Conditioning of Cold Low-Mineralized Groundwater

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Abstract

A novel technology has been developed for conditioning cold mineralized groundwater inherent in the northern Tyumen Region, Russia. The technology involves the use of three chemicals such as hydrogen peroxide, potassium permanganate and sodium hydroxide to provide purifying the water from iron, manganese, hydrogen sulphide and silicon up to the standards of drinking water, as well as the stabilization treatment of water. Rationale for choosing the type of reagent for stabilization treatment and the results of testing the technology are presented.

Key words: groundwater, iron, manganese, hydrogen sulphide, silicon, stabilization treatment, hydrogen peroxide, potassium permanganate, sodium hydroxide, water conditioning technology

INTRODUCTION

In 2001–2007 we have developed a new technology for conditioning groundwater aimed at drinking water supply [1–5]. This technology quite adequately takes into account the composition and physical properties of groundwater in northern Tyumen Region (extremely low temperature, alkalinity, hardness, salinity). Because of the specificity of these waters the attempts to apply thereto the processes specified by current regulations [6, 7], proved to be ineffective and did not provide the standard quality of purified water [8].

The basis of the new technology consists in the process of iron 2+ and hydrogen sulphide oxidation by hydrogen peroxide:

$$2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$$

$$\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S}^0 + 2\text{H}_2\text{O}$$

as well as the oxidation of manganese 2+, iron 2+ and hydrogen sulphide final oxidation and the oxidation of residual hydrogen peroxide by potassium permanganate:

$$3\text{Mn}^{2+} + 2\text{KMnO}_4 + 7\text{H}_2\text{O} \rightarrow 5\text{MnO(OH)}_2\downarrow + 2\text{K}^+ + 4\text{H}^+$$

$$3\text{Fe}^{2+} + \text{KMnO}_4 + 4\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{K}^+ + \text{MnO(OH)}_2\downarrow + \text{H}_2\text{O}$$

$$3\text{H}_2\text{S} + 2\text{KMnO}_4 + 2\text{H}^+ \rightarrow 3\text{S}^0 + 2\text{K}^+ + 2\text{MnO(OH)}_2\downarrow + 2\text{H}_2\text{O}$$

$$3\text{H}_2\text{O}_2 + 2\text{KMnO}_4 \rightarrow 2\text{MnO(OH)}_2\downarrow + 3\text{O}_2\uparrow + 2\text{KOH}$$

The separation of insoluble reaction products is performed via filtration through quartz sand.

The proposed technological solutions are protected by RF patent [9]. Thereby we certified hydrogen peroxide and potassium permanganate as reagents for drinking water supply [10, 11]. The technology developed has been successfully implemented in the cities of Noyabrsk and Novy Urengoy, where city water treatment plants (WTP) were established with the productivity of 75.0 and 65.0 m$^3$/day, respectively. In The WTP of the Noyabrsk City was put into continuous operation in September, 2006, whereas that of the Novy Urengoy City was turn over for continuous operation in December, 2007.

As far as the elemental content is concerned, the treatment facilities in general provided a standard quality of water (mg/dm$^3$): iron < 0.1, Mn < 0.05, H$_2$S < 0.001, residual H$_2$O$_2$ < 0.1.
As it is known, the use of reagents in the purification of drinking water is usually accompanied by secondary water pollution with the impurities thereof. The most common impurities of mineral reagents are presented by heavy metals. Table 1 demonstrates data concerning the content of some heavy metals in raw and purified water at the WTP in the Novy Urengoy City. The analysis was performed two years after starting the continuous operation, the water was taken from the raw water reservoirs (RWR) and pure water reservoirs (PWR).

It can be seen that the flowchart of chemical treatment does not result in a deterioration of water quality with respect to the content of heavy metals. Reducing the content of some components (barium, beryllium, and cobalt) occurs, to all appearance, due to the coprecipitation of reaction products such as iron hydroxide and manganese dioxide hydrate. The latter has a developed surface and thus it represents an efficient sorbent.

