

# Transformation of Groundwater Chemical Composition in the Zone of Influence of the Chita TPP-1 Ash Dump (Transbaikalia, Russia)

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**Abstract** –The filtrational leakages from the ash dump of the Chita TPP-1 led to the change of the natural hydrogen carbonate and sulfate hydrogen carbonate composition of groundwater to the sulfate and the hydrogen carbonate sulfate, and to the formation of the aureola of nonstandard drinking water with the excess of MPC for  $\text{SO}_4^{2-}$ , Mg, F, Si, total hardness and salinity level in the area of about 10 sq. km. The increase in Mg concentrations occurs in the most aquifer system, in the rest criteria - by means of ash dump waters. One of the characteristic features is high alkaline. The authors explain this by the hydrolysis of calcium oxide CaO in the ash. Inflowing of mineral substances from watercourses, draining the groundwater of the aureole, and subaqual discharge into the lake Kenon, the cooling pond and the source of technical water supply for TPP-1 caused the changes in the hydrochemical characteristics and deterioration of the quality of the lake water, which are not restored by pumping less mineralized water from the river Ingoda.

**Keywords** – ash dump; groundwater; chemical composition; maximum permissible concentrations; pollution.

## I. INTRODUCTION

In the Russian Federation, there are more than 170 coal power plants generating up to 30 million tons of ash and slag waste annually. More than 90% of them are stored in ash dumps [1], which are the sources of permanent pollution of air, soil, surface and groundwater. Surface water pollution is considered mainly due to the effect on the biotic components of aquatic ecosystems. In this respect, the lake Kenon, a cooling reservoir of the Chita TPP-1, stands out for its studying. [2-4 and others] There are few publications describing the influence of coal energy on the geochemical characteristics of groundwater. In addition to our own works [5, 6] we consider works of other scientists [7–9]. The purpose of this study is to present the nature and extent of the technogenic changes in the chemical composition of groundwater as a result of filtration leakages of one of the ash dumps, hence, expanding the database on the problem under consideration.

## II. OBJECTS AND METHODS

The objects of the study are the hydraulic ash dump (HAD) of the Chita TPP-1 (52.09787° N, 113.30390° E) and the water seepage below it along the relief and groundwater flow. HAD is located 3 km north-west of the TPP and the lake Kenon (Fig.

1). It is a dammed up storage in lowering of the relief of the Chitino-Ingodinsky intermountain valley. The area of the storage is about 115 hectares. More than 10 million tons of ash and slag wastes were accumulated in it during operation since 1973. So far, HAD has been almost filled, its second stage is under construction phase in the area, adjacent to the existing sections from the west.



Fig. 1. The Location TPP-1, ash dump and sampling points for ground and surface water: 1 - on the pulp discharge of the HAD; 2, 3, 8-10 - wells; 4, 7 - river Kadalinka; 5 - stream; 6 - spring. The arrows indicate the direction of groundwater movement.

The geological section of the ash dump foot is represented by a thin layer (up to 2 m) of quaternary sabulous deluvium, overlying interlaminated lower cretaceous sandstones, aleuolites and argillites. The aquiferous complex confined to them has high filtration coefficients (up to 35 m/day) and piezoconductivity (up to 3.9 106 sq m/day). According to the measurements of 2018, the groundwater level near the southern edge of the ash dump (point 3, Fig. 1) had been changed in the range of 10–16 m, depending on the filling of the settling sump. The hydraulic ash dump was filled with pulp without insulation of the basement rocks by a watertight screen, which led to significant filtration water losses (about 550 m<sup>3</sup> / h) and flooding of the TPP-1 site area and the airport runway in the

first years of the operation. To eliminate flooding, a complex of drainage works was performed. The natural drainage of groundwater in the HAD area is the river Kadalinka (points 4 and 7 in Fig. 1) and lake Kenon.

We used titrimetric (CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>), turbidimetric (SO<sub>4</sub><sup>2-</sup>), potentiometric (pH, Cl, F), photometric (Si, P, permanganate oxidizability), atomic absorption (basic cations, strontium, other metals) and other methods of analysis. For atomic absorption analysis we acidified the samples with chemically pure nitric acid to pH 2.0.

