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Hydrogeochemical characteristics of water intakes from groundwater sources in Seversk

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Abstract. The article describes the hydrogeochemical environment behavior analysis of groundwater intake which, in its turn, provides the utility and drinking water supply for Seversk. The reasons for temporary changes of the hydrogeochemical aquifer indicators in the producing areas have been highlighted. The main factor could be upset hydrodynamic conditions during long-term operation. Changed hydrogeochemical indicators have been revealed not only during the technological water treatment process but also during water transportation to consumers. Chemical composition water changes are related to secondary mineral and sludge formation on technological equipment. Precipitation is a polymineral mixture predominantly a ferrous phase, whereas phosphate and carbonate phases are secondary. Clay minerals are also found.

1. Introduction

One of the most common types of human activities involves water supply, which, in its turn, results in significant. The study of the chemical and mineral precipitation composition, its structure and formation mechanisms is of both theoretical and practical interest. The authors have been studying precipitation formations within water supply systems of the water intakes from Tomsk and Tomsk Oblast groundwater sources [1-5]. Based on investigation results, the precipitation composition and structure were identified, as well as the precipitation property- water aeration regime and **tile line** relationship. This research is focused on studying the variability of hydrogeochemical environments and accumulation of secondary solid mineral neocrystallizations in Seversk water intake facilities.

2. Research target characteristics

The utility and drinking water in Seversk, the second largest city in Tomsk Oblast, is supplied from two groundwater source intakes, located on the right Tom River bank and embracing aquifers of the West Siberian Megabasin (fig.1). Water intake facility No.1, operating since 1965, includes 32 wells within Paleogene aquifer. Water intake facility No.2 operating since 1971, includes 22 wells within Paleogene and Upper Cretaceous aquifers. All the wells and water intake facilities are equipped with wire-wrapped screens and submersible pumps. Their depth varies from 84 to 129 meters while their productivity is from 40 to 120m³/day. Total productivity is about 50 thousand m³/day.



Operating regulations for analyzing and predicting hydrogeological condition changes within the areas of water intake facilities are stipulated by the monitoring system for groundwater level and quality. Analytical work was performed in accredited laboratories of OJSC Seversk Vodokanal and OJSC Tomskgeomonitring.



Figure 1. Layout of Tomsk and Seversk water intake facilities: 1 – lines of water intake production wells in Tomsk; 2 – water intake facilities in Seversk.

3. Groundwater chemical composition

Chemically, water in production wells is exclusively hydrocarbonate in composition with different calcium and magnesium ratios and could be classified as fresh, neutral and weakly alkaline, moderately hard water (Table 1).

This groundwater is typical of taiga and subtaiga landscapes in geochemical ferromanganese province of Western Siberia. Water values exceeding maximum allowable concentrations for drinking and household water include iron, manganese and silicon, whereas iron and manganese are found in practically 100% of all investigated cases. Chemical composition variation indicators, changing patterns and their magnitude depend on spatial location and lithologic and facies rock characteristics, as well as the temporal sampling coordinates.

Table 1. Groundwater chemical composition and technological water cycle in water intake facilities (based on water intake facility service data of 2012-2014).

Indicators	Water intake facility No.1			Water intake facility No.2		
	Water in production well	*Technological water	**Water supplied to networks	Production well waters	*Technological water	**Water supplied to networks
Dry residues, mg/dm ³	<u>244...895</u> 355	<u>319...320</u> 1	330	<u>200...306</u> 247	<u>257...264</u> 7	252
TDS, mg/dm ³	<u>375...1066</u> 520		485	<u>318...474</u> 377	<u>377-364</u> -13	375
pH	<u>7.1...7.6</u> 7.3	<u>7.0...7.5</u> 0.5	7.6	<u>6.9...7.3</u> 7.1	<u>7.0...7.4</u> 0.4	7.5
Hardness, mg-eq/dm ³	<u>4.1...6.9</u> 5.1	<u>4.9...4.85</u> -0.5	5.3	<u>3.5...6.1</u> 4.2	<u>4.2...4.0</u> -0.2	4.0
HCO ₃ ⁻ , mg/dm ³	<u>262...386</u> 330	<u>351...330</u> -21	311	<u>228...366</u> 260	<u>271...271</u> 0	245
Cl ⁻ , mg/dm ³	<u>2...253</u> 29	<u>23.5...25.5</u> 2	19.3	<u>2.0...5.1</u> 2.3	<u>0.2...2.4</u> 2.2	4.4
SO ₄ ²⁻ , mg/dm ³	<u>2...36</u> 8	<u>19.5...5.86</u> -13.64	6.1	<u>2.0...14.2</u> 5.3	<u>16.6...2.8</u> -13.8	5.5
Ca ²⁺ , mg/dm ³	<u>60...242</u> 85	<u>78.2...82.2</u> 4	77	<u>50...81</u> 63	<u>62...65</u> 3	62
Mg ²⁺ , mg/dm ³	<u>4...34</u> 16	<u>12.6...9.45</u> -3.15	13	<u>7...28</u> 13	<u>13.7...8.7</u> -5.0	11

