Geochemical peculiarities of underground and surface waters in the area of influence of the ash dump of the Chita CHPP-1

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Abstract. As a result of filtration leaks from the ash dump, an envelope with a length of over 3 km up to the lake Kenon has been formed along the flow of groundwater bicarbonate-sulphate waters with a mineralization of more than 1.0 g/l, substandard in terms of drinking waters relative to the total mineralization, the magnitude of stiffness and the content of magnesium and silicon. Pollution of natural waters in the areas of disposal of ash dumps is a common problem of coal power plants and thermal power plants [1, 2]. In this regard, the Chita CHPP-1 is no exception. The purpose of this message is to show the change in the chemical characteristics of groundwater and surface water in the zone of influence of its hydraulic ash dump, based on the results of the work performed by the authors. The study was based on the results of hydrogeochemical studies of natural and man-made objects for 2002, 2008 and 2015. Samples were taken in the autumn-summer period (open water period), which, given the fairly stable hydrogeochemical regime within the annual cycle, is fairly representative.

1. Introduction
Pollution of natural waters in areas where ash dumps are located is a common problem of coal-fired state district power stations and thermal power plants [1, 2]. In this respect, Chita CHPP-1 is no exception. In addition to the ash dump itself, the objects of research were the groundwater points in the area of its location, as well as the brook, Kadalinka and Lake Kenon, falling into the zone of influence of the ash dump.

The ash disposal area (GZO) of the Chita CHPP-1 is located 3 km north-west of its site and the lake. Kenon (figure 1) is a reservoir enclosed by dams in the lower relief of the Chita-Ingodinsky intermontane depression. Its area is about 115 hectares, it has been in operation since 1973. To date, the GZO is practically filled, its second stage is under construction on the site adjacent to the existing sections from the west.
Figure 1. The location of the ash dump of Chita CHPP-1 and the points of water sampling: 1 – ash dump settling pond; 2 – pulp discharge section; 3 – pipe draining the pulp discharge section; 4 – spring discharge; 5 – well in the village Cheryomushki; 6 – well in the valley of the Kadalinka River; 7, 8 – Kadalinka River.

In hydrogeological terms, the site is confined to the axial part of the Chita-Ingodinsky artesian basin in the transit zone of the underground waters of the aquifer complex of the Lower Cretaceous normal sedimentary deposits of the Doroninsky suite. The rocks of the complex to a depth of 500–600 m are mainly represented by siltstones and sandstones with an approximately equal ratio of members with a thickness of 50–70 to 110–130 m. Sandstones are predominantly aquifers. The filtration properties of rocks vary greatly, the maximum filtration coefficients of sandstones reach 35 m/day. The waters of the complex in the upper hydrodynamic zone (at the first aquiclude) are groundwater, with depth they become pressurized.

2. Materials and methods
Chemical-analytical determinations of macro- and microcomponents were carried out in a certified laboratory of INREK SB RAS using standardized methods. Titrimetric (CO$_2$, HCO$_3^-$, CO$_3^{2-}$), turbidimetric (SO$_4^{2-}$), potentiometric (pH, Cl, F), photometric (Si, P, permanganate oxidizability), atomic absorption (basic cations, strontium, other metals) and other methods of analysis. Water saturation for possible secondary mineral phases was determined by thermodynamic calculations using the HydroGeo program [3].

3. Results
The chemical composition of the water in the ash dump settler was sulphate magnesium-calcium, the content of sulphate ion did not exceed 600 mg / L. The main source of its high concentrations is sulphide sulfur (in the form of pyrite, marcasite) contained in the burning coal and in the mineral ash-forming components. Some contribution is also made by sulfuric acid used by CHPP-1 when cleaning boilers from scale. The salinity of water, according to data for 2002-2020, in the summer period varied from 0.77 to 1.14 g / L. These fluctuations are due to the dynamics of the composition of the water used for ash removal, the different composition of the CHP-1 process waters discharged into the ash dump, etc. The pH value of the settler water is alkaline (pH up to 9.4). Another characteristic feature is high fluorine concentrations. Data on the chemical composition of the sedimentation tank and groundwater in the zone of its influence for three sampling periods are presented in Table 1.

