Groundwater composition fluctuation within technogenic zones (case study: flooded coal mines in Primorsky Krai, Russia)

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Abstract. The paper considers groundwater composition fluctuation within technogenic zones based on evidence from the flooded coal mines of Primorye. The authors have determined the regularities of hydrogeochemical processes, specified the groundwater composition fluctuation within the technogenic complexes located in the liquidated mine areas, and identified the equilibrium phases between the studied waters and specific secondary minerals. It has been proved that water within natural-technogenic complexes in the liquidated mine areas are saturated with silicates, carbonates, sulfates, oxides, and hydroxides, which should be taken into account when designing technologies for groundwater treatment.

1. Introduction

Today, coal mining is practically interrupted in Primorsky Krai, with 15 mines being flooded. This resulted in the change of the hydrogeological properties of Partizansky, Razdolnensky, and Uglovsky sedimentary basins. Moreover, this increased the permeability in the layers above coal seams, influenced groundwater natural regime and circulation, developed hydraulically bound technogenic aquifer systems, and caused the transformation of groundwater composition and formation of new water type, termed as "technogenic". This term implies the diversity of exogenous and technogenic processes occurring within newly-formed natural-technogenic complexes.

It is important to study the chemical composition and regularities of groundwater formation within natural-technogenic complexes located in the areas of liquidated coal mines. This will allow developing hydrochemical prognosis principles, as well as measures to mitigate environmental impact.

2. Materials and methods

The present paper deals with the chemical groundwater composition changes within technogenic zones, where the 200–800 m water-bearing strata were disturbed by mining works. We have examined the following liquidated mine areas in Primorsk Territory, RF (Figure 1): Partizansky (Glubokaya, Nagornaya, Avangard, Severnaya, and Uglekamenskaya mines), Razdolnensky (Ilyichevskaya and №

4 mines), and the Uglovsky (Artem) coal basins, as well as Podgorodnensky and Khasanovsky deposits (Podgorodnenskaya and Khasanovskaya mines, respectively).

The ground water samples were collected from wells screened of a particular aquifer or connected to filter-equipped mines in undermining sections. The samples were also collected from surface water seepage. To test cations and sulphate ions, hydrochemical water was sampled through cellulose filter (0.45 μm) in situ so as to remove suspended solid particles and then was acidified with nitric acid. For testing anions, the samples were also filtered and collected into polyethylene containers without acidification. Unstable parameters were determined at the sampling point as well. Mineralogical sampling was conducted single point method in sealed glass weighing bottles.
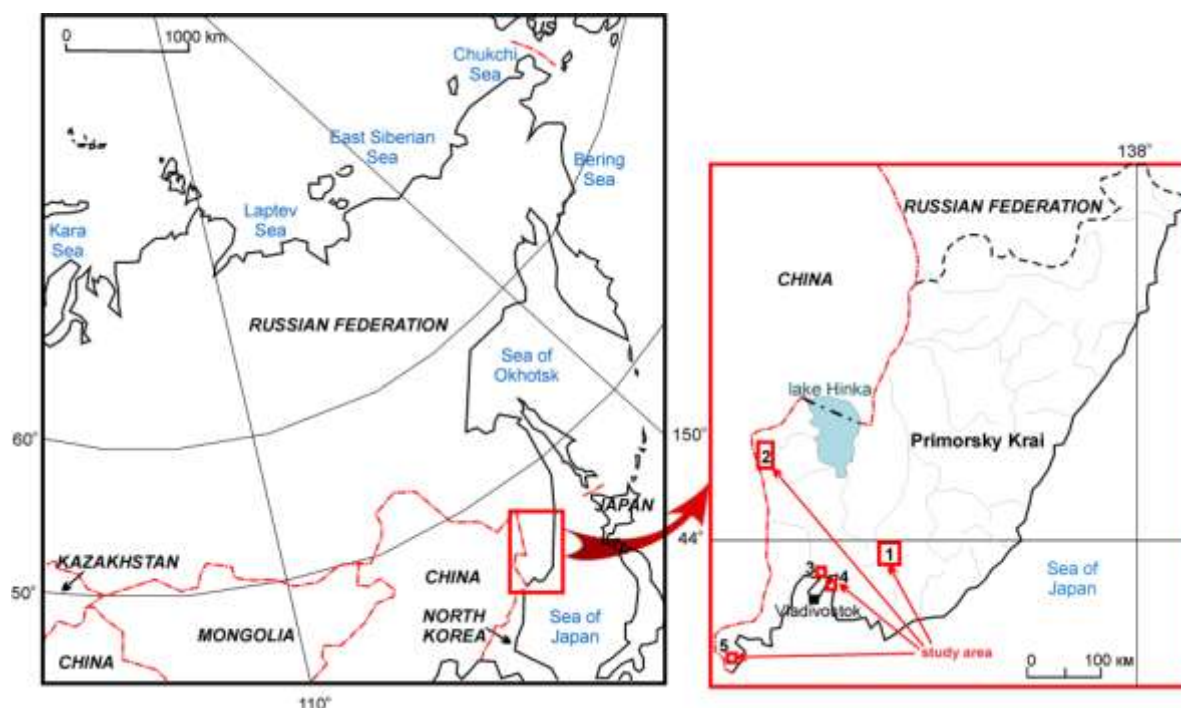

