Technogenic effect of liquidation of coal mines on earth’s entrails: hydrogeochemical aspect

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Abstract. The authors of the paper have established the geochemical features of the composition of underground waters and regularities of their formation in the areas of the liquidated coal mines of Russia and Ukraine. It is shown that the mine flood resulted in the formation of technogenic waters which geochemical specificity originates in the feeding field and is transformed in the direction of the filtration flow. It depends on the geological structure of sedimentary basins and the presence in the coal and supra-coal beds of the marine, salt-bearing and freshwater groups of geological formations. The water types are distinguished characterizing the conditions and processes of their formation that may be the regional markers in the hydrochemical and geological constructions. The technogenic waters influenced the safety of the underground waters, sources of water supply of the regions, and surface water channels. The pollutions are of local character in space.

1. Introduction

The relevance of this study is defined by the wide development of the processes caused by the flooding of coal mines. The flood of big volumes of the underground workings is a poorly known factor of the technogenic action on the entrails, causing the change of the hydrochemical background and forming in the upper part of the underground hydrosphere the new geochemical types of waters not characteristic of it before. So all such investigations are of great importance [1–4]. This paper presents the results of investigations of waters in the areas of the liquidated coal mines of such large coal basins of Russia and Ukraine as Sakhalinsky, Razdol’nensky, Partizansky, Uglovsky, Kuznetsky, Chelyabinsky, Kizelovsky, Pechorsky, and Donetsk (Fig. 1). The investigations are directed at the determination of geochemical features and formation regularities of the underground water composition in the districts of the liquidated coal mines. The tasks set covered a wide range of problems from the formation conditions of the water composition in the natural-technogenic structures to the concrete effect of the technogenic waters on the natural environment. These tasks are directed at the solution of a complicated scientific-practical problems of the rational nature management.
2. Objects and methods of investigation
The work is based on the continuous, standardized by methodology and technique, process of observations and measurements of the indicators characterizing the hydrodynamic features of the coal mine flood, as well as the fluctuations of compositions of the underground and surface waters. The hydrogeochemical samples for analysis of cations and sulfates were filtered through the cellulose filter (0.45 mm) at the place of sampling to remove the suspension and acidified with nitric acid. To determine the ions, the samples were also filtered and gathered into the polyethylene vessels without acidifying. The unstable parameters were determined at the place of water sampling. The analytical investigations were carried out at the Analytical Center of the Far East Geological Institute, FEB of RAS (accreditation certificate N ROSS RU.0001.518986). The element contents in waters were determined with the methods of mass-spectrometry with plasma coupled by induction at the spectrometer Agilent 7700 (Agilent Technologies, USA) and atomic-emission spectrometry with plasma coupled by induction at the spectrometer iCAP 6500Duo (Thermo Scientific Corporation, USA). Roentgenographic analyses of mineral phases were performed with a DRON-3 diffractometer with monochromatized radiation and a D8-Discover microdiffractometer. The micromorphology and composition of mineral phases were studied using the scanning electron microscopy ZEISS EVO 50XVP equipped with the roentgen energy-dispersion spectrometer INCA Energy.

3. Results of investigations and discussion
The hydrodynamic observations established that the regime of the mine flood was defined by the hydrogeological stratification of the supra-coal and coal masses, conditions of development of coal beds, the quantity of the water inflow, and the capacity characteristics of the drained massive.

Through the coal mine flood the underground water-bearing horizons form the hydraulically related technogenic water-bearing complex that differs from the natural one in the filtration, level, and chemical characteristics [5, 6]. The waters show specific features and parameters of chemical composition that originates in the feeding field and is transformed in the direction of the filtration flow (Fig. 2).

The comparison of ratios of the main ions and cations of the underground waters testifies to the regional regularities in the distribution of the macrocomponents. The regularity of the macrocomposition change is most clearly traced in the distribution of hydrocarbonate and sulfate ions.
The underground waters of the basins situated in the west of Russia and in Ukraine (Chelyabinsky, Kizelovsky, Donetsky) have higher concentrations of sulfate-ion (up to 100% equivalent) and chlorine (up to 80% equivalent). The contents of hydrocarbonate ions here decrease to 7% equivalent, and in Kizelovsky basin – to 0% equivalent. The basins located to the east (Kuznetsky, Razdol’nensky, Partizansky, Uuglovsky, and Sakhalinsky) contain higher concentrations of hydrocarbonates (30 to 100% equivalent) and variations of the sulfate-ion contents to 70% equivalent. In this case the pH of the waters in Razdol’nensky, Partizansky, Uuglovsky, Sakhalinsky, Kuznetsky, Donetsky, Pechorsky, and Chelyabinsky basins varies from 5.8 to 10.4 and in Kizelovsky from 7.9 to 2.5.