Table 1. The physicochemical characteristics of the waters of the settling pond of the hydro-ash dump of the Chita CHPP-1, ground and surface waters in the zone of its infiltration influence (in mg / L, except for pH).

| Component | Ash dump | Spring discharge | Well | Kadalinka river |
|-----------|----------|------------------|------|-----------------|
| pH        | 9.38     | 9.33             | 9.85 | 9.27            | 6.64 | 6.84 | 7.58 | 7.29 | 7.26 | 8.06 |
| CO₂⁺      | 0.0      | 0.0              | 0.0  | 0.0             | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| HCO₃⁻     | 126.8    | 104.7            | 18.9 | 433.1           | 303.1| 554.1| 263.5| 281.1| 226.3| 208.6|
| CO₂⁻      | 10.8     | 9.0              | 13.8 | 0.0             | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| SO₄²⁻     | 600.0    | 453.0            | 592.9| 504.0           | 378.0| 409.2| 576.0| 415.0| 455.7| 252  |
| Cl⁻       | 70.8     | 102.4            | 122.6| 39.8            | 52.5 | 66.5 | 50.2 | 67.6 | 66.5 | 16.2 |
| F⁻        | 16.9     | 15.8             | 8.68 | 0.91            | 0.46 | 0.50 | 1.12 | 2.08 | 2.23 | 0.66 |
| NO₃⁻      | 0.71     | 6.2              | 2.66 | 0.68            | 2.97 | 0.88 | <0.62| 1.96 | 0.44 | 0.60 |
| Ca²⁺      | 195.0    | 101.6            | 212.9| 136.3           | 141.1| 177.4| 156.5| 166.8| 150.8| 110.8|
| Mg²⁺      | 48.5     | 56.2             | 25.8 | 112.0           | 63.2 | 102.9| 86.4 | 48.4 | 63.7 | 28.8 |
| Na⁺       | 62.3     | 90.8             | 85.2 | 50.4            | 44.3 | 46.2 | 55.4 | 63.8 | 52.8 | 23.7 |
| K⁺        | 11.1     | 4.5              | 2.9  | 9.2             | 2.9  | 2.9  | 6.8  | 2.7  | 1.9  | 0.67 |
| NH₄⁺      | 0.21     | -                | -    | 0.45            | -    | -    | 1.11 | 0.2  | -    | -    |
| Σ ions    | 1144     | 949              | 1086 | 1286            | 986  | 1360 | 1196 | 1050 | 1021 | 641.5|
| P         | 0.205    | 0.145            | 0.058| 0.099           | 0.083| 0.072| 0.14 | 0.095| 0.065| 0.075|
| Si        | 6.5      | 12.2             | 15.8 | 11.5            | 11.1 | 12.3 | 11.4 | 10.9 | 11.5 | 4.8  |
| Sr        | 2.00     | 1.30             | 14.9 | 1.00            | 1.29 | 5.99 | 0.60 | 1.21 | 2.84 | 0.16 |
| PO₄³⁻, mg O₂ / l | 3.67 | 2.00 | 1.02 | 3.01 | 1.60 | 1.27 | 3.60 | 4.20 | 1.10 | 3.80 |

According to the content of the hydrocarbonate ion in the sump water, the sample stands out sharply at the last sampling period. The reason for this decline is unclear but it may be associated with the increasing calcium entry into an aqueous medium, and with the reduced content carbonate components in the incinerated charcoal. In the first case the formation of secondary carbonates has to amplify, especially the dolomite in which the water supersaturated (table 2). In particular, the equilibrium weight of dolomite CaMg(CO₃)₂ according to the samples taken from the settler for 2002 and 2015 g of are equal to 32 and 5.3 mg (per 1 liter, respectively, with an insignificant mass of calcite CaCO₃ in both cases (less than 0.01 mg). It is known that in the case of the high-calcium and bottom-ash waste the carbonate scale formations grow, and as a consequence, the filtration properties of the underlying rocks ash dumps significantly alter, as a result of secondary carbonate formation. Thus, we noted a decrease in filtration losses from 14.5 to less than 1.0 thousand M³/day at Berezovsky TPP (KATEK). Whereas the filter coefficient of the underlying rocks by 1998 was estimated at 0.04 m /day at 5–10 m/day at the end of the 1950s, before the GZO was put into operation [4]. So far, no such thing has been observed in the ash dump of the Chita CHPP-1. But the saturation of carbonate
minerals, and a higher one at that, obtained on other aqueous samples, including the terrestrial waters. And the hydrogen concentration there is by more than one order higher. Therefore, the second reason is more likely, if we exclude the possibility of others.