Figure 1. Study areas: 1 – Partizansky coal basin; 2 – Razdolnensky coal basin; 3 – Shkotovsky deposit; 4 – Podgorodnensky deposit; 5 – and the Khasanovsky deposit.

The water samples were examined via standard analytical methods ICP-MS; ICP-OES, Furye-spectrophotometer IR FTIR-84008. To study the composition of neocrystallizations, chemical, spectral, and roentgen-phase (diffractometer D8 Discover with CuKα; Dron-3 with FeKα) analyses were used, as well as IR spectroscopy method (IR Furye-spectrometer NICOLET, Termo).

To store, integrate, and process geochemical data, we applied the mathematical methods of statistics and physicochemical modeling – equation solving (with thermodynamic equilibrium constants – program Aqua-Chem V. 5.1 [1]) and Gibbs free energy minimization method (program Selector-Windows [2–4]).

3. Results and Discussion
The analysis data showed that within Primorye liquidated coal mine areas, the groundwater in porous Quaternary and Neogene sediments**,** as well as in fractured aquifer systems of Cretaceous sediments and fracture-veined aquifer systems in zones of tectonic dislocations and intrusive contacts in Cretaceous sediments are fresh (mineralization 0.3–0.4 g/dm^3), low hardness, pH-neutral, and bicarbonate. Cationic water varies from magnesium-sodium-calcium to calcium-magnesium. Chemical water composition variation within natural-technogenic complexes is attributable to mineralization

(from 0.3 to 8.0 g/dm^3). Sodium, magnesium, bicarbonate, and sulfate ion accumulations are involved in the increasing water mineralization. Within newly-formed natural-technogenic complexes, the following brackish water types [5–7] exist: 1)sulphate bicarbonate, bicarbonate-sulphate, and sulphate magnesium; 2) sulphate bicarbonate, bicarbonate-sulphate, and sulphate sodium (Figure 2). The ion-exchange transformation is restricted to pH values from 5.8 to 9.4. Na$^+$ or Mg^{+2} accumulation in the above series is governed by the coal-overlaying formation rock. This fact is confirmed by the results of physicochemical "water-rock" system modeling based on minimization of isobar-isothermal potential (program complex "Selector-Windows")
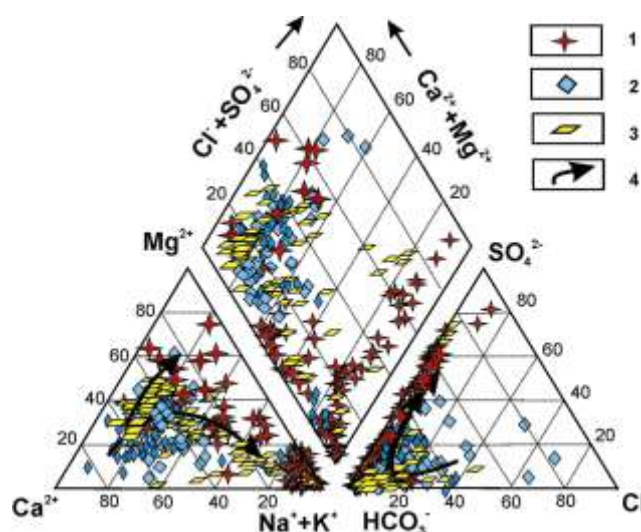

Figure 2. Piper diagram of water samples from areas of liquidated coal mines in Primorye: 1 – water within natural-technogenic complex; 2 –water within alluvial horizon; 3-water in fractured and fracture-veined complexes; 4 – water composition variation.