However, during the first year of WTP operation at individual points of the distribution network of the Novy Urengoy there were cases noted of the secondary pollution of water with iron and manganese. The studies we performed [12] allowed revealing that the mentioned phenomenon is caused by a low stability level of water and the dissolution of long-term sediments accumulated in the pipes.

In this connection, the technology developed earlier has been supplemented with the stage of stabilization treatment.

**EXPERIMENTAL**

The comparative tests of available reagents for the stabilization treatment (slaked lime Ca(OH)\textsubscript{2}, caustic soda NaOH, soda ash Na\textsubscript{2}CO\textsubscript{3}) under the laboratory conditions (Fig. 1) indicate the fact that the use of caustic soda is appropriate: the required dose thereof is twice less than the corresponding dose of soda ash. Unlike the lime, the NaOH is sufficiently pure for drinking water supply and has no insoluble part.

When choosing a grade for the reagent for stabilization treatment the preference was given to caustic soda produced in China (standard GB 5175–2008). In Europe and America, this product is certified as a food additive (acidity regulator), whereas in Russia it is certified as a reagent for drinking water supply [13].

The pilot testing performed confirmed the efficiency of the solution proposed. Below there are characteristics presented for the water fed to the pilot plant within the period of testing,
after treating thereof with hydrogen peroxide:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.9–6.1</td>
</tr>
<tr>
<td>Total alkalinity, mg-eq/dm³</td>
<td>0.18–0.22</td>
</tr>
<tr>
<td>Mineralization, mg/dm³</td>
<td>22–28</td>
</tr>
<tr>
<td>Calcium mg/dm³</td>
<td>15.0–18.0</td>
</tr>
<tr>
<td>Langelier Index</td>
<td>-2.4–-2.8</td>
</tr>
<tr>
<td>Total iron, mg/dm³</td>
<td>5.4–7.2</td>
</tr>
<tr>
<td>Iron 2+, mg/dm³</td>
<td>0.20–0.50</td>
</tr>
<tr>
<td>Manganese, mg/dm³</td>
<td>0.32–0.48</td>
</tr>
<tr>
<td>Hydrogen sulphide (sulphides), mg/dm³</td>
<td>0.02–0.04</td>
</tr>
<tr>
<td>Hydrogen peroxide, mg/dm³</td>
<td>0.30–0.50</td>
</tr>
<tr>
<td>Silicon, mg/dm³</td>
<td>11.0–12.5</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>4.3–5.9</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

Figure 2 demonstrates changing the basic indicators of the stabilization water treatment in the course of the pilot test. It is seen that in order to achieve the water acidity corresponding to pH 7.25–7.50 one needs the dose of reagent ranging within 15–18.5 g/m³. Within this dose range the alkalinity level increases up to 0.53–0.59 mg-eq/dm³, whereas the Langelier index remains within the range of the negative values. At a dose of reagent ranging within 5–10 g/m³ the water acidity corresponds to varying within the range of pH 6.5–7.0, which, to all appearance, could be considered to be an optimal solution for the waters of the Novy Uren-goy. At NaOH dose equal to 10 g/m³ the sodium content in the drinking water would increase to a maximum extent up to 6 mg/dm³. Owing to a low salinity level of water, the dose of the reagent introduced can reach 100 g/m³ with no the hazard of exceeding the standard content of sodium in drinking water (200 g/dm³).

The alkaline reagent is proposed to be introduced simultaneously with potassium permanganate. In order to simplify the process flowsheet in pilot tests, we used a combined reagent such as an alkaline solution of potassium permanganate.

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Fig. 1. Active reaction of treated water (a) and Langelier index depending on (b) the dose of reagents ($D$) in the comparative tests: 1 – CaO, 2 – NaOH, 3 – Na$_2$CO$_3$.

