

## Complexed iron and a groundwater treatment technology

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**Abstract.** The quality parameters and a possible treatment technology of the groundwater in Kogalym (Russian Federation) are discussed. The key problem is stable complexes of di- and trivalent iron and organics in groundwater, which after aeration tend to pass through the hydroanthracite–sand gravity filters. The total organic carbon concentration in raw groundwater is in the range 3.2–6.4 mg/L, total iron concentration is 2.7–6.0 mg/L, and divalent iron concentration 2.4–4.0 mg/L. The humic matter fraction separated from Kogalym groundwater by XAD-16 adsorbent was homogeneous, with only one peak on the chromatogram with maximum  $R_t = 10.75$  min and the corresponding molecular mass of about 2000. The final treatment technology elaborated consists of intensive aeration of raw water in the Gas–Degas Treatment unit followed by sequent filtration through hydroanthracite and special anthracite Everzit.

**Key words:** groundwater, iron, organics, iron and organic complexes, aeration, filtration.

### INTRODUCTION

Production of safe and reliable drinking water from groundwater is in many cases complicated by the increased content of iron and manganese, hydrogen sulphide and sulphides, free carbon dioxide, radon, and other dissolved gases as well as of iron and/or sulphur bacteria. Iron and manganese are present in groundwaters in their most reduced and most soluble forms: Fe(II) and Mn(II). Waters containing iron can be divided into two main groups: waters that separate iron just after aeration and waters where iron remains in the solution after aeration for endlessly long periods [1]. In the latter case we have groundwater in which the iron behaviour depends on types and concentrations of organics. Organic substances (or

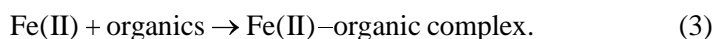
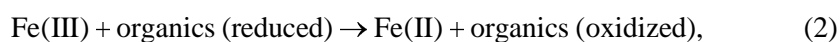
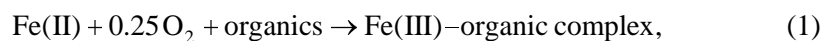
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in some cases silica) in water may interfere with the iron removal process, forming stable complexes with iron, both Fe(II) and Fe(III). The Fe(III)–humic complexes are stronger and more stable than Fe(II)–humic complexes.

Soil scientists have been quite consistent in stating that organic substances that cause these complexes or peptized small metal colloids are of relatively high molecular mass (greater than 2000), whereas water chemists generally concede that low molecular weight organics are responsible for holding iron [2]. These contradictory statements inspired us to carry out our own analyses of humic matter in the groundwater of the town of Kogalym, Tyumen, Siberia, Russian Federation.

In [3] it was established that in the presence of organic matter, the Fe(II)–Fe(III) redox couple acts as a catalyst for the oxidation of the organic matter. In such systems, both complexation of Fe(II) and reduction of Fe(III) by organic matter is possible:



In such cases, the ferrous–ferric system acts as an electron transfer catalyst for the oxidation of organic material. Depending on the relative rates of Fe(II) oxygenation and Fe(III) reduction by organic material, substantial retardation of the overall oxidation of Fe(II) by organic material is possible [4]. The higher the pH, the more the oxidation process of the Fe(II)–organic complex is retarded. For example, at pH 8, a decrease in the rate constant by a factor of 10 results in doubling the half-life of the Fe(II)–organic complex with respect to oxidation [5]. It is well known that temperature plays a key role in chemical reactions kinetics. Unfortunately, no data are available on the oxidation rate of divalent iron or iron complexes at lower temperatures (below 10°C).

Some researchers have expressed an opinion that utilization of a strong oxidizing agent like ozone to break the organic molecules, thus reducing the colour, can also make the organic substance much less tenacious as a complexing agent [6].

