Clear of underground water from ferric and manganese modified filtering material active pink sand

Yury Skolubovich¹, Evgeny Voytov¹, Alexey Skolubovich¹ and Lilia Ilyina¹
¹Novosibirsk State University of Architecture and Civil Engineering (Sibstreen)
113, leningradskaya str., Novosibirsk, 630008, Russia
E-mail: michmacha@mail.ru

Abstract. The article analyzes the methods of purification of groundwater from iron and manganese. A particular problem is the removal of the manganese compounds from water. For the water treatment plants of small and medium capacity economically viable use of the modified filter materials. This research paper presents the technological characteristics of different catalytically active materials. The article describes the results of a study of a new modified material Active pink sand to clean groundwater from iron, manganese and other impurities.

1. Introduction
The iron removal technologies and demanganation water processes are based on the oxidation of iron and manganese compounds and converting them into insoluble compounds that are removed by clarification and filtration.

The variety of iron removal methods and demanganation water can be reduced to two basic types: reagent and reagentless.
Known methods reagentless demanganation iron removal and can be used when the raw water is characterized by: pH - not less than 6.7; alkalinity - not less than 1.0 mmol/l; carbon dioxide content of 60 mg/l, and hydrogen sulfide to 1 mg/l; permanganate oxidation - no more than 2 mg O₂/l; an iron content of not more than 5 mg/l; a manganese content of not more than 0.3 mg/l; water hardness not more than 7 mmol/l; ratio Fe⁺²/Mn⁺²>5 [4]. In other instances, are used methods of reagent treatment [7, 8].

When iron and manganese are complicated hard oxidized complexes with organic water impurities (fulvic acids, humates and others) are also necessary to use reagents: strong oxidizing agents (ozone, potassium permanganate, chlorine and its compounds), coagulants, flocculants, lime, copper salts, phosphates.

2. Materials and Methods
Of particular difficulty is the removal of manganese compounds from water. Divalent manganese oxidation rate greatly depends on the pH of water. At pH <8 without catalyst divalent manganese oxidation does not take place. Для деманганиации воды в водоподготовке в качестве окислителя широко применяется перманганат калия [5, 9].

Demanganation water by potassium permanganate is based on its ability to oxidize the manganese (II) to form a sparingly soluble dioxide of manganese

\[ 3\text{Mn}^{2+} + 2\text{MnO}_4^{-} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2\downarrow + 4\text{H}^+ \]
An important aspect of the use of potassium permanganate for water purification from manganese is the formation of particulate sediment of dioksida manganese MnO$_2$, which has a large specific surface area (300 m$^2$/g), is effective sorbent and, as mentioned above, has catalytic properties with respect to the process of oxidation of iron ions (II) and manganese (II) by oxygen.

The use of potassium permanganate as a strong oxidizing agent allows you to destroy the organometallic complexes enables to further oxidation of divalent manganese ions, iron with coagulation of oxidation products. However, the use of additional reagents that activate the oxidation of organic matter, iron and manganese in surface water significantly increases the price of its treatment for drinking water supply. Therefore, it is advisable to use filters with modified filtering medium on new purification plants of small and medium capacity.

It is found that the pre-deposited on the surface of filter media grains manganese oxides have a catalytic effect on the oxidation process of the iron ions (II) and manganese (II) by oxygen. Filtration water containing manganese, through the sand load over time on the surface of the sand grains, a layer consisting of a negatively charged hydroxide precipitate manganese Mn(OH)$_4$, which adsorbs the positively charged ions of manganese (II). These ions react in the hydrolysis process with the precipitate of Mn(OH)$_4$, forming well-oxidizable sesquioxide Mn$_2$O$_3$ the reactions:

\[ \text{Mn} (\text{OH})_4 + \text{Mn} (\text{OH})_2 \rightarrow \text{Mn}_2\text{O}_3 + 3\text{H}_2\text{O} \]
\[ 2\text{Mn}_2\text{O}_3 + \text{O}_2 + 8\text{H}_2\text{O} \rightarrow \text{Mn} (\text{OH})_4 \downarrow \]

Thus, as a result again formed manganese hydroxide (IV), which again is involved in the oxidation catalyst.

Using this property of manganese oxide give the opportunity to apply in practice, water conditioning method of its filtration through a modified filter material - sand, the grains of which pre-coated with a film of manganese oxide (so-called "black sand"). For this purpose an ordinary quartz sand grain size 0.5...1.2 mm treated sequentially with 0.5 percent solution of manganese chloride and potassium permanganate.