Fetotal, mg/dm ³	$\frac{3.0...6.7}{4.8}$	$\frac{4.74...0.1}{-4.73}$	0.1	$\frac{1.1...4.5}{2.4}$	$\frac{2.4...0.1}{-2.3}$	0.11
Mn, mg/dm ³	$\frac{0.2\ 0.6}{0.4}$	$\frac{0.29...0.2}{-0.09}$	0.26	$\frac{0.02\ 0.39}{0.24}$	$\frac{0.23...0.20}{0.03}$	0.29
Si, mg/dm ³	$\frac{10.3...14.8}{12.0}$	$\frac{12...11.7}{-0.3}$	9.6	$\frac{11...14}{12}$	$\frac{13-14}{1}$	10
Oxidability, mg O ₂ /dm ³	$\frac{1.4...4.7}{2.4}$	$\frac{2.04...0.88}{-1.16}$	1.1	$\frac{0.8...2.3}{1.5}$	$\frac{1.3...0.7}{-0.5}$	1.5
Number of values	25	10	4	21	10	4

Note. *numerator- range and denominator – mean value of the indicator.

**numerator - value indicator range of water supplied to and in water treatment cycle, denominator – change of indicator values

4. Hydrogeochemical characteristic changes during field development

Operating water intake facilities furthered depression cone formation in developing Paleogene and overlying Neogene-Quaternary aquifers. In both aquifers the depression cones are separated by groundwater divisions, spatially coinciding with orographic water division. The cone configurations and dimensions have not practically changed in recent years, while their level surface ranges from 0.5 to 1.0 m depending on water intake rate. In highly intensive production wells cone depression surface level decreases to 10...23 m.

It is obvious that hydrodynamic condition changes lead to variations of extracted water quality. The main mechanisms of these changes are the following: (1) subsurface aeration occurring within forming depression cones and aeration water flows from overlying aquifers and (2) as a result of elastic deformation processes occurring in bedded formations during hydro-technical utilities and the active areal water flows from underlying aquifers which could be rather intensive in lithologic windows [5]. Spatially, both mechanism changes of hydrogeochemical conditions embrace a wide areal distribution. In terms of continuous water intake facilities operation and underinvestigated Tomsk water intake facility [2] these processes result in the chemical groundwater composition within the aquifers. Year-to-year observation data indicated a rather pronounced increase in mineral content, especially chloride ion, as well as iron content decrease in the waters of developed aquifers. Such changes are apparently associated with intensive water flows from deep aquifers. Iron content decrease is associated with solution-solid transformation during water flows from overlying oxygen-enriched Neogene-Quaternary aquifers.

According to data analysis, water supplied to the water treatment process cycle comparable to production well water is characterized by a low variability of indicators due to equalization (table 1). The quality of production well water is enhanced to drinking standards via water treatment technology based on natural processes. In terms of its physical nature this could be an analog to groundwater discharge at the surface. This water treatment technology includes deferrization of simplified aeration, further penetration into a contact chamber and filtration through granular medium, as well as hypochlorite sodium purification. Water treatment reduces the indicator values (table 1). Iron content in after-treatment water does not exceed maximum allowable concentrations. Water of required hygienic standards is supplied to consumers via distribution networks being about 200 km. Water composition and quality indicators also change.

5. Changes of hydrogeochemical indicators and secondary mineral formation

Water chemical composition changes are accompanied by secondary mineral formation and precipitation on water intake equipment. Precipitation accumulates near the wellbore in pre-filtering zone and on well equipment (pumps, water gauges, pipes) (fig. 2), on filters of water intake facilities and distribution networks, plumbing equipment and household appliances.

Two morphological types of mineral neocrystallization are formed on the equipment of water intake facilities: structureless ochreous (iron) masses and mineral aggregate having rigid-structured framing. There are no significant genetic differences between these precipitation types: both are formed due to physical-chemical environmental condition changes, whereas their morphological peculiarities are predominantly associated with the hydrodynamic depositional environment [4].



Figure 2. Precipitate in an ascending pipe in well No. 14.

Ochreous (iron) masses accumulate in dynamic water flow conditions on the filters and production well ascending pipes, on submersible pumps and measurement equipment. They also accumulate in granular medium filters after water purification. They have different consistency: near the surface – thick creamy liquid and internal layers- dense, paste-like; harden during drying up and easily triturable into dust.