This paper presents the results of three-time hydrogeochemical testing over the monitoring network of the Chita TPP-1 for 2018, supplemented by a single sampling at points 2, 5 and 6 (Fig. 1). Water samples from wells, excepting self-pouring in the valley of the river Kadalinka (Fig. 1, point 2), were selected after pumping at least four volumes of the water column in each of them.

The chemical and analytical studies of water samples were carried out in accordance with the standard procedures in the INREC SB RAS laboratory of geo-ecology and hydrogeochemistry, certified for the production of natural water analyzes. We used titrimetric (CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>), turbidimetric (SO<sub>4</sub><sup>2-</sup>), potentiometric (pH, Cl, F), photometric (Si, P, permanganate oxidizability), atomic absorption (basic cations, strontium, other metals) and other methods of analysis.

For atomic absorption analysis, the samples were acidified with chemically pure nitric acid to pH 2.0.

The name of the chemical composition of water is given from 20% mg-eq. increasing the content of basic ions according to the standard OST 41-0-263-86 during hydrogeological works in Russia.

### III. RESULTS

The results of determination of the water samples chemical composition are presented in the table 1. For ash dump, a sample of June 7th was taken from a pond, the other two were taken from the pipeline in the discharge of pulp. Outside the flowing zone of filtration leakages is borehole 1068 (Fig. 1, p.10), the composition of its water can be considered as background. Kenon Lake was tested near the 24 kn well (p.9). In order to compare the table includes data from one of the boreholes of the Central Water Intake of Chita city, which is piping the same aquifer system of lower cretaceous water deposits as the boreholes in the area of the ash dump.

The chemical characteristics of water infiltration leakages of the ash dump are determined by the initial composition of the water used to transport the pulp, its interaction with ash in the pipeline, geochemical processes in the sump and during filtration through the bottom ash layer.

TABLE I. MACROCOMPONENT COMPOSITION OF WATERS OF THE ASH DUMP IN THE CHITA TPP-1 AND WATER POINTS IN THE AREA OF ITS INFILTRATION INFLUENCE