Cromley & O'Connor [7] compared ozone with oxygen for the oxidation of iron in a groundwater of high concentration of dissolved organic carbon (DOC). They found that ozone resulted in more rapid precipitation of the iron, although it was not clear how much of this iron was organically bound. These authors proposed that high ozone doses resulted in the formation of very stable trivalent iron–organic complexes, which could not be oxidized subsequently, i.e., ozonation need not always be superior to simple aeration in the removal of iron by filtration.

It was established by Reckhow et al. [8] that ozone oxidizes iron very quickly in the absence of organic matter. However, in the presence of humic substances at pH 6.3, iron may be completely protected from oxidation and precipitation, if the iron–organic complexes were formed under reducing conditions.

**Table 1.** The main raw water quality parameters

Parameter	Unit	Range
pH	–	6.60–6.80
Conductivity	µS/cm	178–208
Dry residue (105 °C)	mg/L	140–165
Colour	mg/L Pt	26–55
Turbidity	NTU	4–28
Fe <sub>total</sub>	mg/L	2.7–6.0
Fe <sup>2+</sup>	mg/L	2.4–4.0
COD <sub>Mn</sub>	mgO <sub>2</sub> /L	4.8–6.6
COD <sub>Cr</sub>	mgO <sub>2</sub> /L	8–13
TOC	mg/L	3.2–6.4
NH <sub>4</sub> <sup>+</sup>	mg/L NH <sub>4</sub> <sup>+</sup>	1.34–1.65
Mn	mg/L	0.09–0.16
Alkalinity	mg–eq/L	1.95–2.15

Among the technologies now in use for dealing with these challenges are the injection of air, oxygen, or ozone into water streams for stripping unwanted gases; oxidation of hydrogen sulphide, sulphides, iron, and manganese; filtration of the precipitate; and post-disinfection [9]. Iron and manganese can also be removed using biological as opposed to physical/chemical means. However, biological treatment requires specific raw water qualities and conditions, and not all groundwaters or surface waters can be treated economically using this technique [10].

The aim of the present study was to determine the main quality parameters of the raw groundwater in Kogalym and to elaborate for it a contemporary treatment technology of high efficiency with minimum chemical reagents consumption. The town of Kogalym is supplied by groundwater from 42 wells of 170 m in depth. The water is quite cold (from 0 to +2 °C), it contains free dissolved carbon dioxide (50–60 mg/L), colloidal iron (2.7–6.0 mg/L), some hydrogen sulphide, organic compounds (total organic carbon (TOC) 3.2–6.4 mg/L), and silica (40 mg/L SiO<sub>2</sub>). About 63% of all the samples taken from the local groundwater in Kogalym do not meet the Russian standards on drinking water quality. Table 1 summarizes the ranges of the main raw water quality parameters.

## EXPERIMENTAL

### Studies on the composition of humic matter and metal–organic complexes

Preliminary laboratory tests of raw water aeration and oxidation indicated clearly that iron in raw water was complexed by organic compounds when oxidized by ozone up to the trivalent state, iron stayed in the solution and was not precipitated. The total iron guideline for the treated water (drinking water) in Russia is 0.3 mg/L (in Estonia and EU countries this guideline is now 0.2 mg/L).

Then the humic matter in raw groundwater was analysed using exclusion chromatography [11]. Also the amount of metal bound with organic matter was established. A groundwater sample was filtered through a 0.45  $\mu\text{m}$  filter and then acidified with concentrated  $\text{HNO}_3$  instead of  $\text{HCl}$  to the pH value 2.0. Humic matter was extracted by filtration of 2 L of acidified water through the adsorbent XAD-16. The concentration of metals was established in the acidified water as well as in the filtered water. The amount of organically bound metals was calculated from the difference:

*Organically bound metals = total metals content in acidified water – metals content after adsorption onto XAD-16.*

