Hydrogenous mineral neoformations in Tomsk water intake facility from underground sources

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Abstract. The article considers study outcomes of hydrogenous mineral neoformations precipitated on deferrization filters of Tomsk water intake facility from underground sources. Compositionally, these precipitations are colloform and polymineral including ferrous, carbonate and aluminosilicate mineral phases. Ferrous phase predominates and embraces ferric hydroxides (ferrihydrate, goethite, hematite and lepidocrocite) and ferrous hydrophosphates (vivianite, strengite, strunzite and rockbridgeit). Carbonate and aluminosilicate minerals are calcite and kaolinite-group, respectively.

1. Introduction

Water supply is one of the most common human activities that is accompanied by the formation of significant precipitation. In many cases problems crop up from operating water intake facilities, such as incrustation, water supply pipe network incrustation, which, in its turn, reduces tap drinking water quality. Researchers consider such a factor as "water intake facility ageing" and identify the following environmental degradation causes at water supply facilities: equipment corrosion, sanding, ochering, deposition of various chemical elements and slimming caused by microorganism growth.

Studies of chemical and mineral composition of the precipitation, its morphology, formation behavior patterns are of both theoretical and practical importance. There are two sides of this issue: on the one hand, such data is necessary in selecting the relevant water treatment technology and further optimization of the water intake equipment operation; on the other hand, up-dated model of hydrogenous mineral formation allows observing the formation of minerals from the first moment of their origin.

The authors have been studying precipitations forming in water supply systems of water intake facilities from underground sources in Tomsk and Tomsk Oblast [1-3]. Studies revealed data on precipitation composition and morphology and the precipitation properties – water aeration regime relation, as well as type of water load.

Research findings proved the fact that such precipitations could be used as raw sources, i.e. sorbents to purify water from petrochemicals and phenols [4], as well as catalysts in the hydrocarbon oxidizing process [5].

2. Study subject

Tomsk water intake facility from underground sources is one of the largest intake facilities in Russia (Figure 1) and it develops Paleogene aquifers being main water supply source for the majority of West-Siberian populated areas. The chemical composition of ground waters has been studied during the entire development period of this ground water basin. According to research data [6], production wells are compositionally hydrocarbonate with various calcium-magnesium ratios; fresh waters with mineralization varying from 196 to 600 mg/dm^3; weak-acid to weak-alkaline (pH: 6.2 – 8.0); very soft to hard (from 0.6 to 7.0 at a mean value of 3.8 mg-equivalent/dm^3), and predominately hard. Concentrations of most analyzed components do not exceed the maximum allowable concentration (MAC). Ferrum and manganese content is higher than MAC, whereas ferrum concentration exceeds the MAC in 100% cases. Proposed water treatment scheme includes simplified aeration followed by filtering through granular loading and decontamination. In general, water treatment shows rather positive results – water through technological treatment responds to the existing regulatory documents.

