determine that pH of alkaline waters varies considerably during sample storage. The *in situ* value decreased from 9.5–11.2 to the close to neutral values of 7.2–7.8. The effect of the alkali neutralization is associated with absorption of CO<sub>2</sub> from the air while taking aliquots from the sample during chemical analysis. The concentration of NO<sub>3</sub> decreased to 75% of the initial values, measured by the hydrogeochemical probe during the two or more weeks of sample storage. Nitrate destruction took place probably through microbiologic denitrification in the laboratory temperature environment (about 20°C), which is not realized in the 5–7°C environment of the water-bearing horizon.

*These examples highlight the need to determine basic hydrogeochemical parameters directly in the reservoir environment, because the long-term storage of water samples may significantly distort the actual physico-chemical environment.*

The computing program CARST (Solodov et al., 1993) was used in the successive processing of the hydrogeochemical data. The ionic-molecular composition of the water solution was determined using Gibbs' free-energy minimization method, and the solution saturation index (SI) relative to the natural-technogenic mineral associations was calculated using Barnes and Clarke's method [1969]. The matrix of the mass balance in the physico-chemical model of the solution, which included all chemical types of waters from the investigated region, included 16 independent components (H, O, NH<sub>4</sub>, K, Na, Ca, Mg, Sr, UO<sub>2</sub>, CO<sub>2</sub>, Cl, SO<sub>4</sub>, CH<sub>3</sub>COO, Si, NO<sub>3</sub>, NO<sub>2</sub>), 104 dependent species in aqueous solution, and 38 solid phases. Isobaric isothermal potentials of species in the aqueous solution and solid phases were taken from works by Naumov et al., 1971; Mel'nik, 1972; Langmuir, 1978; Johnson et al., 1991. Except for those operations above, mentioned the program calculates the ionic strength of the solution, activity coefficients, and to be dissolved solids, and evaluates the percentage of the analytical error. The last procedure is executed by comparison of equimolar numbers of positive and negative charged particles. The error evaluation was feasible owing to the removal of restrictions on electrical neutrality, which is required in most similar programs [Metody. Geokhimicheskogo Modelirovaniya i Prognozirovaniya v Gidrogeologii, 1988]. Activity coefficients were calculated using the Debye-Hückel equation in the third approximation. Ionic radii for this calculation were obtained from the corresponding manuals, and in the absence of such information, they were assumed to be: equal to singly-charged ions—0.45, double-charged—0.60–0.70, triple-charged—0.78 nm. The coefficient, C, in the third term of the equation is 0.1.

# EVOLUTION OF THE CHEMICAL COMPOSITION OF NATURAL AND CONTAMINATED SUBSURFACE WATERS

## NATURAL SUBSURFACE WATERS

In the regional hydrogeological framework, Lake Karachai and vicinity is a small area within the vast recharge area of the Tobol artesian basin. The boundary between emerging basement rocks and water-bearing rocks of the sedimentary cover is 50–70 km to the east of the investigated region. The Tobol basin is part of Western-Siberian artesian megabasin, the largest in the world. In hydrodynamic terms, the Lake Karachai area is a zone of intensive water recharge.

The major source of subsurface waters of the water-bearing horizon in the fissured volcanic bedrocks is surface water. The magnitude of its flow into the fissured rocks of the water-bearing horizon and variations in its chemical composition through reaction with the enclosing rocks depends directly on the relief and the thickness of unconsolidated, relatively impermeable sediments. An analysis of the principal factors affecting the chemical composition of subsurface waters allowed us to distinguish two hydrodynamic subzones with distinctive hydrogeochemical properties.

### Subzone of Active Vertical-Lateral Circulation of Infiltrating Waters (SZ-1)

The subzone, SZ-1, of active vertical-lateral circulation of infiltrating waters is confined to elevated areas of bedrock relief, where fissured rocks outcrop or are covered by a thin layer of soils and loams. Here the lower boundaries of the disintegration zone of the weathered profile occur at depths of no more than 40 m. The subzone is characterized by the distribution of slightly acidic and close to neutral (pH 6.4–7.2) oxidizing (Eh 200–480 mV), oxygen bearing slightly mineralized (M 90–200 mg/l) waters (Table 2). These characteristics indicate that this water is close in composition to the surface water. When water is in equilibrium with atmospheric CO<sub>2</sub>, it is slightly acidic (pH = 5.7; Garrels, 1960) and possesses high Eh values (+200...+650 mV), which are typical of the oxygen-potential controlling systems [Krainov et al., 1992].

The subzone waters are chemically reactive in relation to the enclosing rocks, because they are not in equilibrium with most of the dispersed carbonate, sulfate, and silicate minerals (Table 3). This indicates the existence of active vertical and horizontal circulation of surface waters throughout its entire thickness in this area, and these waters are subject to only slight modification under the influence of enclosing rocks.

The above mentioned properties of subsurface waters of this subzone reflect the results of measurements *in situ*, executed in wells located to the south from the Mishelyak river, and beyond the influence of contaminant sources (Figs. 2 and 8). In this case it is an isolated body of water, represented to the right in the hydrogeochemical section (Fig. 8).

### **Subzone of Delayed Lateral Infiltration of Subsurface Waters (SZ-2)**

The subzone of delayed lateral infiltration of subsurface waters, designated SZ-2, is associated spatially with depressed areas of bedrock relief that often coincide with tectonically relaxed regions. Here the weathered rock thickness reaches 80 m and the fissured volcanogenic bedrocks are covered with slightly permeable elluvial, deluvial-proluvial, and alluvial flood plain sediments. The waters predominating in this subzone are slightly oxidizing ( $Eh < +200$ , in the lower part of the horizon to  $+50...+120$  mV) practically oxygen-free, and slightly alkaline (pH 8.0–8.5) (Table 2). The total dissolved salts (TDS 400–600 mg/l) increases in the waters as they attain partial equilibrium with the enclosing rocks (Table 3). Lateral migration, less intensive in subzone SZ-1, predominates in SZ-2.

*Hydrogeochemical analyses of natural environmental conditions allows us to assume that between Lake Karachai and the Mishelyak river, prior to liquid radioactive waste deposition in the lake, an environment typical of subzone SZ-2 should have predominated.* In the area of the northern branch of the Paleomishelyak river, slightly alkaline and slightly oxidizing waters should form. As will be shown below, technogenic geochemical processes have drastically changed this environment.

The spatial interrelation of the identified subzones is shown in Fig. 8. In the upper part of the section, there is a distinct anomaly of alkaline (pH 8.5–9) with  $Eh < 120$  mV subsurface waters, and this anomaly coincides directly with the location of the fly-ash impoundment, A-1. The oxidizing slightly acidic waters of subzone SZ-1 penetrate the fissured rocks and separate waters of subzone SZ-2 from the alkaline technogenic waters. [Is this OK?]

### **CONTAMINATED SUBSURFACE WATERS ASSOCIATED WITH FLY-ASH IMPOUNDMENT A-1**

The most alkaline (pH to 11.2) and reducing ( $Eh$  from  $-150$  to  $-250$  mV) waters are observed near the Novogornenskii water intake in the area of observation well cluster 205 (Figs. 2 and 9). They are distinguished by the discrete hydrogeochemical logging of observation wells in the area between the Mishelyak river and the observation well cluster [Velichkin et al., 1993]. The distribution of pH, Eh, T and active concentrations of  $NO_3$  and Na with well depth was studied in logging increments of 2–5 m.

The logging investigations in the area of cluster 205 allowed us to study the isolated body of uncontaminated subsurface water and plumes of alkaline waters that flow towards the water intake (Fig. 9). It can be seen from these data that the alkaline waters occur in the upper part of the water-bearing horizon. The nature of this phenomenon became clear after evaluation of the chemical compositions of these waters (Table 2) and determination of their saturation indices in relation to the typomorphic minerals (Table 3). The alkaline waters contain less than half of the total dissolved solids of ambient natural subsurface waters. The demineralization is associated with the removal of carbonates and hydroxides of Ca and Mg, and the removal of Si from the aqueous phase. They are therefore enriched slightly with typomorphic elements from the fly ash, i.e., K, Na, Al, and B [Tauson, 1986; Tauson et al., 1986]. The low concentration of SiO<sub>2</sub> in solution is obviously controlled by the solubility of Ca and Mg silicates. Solutions from the subzone of technogenic alkaline waters (A-1) are saturated in relation to Ca and Sr carbonates, portlandite, and brucite.

The aqueous demineralization process leads to a lowering of the density of the fly-ash derived waters. In contrast to the dense contaminants from Lake Karachai, which are expected to subside, the depleted less dense solutions from the fly-ash impoundments are presently found at the top of the hydrogeological section.

The results of the hydrogeochemistry study of the water-bearing horizons in fissured bedrocks using hydrogeochemical logging (Fig. 9) allow us to explain the zonation of the subsurface waters and to evaluate the capabilities of direct hydrogeochemical logging of wells. The formation of the vertical pH-Eh zonation under the given conditions may be explained as follows. Slightly acidic (pH 5.7) surface waters with Eh +300 to +650 mV, infiltrate the fissured rocks and become gradually slightly alkaline and less oxidizing due to the reducing and neutralizing capacities of enclosing rocks. The neutralization takes place mainly through the influence of carbonates, chlorites, pyroxenes and other rock-forming minerals. In the absence of reducers, the Eh value in oxygen-bearing waters changes depending on pH and it is described by the empirical equation: Eh = 0.89 - 0.059 pH (at 25°C) [Krainov et al., 1992]. Using this dependence in the range of all measured values of pH = 6.4-11.4, Eh should change in the range of +200 – +510 mV. The appearance of Eh values below this range indicates the presence of oxygen reducers in the system. They may be Fe(II), Mn(II), organic matter or other unidentified reductants. The neutralizing and reducing capacities of the enclosing rocks is higher the lower the migration velocity, and consequently the lower the rock permeability.