For the characterization of organic matter the humic fraction adsorbed onto XAD-16 was eluted using 0.2 M solution of  $\text{NaOH}$  and immediately neutralized. Exclusion chromatograms of the initial raw water and separated humic matter fraction were taken from [11]. The column was calibrated using the protein standards. The calibration straight line corresponded to the equation:

$$\log M_w = -0.4721Rt + 8.3543 \quad R^2 = 0.9778, \quad (4)$$

where  $Rt$  is retention time, min, and  $M_w$  is mass-average molecular mass. The average molecular masses of humic matter were calculated according to the equations:

$$M_n = \frac{\sum h_i}{h_i/M_i}, \quad (5)$$

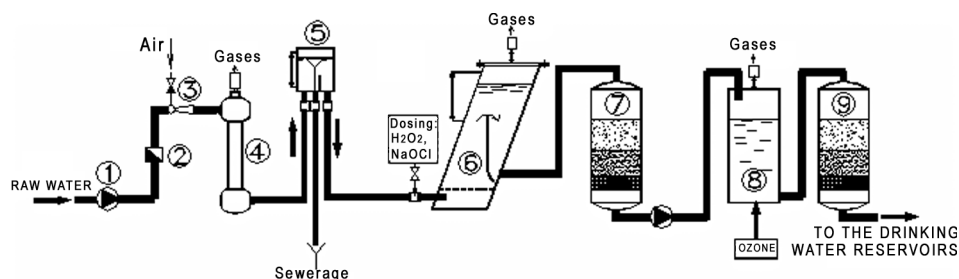
$$M_w = \frac{\sum (h_i \cdot M_i)}{\sum h_i}, \quad (6)$$

where  $M_n$  is numerical-average molecular mass,  $h_i$  is the height of the chromatographic peak at certain retention volume  $V_i$ ,  $M_i$  is the corresponding molecular mass found by the calibration curve.

If the polymer is uniform,  $M_n = M_w$ . The ratio  $d = M_w/M_n$  is called the polydispersity factor. If  $d = 1$ , the polymer is monodispersal. If  $d$  is close to 1, the polymer has a narrow distribution of molecular masses.

### **Pilot plant tests for elaborating the groundwater treatment technology**

For the elaboration of an optimum treatment technology for the raw water of the city of Kogalym a pilot plant was constructed (Fig. 1). The maximum flow rate of water at the pilot plant was 5  $\text{m}^3/\text{h}$ . The main tests were carried out at a flow rate of 1.58  $\text{m}^3/\text{h}$ . The experimental set-up consisted of a novel Gas–Degas Treatment aeration unit (GDT DS-100-316) from the GDT Corp. (Phoenix, Arizona, USA), a water collection reservoir ( $D = 0.8$  m;  $H = 0.5$  m), contact column ( $D = 0.61$  m;  $H = 3$  m), ozonation bubble column ( $D = 0.14$  m;  $H = 2.5$  m), ozone generator GOC-2 (8  $\text{gO}_3/\text{h}$  from oxygen), oxygen generator



**Fig. 1.** Schematic of the pilot plant: 1 – water pump; 2 – flow meter; 3 – injector Mazzei; 4 – degassing separator; 5 – feed tank; 6 – reactor; 7 – first-stage filter; 8 – ozonation column; 9 – second-stage filter.

AS-12 (5 LO<sub>2</sub>/min), two sequent filters (both with  $D = 0.72$  m;  $H = 3.96$  m) with different filter media. The filter media in the first filter were hydroanthracite (diameter of particles 1.4–2.5 mm;  $h = 1.1$  m) and sand (0.4–0.8 mm;  $h = 1.0$  m) and in the second filter Pyrolox (20/40 mesh;  $h = 1.2$  m) or special anthracite Everzit (0.6–2.0 mm;  $h = 1.4$  m) and sand (0.4–0.8 mm;  $h = 0.5$  m). The set-up also included a dosing system for the injection of different oxidants (ozone, hydrogen peroxide, chlorine (NaOCl)).