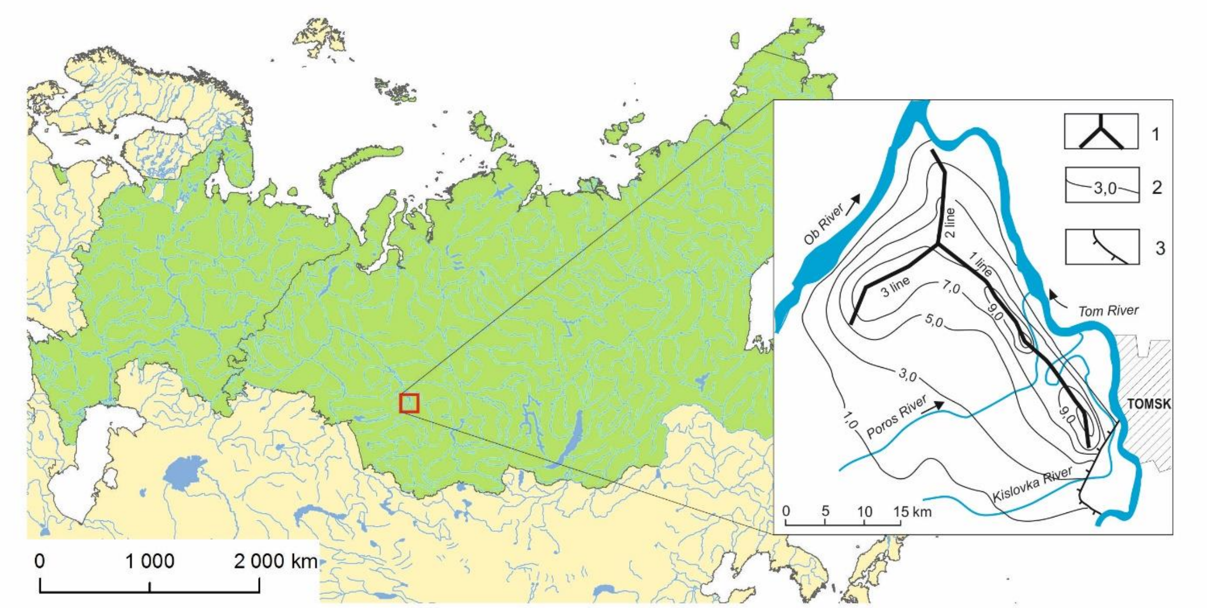

Figure 1. Layout of Tomsk water intake facilities: 1-production well line of water intake facility; 2 – contours of decreasing groundwater level, m; 3 – Paleozoic basement protusion borderline.

3. Materials and methods

Investigated precipitation samples from processing water intake equipment embrace a mixture of finely-dispersed and poorly-crystallized minerals which are problem objects under conventional research methods. In this case, the authors applied methods used to investigate dispersed rocks, soils and clay minerals, as well as a series of physico-chemical methods including: 1) silicate chemical analysis; 2). X-ray analysis; 3) infrared spectroscopy (IS); 4) thermogravimetric analysis; 5) spectrometry – ED (on SEM); 6) microdiffraction and spectrometry via electron transmission microscopy (ETM) and 7) composition analysis via scanning electron microscopy VEGA II LMU, equipped with energy-dispersed spectrometer INCA Energy.

4. Results and discussion

Precipitation samples were selected from the filters of Tomsk intake facility from underground sources including operation time of the filters. Quartz sand and crushed albitophyre were used as a filter bed. Sand grain sizes vary from 0.2 mm to 1.5 mm, while albitophyre grains: 5 – 7 mm.

Suspended particles in the filtered water settle down on the grain surface forming a layered film, which, in its turn, forms rounded brown aggregates related to oolites. The size and specific morphology of oolites depend on filter bed type and operating filter time. In operation time the precipitation film thickness varies from a thinnest layer on filter bed grains to large -sized oolites (3-4 times more than grain size) (Table 1). After air drying, the precipitation structure preserved and only mechanically disintegrates.

Table 1. Morphological characteristics of mineral neoformations.

Filter №	Filter operation time, years	Filter bed composition	Oolites size (diameter) and shape
11	21	quartz sand	5.8 – 6.5 mm (spheroidal)
19	19	quartz sand	3.5 – 4 mm (spheroidal)
7	6	albitophyre	5 – 10 mm (spheroidal -elliptical)
14	1	albitophyre	≈ equal to the filter bed grain size
17	less than 1	albitophyre	≈ equal to the filter bed grain size

Well-developed oolites in the cross-section revealed a bedded structure: if mechanically disintegrated, upper oolite layer (crust) easily laminates from the inner dense layer (core). The crust differs from the core due to its light color and specific bedding embracing alternating dark and light layers (Figures 2). Oolites have such concentrically-layered structure formed in long-term operating filters.