Modeling methodology included the calculations of "water-rock" system equilibrium. Chemically-natural water-bearing rocks were introduced in relevant proportions. Modeling involved the incongruent dissolution of rock minerals under the following conditions: 1) closed CO$_2$ and atmospheric gases (CO$_2$ – 0.01 kg/1 kg H$_2$O, atmospheric gases – 0.3 kg/1 kg H$_2$O) systems; 2) opened CO$_2$ system (CO$_2$ increased from 0.01 to 1.28 kg/1kg H$_2$O).

According to B. N. Ryzhenko and S. R. Krainova [8, 9], rock mass (R) and water mass (W) ratio in aluminosilicate rocks involves interaction time (conventionally, water exchange time) between rock and water solution. In this regard, the following R and W ratios were used in modeling the systems: 0.001 (step 1); 0.002 (step 2); 0.004 (step 3); 0.008 (step 4); 0.010 (step 5); 0.016 (step 6) 0.032 (step 7); 0.064 (step 8); 0.080 (step 9). Initially, step 1 of computational experiment, partial pressure of carbon dioxide is 10^{-2}bar, which corresponds to the mean groundwater within the regional fractured zone. Model adequacy to natural objects was estimated as the calculated correlation of chemical element composition in water and pH to the mineral composition of newly-formed solids of relevant natural parameters.

Geochemical properties of groundwater within technogenic complexes located in the liquidated coal mine areas generate in the catchment area itself and transform towards the filtration flow accordingly: HCO$_3$–Ca $\rightarrow$ HCO$_3$–Na(Mg) $\rightarrow$ HCO$_3$–SO$_4$–Na(Mg) $\rightarrow$ SO$_4$–Na(Mg) (table 1). Increased magnesium concentration in the groundwater is governed by significant mafic tuffogenic accumulations (40 %) in the stratigraphic sequence [7].

It has been revealed that closed CO$_2$ system (PCO_2 = 10$^{-2,0}$) itself hinders HCO$_3^-$ + CO$_3^2$ concentration increase in the water phase and furthers increasing SO$_4^{-2}$ concentration (if possible). Sulphate ions in the groundwater of study basins is governed by the sulfides (pyrite) in overlaying coal

and coal thicknesses. This process is governed by the CO_2 partial pressure and the presence of O_2. Higher CO_2 partial pressure equilibrium ($> 10^{-1.0}$) and lower O_2 concentration equilibrium result in the expansion of HCO_3–Na water areas within the coal basins.

Chemical element concentration in water is governed by secondary minerals. Physico-chemical calculations identified that components migrate in natural waters as uncomplexed ions. As the mineralization process continues, the number of complexed migrating components increases, which, in its turn, results in the formation of mineral phases. There exists a distinct alteration of groundwater composition during their circulation in the natural-technogenic complexes and composition in the equilibrium secondary mineral phase (Table 1).

Table 1. Modeling data within "rock-water" system, closed CO_2 and atmospheric gases (CO_2 – 0.01 kg/1 kg H_2O, atmospheric gases – 0.3 kg/1 kg H_2O) systems.