We were convinced by the first laboratory tests that to avoid the formation of very strong and stable Fe(III)–organic complexes, the first step of the raw water treatment – aeration – must proceed at the maximum speed and minimum retention time of water. This is why we chose for aeration a very efficient and novel Gas–Degas Technology (GDT). The GDT aeration unit consists of a patented Mazzei venturi injector to dynamically introduce gases (air, oxygen, ozone), a patented centrifugal degassing separator to quickly and effectively remove unwanted entrained gases, a degas relief valve to release the captured gases for processing or venting, and a back-pressure control valve on the water outlet pipeline from the separator. The GDT process has proven to be extremely efficient in dynamically transferring gases into pressurized solutions while removing unwanted entrained or dissolved gases. In addition to its technological benefits, the GDT process features a small footprint; low costs of capital, installation, and operation; easy installation; and nonfouling pressurized operation.

For the pilot plant tests, the smallest GDT unit with the water flow rate of 1.1–11.4 m<sup>3</sup>/h was purchased (Mazzei injector model 885-X together with the degassing separator model DS-100-316). The pilot plant in Kogalym was in operation with some short intervals for more than 2.5 years (December 1999–September 2002). During the tests, the main operating parameters (detention time of water in the GDT aerator, doses and injection points of the oxidants (O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, NaOCl), type of filtration medium, filtration rate, etc.) for determining the quality of filtered water were measured and varied.

The pH and oxidation–reduction potential (ORP) of water were measured by Testo 230 (Testo GmbH & Co), the temperature and concentration of dissolved

oxygen by electrode analyser model MJ 97, the concentration of dissolved CO<sub>2</sub> by the method of Hach Comp. (titration with 0.01 N solution of NaOH), and colour and turbidity by spectrophotometer DR/2010 (Hach Comp.). The colour of water was measured at 455 nm (Pt–Co scale) and turbidity at a wavelength of 860 nm. The iron content (ferrous and ferric) was determined by spectrophotometer DR/2010 at a wavelength of 510 nm.

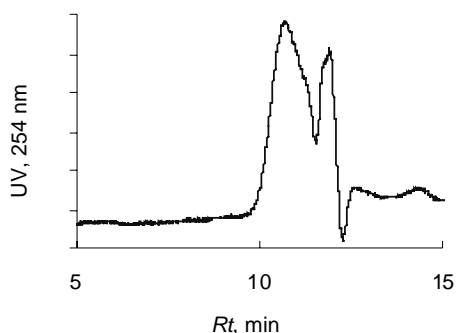
## RESULTS AND DISCUSSION

### Iron and manganese complexes with humic matter

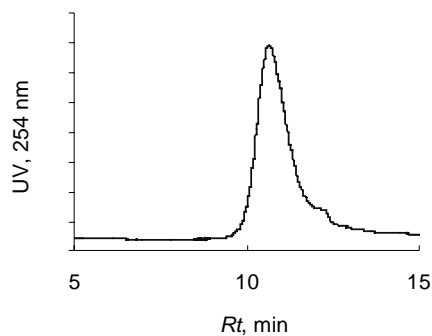
Table 2 presents the results of analyses of metals (iron and manganese) in raw groundwater after filtration through a 0.45 µm mechanical filter. It was established that almost 60% of iron and 7% of manganese were organically bound into complexes. Studies on the Kogalym groundwater humic fraction without humic matter separation (filtered through a 0.45 µm filter) showed that the numerical-average value of the molecular mass  $M_n$  was 1130 and the mass-average value  $M_w$  was 1860 with the polydispersity factor  $d = 1.65$  at the retention time  $Rt = 10.65$  min during exclusion chromatography. The exclusion chromatogram of the raw filtered groundwater is presented in Fig. 2, and the chromatogram of the humic matter fraction separated from the groundwater in Fig. 3. In Fig. 2 two peaks

**Table 2.** Fe and Mn concentrations (µg/mL) in groundwater and the humic fraction

Sample	Fe	Mn
Groundwater	0.21	0.09
In humic fraction	0.125	0.006
Metals organically bound, %	59.5	6.7



**Fig. 2.** Exclusion chromatogram of Kogalym groundwater without separation of humic matter. Column BIOSEP-SEC-S 2000 (300 × 7.5 mm); eluent: 0.02 M phosphate buffer; pH 6.8; I = 0.2 M; flowrate 1 mL/min; UV detector, wavelength 254 nm.