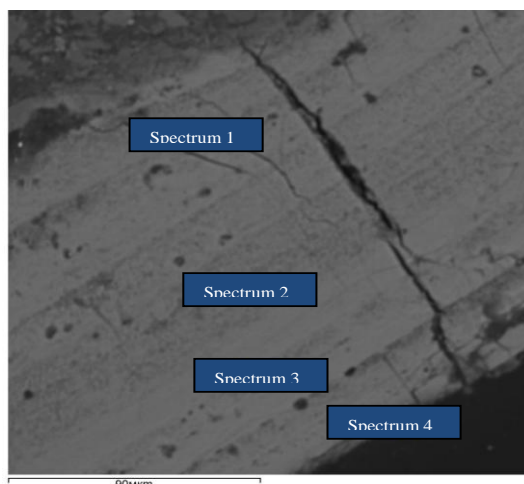
Second-type mineral neocrystallization accumulates on the granular medium filters in water treatment facilities, having concentric layered structure with alternating beds of different thicknesses and color. Based on these characteristic features they could be referred to as oolites [4]. After

air drying, oolite structure is preserved while aggregates can be decomposed only under mechanical effect. Dispersion particles remain on the grain surface forming an increasing thick film due to filter flushing.

Oolite composition and structure were analyzed on the VEGA I LMU scanning electron microscope equipped with INCA Energy dispersive spectrometer in the Analytical Center for Geochemistry of Natural Systems, TSU (by A.S. Kulkov -analyst, assistant, Department of Petrography, TSU). The concentric layered precipitation film structure formed around the grain medium was detected on the electron microscope. The precipitation film thickness depends on filtration operating time and could vary from mm fractions to 1 mm [4]. In our case, separate film layer thickness ranges from 10 to 45 μm (fig. 3).

Precipitation is mainly composed of iron compounds (up to 75.34%), less of silicon (up to 14.52%), calcium (up to 7.71%) and phosphorus compounds (up to 7.89).

Mineralogical identification of investigated material has not been performed yet. However, according to the obtained data, one and the same aquifer is the groundwater source for both Tomsk and Seversk water intake facilities. The ferrous phase includes ferrous hydrite, goethite and hematite and carbonate phase – calcite. Iron hydrophosphates, such as rockbridgeite, dufrenite and vivianite precipitations were identified in Tomsk water intake facility [4].



Besides the main components and mineral neocrystallization, impurity elements are also found and their concentrations in the primary solution depend on both natural factors and the environmental system conditions.

Figure 3. Concentric layered oolite structure formed around grain medium and points of analysis BSE image.

The chemical precipitation composition was studied via energy-dispersive X-ray spectroscopy (EDX) (table 2).

Impurity elements could be removed from water in several ways. Apart from iron mineral formation, the isomorphic or sorption mechanisms of microelement-capture forming mineral neocrystallization is significant. Although many undersaturated microelements in groundwater are not removed during the water migration, for example, iron minerals, they are either sorbed or precipitation of colloidal oxides and iron hydroxides, manganese oxides, clay minerals and carbonates [4].

Table 2. Chemical composition of the newly formed oolite around grain medium (%).

Oxides	Content (mass fraction, %)			
	Points of analysis			
	1	2	3	4
Si ₂ O	11.62	12.96	10.11	14.52
FeO*	75.34	75.24	74.30	75.18
CaO	7.13	7.04	7.71	6.64
P ₂ O ₅	5.91	4.76	7.89	3.66
Total	100.00	100.00	100.00	100.00

Note: FeO* = FeO + Fe₂O₃.

The microelemental composition of precipitation was analyzed on ICP-MS at LLC Chemical-Analytical Center Plasma. The analysis results showed that precipitation formed at different water treatment stages, mainly, in cooling tower and in granular filters, differ in their composition (table 3). The precipitation from the cooling tower has a more ferrous composition (34.6%) comparable to the precipitation from the filters (13.6%). The difference involves the manganese content which is more significant. There are also microelement content differences, which indicate the complex mechanisms of chemical element precipitation during water treatment.

Table 3. Elemental and microelemental composition of precipitation (mass fraction, %)

Sampling No. *	Elements								
	Fe	Mn	Cu	Ni	Cr	Ba	Zn	Co	Sr
1	13.6	26.0	0.0017	0.0005	0.00098	0.55	0.029	0.00057	0.070
2	34.6	0.72	< 0.0001	0.0005	0.00028	0.12	0.018	0.00004	0.024

*Sampling location: 1 – deferrization filters in water intake facility No.1 in Seversk; 2 – precipitation from a cooling tower in water intake facility No.1 (2) in Seversk.

6. Conclusion

Changes of hydrogeochemical conditions during groundwater field development is accompanied by secondary mineral formation and precipitation both in reservoir conditions and during operating water intake facilities, as well as at subsequent stages of water treatment and transportation.

Precipitation from water supply systems are a mixture of finely dispersed and poorly crystallized minerals that are predominantly composed of nanometer-sized ferrous oxide and hydroxide particles, which could be of some interest for researchers involved in nanotechnology development. Based on precipitation from water supply systems, technologies for producing nanomaterials could be developed, which, in its turn, could generate composite materials with specific catalytic and oxidation-reduction properties [6,7].

According to research findings, precipitation formed in service water systems reveal similar composition and structure comparable to those of natural formations [8,9,10]. Analyzing the chemical and mineral composition of these precipitation, their structure patterns and formation mechanisms is of theoretical and practical importance.

Thus, further detailed studies of natural and man-caused precipitation can significantly extend our knowledge of mineral formation in hypergenesis areas of both modern and ancient environments.

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