*To summarize, it may be emphasized that pH-Eh logging allows a qualitative evaluation of inhomogeneities in the permeability of the fissured rocks. Consequently, if the inhomogeneity of pH and Eh distribution is the result of inhomogeneities in the permeability*

of the fissured rock, then the areas with the lowest pH and high Eh are most likely to possess maximum permeability. A nitrate anomaly is associated with one of these areas (Fig. 9), and was probably transported from the near-surface.

## **CONTAMINATED SUBSURFACE WATERS ASSOCIATED WITH THE LAKE KARACHAI**

The position of Lake Karachai on the divide between the Techa and Mishelyak river catchments, together with other factors, predetermines the magnitude of subsurface water contamination. During the time the lake acted as a liquid waste impoundment, it accepted an effluent volume 25 times the volume of the lake basin. The excess volume of solution infiltrated into the water-bearing horizons and displaced of the underlying natural subsurface waters. The high density of the brines favored this phenomenon. As a result, by 1993, a plume of sodium nitrate brine with a volume of  $4.5 \cdot 10^6 \text{ m}^3$  covering an area of 15  $\text{km}^2$  formed in the vicinity of the lake.

*Brine flow in the northerly and southerly directions takes place in response to variations in the relief of the base of the disintegration zone in the volcanic rocks of intermediate-basic composition, to the trend of predominant fissure zones, and to locations of artificial and natural areas of partial discharge of subsurface water near the lake.*

The velocity of the advancing front of the most conservative component [in S.I. Smirnov's opinion (1979)], nitrate, at a depth of 60–100 m, is estimated differently by various authors. According to G.A. Postovalova and A.K. Posokhov, it is 0.4–1.77 m/day (weighted mean value 0.84 m/day); other investigators [Glagolev et al., 1992] estimate the mean value of advance to be 0.23 m/day. It should be pointed out, that the flow velocity during the evolution of the plume has responded to spatial and temporal inhomogeneities, associated with precipitation intensity, which causes the divide between the river catchments in the Lake Karachai area to migrate. Other factors, such as inhomogeneities in permeability, the anisotropy of the fissured bedrock, and changes in brine density at the source of contamination, also influence the rate of plume advance.

The plume is elongated in the N–S direction. The southern front, which is most distant from the contamination source, was 2.5 km distant in 1993. It is necessary to point out, that the actual position of the plume boundary does not correspond to its calculated position, as estimated from the above-cited flow velocities, according to which the contaminated waters should already have reached the water intake or at least would have crossed the Mishelyak river and be at the distance of 1100 m from the water intake. In fact, this is not observed. The explanation for this phenomenon is given below.

The technogenic solutions completely displace the natural subsurface waters. But the chemical composition of the sodium nitrate brines does not remain constant with time. Apart from processes of dilution and precipitation, and hydraulic dispersion, the compositions change under the influence of fission-product radiation and interaction with the enclosing rocks. According to completed investigations (Tables 4–6 and Fig. 10), the following hydrogeochemical environment has formed between the lake and the Mishelyak river.

Waters in the lake and vicinity are slightly alkaline (pH 8–8.5) and oxidizing (Eh about 300 mV). As they migrate away from the lake, they become slightly acidic (pH is decreased to 5.9) and with high oxidizing capacity (Eh is more than 300 mV for the whole thickness of the horizon). The nature of acidification and the high oxidizing capacity is probably explained by the influence of radiation on the subsurface water-rock system.

Radiolysis and associated products of radiolytic disintegration of the water intensify many processes, some of which are not attained in the hypogene zone [<sup>1</sup>Vovk and <sup>2</sup>Vovk, 1979]. Under the influence of the products of radiohydrolysis, feldspar alters to clay minerals and sulfides to sulfates more intensively than in natural waters. As a consequence of radiolytic oxidation of organic matter contained in the water and rocks, carbon dioxide is formed; which dissolves in the subsurface water with the formation of carbonic acid.

In the environment under consideration the radiolytic disintegration of acetate should take place with the formation of carbonic acid, methane, and hydrogen [Allen, 1961]. The concentration of  $\text{CH}_3\text{COO}$  decreases from an initial value of 0.6–20 g/l at the source to 25–150 mg/l in the principal volume of the technogenic brine plume. These processes also appear to be associated with the disappearance of oxalate from solution. It is probable that oxalate was at first removed from the solution in the form of calcium oxalate, which possesses extremely low solubility, and then the solid precipitate disintegrated through radiolysis. It is not inconceivable that nitrate is partially transformed to nitrite (Table 4). Under these conditions, the formation of ammonium ions and molecular nitrogen is quite plausible [Allen, 1961]. *The radiolytic disintegration of nitrate and acetate indicates that they may not be ideal tracers of the contaminated subsurface water.*

The radiolytic disintegration of chemical constituents takes place so intensively, that active gas emanation is observed from all wells within a radius of one km from the lake. One of the gaseous components is carbon dioxide. Its presence obviously explains the appearance of slightly acidic waters in this area of the water-bearing horizon. Waters, containing carbonic acid, become aggressive lixivants in relation to the enclosing rocks, leading to intensive removal of alkaline-earth elements. Calcium and magnesium contents of the plume waters are respectively in excess of 80 and 40 times their concentrations in the lake, and strontium is 850 times more concentrated than it is in the natural subsurface waters.

The oxidizing nature of these waters may be explained by radiolytic processes with regard to the theoretical and experimental data by Gutsalo (1971). The author concluded, that "when water is subject to alpha-radiation, the radiation induced chemical oxidation of dissolved matter is observed more often than reduction (p. 1478)." It is associated with significantly higher diffusive permeability of reductants in comparison with the oxidants, the former diffuse more rapidly away from the region of radiolytic reaction than the latter.

An analysis of the variation of the bulk chemical composition of technogenic solutions (Table 4), the ratio of their saturation in relation to the typomorphic minerals (Table 5), and geochemically significant concentrations of the principle components (Table 6) in proportion to their distance from the lake (Fig. 10) allow us to make the following observations:

1. Nitrate complexes of metals (Na, Ca, Mg, and Sr) appear in the area occupied by sodium nitrate brines.
2. In the system under consideration, the contaminants display different migration rates, but what is most important, nitrate leads practically all the principal stable and radioactive isotopes.
3. Strontium in the aqueous solution occurs mainly in the form of positively charged ( $\text{Sr}^{2+}$ ) and neutral  $(\text{Sr}(\text{NO}_3)_2^0$ ) species. It is adsorbed by rocks owing to the presence of relatively high concentrations of such competitive ions as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ .
4. The migration of strontium at a distance of 1.5-1.9 km from Lake Karachai is controlled by the saturation of solutions with respect to strontianite. Mg and Ca also migrate in the saturated state in the relation to calcite and magnesite, but the area where their concentration is controlled by saturation extends to 2.8 km.
5. Uranium, in an area up to 2 km from the lake, probably migrates in the saturated state in relation to its carbonates. Uranium sorption by rocks is improbable, because it migrates in the technogenic solutions mainly in the form of negatively charged uranylcarbonate complexes.
6. The acid-alkaline and redox environment varies considerably to the north and south of the Mishelyak river. Between Lake Karachai and the river, as was pointed out, oxidizing slightly acidic waters predominate. Between the river and the water intake, the alkaline (pH 9-11) reducing ( $\text{Eh} < 0$ , to -250 mV) waters, associated with the fly-ash impoundment, A-1, are observed with slightly oxidizing ( $\text{Eh} 0-200$  mV) slightly alkaline (pH 7.5-8.0) waters. The former are distributed in the vicinity of the water intake.

## DISTRIBUTION OF THE CONTAMINATED SUBSURFACE WATERS

A fundamental problem is to determine the position of the interface that separates contaminated waters from the natural subsurface waters. In the situation considered here, an isopleth of nitrate concentration was chosen to delineate contaminated from uncontaminated waters. This isopleth corresponds to the permissible concentration of nitrate (45 mg/l) in drinking water. It is expressed in the form  $p\text{NO}_3 = -\lg(a\text{NO}_3) = 3.1$ . The non-conservative components (Na, U,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{60}\text{CO}$ , etc.), are considered to be more strongly retarded than the conservative component,  $\text{NO}_3$ .

Because of differing migration rates of liquids with variable density in the area between the lake and the Mishelyak river, it is necessary to distinguish the *observed* distribution from the *actual* distribution of a specific component in the migrating subsurface water. During geophysical and hydrogeochemical investigations in unflushed observation wells, the observed distribution of dissolved constituents in the liquid phase, results from diffusion and density differentiation in the free space of the well. As will be shown below, density convection is more significant than diffusive redistribution of the chemical constituents. Regarding the results of investigations in unflushed wells, it is impossible to detect the lower limits of contaminant penetration into the fissured bedrock.

The hydrogeochemical cross-sections shown in Fig. 10 provide examples of the observed distribution of the contaminated water. Hydrogeochemical logging investigations in the unflushed observation wells monitor only the leading edge and upper parts of the plume, but permit detailed study of the processes of dilution and dispersion of the dissolved constituents. *In the case of Fig. 10, the lower boundary of the sodium nitrate brine is fictitious, as it corresponds to the well depth.*

Evaluations of the hydrogeochemical sections\* (Fig. 10) permit us to make an important assumption concerning the influence of petrofabric on the distribution contaminated subsurface waters: *The zone of the Mishelyakskii fault and associated faults, together with the infrabed flow in alluvial sediments of the Mishelyak river represents a hydraulic barrier to the flow of contaminated water towards the Novogornenskii water intake. The flow appears to divide into two parts: the upper part is intercepted by the river infrabed flow and carries the contaminated waters eastward toward the fly-ash impoundment A-2, whereas the lower part changes in direction from southerly to southeasterly in conformity with the strike of the Mishelyakskii fault (Fig. 2).*

\*The data of interval sampling of wells, executed in the distribution zone of radioactive waters with contents of  $^{90}\text{Sr} > 10^{-7}$  curies/l, and the results of hydrogeochemical logging investigations were used in the preparation of hydrogeochemical sections. Interpolation of these data is performed using the engineering graphics program, SURFER, by a Kriging method with a grading radius of 500 m.