![Figure 2. Correlation of the main cations and anions in the underground waters of the areas of the liquidated mines of coal basins (1–6): 1 – Razdol’nensky, Partizansky, Uuglovsky (Primorye); 2 – Sakhalinsky; 3 – Kuznetsky; 4 – Chelyabinsky; 5 – Kizelovsky, 6 – Donetsky.](image)

The regional regularities of the composition change of waters formed in the districts of the liquidated mines are defined by the features of the geological structure of sedimentary basins and, first of all, by the presence of the marine, salt-bearing, and fresh-water groups of geological formations in the coal and supra-coal beds. It is shown that in Donetsky, Kizelovsky and Chelyabinsky basins the water composition is defined by the alternating facies of different salinity – marine, salt-bearing, and freshwater ones. In Pechorsky basin it is defined by homogeneous marine facies, and in Kuznetsky, Razdol’nensky, Partizansky, Uuglovsky and Sakhalinsky basins by freshwater facies.

The shift of the water pH value to the acidic field (Kizelovsky basin) takes place when the scales of the CO₂ formation begin to exceed the HCO₃⁻ amount, and the growth of PCO₂ (the partial pressure of CO₂) causes the increase of the hydrogen ion concentration that results in the formation of H₂CO₃ (Table 1). The waters with pH = 2–4 may have a mixed cation composition. Within the pH range of 4–6, the waters turn to be of the calcium (magnesium-calcium) cation composition, and at the pH > 8.0 they become sodic (Fig. 3).

| Form   | pH 2*** | pH 4*** | pH 7**  | pH 8**  | pH 9*   |
|--------|---------|---------|---------|---------|---------|
| H₂CO₃  | 6.65e+02| 8.73e+02| 4.50e+01| 8.18e-01| 1.87e-01|
| HCO₃⁻  | 7.64e-02| 3.35e+00| 2.39e+02| 5.51e+01| 2.88e+01|
| CO₂ ²  | 1.17e-09| 1.47e-06| 1.49e-01| 4.84e+01| 5.62e-01|
| CO₂    | 4.14e+01| 5.03e+01| 3.10e+00| 6.00e-02| 1.00e-02|
| H⁺     | 5.02e+00| 1.19e-01| 8.81e-05| 7.88e-06| 3.52e-06|
| PCO₂   | 3.11e+01| 3.99e-01| 2.05e-02| 3.75e-04| 8.78e-05|

*Note. Systems: * – “dolomites-water”; ** – “limestone-water”, *** – “water-rock” of Kizelovsky
Figure 3. Dependence of the $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Na}^+$/$\text{K}^+$ concentrations of pH in underground waters of coal basins (1–9): 1 – Donetsky, 2 – Kizelovsky, 3 – Kuznetsky, 4 – Partizansky, 5 – Pechorsky, 6 – Razdol’ensky, 7 – Sakhalinsky, 8 – Uglovsky, 9 – Chelyabinsky; 10, 11 – the line averaging the position of figurative points: 10 – after [7], 11 – the authors’ data.

Using the calculation of the following commonly accepted correlations [8, 9]: I Hydrocarbonate class – $r_{\text{HCO}_3^-} > r_{\text{Ca}^2+r\text{Mg}^2}$; II Sulfate class – $r_{\text{HCO}_3^-} < r_{\text{Ca}^2+r\text{Mg}^2} < r_{\text{HCO}_3^-}+r_{\text{SO}_4^{2-}}$, IIIa (magnesium group) – $r_{\text{Ca}^2} > r_{\text{Na}^+}$, IIb (calcium group) – $r_{\text{Ca}^2} < r_{\text{Na}^+}$; III Chloride class – $r_{\text{HCO}_3^-}+r_{\text{SO}_4^{2-}} < r_{\text{Ca}^2+r\text{Mg}^2}$ ($r_{\text{Cl}^-} > r_{\text{Na}^+}$), IIIa (chlorine-magnesium group) – $r_{\text{Cl}^-} < r_{\text{Na}^+}+r_{\text{Mg}^2}$, IIIb (chlorine-calcium group) – $r_{\text{Cl}^-} > r_{\text{Na}^+}+r_{\text{Mg}^2}$; IV Acid waters – $r_{\text{HCO}_3^-} = 0$, where $r$ is the component concentration in mg-eq/dm$^3$, the authors have elaborated the methodological bases of hydrochemical forecasting at the flood of coal mines depending on the formation belonging of the rocks of the supra-coal bed. Three water types have been distinguished that characterize the conditions and processes of their formation in the natural-technogenic structures. It is established that the I $\text{HCO}_3^-–\text{Ca}$, I $\text{HCO}_3^-–\text{Mg}$, IIa $\text{HCO}_3^-–\text{Ca}$, IIa $\text{HCO}_3^-–\text{Mg}$, IIa $\text{SO}_4^{2-}–\text{Mg}$ waters are formed exclusively through the incongruous dissolution of minerals of the volcanogenic-terrigenous water-enclosing rocks of the fresh-water facies. The IIa $\text{SO}_4^{2-}–\text{Na}$, IIb $\text{HCO}_3^-–\text{Na}$, IIb $\text{SO}_4^{2-}–\text{Na}$, IIb $\text{SO}_4^{2-}–\text{Ca}$, IIb $\text{SO}_4^{2-}–\text{Mg}$, IIIa $\text{SO}_4^{2-}–\text{Ca}$, I, IIa, IIb and IIIa $\text{Cl}–\text{Na}$ waters are formed through the congruous dissolution of minerals of the sulfate and chloride rocks in whose paragenesis the limestones and dolomites participate. The IIa $\text{SO}_4^{2-}–\text{Na}$, IIb $\text{SO}_4^{2-}–\text{Ca}$, IIb $\text{SO}_4^{2-}–\text{Mg}$ and IIIa $\text{SO}_4^{2-}–\text{Ca}$ waters are formed through the dissolution of the rock-forming minerals of gypsum-carbonate, predominantly not-salt-bearing, beds. The I $\text{HCO}_3^-–\text{Na}$, I $\text{SO}_4^{2-}–\text{Na}$ and IIb $\text{HCO}_3^-–\text{Ca}$ waters can be formed through both congruous and incongruous dissolution of the rock-forming minerals.

