Physical and Chemical Regularities of Water’s Composition Formation in Natural and Technogenic Geological Structures of Closed Coal Mines (“Water-Rock” Model Verification)

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Abstract. The physical and chemical modelling helped to establish the regularities of the groundwater’s composition formation in the areas of coal mines that are being abandoned. We demonstrated that the unusual features of the composition of the subsurface waters in natural and technogenic structures of Russia and Ukraine resulted from “water–rock–gas” system’s chemical processes. “Aluminosilicates–water” system consecutively produces solutions corresponding to the \( \text{HCO}_3^-\text{Ca} \rightarrow \text{HCO}_3^-\text{Na(Mg)} \rightarrow \text{HCO}_3^-\text{SO}_4^-\text{Na(Mg)} \rightarrow \text{SO}_4^-\text{Na(Mg)} \) series of changes in composition, “limestone-water” system produces solutions corresponding to the \( \text{HCO}_3^-\text{Ca} \rightarrow \text{Cl}^-\text{Ca} \) series, “dolomite-water” system consecutively produces aqueous solutions of the \( \text{HCO}_3^-\text{Mg} \rightarrow \text{Cl}^-\text{Mg} \) series, and “rock salt-water” system produces acidic \( \text{Cl}^-\text{Na} \) type waters. We proved that water composition of technogenic complexes is determined by the features of geological structure of sedimentary basins, relations between reaction water masses and rocks (W/R), \( \text{O}_2 \) and \( \text{CO}_2 \) closeness-openness of W/R system.

1. Introduction

Our previous research showed that flooding (liquidation) of coal mines results in formation of a technogenic water-bearing complex that differs from a natural one in its filtration, level, and chemical characteristics. The comparison of underwater’s principal ion and cation ratios in the areas of closed mines of coal basins in Russia and Ukraine (Sakhalinsky, Razdolnensky, Partizansky, Uglovsky, Kuznetsky, Chelyabinsky, Kizelovsky, Pechorsky, and Donetsky) demonstrates regional patterns in the distribution of basic macrocomponents. The macrocomposition change pattern is best seen in the distribution of hydrocarbonate and sulfate ions [1–5]. Groundwater of basins situated in the west of Russia and in Ukraine (Donetsky, Chelyabinsky, Kizelovsky) have high concentrations of sulfate ion (up to 100 % equivalent) and chlorine (up to 80 % equivalent). However, concentrations of hydrocarbonate ions decrease here to 7 % equivalent, in the Kizelovsky basin to 0 % equivalent. Basins situated farther in the east of Russia (Kuznetsky, Razdolnensky, Partizansky, Uglovsky, and Sakhalinsky) are characterized by high concentrations of hydrocarbons (30 to 100 % equivalent), variation in contents of sulfate ion to 70 % equivalent, and high predominance of sodium ions in technogenic complexes’ waters. Moreover, pH of waters in the Razdolnensky, Partizansky, Uglovsky, Sakhalinsky, Kuznetsky, Donetsky, Pechorsky, and Chelyabinsky basins varies from 5.8 to 10.4, while in the Kizelovsky basin it varies from 7.9 to 2.5 (Figure 1).

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The results of the study of coal basins’ geology led us to infer that the specific features and parameters of the chemical composition of waters, formed in the natural and technogenic structures of liquidated mines, are associated with the interregional distribution of coal basins. They are also highly dependent on the characteristics of the geological structure of sedimentary basins. Prevalence of sea sedimentation and feeble manifestation of oscillatory motions on the East European platform, compared to more intensive upward-downward motions in the regions farther in the east, determined the presence in the strata lithological composition of carbonate, chloride and sulfate rocks in the western part of the territory, and terrigenous and volcanogenic rocks in the basins in the east. Thus, we showed that the material composition of rocks of supra-coal stratum in the Donetsky, Kizelovsky and Chelyabinsky basins is characterized by alternating facies of different salinity – sea, salt-bearing, and limnetic facies. The Pechorsky basin is characterized by homogenous sea facies, while the Kuznetsky, Razdolnensky, Partizansky, Uglovsky, and Sakhalinsky basins by limnetic facies.