Sampling points (Fig. 1)	Sampling points	Index, mg/L (except pH and *Hd)												
		pH	CO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	F <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	TDS	Si	Hd**
Lake Kenon	07/06/2018.	8.60	9.00*	122.0	231.4	75.9	1.44	49.5	48.4	61.0	4.37	604.7	<0.50	6.51
	26/09/2018	7.80	8.80	167.8	188.0	56.8	1.34	47.5	41.8	45.5	3.72	555.4	2.07	5.85
	21/11/2018	8.20	1.76	198.3	206.4	66.8	1.31	69.1	48.3	41.1	4.78	639.8	1.22	7.48
1 – ash dump	07/06/2018	8.90	12.0*	44.2	717.5	114.1	9.97	199.3	45.7	84.3	7.47	1242	16.0	13.8
	26/09/2018	8.33	4.80*	68.3	513.9	65.2	1.77	148.2	49.4	56.6	5.53	919.0	17.8	11.5
	21/11/2018	9.30	36.0*	37.8	511.7	69.8	10.4	372.1	56.6	47.1	6.99	1205	17.0	23.3
2 – borehole	07/06/2018	7.10	25.7	215	657.7	70.5	0.39	140.6	109.3	61.4	6.58	1261	11.5	16.1
3 – borehole 241	07/06/2018	7.20	48.0	237.9	719.5	93.4	3.46	148.6	122.0	67.5	7.68	1406	7.18	17.6
	26/09/2018	7.10	93.1	478.2	567.8	85.0	1.75	119.9	175.7	26.2	4.34	1464	5.61	20.6
	21/11/2018	7.20	33.9	282.4	591.5	91.2	3.38	155.1	111.8	49.4	6.94	1307	5.64	17.1
4 – Kadalinka river	07/06/2018	8.00	6.16	350.8	509.2	41.7	0.97	129.1	96.9	54.8	4.71	1191	7.55	14.5
	26/09/2018	7.90	4.18	128.7	92.3	7.50	0.43	32.7	18.5	13.3	1.61	297.5	7.08	3.18
	21/11/2018	7.40	16.5	201.9	168.2	14.4	0.46	61.1	34.7	19.8	2.53	507.2	8.45	5.94
5 – creek	21/06/2018	8.00	14.7	777.8	542.5	6.53	0.19	148.5	186.7	29	5.17	1696	7.08	23.0
6 – spring	21/06/2018	7.20	26.0	259.8	637.8	82.2	0.57	155.2	116.4	57.0	6.70	1316	10.1	17.5
7 – Kadalinka river	07/06/2018	8.40	6.00*	253.2	68.6	5.02	0.43	23.8	42.8	25.5	2.71	429.4	4.86	4.76
	26/09/2018	7.90	2.64	80.5	24.2	2.65	0.33	16.9	4.08	7.34	1.20	139.4	7.61	1.19
	21/11/2018	7.40	7.48	101.3	25.6	3.25	0.33	22.1	6.78	8.93	1.64	174.7	8.13	1.67
8 – borehole 26kn	07/06/2018	7.20	67.3	230.3	654.2	58.8	1.65	121.0	129.3	55.6	7.56	1263	10.5	16.8
	26/09/2018	6.90	54.8	237.3	630.3	58.0	1.70	105.3	125.3	43.4	6.32	1212	11.4	15.7
	21/11/2018	6.80	59.8	237.9	633.6	60.5	1.65	140.9	96.3	65.8	6.83	1258	11.3	15.1
9 – borehole 24kn	07/06/2018	7.53	24.6	437.7	84.0	46.8	1.31	85.4	40.0	63.2	7.09	769.0	9.34	7.60
	26/09/2018	7.80	22.2	420.9	64.8	56.6	1.85	83.0	35.0	56.3	6.15	728.4	9.30	7.06
	21/11/2018	7.70	15.2	429.4	85.8	56.5	1.54	89.2	40.2	51.2	6.54	768.2	9.20	7.81
10 – borehole 1028	07/06/2018	7.20	30.4	212.0	46.5	7.30	0.30	48.7	15.0	14.2	2.50	349.9	8.33	3.69
	26/09/2018.	7.40	20.5	216.6	63.4	7.27	0.28	54.1	17.4	14.0	1.72	378.1	8.24	4.16
	21/11/2018	7.20	21.3	215.3	59.8	7.10	0.25	53.5	15.6	13.4	2.09	375.7	8.09	3.98
Water intake borehole MPC	2008	7.58	59.7	224.5	31.6	15.8	0.29	27.7	5.3	65.5	0.8	361.5	7.2	1.83
	-	-	-	500	350	1.2	-	40	-	-	-	1000	10.0	7.0

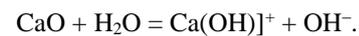
Note: \* – CO<sub>3</sub><sup>2-</sup>, \*\*Hd – hardness, rCa<sup>2+</sup> + rMg<sup>2+</sup>, mg-eq/L.

Technical water supply of the Chita TPP-1 has been carried out from lake Kenon since its launch in 1965. For the first twenty years, the composition of lake water had been changed from hydrogen-carbonate sodium-magnesium or magnesium-sodium to sulphate-hydrocarbonate thriple-component by cations. The most significant changes occurred in the basic anions. During the permissible period, the content of HCO<sub>3</sub><sup>-</sup> was 385-445 mg / l, and the sulfate ion was not exceed 25 mg / l, while its share in the amount of anions was 6.5-7% -eq. Over the years of the TPP operation the content of hydrogen carbonate was decreased almost threefold to the maximum, while the sulfate ion was increased more than 10 times.

On the one hand, the various directions of these components dynamics are determined due to a change in the water balance items, and, on the other hand, to the new sources involving in the formation of the salt balance of the lake water masses. The decrease in the concentration of carbonate components is caused by the injection of low-mineralized water (100-120 mg / l) from the river Ingoda to compensate losses in heat networks of water intake for the ash transportation and an increased free-water lake surface evaporation due to the warm water discharge from the turbines cooling system. The increase of SO<sub>4</sub><sup>2-</sup> concentrations is determined due to the influence of the existing and previous ash dumps located on the lake shore, and sulfur oxides in the composition of the gas and smoke emissions from TPP-1, as well as the discharges of industrial water from water treatment units and after cleaning the boilers, where sulfuric acid is used as one of the main reagents.