This assumption will require thorough verification through focussed and comprehensive investigations. If correct, then the noted difference between the actual and calculated position of the southern front of the contaminated water can be explained.

*The actual flow pattern is reflected by the true distribution of component concentrations in the interstitial and fissured volume of the bed rock at the time of investigation. In the absence of free gravitational convection in the well with its accompanying extensive exchange of water, and when molecular diffusion is insignificant, hydrogeochemical logging can define the actual distribution of components in the undisturbed flow. The observed distribution of natural and alkaline technogenic waters may then be representative of the actual migration patterns.*

*We may then state, that under the conditions of migrating liquids of uniform density, the observed and actual distributions coincide as a rule. With the appearance of density convection due to significant differences of fluid velocity in open fractures and interstitial pores [Smirnov, 1971], the distribution is different. This difference increases as the density gradient increases.*

To determine the actual pattern of flow in the region containing solutions with higher density, comprehensive investigations were conducted. The deepest observation well, 176 (the location of which is shown in Fig. 11), was chosen for this purpose. The well was initially logged hydrogeochemically (Fig. 11), allowing us to determine that: (a) diluted sodium nitrate solutions with an activity of  $\text{NO}_3$  of  $10^{-1.8}$  mol/kg and Na of  $10^{-3.3}$  mol/kg, and with an electrical conductivity  $-0.7$  Sm/m, were observed at a depth of 55 m; (b) these parameters increased below 55 m, reaching maxima at a depth range of 65–70 m; (c) undiluted contaminated waters were distributed throughout the interval from 65 m to 220 m, *i.e., the apparent thickness of the contaminated waters was 155 m* (but as will be shown below, this is the result of gravitational redistribution of solutions in the well); (d) of all parameters, only electrical conductivity (E) and redox-potential (Eh) allowed us to determine the actual interval of the contaminated water. On the logging curves of these parameters, the contaminated water was identified as positive anomalies at a depth of 65–95 m (Fig. 11); (e) the Eh-anomaly displacement in relation to the true Eh-anomaly is the result of the persistence of redox-potential measurements during continuous logging (Fig. 11); (f) the disagreement between the equimolar concentrations of sodium and nitrate and the ubiquitous predominance of the  $\text{NO}_3$  over Na is additional proof that  $\text{NO}_3$  is transported without retardation by the rocks. Na takes part in ion-exchange reactions, and is probably adsorbed by rocks.

To exclude the influence of the density convection, the well was flushed with fresh water, using a drilling rig. For this purpose the drill string was run in to a depth of 180 m, and

the well water was pumped from the bottom up. This method permitted flushing of the interval from 180 m to 70 m. The brines, lifted from the lower part of the well, remained unflushed above that interval. The drill string was run out of the well in 26 minutes. As soon as it was brought to the surface, resistivity logging measurements were started (Fig. 12). These observations reflect two processes: (a) gravitational depression of the upper boundary of dense solutions with the velocity of 1.7–5.9 m/hour (mean value 3.7 m/hour); (b) brine flushing by diluted solutions (in this case, the method of artificial salinization was simulated, as is often used during resistivity measurements) with maximum bulk velocity of 0.3 l/sec., as determined using a flow meter (Fig. 13). With the resistivity data, A.V. Zharikov conducted a layer by layer evaluation of the flow rate throughout the whole of the permeable interval and determined that the hydraulic conductivity varies between 0.03 and 0.96 m/day. The maximum permeability coincides with the 55–70 m interval, within which intensive inflow of contaminated waters is observed (Fig. 12). This inflow stabilized at the end of the first day of observation, and was reflected in the nitrate logging data (Fig. 13). *It is seen from these data that the actual thickness of the contaminated water zone does not exceed 15 m in the investigated section.*

*In the plume of radioactive water, the technogenic gamma-anomalies, detected by gamma logging, may serve as additional indicators of permeable fissures, hydraulically connected to the source of contamination.* A comparison of gamma logging investigations with caliper logging supports this assumption (Fig. 14). It is obvious from these data, that maximum areal gamma anomalies coincide with the most permeable zone in the interval of 55–70 m, identified earlier with other methods.

On the basis of the entirety of knowledge on the structure of the transport medium, a qualitative model of the contaminated water plumes from Lake Karachai and the fly-ash impoundment, A-1, are represented in Fig. 15. The factors that may delay the flow of contaminated waters to the Novogornenskii water intake may be represented on a quantitative level as follows:

1. Hydraulic processes of dilution by precipitation and by surface waters (distributed to the depth of 20–40 m) and dispersion of the leading edge of the plume.
2. Free gravitational convection in the fissured bedrock, and immobilization and of sodium-nitrate brines by structural and lithological traps.
3. Ion-exchange and sorption of contaminants by the enclosing rocks.

4. Transfer of contaminants from the liquid to solid phase during chemical transformations at the subsurface water-rock interfaces.
5. Radioactive decay.

The principal aim of further investigations is an evaluation of the significance of these phenomena and selection of major factors that should constitute the basis for a quantitative prediction of migration of stable and radioactive isotopes in the groundwater system.

## **GEOCHEMICAL TECHNOLOGIES FOR SUBSURFACE WATER QUALITY RESTORATION**

The most dangerous of all radionuclides entering the subsurface waters from Lake Karachai is  $^{90}\text{Sr}$ . In order to decrease the rate of migration of its concentration front to the Novogornenskii water intake, AI "Mayak" intends to intercept the contaminated water and pump it to the surface. The extraction of the ecologically dangerous radionuclides from waters pumped to the surface is envisaged using various technologies. During the application of these technologies, the total content of the stable plus radioactive isotopes is of more fundamental importance than the concentration of the radioisotope. Thus, for Ru, Co, and Cs, the total concentrations of which are fractions of milligrams per liter, these elements, contaminated by radioactive isotopes, will be concentrated at the surface. But a quite different situation occurs with the extraction of  $^{90}\text{Sr}$ , because the total concentration of Sr in solution is between 50–300 mg/l. It is easy to calculate that the total quantity of strontium, contaminated by its radioactive isotope, when concentrated at the surface after the treatment of  $4.5 \cdot 10^6 \text{ m}^3$  of solution, will be very large. It is therefore preferable to develop methods of *in situ* immobilization. In these calculations we simulated theoretically three versions of the application of geochemical technologies to decrease the strontium concentration in solution.

- Artificial geochemical barriers were considered, in the form of geochemical buffers, created ahead of the contaminated water front. Technically, these buffers are represented by ditches, cut through the sedimentary rocks into the fissured rocks. The ditches are filled with mineral carbonates or sulfates of alkaline or alkaline-earth metals. The sulfates or carbonates in the ditches are flushed with surface waters in order to create the buffer. The water enriched with carbonate or sulfate anions penetrate the region of the predominant strontium migration through natural gravitational convection. The selection of sulfate and carbonate minerals as anionic fixers of strontium is justified by two considerations: (1) the relatively low solubility of celestite and strontianite; (2) the possibility of using local materials, such as gypsum or limestones, i.e., as sources of anionic fixers of strontium.

Some parameters of the buffer are as follows: With the solubility product of celestite of  $2.14 \cdot 10^{-7}$  in equilibrium conditions in pure water with  $\text{SrSO}_4$  saturation there should be 81 mg/l of Sr and 89 mg/l of  $\text{SO}_4$ ; with the variation of sulfate concentration from 10 to 1000 mg/l, the Sr concentration varies from 720 to 7 mg/l [Krainov et al., 1987]. In real mineralized solutions, containing other metals that form complexes with sulfate, these ratios may change.

Physico-chemical modeling, executed with the CARST program, with the application of actual compositions of sodium nitrate brines, indicated that, with the sulfate concentration in equilibrium with gypsum the strontium concentration did not reach equilibrium with celestite, and in this case Sr was not removed from the solution. This occurs because of the formation of sulfate complexes with Na, Ca, Mg, and partially with U.

Geochemical technologies of such kind are not effective because of the reversibility of the created geochemical barriers. To achieve an irreversible transition of matter from the solution to the solid phase, the concentration of the anion-fixer in the infiltrating flow must be constantly maintained at the calculated level. Furthermore, the duration of this artificial process should be close to the decay period of the radioactive strontium to the permissible level.

- Application of the conserving properties of carbonate formations in relation to strontium were also considered. In the given geological environment the most suitable for this purpose is limestone, outcropping 7 km north to northeast of Lake Karachai.

The possibility of this method working under natural conditions is proved by observations during study of natural strontium migration in carbonate formations. In saturated waters the ratio of Ca concentrations, which are in equilibrium with calcite and strontianite, to Sr has a value of 5–15 [Krainov et al., 1987]. Our calculations show that equilibrium strontium concentrations are at the level of 0.1–0.3 mg/l in equilibrium with carbonate-bearing volcanic rocks.

Strontium deposition in the form of carbonate compounds is more effective than that of sulfates, as shown by the activity product for strontianite ( $1.68 \cdot 10^{-9}$ ), which is two orders of magnitude lower than that for celestite. This suggests that during migration of technogenic solutions through carbonate rocks and achievement of equilibrium, the concentration of total and, correspondingly, radioactive strontium will be decreased by 3–4 orders of magnitude. For this technology to work it is necessary to treat the solutions pumped to the surface containing the most dangerous radionuclides, and then to reinject them into the carbonate formations.