**Figure 1.** Scatter plot of common anions and mineralization in the groundwater of the technogenic complex of coal basins in Russia and Ukraine.
We aimed at confirming the aforementioned statement and identifying the geochemical regularities of formation of the composition of groundwater in the area of liquidated coal mines by the means of physical and chemical modeling.

2. Objects and methods of investigation

This article is based on the data obtained as the result of continuous, methodologically standardized process of observations and measures of indicators showing the differences in waters’ composition. The investigations were carried out in the analytical center of the Far East Geological Institute FEB of RAS (accreditation certificate N POCC RU.0001.518986). The content of elements in water was determined by the methods of inductively coupled plasma mass-spectrometry using Agilent 7700 (Agilent Technologies, USA), and inductively coupled plasma atomic emission spectroscopy using iCAP 6500Duo (Thermo Scientific Corporation, USA).

We decided to use the “Selektor” software package for modeling [6]. “Selektor” implements the approach of convex programming to calculate the equilibrium in heterogeneous systems by minimizing the Gibbs free energy. The Gibbs chemical thermodynamic device allows to describe in a formalized way the hydrogeochemical processes and to express them in relevant physical and chemical models.

The technique of the physical and chemical modeling of the hydrogeochemical processes consisted in performing several calculations of the equilibrium state of the “water-rock” system. We set internal conditions for the system (temperature, total pressure and chemical potential of each perfectly mobile component), injected the natural chemical composition of water-bearing rocks having recalculated the number of moles for each component. Moreover, we made a set of phases and forms of the chemical elements’ existence in the simulated system. During the selection we considered the forms of chemical elements’ migration calculated in «Aquachem V. 5.1» as well as the components of secondary mineral formation.

3. Results of investigations and discussion

In order to make a quantitative assessment of the regularities of hydrogeochemical processes, and to determine the ways of groundwater composition changes and irreversible natural mineral formation in the area of liquidated coal mines we developed simulation models of dissolution of the terrigenous and volcanogenic (aluminosilicate), carbonate, gysiferous, and saliferous deposits. Models of “aluminosilicate rocks–water”, “limestone–water”, “dolomites–water”, “gypsum–water” and “rocky salt–water” systems were created. The modeling simulated dissolution of minerals (rocks) in the following conditions: 1) in a closed CO₂ and atmospheric gas system (CO₂ = 0.01 kg/1 kg H₂O, atmospheric gas = 0.3 kg/1 kg H₂O); 2) open CO₂ system (CO₂ was increasing from 0.01 to 2 kg/1 kg H₂O) at a temperature of 25°C. We used thermodynamic properties of minerals gases and water solution components adapted and found in Selektor- Windows data bases: a_Shock [7–12], g_Reid [13], s_dump, s_Robie Hemingway [14], b_Sidorov, s_Yokokawa [15]. Each system was described with a matrix of 16 independent components (Ca, K, Na, P, Al, Fe, Mg, Mn, Si, Ti, C, S, N, H, O, e) and 235 dependent components, including 43 mineral phase components and 12 dependent gas phase components. Initially (step 1 of calculation experiments) the partial pressure of the carbonic acid was assumed to be 10⁻²⁻⁸ bar and more, which on the average matches underground waters of the regional fracture zone.

It was established that the increase in water/rock relations for all systems is followed by an increase in mineralization of the water solution.