Step number	1 (1g rock / 1 kg H₂O)	2 (2 g rock / 1 kg H₂O)	3 (4 g rock / 1 kg H₂O)	4 (8 g rock / 1 kg H₂O)	5 (10 g rock / 1 kg H₂O)	6 (16 g rock / 1 kg H₂O)	7 (32 g rock / 1 kg H₂O)	8 (64 g rock / 1 kg H₂O)	9 (80 g rock / 1 kg H₂O)
Water solution, mg/kg H_2O									
TDS	273.63	488.07	749.71	1104.24	1292.85	1898.61	3605.25	6666.75	7945.08
pH	6.69	7.03	7.21	7.33	7.38	7.48	7.56	7.63	7.61
Eh. B	0.821	0.80	0.79	0.78	0.78	0.78	0.77	0.77	0.77
Ca^{+2}	2.40e+01	4.52e+01	4.96e+01	2.94e+01	2.39e+01	1.56e+01	1.08e+01	7.80e+00	8.35e+00
Na^+	9.47e+00	1.88e+01	3.70e+01	7.02e+01	8.35e+001	1.02e+02	5.18e+01	5.26e+00	1.75e+00
Mg^{+2}	6.06e+00	1.15e+01	2.20e+01	4.20e+01	5.14e+01	7.84e+01	1.49e+02	2.36e+02	2.53e+02
HCO_3^-	1.03e+02	2.25e+02	3.45e+02	4.61e+02	5.18e+02	6.57e+02	8.18e+02	1.01e+03	9.99e+02
SO_4^{2-}	2.36e+01	4.49e+01	8.88e+01	1.83e+02	2.30e+02	3.69e+02	7.29e+02	1.39e+03	1.70e+03
Cl^-	1.50e+01	1.50e+01	1.50e+01	1.50e+01	1.50e+01	1.50e+01	1.50e+01	1.49e+01	1.49e+01
Si	6.42e+00	6.43e+00	6.43e+00	6.44e+00	6.44e+00	6.45e+00	6.44e+00	6.43e+00	6.41e+00
Gas parameters									
PCO_2	2.16e-02	2.16e-02	2.16e-02	2.17e-02	2.18e-02	2.20e-02	2.23e-02	2.34e-02	2.40e-02
PO_2	2.06e-01	2.05e-01	2.04e-01	2.03e-01	2.02e-01	1.99e-01	1.92e-01	1.77e-01	1.69e-01
PN_2	7.73e-01	7.73e-01	7.74e-01	7.76e-01	7.77e-01	7.79e-01	7.86e-01	8.00e-01	8.07e-01
Mineral phase. %	goethite – 3.35; montmorillonite – 29.17; quartz – 67.48	goethite – 3.32; montmorillonite – 28.98; quartz – 67.70	goethite – 3.23; montmorillonite – 28.17; quartz – 66.14; calcite – 2.46	goethite – 3.15; montmorillonite – 27.45; quartz – 64.60; calcite – 4.71; rhodochrosite – 0.10	goethite – 3.13; montmorillonite – 27.32; quartz – 64.34; calcite – 5.05; rhodochrosite – 0.15	goethite – 3.12; montmorillonite – 27.18; quartz – 64.05; calcite – 5.44; rhodochrosite – 0.21	goethite – 3.11; montmorillonite – 27.11; quartz – 63.92; calcite – 5.62; rhodochrosite – 0.24	goethite – 3.10; montmorillonite – 26.99; quartz – 63.67; calcite – 5.30; rhodochrosite – 0.24; dolomite – 0.69	goethite – 3.09; montmorillonite – 26.92; quartz – 63.51; calcite – 5.00; rhodochrosite – 0.24; dolomite – 1.23

AquaChem program V. 5.1 showed that underground water with mineralization > 0.6 g/dm³ are saturated with calcium and magnesium carbonates, which corresponds to the findings by S. L. Shvartsev [10, 11] and other scientists [12, 13] concerning cation behavior in the groundwater within different landscape zones. If mineralization is >1.5 g/dm³, equilibrium with magnesium sulphate – epsomite (Razdolnensky coal basin) could be found. As for surface water seepage in technogenic complexes, a steady equilibrium between above-discussed water types and sodium mineral series thermonatrite ($Na_2CO_3 \cdot H_2O$), tenardite (Na_2SO_4), etc. is established. All waters have been identified to be in equilibrium with kaolinite. Further water-rock interaction results in increasing silicon,