The irreversibility of technogenic geochemical barriers created by the proposed method is provided by the rocks themselves, which are a continuous source of carbonate anions.

- Large fly-ash impoundments, located near Lake Karachai, are simultaneously both natural and artificial geochemical barriers. Because the impoundments are situated on swamp sediments, both the fly-ash and swamp sediments possess the sorption, reduction, and neutralizing capacity to cause the complete immobilization of practically all contaminants contained in the contaminated subsurface waters. The task is to direct the contaminated waters to the area where these deposits are found, which it is quite feasible, technically.

This last method is the most attractive of the three considered. It avoids the pumping of radioactive waters to the surface and their treatment and reinjection. For a practical accomplishment of this method, it will be necessary to conduct comprehensive geologic, hydrogeologic, and geophysical investigations.

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Table 1. Technical characteristics of the information-observation system used for hydrogeochemical logging of observation wells.

Parameter	Measurement Unit	Range	Error	Resolution
Temperature	degrees C	-2...+60 3	0.01	0.001
Electrical conductivity	Sm/m	<6.5	0.001	0.0002
Hydrostatic pressure	MPa	0...15	0.15% (to the measurement range)	0.005
Hydrogen index, pH	pH unit	0...12	0.05	0.005
Redox potential, Eh	mV	-500...+1800	10	0.5
Dissolved oxygen	mg/l	0...20	0.3	0.05
Overall dimensions of submersible part		Length 980 mm Diameter 65 mm		
Mass of the submersible part		5 kg		

Table 2. Chemical composition of natural and technogenic alkaline subsurface waters. Right bank of the Mishelyak river. September 1992.

Component	Measurement unit	Subzone of active circulation of infiltration waters (SZ-1)	Subzone of delayed lateral filtration (SZ-2)	Alkaline waters, associated with the fly-ash impoundment A-1 (A-1)
pH <sub>p</sub>		6.45	8.50	11.2
Eh <sub>p</sub> (Pt)	mV	+400	+190	-185
HCO <sub>3</sub>	mg/l	98	230	67.1
Sum of CO <sub>2</sub>		77	121	8.8
SO <sub>4</sub>		26.9	115	38.4
Cl		7.1	53.2	36.7
SiO <sub>2</sub>		17	15	5.4
NO <sub>3</sub> p		1.5	6.2	28
NO <sub>2</sub>		<0.01	1.5	2.0
NH <sub>4</sub>		<1.8	<1.8	<1.8
Na		4.5	16	28
K		0.9	2.0	17.0
Ca		22	76	4
Mg		8.4	30	0.04
F	μg/l	300	300	300
Al		220	410	1200
Sum of Fe		43.4	580	16.7
Mn		15.2	41	10
Sr		210	290	120
Ba		17	27	14
Zn		43	120	24
Pb		<2	<2	4.8
B		15	58	24
Ti		11	41	72
Cu		4.3	4.1	7.2
Ni		1.5	2.4	2.4
Mo		15	5.5	0.5
U		3.8	1.2	0.65
Ga		0	0	1.2
Ta		0	0	2.8
Total Dissolved Solids	mg/l	181	430	191

Table 3. Saturation indices, SI, of subsurface waters in relation to typomorphic solid phases in subzones.

Solid Phase	Name	SZ-1	SZ-2	A-1
$\text{CaCO}_3$	calcite	0.016	<b>2.472*</b>	<b>2.465</b>
$\text{MgCO}_3$	magnesite	0.004	<b>2.728</b>	0.110
$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$	lansfordite	1.5E-5	0.012	4.8E-4
$\text{SrCO}_3$	strontianite	4.5E-4	<b>0.980</b>	0.401
$\text{UO}_2\text{CO}_3$	rutherfordine	0.003	1.5E-6	2 E-9
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	gypsum	0.003	0.024	5.8E-4
$\text{SrSO}_4$	celestine	1.8E-4	7 E-4	1.5E-4
$\text{Ca(OH)}_2$	portlandite	2.3E-9	4.7E-4	<b>0.980</b>
$\text{Mg(OH)}_2$	brucite	1.1E-7	0.004	<b>2.263</b>
$\text{Sr(OH)}_2$	—	3.0E-13	4.0E-8	0.002
$\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$	skupite	2.9E-5	7.1E-7	8.8E-5
$\text{SiO}_2$	amorphous	0.133	0.112	0.001
$\text{Ca}_2\text{SiO}_4$	—	6.8E-24	6.5E-15	1.1E-8
$\text{CaMgSiO}_4$	monticellite	4.8E-15	4.8E-6	<b>1.667</b>
$\text{Mg}_2\text{SiO}_4$	forsterite	4.1E-14	4.2E-5	<b>2.812</b>
$\text{Sr}_2\text{SiO}_4$	—	6.8E-34	1.2E-25	1.6E-17

\*Indices appropriated to the saturated solutions of relative solid phase are designated in bold type.

Table 4. Chemical composition (in mg/l) of sodium nitrate brines and subsurface waters in the lower part of the water-bearing horizon (40–100 m from the surface) along their flow path from Lake Karachai to the Novogornenskii water intake. August 1993.

Wells	41/77*	63/68*	10/68*	3/68*	9/68*	176	50/79	209
Dist., m	50	1100	1500	1900	2150	2500	2800	4000
Depth, m	45	100	100	90	100	80	40	40
pH	8.1	7.3	6.6	6.5	5.9	7.33	8.42	7.62
NO <sub>3</sub>	45000	45000	52000	32000	27100	3910	43.0	0.0
NO <sub>2</sub>	4100	3600	6000	3800	3200	250	0.7	0.0
HCO <sub>3</sub>	4760	1220	1830	1160	952	251	220	129
SO <sub>4</sub>	360	400	350	165	287	200	111	42.2
Cl	120	90	105	80	88	162	54.0	46.9
CH <sub>3</sub> COO	25	150	90	~50	300	0.18	<0.02	0.02
F	2	1.5	2	1.3	1.5	0.8	0.3	0.3
Humus	—**	—	—	—	—	22.4	3.5	<0.1
C <sub>2</sub> O <sub>4</sub>	<5	<5	<5	<5	1.8	0.009	<0.001	<0.001
SiO <sub>2</sub>	2	6	6	16	16	21	21	2.5
Na	19000	16000	9000	3500	2200	46.3	42.5	35
K	310	260	140	130	60	18	22	4
Mg	300	200	2900	2500	2100	408	23.8	3.8
Sr	210	260	250	250	180	2.2	0.31	0.03
Ca	10	1400	6300	5300	4800	720	66.4	1.6
NH <sub>4</sub>	48	20	52	26	25	2.9	0.0	1.8
U	41	35	41	28	23	0.0037	0.0042	0.0017
Cs(μg/l)	<300	<300	<300	<300	<300	<4.5	<4.5	<4.5
Mineralization, g/l	71.81	68.03	79.14	48.10	40.89	5.92	0.547	0.215

\*Chemical analyses for wells 41/77, 63/68, 10/68, 3/68 and 9/68 were performed at the Chemical Laboratory of the "Mayak" Central Plant Laboratory under the supervision of M.A. Tungusov. The components Ba, P, Fe, and Al are present in concentrations of less than 1 mg/l and are not included in the Table.

\*\*A dash (—) means the absence of data.

Table 5. Variation of the saturation index of technogenic solutions in relation to typomorphic minerals along of the solution migration path from Lake Karachai to the Novogornenskii water intake.

Solid Phase	SI							
	41/77	63/68	10/68	3/68	9/68	176	50/79	209
Well	41/77	63/68	10/68	3/68	9/68	176	50/79	209
Distance, m	50	1100	1500	1900	2150	2500	2800	4000
<b>MgCO<sub>3</sub></b>	<b>4.19*</b>	<b>1.65</b>	<b>2.88</b>	<b>1.95</b>	<b>-0.09</b>	<b>0.99</b>	<b>0.85</b>	<b>-3.09</b>
MgCO <sub>3</sub> ·5H <sub>2</sub> O	-1.25	-3.78	-2.55	-3.48	-5.53	-4.44	-4.58	-8.53
Mg <sub>2</sub> (SiO <sub>4</sub> )	-12.5	-17.4	-17.1	-18.1	-24.0	-15.1	-10.8	-23.2
Mg(OH) <sub>2</sub>	-6.11	-9.03	-8.93	-9.78	-12.7	-8.36	-6.20	-11.5
CaCO <sub>3</sub> ·(arag)	0.57	2.93	2.75	2.14	0.26	1.67	2.08	-3.74
CaCO <sub>3</sub> ·(calc)	0.91	3.26	3.08	2.48	0.60	2.01	2.41	-3.41
CaMg(CO <sub>3</sub> ) <sub>2</sub>	8.85	8.67	9.71	8.18	4.25	6.75	7.02	-2.76
CaSO <sub>4</sub> ·2H <sub>2</sub> O	-7.47	-1.94	-2.04	-2.61	-1.96	-2.60	-4.31	-8.51
Ca(OH) <sub>2</sub>	-25.2	-23.2	-24.5	-25.0	-27.8	-23.1	-20.4	-27.6
SrCO <sub>3</sub>	<b>5.14</b>	<b>2.92</b>	<b>1.13</b>	<b>0.91</b>	<b>-1.19</b>	<b>-2.63</b>	<b>-1.83</b>	<b>-6.32</b>
SrSO <sub>4</sub>	-1.90	-0.95	-2.65	-2.84	-2.42	-5.90	-7.22	-10.0
Sr(OH) <sub>2</sub>	-35.8	-38.4	-41.3	-41.5	-44.5	-42.6	-39.5	-45.4
Sr(NO <sub>3</sub> ) <sub>2</sub>	-10.1	-9.13	-9.17	-9.61	-10.1	-18.0	-28.6	-73.3
UO <sub>2</sub> (CO <sub>3</sub> )	-9.13	-2.89	0.43	0.75	2.33	-9.30	-12.4	-9.54
UO <sub>2</sub> (OH) <sub>2</sub> ·H <sub>2</sub> O	-13.5	-7.70	-5.50	-5.10	-4.44	-12.7	-13.6	-12.0

\*Indicates appropriated to the saturated solutions of relative solid phase are designated by bold type.