The initial increase in the concentrations of SO<sub>4</sub><sup>2-</sup> in the water entering the ash dump occurs during the transportation of ash, while the concentrations of calcium, silicon and strontium increase as well, the water salinity increases almost 2 times, but herewith the content of HCO<sub>3</sub><sup>-</sup> decreases several times. We explain the latter by the formation of CaCO<sub>3</sub>, according to which the water isoversaturated, as thermodynamic calculations showed it via HydroGeo program [10]. Further accumulation of sulfate occurs in the ash dump as a result of leaching it from the ash, the concentration of siderophil elements (Table II). On the contrary, pH decreases due to the limit of water migration of their high values.

The alkaline environment is one of the geochemical features of the water pulp and sedimentation tanks. For the ash dump of TPP-9 in Irkutsk, pH values varied in the range of 8.16–11.25 [8], and for the ash dump of TPP-1, taking into account the previously obtained data, were within 8.16–9.40. In our opinion, the reason for the high alkalinity is hydrolysis of calcium oxides, in this form the element is in the ash and slag waste, which can be seen in the reaction:



Not only the different proportions of water and ash in the pulp cause fluctuations in pH values, as it was explained by Pavlov [8], but also by the heterogeneous composition of the ash.

TABLE II. MICROELEMENTS IN WATERS OF ASH DUMP IN THE TPP-1

Sampling points (Fig. 1)	Index (Mn-Sr - mg/L, Co-Cu - µg/L)					
	Mn	Fe	Sr	Co	Ni	Cu
Lake Kenon	0.004	0.01	1.08	<0.30	2.06	3.42
	0.04	0.02	0.91	<0.30	4.08	4.86
	<0.01	<0.01	1.01	<0.30	<0.36	0.91
1 – ash dump	0.008	0.05	5.11	<0.30	<0.36	2.27
	0.07	0.56	3.03	<0.30	5.79	5.44
	1.09	42.3	6.86	2.92	149.6	78.0
2 – borehole	0.48	0.28	1.98	-	-	-
3 – borehole 241	0.62	1.87	2.31	2.56	6.79	2.16
	1.10	1.25	1.23	0.99	12.6	3.64
	0.19	9.55	1.90	1.20	1.11	3.62
4 – Kadalinka river	0.18	0.15	1.50	7.84	8.75	1.62
	0.09	0.07	0.38	5.11	6.29	3.80
	0.36	0.25	0.64	6.31	4.60	0.31
5 – creek	0.03	0.26	2.13	-	-	-
6 – spring	0.11	0.21	1.97	-	-	-
7 – Kadalinka river	0.01	0.15	0.36	<0.30	2.16	3.06
	0.03	0.06	0.16	<0.30	16.2	8.94
	<0.01	0.20	<0.01	<0.30	2.47	0.78
8 – borehole 26kn	1.52	1.07	0.83	39.4	90.5	2.42
	1.44	1.15	0.85	32.7	43.7	3.80
	1.31	9.85	0.82	117.5	110.0	2.98
9 – borehole 24kn	0.17	0.65	1.24	0.33	2.44	1.01
	0.08	0.79	1.30	<0.30	3.77	2.29
	0.12	3.86	1.20	2.28	12.9	2.60
10 – borehole 1028	1.13	0.84	0.37	3.54	6.04	2.18
	1.05	1.52	0.38	<0.30	1.88	2.11
	1.08	6.46	0.37	3.32	<0.36	<0.18
MPC	0.1	0.3	7.0	100	100	1000

Infiltration of the sulphate waters of the sump led to a change in the natural hydrocarbonate, as in the borehole intake, or in the sulfate-hydrocarbonate, as in well. 1068 (table I), on sulphate (borehole 241) or hydrocarbonate-sulphate types. Due to the groundwater feed, including through flowing borehole (Fig. 1), sulphate is included in the definition of the chemical type of water and the river Kadalinka, in drought period and in low water it dominates. With an increase in the river flow due to the influx from headwater, the concentrations of  $\text{SO}_4^{2-}$  decrease in the river water, but at the lower point it is constantly higher than at the top. The ratio of water concentrations of sulfate in the ash dump and in some water points in its zone of influence is presented in Fig. 2. The data from the last two measurements in the point 1 refer to the pulp.