Depending on the regional features of the location of the natural-technogenic structures, the hydrochemical aureoles of the underground waters originate with higher contents of different components governed by the natural geochemical processes favorable for their migration and accumulation. A set of the components and their migration forms and concentrations have been determined and respectively limited with regard to the thermodynamics. Acid waters of the Kizelovsky coal basin with high values of the redox potential ($\text{pH} < 5$; $\text{Eh} > 400$ mB) concentrate $\text{Be}$, $\text{Cd}$, $\text{Co}$, $\text{Li}$, $\text{Ni}$, $\text{Mn}$, $\text{Pb}$, $\text{Zn}$, $\text{B}$, $\text{Fe}$, $\text{Si}$, $\text{Al}$, and also can accumulate $\text{Hg}$, $\text{Be}$, $\text{As}$, $\text{S}$, $\text{Cr}$ (VI), $\text{NO}_3^-$, and others. According to data of N.G. Maksimovich with coauthors [10], significant concentration of iron in Kizelovsky basin (up to 5 g/dm$^3$) result in the contamination of rivers over tens of kilometers. Under this technogenic effect, about 80 tonnes of hydroxides of iron and aluminium with high contents of $\text{Mn}$, $\text{Cu}$, $\text{Ni}$, $\text{Zn}$, $\text{Pb}$ and $\text{Cd}$ deposit on the stream beds every day [10]. Dissolution and diffusion desalting of the rocks of carbonate, sulfate, and halogen formations (Donetsky and Chelyabinsky basins) favor the concentration of the $\text{Cl}^-$, $\text{CO}_3^{2-}$, $\text{HCO}_3^-$ и $\text{SO}_4^{2-}$ ions in the water solution. It is apparent that the thicker carbonate, sulfate, and halogen horizons in a coal bed, the more dangerous are the underground waters in the technogenic complexes of the natural-technogenic basin.
structures from the position of the ecological contamination. The near-neutral waters with high values of the redox potential ($\text{pH} = 6–9; \text{Eh} > 250 \text{ mB}$) (Sakhalinsky, Razdol’nsky, Partizansky, Uglovsky, and Kuznetsky basins) concentrate $\text{Na}$, $\text{SO}_4^{2-}$, $\text{HCO}_3^-$, $\text{Sr}$, $\text{Mg}$, $\text{Fe}$, $\text{NH}_4^+$, $\text{Pb}$, $\text{NO}_3^-$, $\text{As}$, $\text{Cd}$, $\text{Sr}$, $\text{Zn}$, $\text{Cu}$, $\text{Cr}$, $\text{Mn}$, $\text{F}$, as well as $\text{Be}$, $\text{Sb}$, $\text{Se}$ and others.

The elaborated digital models of the hydrochemical fields allowed us to visualize the today’s situation in the districts of the liquidated coal mines and to demonstrate that the waters of the technogenic complexes with their chemical composition initiate the center of contamination and influence the safety of the underground water basin and thus the main sources of water supply and the surface water channels. However, the pollutions are local in space and defined by the area of distribution of the zone of the water-passing fractures and by the steady water level of a technogenic complex.

4. Conclusion
The study of the features and regularities of formation of the underground water composition resulted from the liquidation (flood) of coal mines has established the following facts:

1. The regime of the mine flood is defined by the features of the hydrogeological stratification of the supra-coal and coal beds, conditions of development of coal seams, volume of water inflow, and capacity characteristics of the drained massif.
2. Water composition of the technogenic complexes strongly depends on the features of the geological structure of sedimentary basins and stratigraphic position of the natural-technogenic structures.
3. The distinguished water types, characterizing the conditions and processes of their formation, may be the regional markers in small-scale hydrochemical and geological constructions.
4. The waters of technogenic complexes with their chemical composition initiate the center of contamination, but the contaminations are local in space and defined by the scales of distribution of the zone of the water-passing fractures and steady water level.

The results obtained are important in the elaboration of the bases of hydrogeochemical predictions, measures for management of the underground water quality, and prevention of the environmental pollution in the districts of the liquidated coal mines. They may be useful for planning and production organizations, services of ecological monitoring, and scientific-research institutes that plan and realize the works on providing the ecological safety of the underground water basin, sources of water supply, and surface water channels.

5. Acknowledgments
The research was supported financially by the Russian Foundation for Basic Research (project No. 17-05-00051a).

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