Formed the fine suspension of MnO$_2$ is moving closer to the surface of the grain loading and under the influence of forces (molecular, Coulomb, gravity) sticks to it, forming around each grain clusters of particles of manganese oxide.

By using such a filtering medium manganese oxidation by dissolved oxygen of air in the water may be carried out at pH values much smaller than usual (pH≤7.5). This eliminates the need for additional alkalizing water.

However, the method of water filtration through a modified medium using as reducing agent the manganese chloride has the disadvantage of gradual crushing of the particles forming the coating loading grains and their breaking through into the filtrate. Another disadvantage demanganation filtration through "black sand" is a significant consumption of potassium permanganate.

To eliminate these shortcomings developed a method for "black sand" and demanganation water by filtration through a modified media, prepared by the sequential pass upwards through the quartz sand solution ferrous sulfate and potassium permanganate.

Modification of the filter material described by the following equation:

\[ 3\text{FeSO}_4 + \text{K MnO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2 (\text{SO}_4)_3 + \text{Fe} (\text{OH})_3 + \text{MnO}_2 + \text{KOH}. \]

For fixing of the resulting film of iron hydroxide and manganese oxide on the grains of the filter medium her then further treated by threesodiumphosphate or sodium sulfite. The treated water is filtered from top to bottom with velocity 8...10 m/h.

Using of this method allows you to save the expensive potassium permanganate. Formed on the surface of filter media highly active film consisting of iron and manganese oxides, promotes the oxidation of iron and manganese in the water.
Is also known to produce catalytically active particulate filter material MFO-47, including the modification of a natural material - crushed and sorted burnt rocks with a solution of potassium permanganate, and then the second reagent - sodium sulfite and subsequent drying, which contributes to the formation on the surface of the carrier manganese oxide [3].

A common shortcoming of these ways is obtaining oxide compounds on the surface of modified filtering material grains without drying after impregnation with a solution of potassium permanganate, and the second reagent after impregnation - sodium sulfite at temperatures sufficient to form a strong chemical bonds formed between the oxides and the grain surfaces boot. Active film formed of iron and manganese oxides is kept mainly due to the adhesive properties of the surface of the grains of the carrier material. As a result, there is erosion of the oxide film from the surface of the grains of the filter material in washing, which excludes the possibility of subsequent regeneration of filter media and requires virtually complete repeat their modifications after backwashing to restore the catalytic properties of the load, which increases operating costs.

In world practice widely used filter materials for the removal of iron and manganese known under the trade names Birm Fine, Manganese Greensand, MTM. All these downloads work on the principle of catalytic oxidation on the surface of grains of manganese-filtering materials [6].

These materials allow for their periodic backwashing and, if required, subsequent regeneration of KMnO4 solution without repeating the modifications, providing long-term continuous service.

The main drawback of these materials is their high cost of delivery (about $ 2.5 per 1 kg in Russian).

The catalytically active granular filter material MZF (the company "Alliance-Neva", Saint-Petersburg) is obtained by crushing, classification, annealing dolomite and subsequent treatment with a solution of divalent manganese. The material has a sorption capacity and purifies water from iron and manganese. Delivery cost - $ 1.5 per 1 kilogram. However, the method according to the resulting material has low mechanical strength (friability of 0.5%), which reduces its durability.

A great prospect has filter material "Sorbent AC" (analogue of Birm). Sorbent AS (manufactured by "Aqua Terra", Russia) - an aluminosilicate catalyst multifunctional sorbent of new generation. It is designed primarily to remove iron. AS acts as a catalyst of oxidation in reactions of interaction dissolved oxygen with iron compounds (II) and (III), hereby forming iron hydroxide (III), which compound is insoluble and is easily removed by passage of flushing water. During the passage of filtered water through the material at its granules formed film of iron hydroxide, which further enhances the sorption properties of the material not only on iron but also hydrogen sulfide, manganese, aluminum, strontium, chromium, barium, heavy non-ferrous metals, phenol, fluorine, radionuclides and translates them into coarse particles. Sorbent is not processed further by any chemicals to create an active film on the surface of grains of sand on the basis of manganese or other catalytically active metal, which eliminates the possibility of failure of the material for exhaustion or flushing of the film. The catalytically active components included in the structure of the sorbent granules. This is one of the fundamental differences between the sorbent from the mediums such as "Birm", "Green Sand", "IWF", black sand, etc. The disadvantage of this material is its preferential treatment of water from the iron. The cleaning efficiency of manganese and other contaminants to drinking water regulations require additional research. Moreover, the cost of the filter material, but not exceed the cost of medium Birm, but still remain high.