Fig. 2. Active reaction of the pilot plant filtrate (a) and the Langelier index (b) depending on the dose of reagent ($D$).
TABLE 2
Residual content of iron and manganese in the pilot plant filtrate

<table>
<thead>
<tr>
<th>Alkali dose, g/m³</th>
<th>Residual content, g/m³</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>at a dose of KMnO₄, g/m³</td>
<td>1.5</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>0.15</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>15</td>
<td>0.10</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>20</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>25</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>30</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

In order to study the effect of the stabilization treatment procedure on the main technological processes of the WTP such as deironizing and demanganation, we made additional measurements (Table 2).

It is seen that at a dose of the caustic soda equal to 15–20 g/m³ the residual content of iron and manganese do not exceed 0.1 and 0.05 mg/dm³, respectively. As far as the residual concentrations of hydrogen sulphide and hydrogen peroxide are concerned, these values also meet the requirements of the Russian sanitary standards (SanPin).

The working dose of potassium permanganate at the WTP of the Novy Urengoy without using the stabilization treatment technology amounts to about 2.0 g/m³. With using the stabilization treatment this value could be reduced by 25% with no detriment to the quality of the filtrate.

We should note a decrease in the silicon content to the standard values as an additional effect of the novel water treatment technology. Figure 3 demonstrates a plot for the residual silicon content in the filtrate depending on the alkali dose obtained in the course of the pilot

![Fig. 3. Residual content of silica in the filtrate of the pilot plant (Si) depending on the dose of caustic soda (D). The dose of potassium permanganate (g/m³): 1.5 (1), 2.0 (2).](image)

![Fig. 4. Flowsheet for the conditioning of cold mineralized groundwater: 1 – input unit for hydrogen peroxide, 2 – raw water reservoirs, 3 – input unit for reagents, 4 – contact capacity, 5 – filter station, 6 – pumping station for second lifting, 7 – pure water reservoirs, 8 – pumping unit for filter washing, 9 – flocculant mixer, 10 – wash water clarifiers, 11 – receptacle, 12 – pumping station for wash water, 13 – metering pump for hydrogen peroxide, 14 – tanks for hydrogen peroxide solution, 15 – tare capacity for hydrogen peroxide, 16 – pump for commercial hydrogen peroxide solution, 17 – metering pump for potassium permanganate, 18 – solution supply tanks for potassium permanganate, 19 – flocculant metering pump, 20 – solution supply tanks for flocculant, 21 – metering pump for alkali reagent, 22 – solution supply tanks for reagent.](image)
testing at the two doses of the oxidant equal to 1.5 and 2.0 g/m³.

It is evident that the technology we proposed provides decreasing the silicon content down to the values lower than the MPC; thereby this effect can be achieved also with reducing the working dose of potassium permanganate from 2.0 to 1.5 g/m³.

Figure 4 demonstrates a flowsheet of conditioning cold mineralized groundwater we have proposed for use at the WTP of the city. According to the scheme, the raw water from the boreholes is treated by hydrogen peroxide to be supplied to a raw water reservoir, where there is an almost complete oxidation of divalent iron with no formation of a suspension as well as partial hydrogen sulphide oxidation.

Water heating in winter via burning the gas allows one to avoid freezing the water in the course of transferring to the city through a land pipeline. For the purpose of performing the stabilization treatment, as well as the final oxidation of divalent iron and hydrogen sulphide, the oxidation of manganese and the reduction of the residual hydrogen peroxide, water is added with the solutions of caustic soda and potassium permanganate. In order to separate insoluble reaction products, sand filters are used. The filtered water is fed into the reservoir unit with pure water, wherefrom it is supplied to consumers.

In June 2010, the technology perfected passed industrial tests at the WTP of the Novy Urengoy, with the productivity of about 30 m³/day. The results are consistent with data obtained in the course of the pilot testing.

CONCLUSION

A novel technology has been developed for conditioning underground water, that allows one to obtain water with drinking water quality in the cases when the classical methods of water purification from iron, manganese and hydrogen sulphide are inefficient (at low temperature, salinity, alkalinity and water hardness). The technology proposed involves also the procedures of stabilizing treatment. The results of tests confirmed that the proposed technology is of high efficiency, which allows using them for the design and reconstruction of water treatment plants in the northern regions of Russia.

REFERENCES