**Fig. 3.** Exclusion chromatogram of the humic matter fraction separated from groundwater Column BIOSEP-SEC-S 2000 (300 × 7.5 mm); eluent: 0.02 M phosphate buffer; pH 6.8, I = 0.2 M; flowrate 1 mL/min; UV detector, wavelength 254 nm.

of organic matter fractions with different molecular masses can be easily identified. The first one represents humic matter, the second one represents the mixture of monodispersal polymer. The humic matter fraction separated from water by XAD-16 was homogeneous, there is only one peak on the chromatogram in Fig. 3 with the maximum  $R_t = 10.75$  min and the corresponding molecular mass of about 2000. Thus, according to our investigation and differently from the soil scientists' statement, the organic matter responsible for metals complexing in this case is not of high molecular mass (>2000).

### **Elaboration of the most efficient treatment technology for the groundwater of Kogalym**

In 1999–2000 several flowsheets (schemes) for raw well water treatment were tested on the pilot plant in Kogalym (Fig. 1). Below the main results are shortly summarized and the final flowsheet for full-scale application is selected. As the main quality parameters of treated water, the total and divalent iron concentration, colour, and turbidity were chosen. At the first stage of the pilot tests our attention was focused on a new efficient catalytic filter medium for iron oxidation and removal – Pyrolox (American Minerals). Pyrolox is a very rare form of almost pure (100%) manganese dioxide. This material is extremely hard, like garnet, and heavy (hardness 1–2, density 4.5–5.0 g/cm<sup>3</sup>). It does not need chemical regeneration with a solution of potassium permanganate like Birm, Filox, and Manganese Greensand, but only mechanical backwash at a rate of 60–70 m/h in 24 h, and dosing of a relatively small amount of active chlorine (0.1–1.0 mg/L) at the inlet of the filter to keep the medium active.

Unfortunately, Pyrolox does not remove the complexed iron. In order to break down the iron complexes formed in the aerated water reservoir, ozone

(0.5–1.6 mg/L) was injected into water before the Pyrolox filter. The best quality parameters of water filtered through Pyrolox were obtained in the case preozonation was used: the total iron concentration was reduced by 93% and divalent iron concentration by 98.7%. The colour of the filtered water was 1 deg. (Pt–Co) and turbidity 0 mg/L. However, by the end of this cycle of pilot tests Pyrolox had lost about 50% of its initial activity due to the formation of a quite tight yellowish precipitate (iron phosphates) on the surface of its particles.

In 2000 the scheme of the pilot plant was modified: as the protecting prefilter, a filter with hydroanthracite (40% sand of 0.35–1.0 mm) was connected to the scheme, the aerated water was led directly to the hydroanthracite filter without the water reservoir to avoid the formation of very strong trivalent iron complexes, and about 35% of sand was added to the Pyrolox filter to improve the filtration properties. At the second stage of the pilot tests the impact of different oxidants, postozonation, prefiltration, and granular activated carbon (GAC) filtration was studied. The tests with hydroanthracite prefilter clearly indicated that in the case of using both filters the total iron content in filtered water was 1.7 times and colour 1.5 times lower than when only Pyrolox filter was used.

However, analysis of the contribution of the two filters in total iron removal revealed that the hydroanthracite prefilter removed about 90–94% of total iron and the Pyrolox filter 6–10%, i.e. the average efficiency of total iron removal of hydroanthracite was almost the same as that of the Pyrolox filter (92%) when used as a first stage filter. It was also established that postozonation had a quite positive additional impact on the filtered water quality: the  $\text{COD}_{\text{Mn}}$  was reduced by 20%, the colour was reduced further by 10 deg., and instead of a total 22% of colour reduction in the scheme, 54% was achieved. However, there was no impact of postozonation on the degree of total iron reduction (92–94%).