There are prospects for new modified filter materials, developed in recent years at the Institute of mining of the Siberian Branch of the Russian Academy of Sciences (SB RAS) - brusit and manganese ores.

Brusit, Mg (OH)2 - natural crystalline magnesium oxyhydrate, containing up to 69% MgO c variable amount of silicate and carbonate minerals impurities [1]. Modification of brucite is held of its heat treatment by calcination in a muffle furnace at a temperature 400-600ºS. Thus brusit is shifting from gidrookisnyh mineral form to oxide compound. Structural changes lead to an increase in the sorption properties of brucite on iron ions in 2.5-5 times and manganese ions by - at 10-18 times. Removal of sludge from the granular medium and restore the filtering properties of brucite carried by reverse washing water.
Manganese ores - cheap natural mineral that is widely distribute on the territory of Russia. The Institute of Mining of SB PAC researched ore of deposits of the Kemerovo region. It is carbonate manganese ore (rhodochrosite) MnCO₃, belonging to the class of the group of carbonates calcite oxide manganese ore - psilomelan (Romanechite) BaMn²⁺Mn⁴⁺O₁₆·2H₂O class of complex hydrated oxide. Ores thermally modified at a temperature 400-600°C and are active sorbents and catalysts for the oxidation of Fe²⁺ ions and the Mn²⁺ by atmospheric oxygen dissolved in the water, to poorly soluble oxides detained as sediment in the deep of filter media. Sorbents rhodochrosite, psilomelan freed from the precipitate by their periodic backwash water, do not require chemical regeneration of catalytic properties and also provides a normative concentration of iron and manganese in the filtrate.

However, it should be noted that the data on the use of modified natural sorbents for iron removal and demanganation of water until are preliminary and need to address the delivery of raw materials, industrial production and certification of the filter material.

It developed a new catalytically active filter material "Active pink sand" (APS) at the Novosibirsk State Architecture and Construction University [2], currently manufactured by the enterprise "Infraspak-Lab" Novosibirsk. The filter material APS is a modified argillite rocks (pink sand) of field "Distant Mountains" various factions. The starting material is manufactured in accordance with the specifications 5712-001-48634843-99 and has sanitary-epidemiological conclusion on the admissibility of its application as a filter material for water purification. The material meets the standard requirements of the filter materials for mechanical resistance (abrasion, grind ability) and chemical resistance.

Modified pink sand is prepared by covering the surface of the starting material of manganese oxide (MnO₂) and iron (Fe₂O₃) using infiltration techniques and their soluble salts stage-heat treatment. The resulting material acquires catalytic activity in the oxidation of divalent iron ions and manganese contained in natural water by oxygen. The resulting catalytically active filter material has on the grains surface particulate firmly fixed, resistant to deterioration during periodic backwashing and regeneration the oxide film.

Oxidative capacity of the filter material at the joint purification underground water from iron and manganese is about 1.2 g of iron per 1 liter material and 0.2 g of manganese per 1 liter, which exceeds the known oxidation catalysts imported to Russia green sand and Burm. At the same time, ATM cost 15-20 times lower than similar imported. Regeneration of sorption-catalytic activity of contaminated catalytic material obtained by the proposed method during the exploitation, is carried out by pre-water washing and subsequent regeneration using potassium permanganate (KMnO₄). Filters loaded with APS efficiently incorporate to water treatment plants after the fast filters when there is high content of iron and manganese in natural water.

Research on treatment of groundwater at filters with modified loading of APS conducted in a semi industrial conditions of water treatment station in Novosibirsk (Akademgorodok) on the experimental setup shown in Fig. 1.

The model was made as a column of organic glass section 100x100 mm, loaded with active pink sand with a grain size of 0.8-1.5 mm. The height of the modified layer of media was 1.0 m.

Underground water from wells after their degassing without chemical treatment was supplied through the tank dispenser 5, air separator 1 and the reactor-clarifier 2 to the model of the prefilter 3 with inert sand load, and then on the sorption filter 4 with a modified filler. Water also could come from the tank dispenser directly to the filter with modified material without prefilter. 1 - air separator; 2 - reactor-clarifier; 3 - prefilter; 4 - filter with a modified filler.; 5 - tank dispenser; 6 - reagent tanks; 7 - dosing pumps; 8 - piezometric shield.