magnesium, calcium, sodium concentration in the solution and formation of montmorillonites and chlorites. When K^+ ions that are closely connected with the weak acid anionites (HCO_3^-) accumulate, illite and sericite are formed. If mineralization is > 4 g/dm^3, equilibrium with analcime, a typical mineral in alkaline sodium water, could be found. According to R.M. Garrelse and C. L. Kraist [14], this mineral could indicate the formation of amorphous silica.
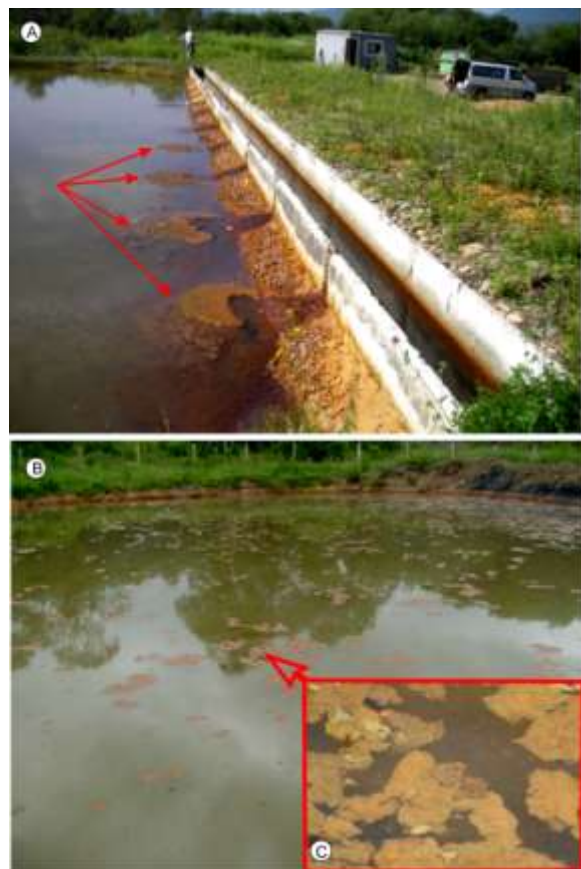

As there exists an equilibrium between the studied water and secondary minerals series on the earth surface, the intensive coagulation of newly-formed minerals and flaky fine-dispersed masses is observed (Figure 3). Phase (mineral) composition of fine-dispersed fraction was determined via IR Furye-spectrometry; and the following four mineral series were identified: carbonate, quartz, and montmorillonite; montmorillonite and quartz with insignificant iron hydroxide impurities; montmorillonite, quartz, and carbonate with significant iron hydroxide impurities; iron hydroxides.

Thus, it has been established that the water within natural-technogenic complexes in the liquidated mine areas are saturated with different silicates, carbonates, sulfates, oxides, and hydroxides. This fact should be taken into account when designing groundwater treatment facilities and developing measures to mitigate the environmental impact caused by existing coal mines.

It is noteworthy that the design and construction of the reagent-free water treatment facilities with filtration dikes are not always appropriate for mine water treatment, as there is an equilibrium between the studied waters and secondary mineral series on the earth surface, intensive coagulation of newly formed minerals and flaky fine-dispersed masses. This, in its turn, causes intensive silting of the dike filters, water level increase in the storage pond, overflow, and destruction of the hydro-technical construction.

Figure 3. Reagent-free water treatment facilities with filtration dike (Uglekamenskaya mine): A – coagulation of clay minerals at the outlet of the distributive tray; B – mineral formation on the surface of the pond-storage; C – fine-dispersed mineral fraction.

4. Conclusion

Based on the research results, it is possible to conclude that:

- coal mine flooding in Primorsky Krai causes changes in ground water circulation and leads to formation of hydraulically bound technogenic aquifer systems;
- geochemical properties of groundwater within technogenic complexes located in the liquidated coal mine areas generate in the catchment area itself and transform towards the filtration flow;
- increased magnesium concentration in the groundwater is governed by significant mafic tuffogenic accumulations (40 %) in the stratigraphic sequence;
- closed CO_2 system ($PCO_2 = 10^{-2,0}$) itself hinders $HCO_3^- + CO_3^2$ concentration increase in the water phase and furthers increasing SO_4^{-2} concentration (if possible); higher CO_2 partial pressure

equilibrium (> $10^{-1.0}$) and lower O_2 concentration equilibrium results in the expansion of HCO_3–Na water areas within the coal basins.

- existing steady equilibrium between the studied waters and secondary mineral series (silicates, carbonates, sulfates, oxides, and hydroxides) should be considered when designing measures to mitigate the environmental impact caused by the waters formed within the natural-technogenic complexes.

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