When a filter with GAC was connected after the postozonation column, the total iron content in the filtered water was 0–0.07 mg/L (reduction by 98–100%), colour 2–5 deg., turbidity less than 0.58 mg/L, and pH 7.0–7.8. The excellent quality of treated water can be explained by the impact of the GAC filter. It is well known that GAC is a very good adsorbent for heavy metals, organics, residual oxidants, and that on its surface several oxidation processes proceed, especially when ozone is added at the inlet to the filter. However, due to its quite high price, it was decided to give it up, and to replace Pyrolox in the second filter by a new special anthracite – Everzit.

Everzit-Special is a rather new filtration material from Germany, which efficiently removes trihalomethanes (THM) and other chloroorganic compounds (AOX), ammonia, and phosphates from water. A great advantage of this material is that it is able to reduce iron and manganese contents in water significantly, including also complexed iron. At the same time there is no need to use strong oxidants such as chlorine, ozone, or hydrogen peroxide. It is only necessary to have enough dissolved oxygen in water (or sufficiently high ORP values) to form a self-regenerating catalytic film of  $\text{FeO}(\text{OH})$  on the surface of the Everzit particles.



Giving up ozone also eliminated problems with the control of ozonation by-products (aldehydes, ketones, etc.). Everzit-Special has particles of 0.6–2.0 mm diameter and specific interfacial area of about 350 m<sup>2</sup>/g. It is used in open filters at filtration rates of 5–10 m/h with the water backwash rate of 30–35 m/h.

Taking into consideration the experience collected during the previous tests, we finally modified the pilot set-up to the following very simple scheme, which served as a basis for the design of the full-scale plant. A scheme of the final flowsheet of the pilot plant is presented in Fig. 4. The raw water is quickly and intensively aerated in the GDT unit and led directly to the first, anthracite filter. The filtered water is enriched with oxygen and then led to the second, polishing filter with Everzit.

For efficient iron removal in the presence of iron–organics complexes the concentration of dissolved oxygen as well as the ORP must be optimized. For example, our pilot plant tests revealed that for noncomplexed iron removal the best conditions at pH = 7.0 are +300 mV < ORP < +500 mV. If ORP << 300 mV, iron is present in water as divalent cations Fe<sup>2+</sup>. If ORP >> 500 mV, iron will dissolve in water in the form of cations Fe(OH)<sub>2</sub><sup>+</sup>.

The given values of ORP are valid only for the pure system Fe–H<sub>2</sub>O. Our ORP measurements on the pilot and full-scale plant in the conditions of iron–organics complexes showed that the iron removal process proceeds successfully when the average ORP of water after the first filter is +(96–100) mV and after the second filter +(200–205) mV. The raw water ORP was in the range –(56–90) mV. The concentration of dissolved oxygen after the GDT was in the range 7.6–9.0 mg/L. If the concentration of dissolved oxygen after the first filter is below 1 mg/L, the water before the second-stage filter must be enriched with oxygen from the oxygen generator.

When the above-described system of two sequent filters was used at the pilot plant, dissolved and complexed iron was quite efficiently removed. The raw water flowrate was 1.58 m<sup>3</sup>/h. Both filters were operated at a filtration rate of 3.89 m/h with air/water backwash in 24 h. The first-stage filter (hydroanthracite) removed 69–96% of divalent iron and 75–95% of total iron. The second-stage filter (Everzit) worked as a good polishing filter reducing the total iron content (including iron complexes) at the outlet of the filter to 0.05–0.12 mg/L, which is much less than the required Russian guideline (0.3 mg/L), and easily meets the EU guideline (0.2 mg/L). The divalent iron content at the outlet of the second-stage filter was zero (Fig. 5). The manganese concentration in the filtered water was 0.1 mg/L, phosphate concentration 0.2 mg/L, and ammonia concentration 1.2 mg/L.