3. Results
As shown by the results of studies is impractical submit of treated water after the degasser-oxidizer directly to the filter with modified filtering material. The fact is that pores of modified filter material quickly clogged by formed precipitate of ferric hydroxide Fe (OH)₃ when high content of iron in the subterranean water (> 3 mg / L) and absent stage of fast water filtration when filter was necessary wash with achieve the maximum permissible loss of pressure (3-3.5 m water column for opened filters [10]).
In a two-stage filtration most of the load on the release of iron from the water took on the fast filter, and the filter with modified medium was used for purification of divalent manganese, which at pH <8.5 from the water without its prior alkalizing deduced out filter slightly. Operating speed downlink filtration on filter with a modified load was equal 8-10 m/h.

The results of efficacy studies of ground water purification filter with modified filter media (ATM) are presented in table 1. As the results of studies filter material "ATM" is effective in reducing not only the content of iron and manganese in the water, and turbidity, color, oxidation, phenol and oil

4. Conclusions
With the deterioration of quality of treated water to the maximum permissible concentration of manganese (0.1 mg/l) filter with a modified media was switched off for water washing and regeneration of the oxide film.

Table 1. The results of research of cleaning efficiency of the underground water on the filters with the modified filter material (APS)

| Points selection samples | The average quality parameters to be cleaned underground water |
|--------------------------|---------------------------------------------------------------|
|                          | Fe_{tot}, mg/l | Mn^{2+}, mg/l | Hardness, mmol/l | Turbidity, mg/l | Chromaticity, degrees | Oxidation, mg O_{2}/l | Oil products, mg/l | Phenol, mg/l |
| Prefilter                | 0.38           | 0.25           | 4.5              | 0.1              | 4.5                | 2.4                | 0.02              | 0.0009       |
| Filter with APS          | 0.11           | 0.01           | 4.1              | 0.0              | 1.8                | 1.1                | 0.00              | 0.0002       |

The duration cycle of filtration was equal to 3-4 days, depending on the quality of initial water content of iron and manganese. The loss of pressure in the filter is loaded with a modified load in this case is - 0.7-1.0 m of water. Oxidative capacity of the filter material at the joint clean underground water from iron and manganese was about 1.2 g of iron per 1 liter of filter material and 0.2 g of manganese per 1 liter. Backwash of filter with modified media conducted by clean washing water with flow rate of 15 l/(s·m^2) during 10 minutes. After washing conducted regeneration of filter media. Regeneration conducted out by treating the media 0.05% potassium permanganate solution. The required weight amount of KMnO₄ for regeneration - 2 g per liter of media. Regeneration time - 30 minutes. After backwash and the subsequent regeneration of the download, the original properties of the modified materials renewed.

During research were conducted 33 cycle of varying duration, the medium had been in operation for 90 days. There were no signs of deactivation material (reducing efficiency) subject to periodic flushing and regeneration, for the removal of iron and manganese from the treated water.

The modified filter material APS was used as a medium of water treatment filters in several cities of north of the Tomsk region.

References
[1] Bochkarev G R and Pushkareva G I 2008 Water-clear, water-preparation, water-supply 10 52 - 56
[2] 1986 Building regulations 2.04.02-84 Water supply External networks and buildings (Gosstroy SSSR, Stroyizdat) pp 45 118
[3] Gubaydulina T A and Pochuev N A 2006 Filterring material for peelings of water from manganese and ferric, way of its reception and way peelings water from manganese and ferric R.F. Patent 2275335 April 27

[4] Gurinovich A D 2001 Drinking water-supply from underground sources: problems and decisions Tehnoprint pp 1-25

[5] McFarland W E and Stearns P E 1985 Plant Engineering (USA) 39(13) 62-66

[6] http://www.updizh.ru/category/filering_materials/ (accessed 27 July 2016).

[7] Skolubovich Y L and Voitov E L 2015 Voda i sanitarna tehnika 5-6 51-57

[8] Voytov E L, Scolubovich Y L and Scolubovich A Y 2007 Solution to the Problem of Production of Drinking Water from Underground Sources of Ecologically Unfavourable Regions In the Proceedings of the 2007 International Forum on Strategic Technology (IFOST) pp 315-317

[9] Voytov E L, Skolubovich Y L, Bredihin M N and Skolubovich A Y 2009 The Way of the reception catalytic active granular filterring material. R.F. Patent. 2363536 August 10

[10] Zolotova E F 1975 Clear of water from ferric, fluorine, manganese and hydrogen sulfide (Stroyizdat) pp 176