Table 6. Ionic-molecular composition of sodium nitrate solutions in the lower part of the water-bearing horizon along the flow path from Lake Karachai to the Novogornenskii water intake.

Well	41/77	63/68	10/68	3/68	9/68	176	50/79	209
pH	8.1	7.3	6.6	6.5	5.9	7.33	8.42	7.62
Ionic strength	0.778	0.683	0.786	0.572	0.514	0.103	0.011	0.004
Component	Equilibrium Concentration, mol/kg							
$\text{NO}_3-1$	0.66	0.63	0.52	0.37	0.32	6.1E-02	6.9E-04	no
$\text{NO}_2-1$	6.4E-02	5.9E-02	0.11	7.6E-02	8.5E-02	5.4E-03	no	no
$\text{HCO}_3-1$	4.9E-02	1.2E-02	7.0E-03	5.3E-03	3.3E-03	3.1E-03	3.4E-03	2.0E-03
$\text{H}_2\text{CO}_3\ 0$	5.5E-04	8.2E-04	2.5E-03	2.4E-03	6.2E-03	2.5E-04	2.6E-05	1.0E-04
$\text{CO}_3-2$	6.8E-04	2.5E-05	3.1E-06	1.8E-06	2.8E-07	5.6E-06	5.5E-05	4.7E-06
$\text{SO}_4-2$	2.3E-03	2.0E-03	2.7E-04	1.6E-04	3.2E-04	8.3E-04	9.8E-04	4.3E-04
$\text{CH}_3\text{COO}-1$	2.8E-04	1.5E-03	2.3E-04	1.7E-04	1.1E-03	no	no	no
$\text{Na}+1$	0.71	0.58	0.31	0.13	8.8E-02	2.0E-02	1.8E-03	1.5E-03
$\text{NaNO}_3\ 0$	5.9E-02	4.6E-02	2.0E-02	5.9E-03	3.6E-03	1.9E-05	2.7E-07	no
$\text{NaHCO}_3\ 0$	2.5E-02	4.8E-03	1.5E-03	4.7E-04	2.1E-04	5.5E-06	7.3E-06	3.9E-06
$\text{Na}_2\text{SO}_4\ 0$	1.0E-03	6.0E-04	2.2E-05	2.3E-06	2.2E-06	4.9E-09	1.0E-08	3.8E-09
$\text{CH}_3\text{COONa}\ 0$	1.2E-04	5.0E-04	4.1E-05	1.2E-05	5.6E-05	no	no	no
$\text{Ca}+2$	1.2E-04	6.3E-03	3.8E-02	4.6E-02	4.8E-02	1.6E-02	1.5E-03	3.8E-05
$\text{CaCO}_3\ 0$	1.5E-05	1.6E-04	1.3E-04	7.4E-05	1.1E-05	5.1E-05	7.9E-05	2.3E-07
$\text{CaNO}_3+1$	6.1E-05	1.7E-02	9.4E-02	6.2E-02	5.2E-02	1.5E-03	1.7E-06	no
$\text{Ca}(\text{NO}_3)_2\ 0$	3.6E-05	9.4E-03	4.3E-02	2.0E-02	1.5E-02	1.0E-04	1.7E-09	no
$\text{CaHCO}_3+1$	2.0E-05	1.4E-03	5.6E-03	4.0E-03	2.4E-03	3.5E-04	3.7E-05	6.6E-07
$\text{CaSO}_4\ 0$	3.0E-06	7.8E-04	6.9E-04	4.1E-04	8.0E-04	4.6E-04	8.5E-05	1.3E-06
$\text{Mg}+2$	8.5E-03	3.5E-03	8.7E-02	7.5E-02	6.6E-02	1.5E-02	8.5E-04	1.5E-04
$\text{Mg}(\text{NO}_3)_2\ 0$	1.5E-03	2.9E-03	5.6E-02	1.9E-02	1.2E-02	5.9E-05	5.7E-10	no
$\text{MgHCO}_3+1$	1.5E-03	7.4E-04	1.3E-02	6.4E-03	3.3E-03	3.4E-04	2.1E-05	2.5E-06
$\text{MgCO}_3\ 0$	4.8E-04	3.9E-05	1.3E-04	5.5E-05	7.1E-06	2.3E-05	2.1E-05	4.0E-07
$\text{MgSO}_4\ 0$	3.8E-04	7.4E-04	2.7E-03	1.1E-03	1.9E-03	7.9E-04	8.5E-05	8.3E-06
$\text{Sr}+2$	1.3E-03	7.3E-04	8.8E-04	1.5E-03	1.3E-03	2.4E-05	3.4E-06	3.3E-07
$\text{Sr}(\text{NO}_3)_2\ 0$	5.4E-04	1.5E-03	1.4E-03	9.3E-04	5.6E-04	2.2E-07	5.4E-12	no
$\text{SrHCO}_3+1$	3.1E-04	2.1E-04	1.8E-04	1.8E-04	8.8E-05	7.3E-07	1.2E-07	7.9E-09
$\text{SrCO}_3\ 0$	5.0E-05	5.5E-06	9.0E-07	7.5E-07	9.3E-08	2.4E-08	5.5E-08	6.2E-10
$\text{UO}_2+2$	3.8E-16	8.4E-13	1.7E-10	5.2E-10	1.7E-08	1.2E-14	3.2E-17	5.1E-15
$\text{UO}_2(\text{CO}_3)_3-4$	1.5E-04	9.9E-05	4.4E-05	1.8E-05	2.1E-06	4.8E-09	1.1E-08	1.2E-09
$\text{UO}_2(\text{CO}_3)_2-2$	1.6E-06	3.0E-05	1.1E-04	8.1E-05	6.1E-05	9.9E-09	4.0E-09	6.1E-09
$\text{UO}_2\text{CO}_3\ 0$	2.1E-10	1.1E-07	2.9E-06	4.2E-06	2.1E-05	2.0E-10	8.9E-12	1.6E-10
$\text{UO}_2(\text{OH})_2\ 0$	7.2E-13	2.6E-10	2.3E-09	3.5E-09	6.9E-09	1.8E-12	8.0E-13	3.7E-12
$\text{UO}_2(\text{OH})_3-1$	3.3E-14	1.8E-12	3.3E-12	3.9E-12	1.9E-12	1.2E-14	5.5E-14	3.9E-14
$\text{UO}_2(\text{NO}_3)+1$	6.3E-15	8.4E-11	1.6E-08	2.6E-08	7.0E-07	4.4E-14	1.4E-18	no

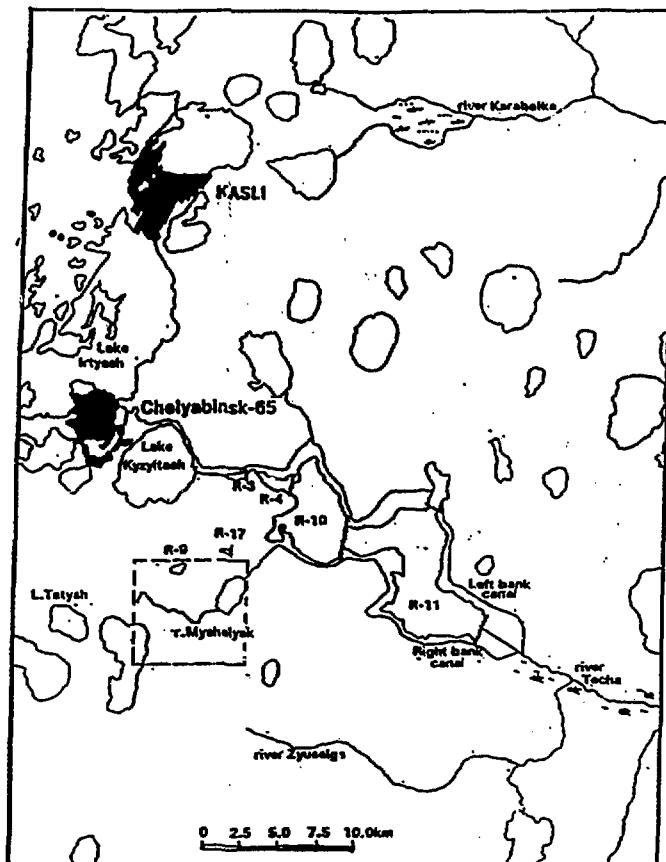


Fig. 1. Distribution of surface water bodies at the "Mayak" site (from the work by Drozhko et al., 1993). The area of detailed hydrogeochemical investigations, represented in Fig. 2, is enclosed by the dashed line.