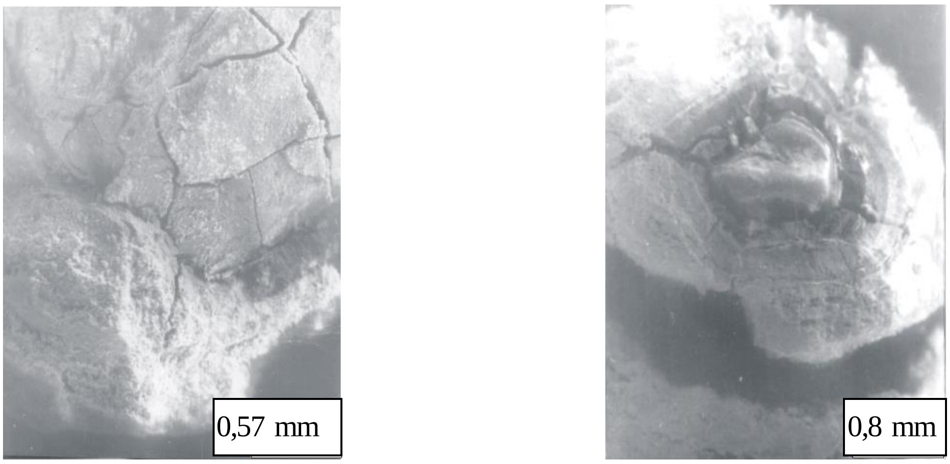

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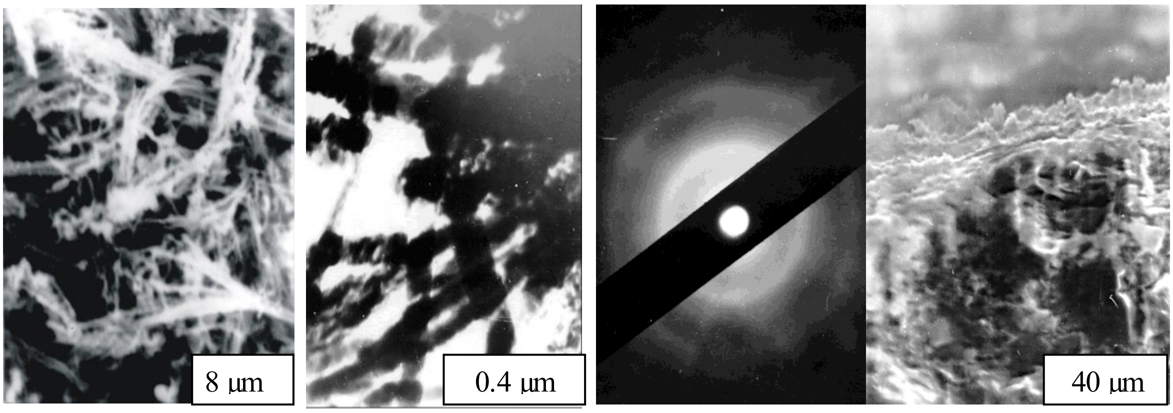
Figure 2. Structure of mineral neoformations from Tomsk water intake facility filters. Oolite is divided into two parts- (1) inner- core, and (2) outer (crust): a) conchoidal-concentric oolite from filter № 7 (cross-section); b) – layered oolite core from filter № 11 (cross-section). (Electron-microscopic analysis was conducted in Electron Microscopy Lab, TSUAB).

Microstructure studies of mineral neoformations indicate the fact that precipitations, as mineral aggregates, have specific microstructures characteristics of which are in direct relationship with the composition and behavior of the hydrogeochemical environment where they are formed. Precipitation structuring formed during the water treatment process is a multi- process as in the natural environment. This, in its turn, is most pronounced in different internal structures of oolites formed on filters of different water intake facilities.

When investigating the precipitations of different ages, it was possible to observe the microstructure evolution itself, practically from its nucleation. Initial stages of the microstructure formation were experimentally investigated. The experiment included: water-cured albitophyre and quartz grains for 48 hours. This water underwent a simplified aeration immediately at Tomsk water intake facility. Scanning and transmission electron microscopes were used to examine the precipitation microstructure and composition. Comparatively different microstructure films formed on albitophyre and quartz were not identified. SEM imaging showed a fibrous structured precipitation film composed randomly of interwoven 0.4 micron fibers and a few micrometers length (Figure 3a). The microstructure is heterogeneous: fibers are interwoven in rope-like bundles which, in its turn, form flaky ultra-microagregates of 3 – 5 μm in diameter by sticking together and inter-twisting. Fibrous microstructure observed in 48-day precipitations is simply a macro- particle aggregate consisting of joint chains. The same fibrous structure was observed in prepared suspended substances. In this case, this fibrous structure included elongated bands and ribbons, laterally about 0.15 μm and 2 μm or more in longitudinal (Figure 3b). The X-ray diffraction pattern of aggregates shows two weak diffusion halos which indicate that the aggregates are small in thickness and are amorphous (Figure 3c). In some sections one can observe twisted and interwoven bands forming micro- dispersed structures.

Six-month aggregates from Filter №17 have the following structure: rounded flakes (particles) of up to 4 μm in diameter (Figure 3c). These flakes (particles) are oriented perpendicular to grain surface of the filter bed (based on SEM results). Particles intertwine laterally forming thin layers. This structure can be characterized as a colloform structure.



a) b) c) d)

Figure 3. Mineral neoformation microstructures from Tomsk water intake facility filters: a) – fibrous precipitation structure formed during the experiment (SEM imaging); b) – ribbon-like aggregates (TEM imaging); c) – microdiffraction image of ribbons; d) flaky aggregates in the precipitation film from Filter № 17 (SEM imaging).