Table 2. Equilibrium amount of sediment of the main minerals (mg / L) according to the samples taken on 27.07.2015.

| Mineral and its formula | settling pond | Water samples | Lake Kenon |
|------------------------|---------------|---------------|------------|
|                        |               | spring discharge | well |                   |
| Quartz; SiO₂           | 28            | 21            | 17       | 0                   |
| Vitlockite (phosphate); Ca₃(PO₄)₂  | 0.083        | 0.1       | 0.1      | 0.11                |
| Fluorite; CaF₂         | 14            | 0            | 0        | 0                   |
| Dolomite; CaMg(CO₃)₂  | 5.3           | 14.0         | 35.0     | 14.0                |
| Celestine; SrSO₄       | 29            | 9.6          | 3.5      | 0                   |

4. Discussions
There are practically no geochemical barriers that significantly limit the accumulation of sulfate in ash dump waters; saturation in gypsum with CaSO₄ 2H₂O is not achieved. The formation of celestite does not markedly affect the concentration of sulfate in the water. Even with the complete sedimentation of celestite in the sample of the sedimentation tank for 2015, the sediment is going to be no more than 15.3 mg / L SO₄²⁻.

Fluorine during filtration through dump-ash sedimentation is already substantially removed from the water medium. When the content in the water in the pulp discharge section was present (point 2 in figure 1) 6.9–16.9 mg / L in the drain from the drainage pipe (point 3), it decreased to 0.48–1.99 mg / L [1]. The removal of fluorine from the filterable waters is due to its precipitation as a result of fluorite formation, in which the pulp and settler waters supersaturated. According to calculations up to 32 mg / L CaF₂ can precipitate from the sump water [5].

Water filtration from ash dump was manifested most significantly in the underground waters in the growth of the sulfate ion content, as seen from the spring unloading and flowing wells in brook valley of Kadalinka (points 4 and 6 in figure 1). In the samples from a recent sampling the concentration of SO₄²⁻ thereon were 409 and 456 mg / L, respectively (table 1). Earlier, at these points, up to 635 and 580 mg / L of sulfates were recorded. The groundwater in the area of the power plant ash disposal area, outside of its impact zone the concentration of sulfate ion varied from 22.8 to 66.0 mg / L (the wells in the Cheryomushki settlement (point 5 in figure 1) near the Kutuzovka settlement and in the Zastep village to the northwest of the ash dump, upstream of the groundwater flow), the anionic composition of the waters is hydrocarbonate. The decrease in the amount of SO₄²⁻ in terrestrial waters compared to the ash disposal is associated with the mixing of filtration leaks with less sulfate aquifer waters, while the content of hydrogen in this case, on the contrary, is higher, as outside of the zone of influence of CHPP-1 it is many-fold higher. So, in the case of a well in the village. Cheryomushki the concentration of HCO₃⁻ was 664.7 mg / L [5]. The high content of hydrogen carbonate in this well’s water is, apparently, due to the local enrichment in carbonates of the water-bearing rocks (sandstones carbonate cement) in the adjacent areas.

As a result of unloading groundwater, the content of SO₄²⁻ in the water of the Kadalinka river at the estuary site (point 8 in figure 1) reached 528 mg / L [6], and in August 2014 even 534 mg / L [7]. Above the sulphate discharge zone, more than 51 mg / L was not observed. The brook discharge outlet thus is one of the ways of sulfates’s penetration into Lake Kenon [8, 9]. They also arrive through the unloading at the groundwater directly into the lake along the northwest coast, which can reach about 1 550 m³ / hour [10].

The enrichment of groundwater with silicon is also associated with the ash dump. The growth of its concentration in the water of the settling tank in comparison with the lake Kenon, from which water is taken for transporting ash, can to some extent be compared with nitrogen terms, and it is determined
by the temperature of the ash and the high alkalinity of the water interacting with it. The source of silicon is aluminosilicate ash components, while at saturation with respect to quartz, its concentrations are mainly controlled by amorphous silica, for which equilibrium is not achieved. The possible formation of secondary clay minerals (beidellites, montmorillonites, illites, etc.) has practically no effect on the silicon content, both in the sedimentation tank water and in the groundwater, their precipitation in total does not exceed 0.1 mg / L.

As a result of filtration from the ash dump of the Chita CHPP-1, a halo was formed with a length of more than 3 km up to Lake Kenon of hydrocarbonate-sulphate waters with a salinity of more than 1.0 g / L, substandard in terms of drinking and of the total mineralization, the value of hardness and the content of magnesium and silicon. Due to the mixing of filtration leaks with groundwater of the aquifer, the content of sulfate ion decreases compared to the ash disposal area, and bicarbonate increases due to its higher content in groundwater, but sulfate remains the dominant anion in the polluted zone. During the period of over 40 years of operation, the ash dump remains a source of groundwater pollution, which indicates the absence of clogging of the underlying rocks, which is significant for reducing filtration losses, and an insignificant scale of secondary mineral formation.

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