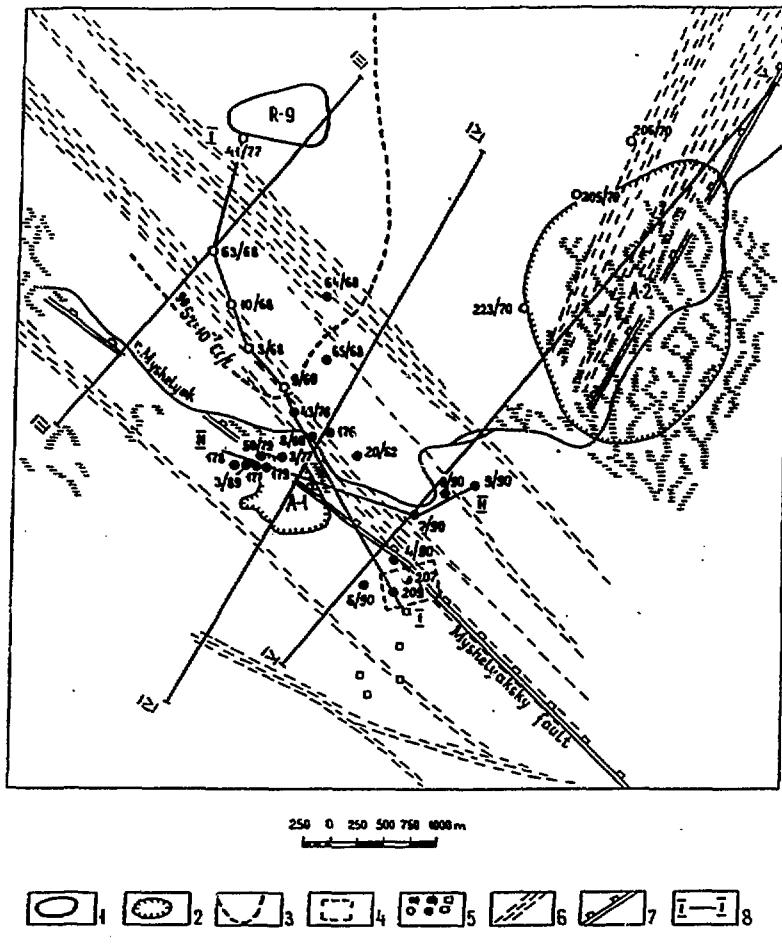


Fig. 2. A map of detailed hydrogeochemical investigations of the area south of Lake Karachai, with elements of hydrography and tectonics (prepared by I.N. Solodov, 1993).

1. Lake Karachai (water reservoir R-9)
2. Fly-ash impoundment of the Argayashskaya TPP
3. Radioactivity isoline of  $^{90}\text{Sr} = 10^{-7}$  curies/l as of March-April, 1993
4. Cluster 205 of observation wells
5. Wells with: (a) interval sampling of subsurface waters, and (b) interval sampling and hydrogeochemical logging; (c) water intake well
6. Zones of schistosity and fracturing
7. Zones of assumed faults
8. Lines of geologic and/or hydrogeochemical crossection

I-V = lines of crossections

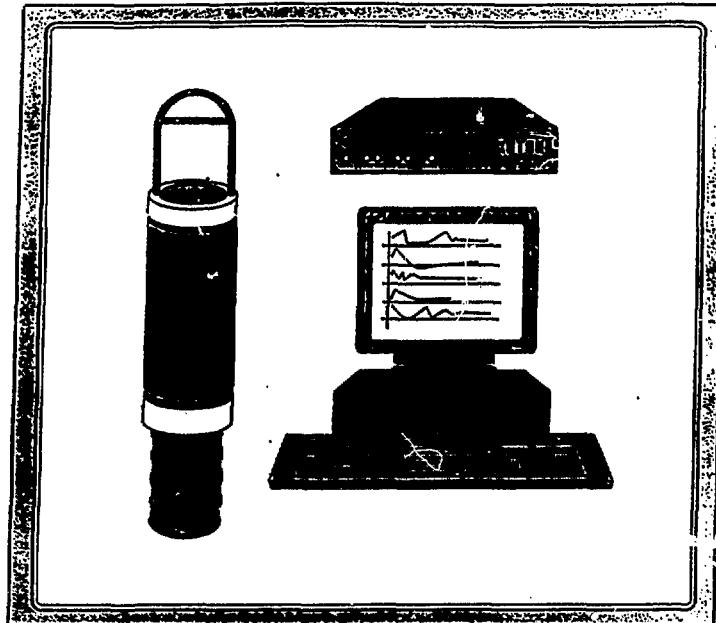


Fig. 3. General view of the information-measurement system, used for hydrogeochemical logging of observation wells.

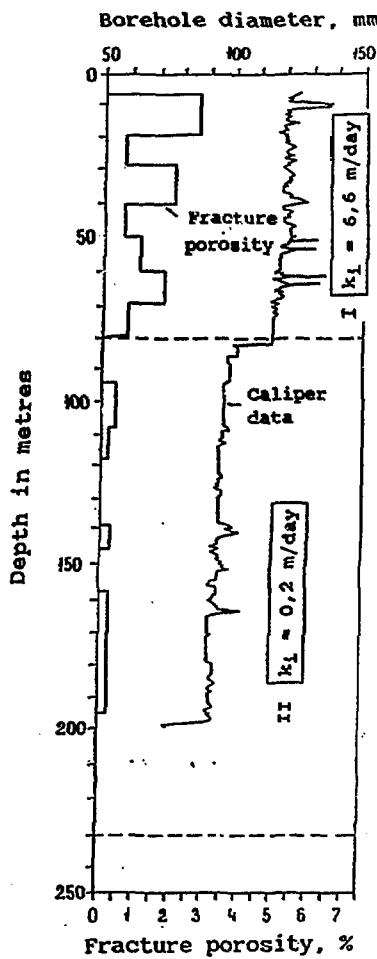


Fig. 4. Cavity histogram and caliper log of well 176.

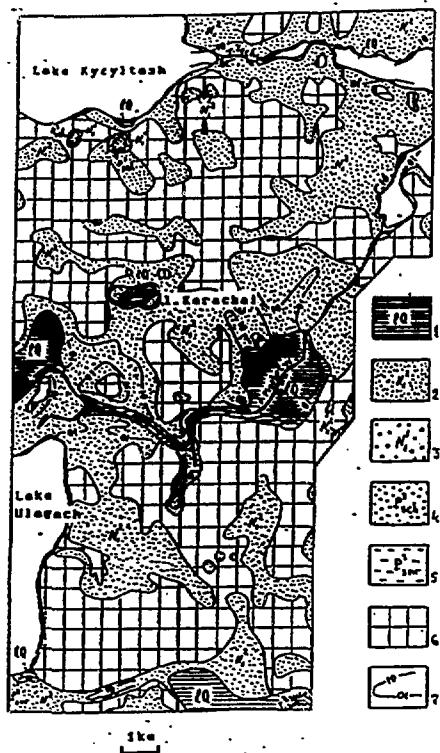


Fig. 5. Map of Cenozoic sediments of the Lake Karachai area (prepared by B.T. Kochkin, 1993).

1. Quaternary lacustrine-swamp and river sediments—peat, silt
2. Late Miocene (Aralian suite) cover-slope, proluvial and alluvial sediments—brown loams with pebbles of quartz, brown clays with intercalations of grey and yellow sands
3. Early Miocene slope sediments—red-brown loams with fragments of quartz and ferrous sandstones
4. Late Oligocene (Chagranian suite) slope sediments—ferrous sandstones with fragments of quartz
5. The Oligocene (Naurzumian suite) sediments—variegated clays
6. Paleozoic bedrocks and surficial loams
7. Isopach of Aralian sediments at 10 m

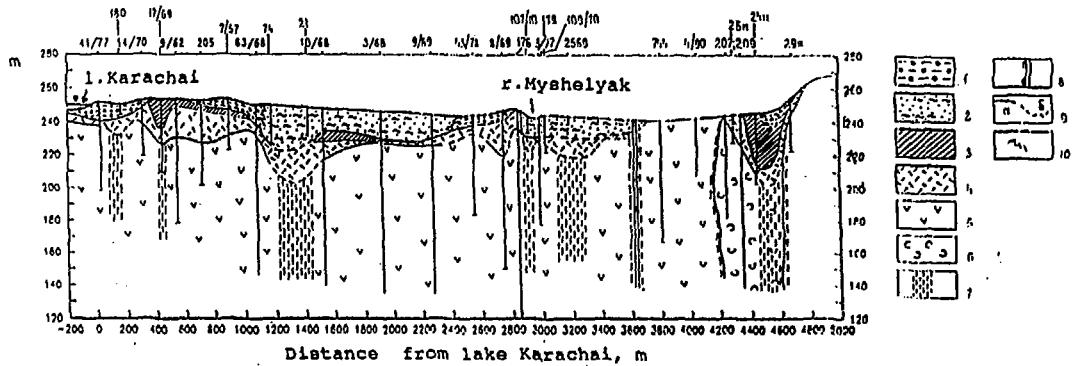


Fig. 6. Geological section I-I, coinciding with the axes of the southern branch of the contaminated water flow, migrating from Lake Karachai (prepared by B.T. Kochkin, 1993).