In all the filters the aggregates from deposited filter bed grains have a colloform structure, differing only in thickness and density of the precipitation itself. Precipitation thickness on albitophyre grains (in Filter №17) is about 16.5 μm. Comparingly, in Filter №14, after a one-year operation, precipitation thickness on albitophyre grains is 0.8-1.2 mm, while in Filter №7, operating over six years, conchoidal-concentric oolites formed on the albitophyre grains (Figure 2a). The thickness of the upper loose precipitation layer (crust) is approximately 0.2 – 0.7 mm, while the thickness of the inner dense layer (core) ranges from 0.8 to 1.2 mm. Oolites formed on the filter bed grains, precipitation thickness of about 2mm during nine-year operation of Filter №19. The research results showed that precipitations have a homogeneous coagulation structure.

Bulk chemical composition of newly-formed oolite particles is given in Table 3 (in analyzing prepared samples filter bed grains were removed). Basically, precipitation composition includes ferrum, aluminum, phosphorus and silicon compounds and precipitations contain a significant amount of water.

Table 3. Chemical composition of precipitations from Tomsk water intake facility filters

Component	Content, %	Component	Content, %
SiO_2	6.34	K_2O	0.42
Al_2O_3	17.44	Na_2O	0.27
Fe_2O_3	28.44	CO_2 carbonate.	1.41
TiO_2	0.06	Ignition loss	29.94
MnO	3.35	Total	95.78
CaO	5.63	H_2O hygroscopic	7.31
MgO	2.70	H_2O inherent	18.65
SO_3	0.12	Humus	4.88
P_2O_5	10.29	$C,_{organicr}$	2.83

NOTE: Analysis was carried out in the laboratory of the Biology Institute, Tomsk State University.

The phase and mineral composition of precipitations have been studied via thermogravimetric analysis and infrared spectroscopy and X-ray diffraction methods. It was established that precipitations are a polymineral mixture composed of ferrous, carbonate and aluminosilicate mineral phases. Ferrous phase is predominate (up to 65 %) and includes ferric hydroxides (ferrihydrate, goethite, hematite and lepidocrocite) and ferrous hydrophosphates (vivianite, strengite, strunzite and rockbridgeit). Carbonate and aluminosilicate minerals include calcite and kaolinite-group minerals, respectively. There are some traces of organic matter as iron organic complexes.

Aggregates consisting of disc-like particles (Figure 4a) formed as a result of Gallionella iron bacterial activity were found in the precipitations via transmission electron microscope. The microdiffraction image (Figure 4b) of aggregates is a combination of circular (ferrihydrate: d □ 2.24, 1.97 and 1.5 Å) and point (hematite: d □ 3.62, 257 and 1.18 Å) X-ray diffraction patterns.

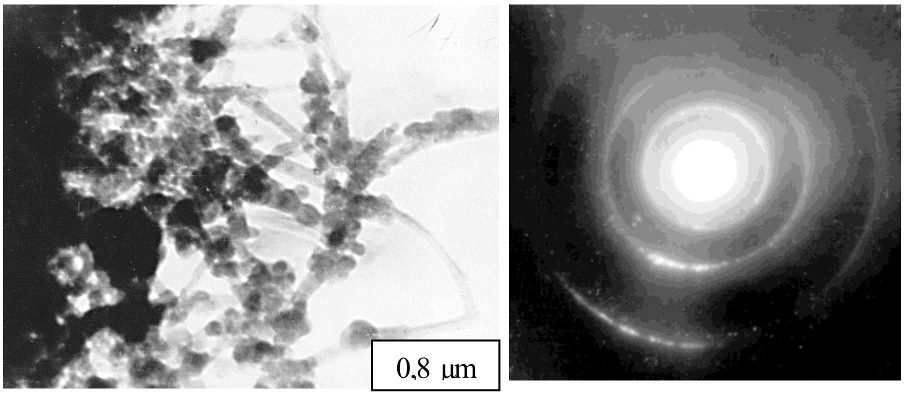


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Figure 4. (a) bacterial disco-like formations (b) aggregate of microdiffraction pattern. TEM imaging.

5. Conclusions

During water filtration treatment concentric-layered aggregates- oolites – are formed on the upper layer of the grain filter bed. Initially, fine -filmed fibrous microstructures are formed on bed grains which gradually evolve into a colloform structure. Colloform structure unit is rounded flakes of about 5 µm in diameter and their intergrowth and recompaction resulting in a layered structure. The precipitation thickness and bedding morphology depend on service time of the filter. Newly-formed oolites predominately include ferrum, aluminum, phosphorus and silicon compounds and are a polymineral mixture whose basic the component is ferrous phase – ferrihydrate, goethite and hematite. Iron bacteria are important in the precipitation of ferric hydroxides. Phosphate and carbonate phases are less. There are clay minerals of kaolinite group in the precipitation.

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