“Aluminosilicate rocks – water” system gradually produces solutions corresponding to the HCO₃⁻ → Ca → HCO₃⁻Na(Mg) → HCO₃⁻SO₄⁻Na(Mg) → SO₄⁻Na(Mg) series of composition changes. Accumulation of Na⁺ or Mg²⁺ in the series is defined by the rock type and attributes specific features to the equilibrium water solution composition. The occurrence of sulfate ions in waters is explained by the presence of sulfides. Closeness of the CO₂ system (PCO₂ = 10⁻²⁻⁸) always means that the water phase is prevented from the increase in HCO₃⁻ + CO₃²⁻ concentration in it and leads to a growth (given
the source exists) of the $SO_4^{2-}$ content. The increase in the CO$_2$ partial pressure ($> 10^{-1.0}$) and decrease of O$_2$ equilibrium concentration expands the area of existence of HCO$_3$–Na type of water in coal basins, and contributes to accumulation of high concentration components in waters. A change in the groundwater composition along with a tendency for components’ concentration growth lead to the authigenic mineral phases’ composition becoming more complex (Figure 2).

Figure 2. Results of evolution modeling of the closed CO$_2$ and atmospheric gas (CO$_2$ = 0.01 kg/1 kg H$_2$O; atmospheric gas = 0.3 kg/1 kg H$_2$O) “aluminosilicate rocks–water” system, a closed atmospheric gas system (A) and an open CO$_2$ (CO$_2$ = 0.01–1.28 kg/1 kg H$_2$O) system (B): 1–6 – hydrophilic rocks: 1 – coal; 2 – argillite; 3 – aleurolite; 4 – sandstone; 5 – rhyolite; 6 – dacianesite; 7–12 – forming mineral phases: 7 – dolomite; 8 – rhodochrosite; 9 – calcite; 10 – quartz; 11 – montmorillonite; 12 – goethite.

A closed CO$_2$ and atmospheric gas “Limestone–water” system forms limnetic (mineralization < 703.09 mg/dm$^3$) hydrocarbonate calcium waters (HCO$_3$–Ca): CaCO$_3$ + CO$_2$ + H$_2$O $\leftrightarrow$ Ca$^{2+}$ + 2HCO$_3^-$, similar in composition to those found in natural and technogenic structures of the Donetsky basin. Due to the increase in mass ratio of W/R we observe a tendency for growth of water’s mineralization, contents of carbonate and chloride ions in the direction of filtrate’s movement. Also the concentration series of Ca > Mg > Na type are preserved. The occurrence of hydromagnesite neocrystallisation in composition is accompanied by a significant decrease in magnesium concentration in a water solution. If the solution’s mineralization > 1263.49 mg/dm$^3$ a transformation of HCO$_3$–Ca type of waters is observed in Cl–Ca.
In an open CO₂ «limestone–water» system the area of existence of HCO₃–Ca type of waters is expanded, which leads to the formation of Cl–Ca type of waters on later stages of water interaction with rocks (if mineralization > 5002.8 mg/dm³, PCO₂ = 6.85ε-01) and to the formation (if mineralization 6181.3 mg/dm³, PCO₂ = 8.135ε-01 bar and PO₂ = 3.8746ε-02 bar) of Cl–Mg type if waters. Thus, the physical and chemical modeling of the «limestone–water» system established that Cl and HCO₃ anion ratios in the water phase are determined by the balance between PCO₂ and W/R mass ratios. As the mineralization of closed CO₂ and atmospheric gas «limestone–water» system increases grows it gradually produces water solutions related to the HCO₃–Ca → Cl–Ca series of composition change. Open CO₂ «limestone–water» system with PCO₂ > 8.1346ε-01 bar and PO₂ < 3.8746ε-02 bar produces water solutions related to, the HCO₃–Ca → Cl–Ca → Cl–Mg series of composition change.

Simulation modeling of a closed CO₂ and atmospheric gas «dolomites - water» system allowed us to state that on the first stages of water’s interaction with rocks HCO₃–Mg type of water is formed and then transforms into Cl–Mg as the mineralization increases. We showed that a closed CO₂ and atmospheric gas “dolomites – water” system gradually produces water solutions related to the HCO₃–Mg → Cl–Mg series of composition change. The modeling of a closed CO₂ and atmospheric gas «gypsum - water» system established that if the ratio of W/R = 0.004 leads to the water equilibrium with gypsum, the SO₄–Ca waters with mineralization up to 1773.97 mg/dm³ are formed. An open CO₂ system (CO₂ = 0.06–1.00 kg/1 kg H₂O) produces solutions related to the SO₄–Ca → HCO₃–Ca series of composition change.