1. Late Miocene deluvial and proluvial loams with rare pebbles of quartz
2. Late Miocene alluvial sands and clays
3. Loams of the weathering crust
4. Weathered bedrocks
5. Porphyrites
6. Tuffs
7. Zones of ancient faults
8. Reactivated fault
9. Rock boundaries, actual (a) and assumed (b)
10. Facies boundaries

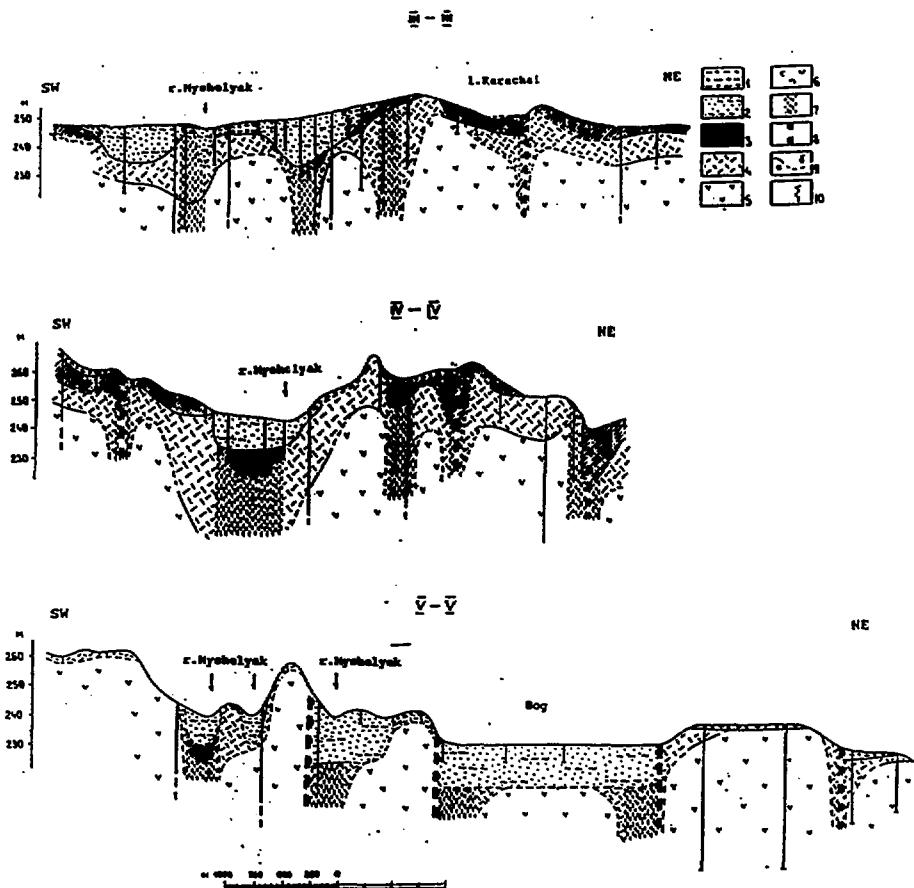


Fig. 7. Geological sections, reflecting structural complexity of contaminated water transport medium in the area of Lake Karachai (prepared by B.T. Kochkin, 1993).

- 1 Late Miocene deluvial and proluvial loams with rare pebbles of quartz
- 2 Late Miocene alluvial sands and clays
- 3 Loams of the weathering crust
- 4 Weathered bedrocks
- 5 Porphyrites
- 6 Tuffs
- 7 Zones of ancient faults
- 8 Reactivated fault
- 9 Rock boundaries, actual (a) and assumed (b)
- 10 Facies boundaries

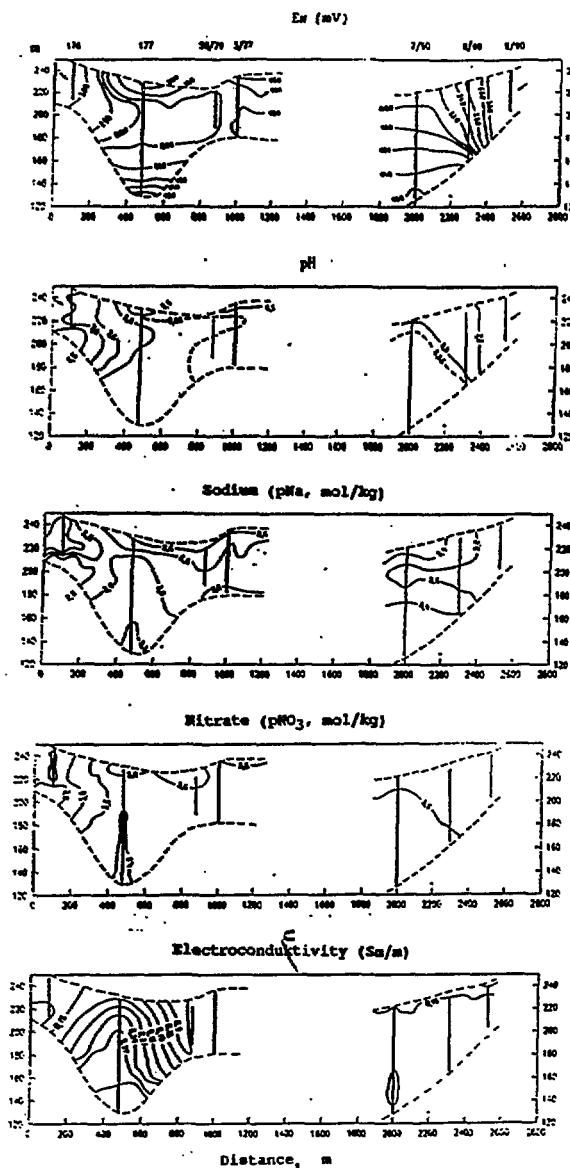


Fig. 8. Hydrogeochemical sections by the line II-II, along the right bank of the Mishelyak river. The area of open observation wells is within a dashed line. The section is prepared from the results of hydrogeochemical logging.

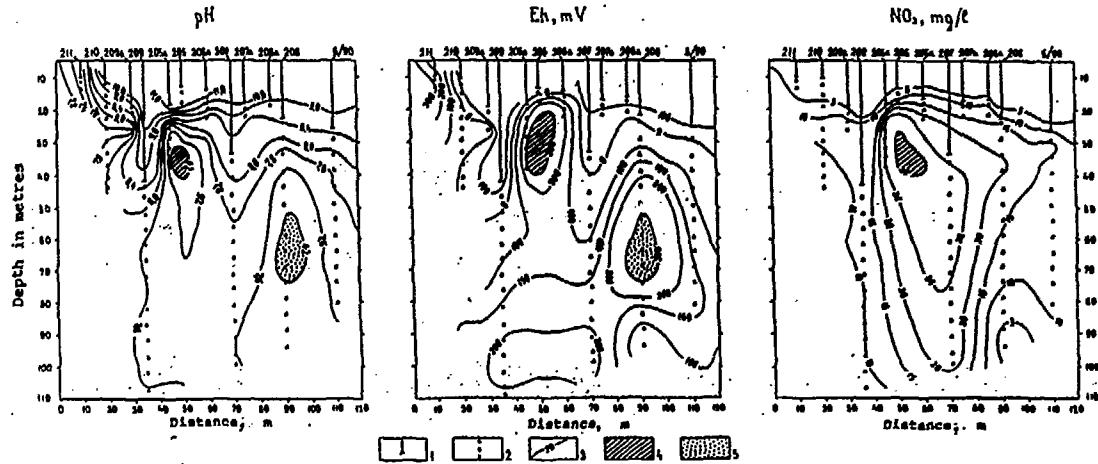


Fig. 9. Hydrogeochemical sections through the line of observation well cluster 205, using discrete hydrogeochemical logging data.

- 1 Well interval, cased with steel
- 2 Uncased well interval and observation points
- 3 Isopleth
- 4, 5 Zones of higher permeability of fissured rocks and, correspondingly, of excessive filtration of subsurface waters
- 4 Combined with the nitrate anomaly
- 5 Relatively pure infiltration waters

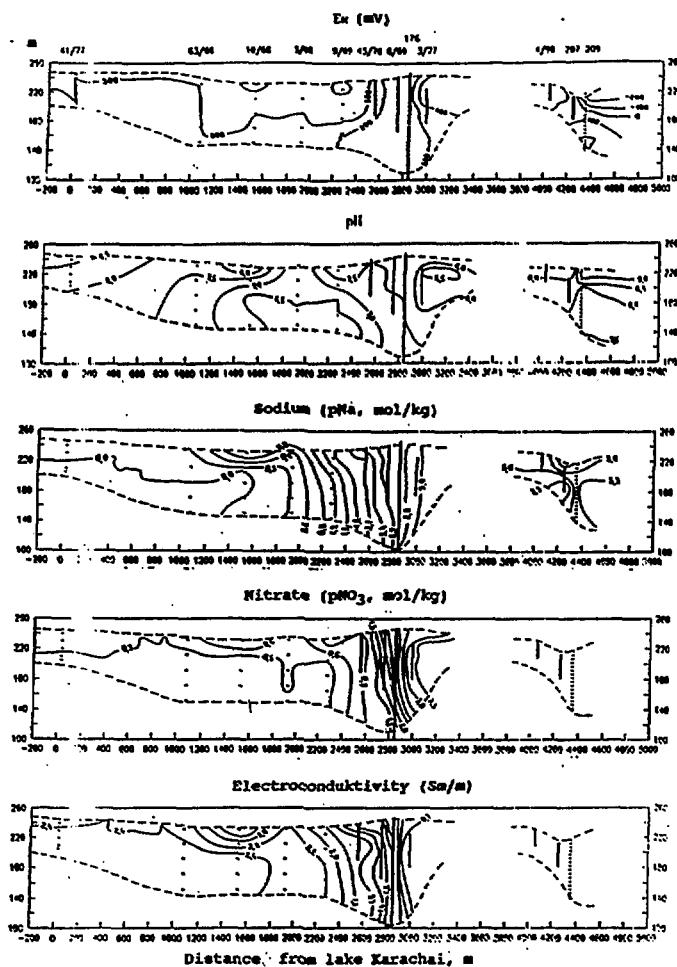


Fig. 10. Hydrogeochemical sections by line I-I, coinciding with the southern branch of the contaminated water plume, migrating from Lake Karachai.

Sections represent the observed structure of the contaminated water plume. The area of open observation wells is within dashed line. Sections are prepared from continuous hydrogeochemical logging data.