The change of the chemical type of water in the zone of the ash dump influence occurs in the upper hydrodynamic zone near the groundwater level or when deep water is mixed when it rises in places of discharge. These cases illustrate the data by the stream in the point 5. The highest concentration of  $\text{HCO}_3$  and water mineralization display the participation of deeper drainage waters in its feeding.

Due to the filtration leakages from the ash dump, a hydro-geochemical aureole in groundwater was formed, it grew to over 3 km with an area of about 10 sq km having excess of maximum permissible concentrations (MPC) for drinking and household water not only in sulphate, but also Mg, F, Si, total hardness and mineralization. The MPC values according to standard adopted in Russia (Sanitary Regulations and Norms 2.1.4.10749-01) are presented in the tables I and II.

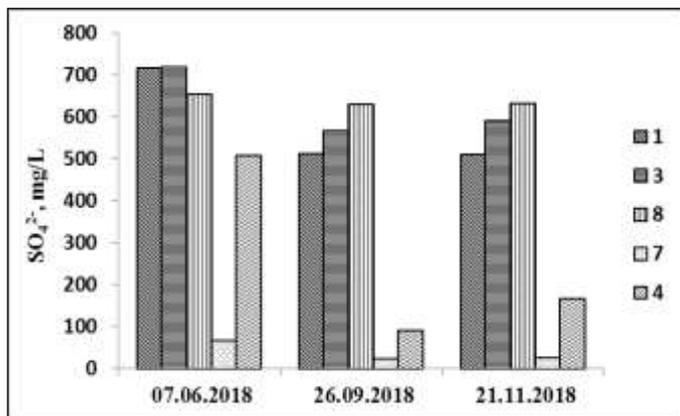


Fig. 2. The ratio of sulfate concentrations in water according to points and timing of testing. Point numbers correspond to fig. 1 and tab. I.

Magnesium stands apart among non-conforming indicators. If for the other components listed above, their intake with leakages from the sump is obvious, then the Mg content in the sump water only slightly exceeds the MPC and is almost the same with Kenon lake water, while in groundwater it increases several times. There are no arguments to prove this phenomenon by the influence of the ash dump; it is rather caused by the natural hydro-geochemical characteristics of the site. Growing concentrations of Mg increase the hardness of the water, which sometimes is below the permissible norm in calcium only.

The enrichment of water in the aquifer system as a result of its interaction with the enclosing rocks is also possible by silicon. Previously, the excess of permissible concentrations by it in borehole samples (point 2, Fig. 1), a spring (point 6) and the river Kadalinka in the drought period, we interpreted [5, 6] as a consequence of the inflow of Si with the infiltration waters of the ash dump. But the data of the borehole 241 (point 3) which is located much closer to HAD and which Si concentrations in water is turned out to be below 10 mg / l (Table I), show that its high contents can be formed in situ, the same nature of high concentrations in excess of MPC for Mn, Fe, Co and Ni. Only by Manganese and Ferum it is determined by the physicochemical conditions of the aquatic environment, whereas for cobalt and nickel a local source is needed in water-bearing rocks.

#### IV. CONCLUSION

Thus, the transformation of the chemical composition of groundwater in the zone of influence of filtration leakages from the ash dump of the Chita TPP-1 manifested itself in the following:

1. Natural hydrogen carbonate and sulfate hydrogen carbonate composition of groundwater has been changed into sulfate and hydrogen carbonate sulfate
2. The total mineralization of water has been increased;
3. A vast areole of groundwater pollution has been formed. It takes over 3 km in the area of about 10 sq. km. having the excess of acceptable concentrations of sulfate ion, magnesium, fluorine, silicon, the values of the total salt content and water hardness for drinking use.

Above the maximum permissible concentration within the boundaries of the aureole there is also the concentration of silicon in water, which may be the result of filtration from the ash dump, as well as it can be formed in the aquifer system during the interaction of water with enclosing rocks. The cases of drinking standards excess for iron, manganese, cobalt and nickel are not related to the effect of the ash dump.

River is the stock draining this areole.

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