The modeling of “rock salt – water” system was also performed for a closed CO₂ and atmospheric gas system (CO₂ = 0.01 kg/1 kg H₂O, atmospheric gas – 0.3 kg/1 kg H₂O) and for an open CO₂ system (CO₂ increased from 0.06 to 1.00 kg/1 kg H₂O). As a raw material we used an average chemical composition of the rocky salt from the Donetsky basin. The rock salt is mostly represented by halite, that, as it is known, [16], has a high solubility – up to 318 g/dm³. The physical and chemical modeling established that a closed CO₂ and atmospheric gas system «rock salt–water» produces highly acidic and acidic (pH = 0.81–3.80) waters of the Cl–Na type with mineralization of 1054.84–34048.36 mg/dm. However, the opening of CO₂ system does not significantly influence the water phase. Thus, it is shown that the non-equilibrium state of solutions and transformations of the chemical composition of the groundwater in the natural and technogenic structures of coal basins’ mines support primarily the main characteristics of such elements and compounds as CO₂, HCO₃⁻, CO₃²⁻, OH⁻, H₂O⁻, H₂CO₃, SO₄²⁻ and Cl⁻. The occurrence of sulfates in the waters of coal basins, supra-coal bed of which is built by aluminosilicate terrigenous or volcanogenic terrigenous rocks, is mainly related to the sulfur content in coals. The sulfate minerals of sedimentary rocks (gypsum, anhydrite etc.) in most cases are the source of the sulfate type of waters in basins, supra-coal bed of which is built by sea carbonate and terrigenous rocks. The formation of hydrocarbuate waters is also of lithogenic nature. Chloride waters’ formation in the natural and technogenic structures results from dissolution of saliferous (halite) and carbonate (limestone, dolomite) deposits.

The obtained results of the physical and chemical modeling showed that acidic waters in the studied basins form when the amount of CO₂ in a solution exceeds the amount of HCO₃⁻, while the increase in concentration of hydrogen ions leads to the formation of carbonic acid. Moreover, waters with pH of 2–4 have a mixed cation composition in most cases. In the pH range of 4–6 they attain calcium (magnesium and calcium) composition, and if pH > 8.0 they become sodium waters.

4. Conclusion
The modeling of processes of the groundwater composition formation in the area of liquidated coal mines of the Donetsky, Kizelovsky, Kuznetsky, Pechorsky, Chelyabinsky, Partizansky, Razdolnensky, Uglovsky and Sakhalinsky basins has established the following:
- Geochemical features of the groundwater in the area of liquidated coal mines are mostly of natural character and result from the geochemical processes in “water–rock–gas” system.
Water composition of technogenic complexes highly depends on the characteristics of the geological structure of sedimentary basins, stratigraphic position of natural and technogenic structures, and it strongly correlates with the presence in coal and supra-coal beds of sea, saliferous and limnetic groups of geological formations.

- Equilibrium in solutions and transformations of the groundwater chemical composition support primarily the physical and chemical characteristics of such elements and compounds as CO$_2$, HCO$_3^-$, CO$_3^{2-}$, OH$^-$, H$_2$O$^-$, H$_2$CO$_3$, SO$_4^{2-}$ and Cl$^-$, and they also influence the ratios of reaction masses of water and rocks as well as the W/R system’s O$_2$ and CO$_2$ closeness-openness.
- pH range of the geochemical transformation of groundwater is determined upon the carbonate equilibrium and it defines the ratio between the concentrations of Ca$^{2+}$, Mg$^{2+}$ и Na$^+$ in the basins’ underground waters.

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