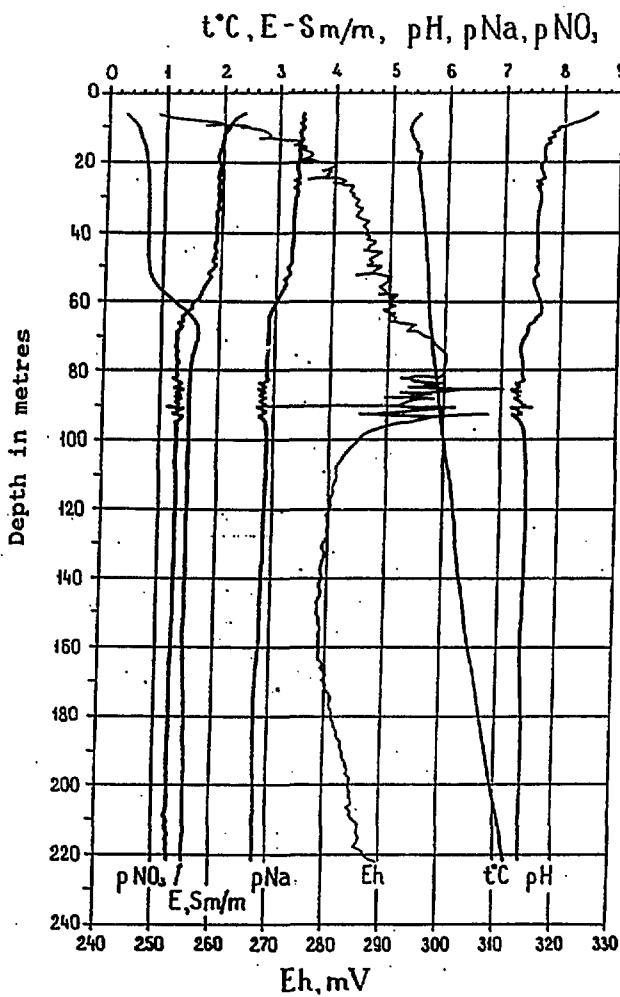


Fig. 11. Results of hydrogeochemical logging of well 176, which was executed before the well flushing with fresh water.

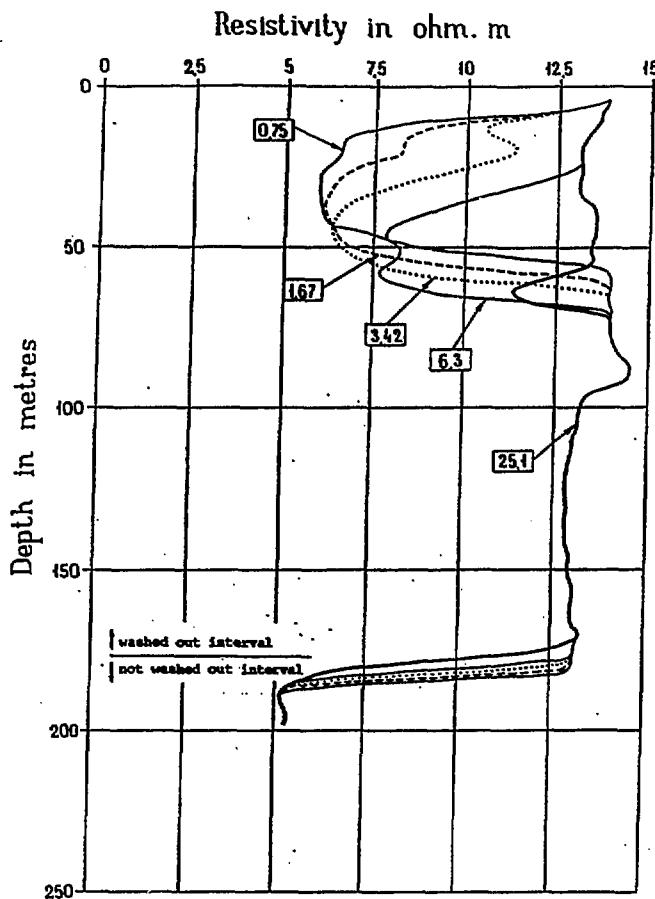


Fig. 12. Results of regime resistivity logging observations in well 176 after flushing with fresh water. Time intervals in hours after termination of well flushing are shown in rectangular boxes.

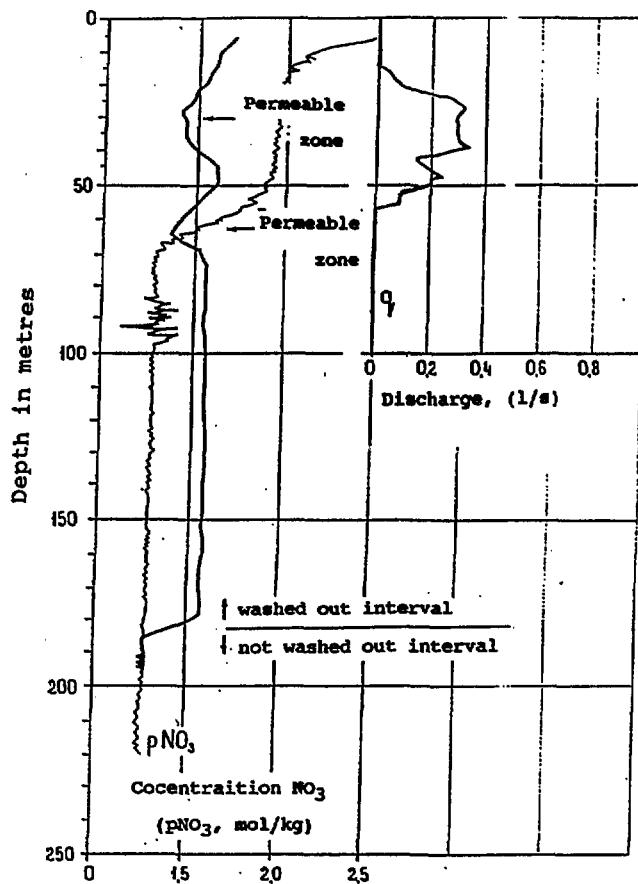


Fig. 13. Correlation of flow rate metering and nitrate logging in well 176. Nitrate logging was executed before (thin line) and after (thick line) the flushing of the well with fresh water.

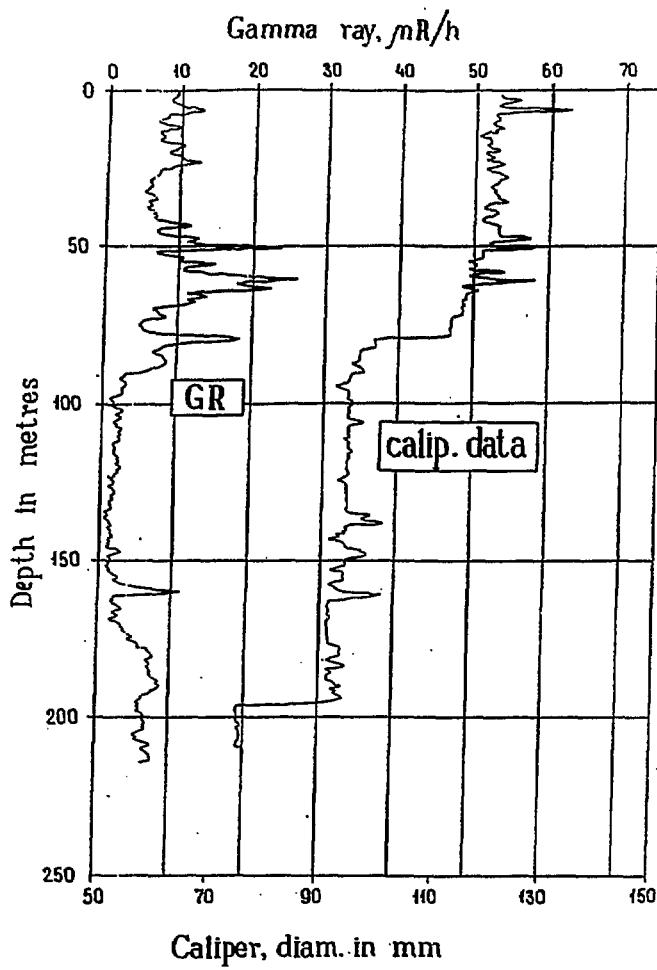


Fig. 14. Correlation of caliper logging and gamma-logging profiles in well 176.

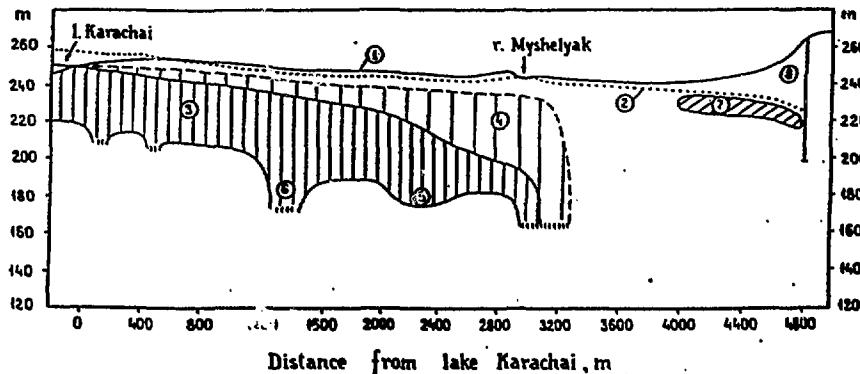


Fig. 15. Qualitative model of the distribution of contaminated subsurface waters, associated with Lake Karachai and the fly-ash impoundment, A-1.

- 1 Land surface
- 2 Interface of dense technogenic brines and fresh waters
- 3 Undiluted sodium nitrate brines
- 4 Sodium nitrate waters, mineralization of which is decreased owing to the dilution processes by surface waters, hydraulic dispersion, and sorption by enclosing rocks and brine structural traps 5 and 6
- 5 Lithological
- 6 Associated with fault tectonics
- 7 Body of alkaline reducing waters
- 8 Water intake well