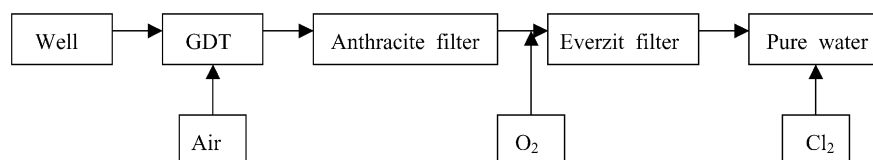
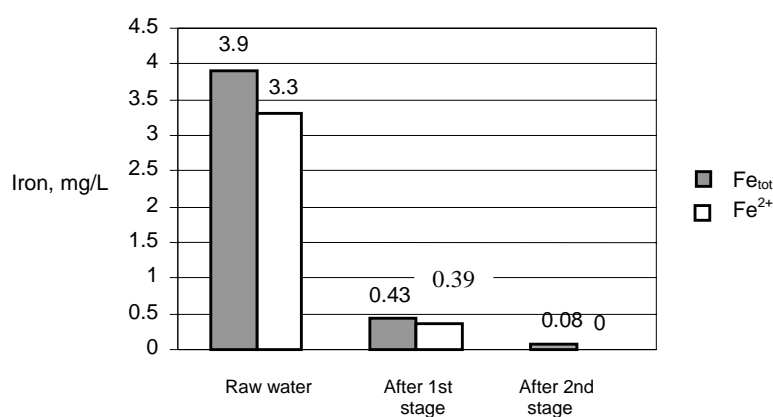


Fig. 4. The final flowsheet (scheme) for the treatment of Kogalym groundwater.

To keep the optimum ORP values of water for iron removal, the amount of air sucked into the injector of the GDT unit was reduced using elevated back-pressure. The CO<sub>2</sub> removal was much less (15–20%) than possible (60–70%) when operating at minimum back-pressure. The pH of the filtered water was in the range 6.40–6.76, which means that post-stabilization of treated water with soda (Na<sub>2</sub>CO<sub>3</sub>) is still needed.

On the basis of the pilot plant tests, the full-scale water treatment plant for Kogalym was designed by the Finnish–Estonian engineering company PIC ESTONIA Ltd. (Tallinn, Estonia) and constructed by the company CUEKS Ltd. (Tallinn, Estonia). The maximum capacity of the plant is 2500 m<sup>3</sup>/h of water. In September 2002, 50% of the plant’s capacity was successfully put into operation. The plant flowsheet is the following: the raw water is aerated in five parallel GDT aeration units (each with a maximum capacity of 750 m<sup>3</sup>/h), and then led to 10 filters of the first stage with hydroanthracite and sand. From the filters of the first stage the filtered water moves by gravity flow to the 10 filters of the second stage with a special anthracite Everzit and sand. Before the filters of the second stage, the water is enriched with oxygen from the oxygen generators to help the formation of the catalytic FeO(OH) film on the surface of the Everzit. After that, the treated water is pumped into two reservoirs of drinking water and disinfected with chlorine. It is also planned to put into operation a unit of drinking water stabilization soon to avoid pipeline corrosion (increasing pH up to 7.5 by dosing 15% solution of soda ash (Na<sub>2</sub>CO<sub>3</sub>)).

By 12 December 2002 Kogalym Plant had already been in continuous operation with the first- and second-stage filters for about three months. The iron removal efficiency of both stages had improved significantly due to the formation of the proper FeO(OH) layers in the filter bed. The behaviour of the full-scale plant has in general been quite similar to that of the pilot plant. The prevailing amount of



**Fig. 5.** Total and divalent iron concentration in raw water at the outlets of the first-stage and second-stage filters on the pilot plant.

total iron (90–94%) is separated in the first-stage anthracite filters. The second-stage polishing Everzit filters enable to reduce the divalent iron concentration to 0.02–0.1 mg/L and total iron concentration to 0.14–0.20 mg/L, which are higher than the values obtained on the pilot plant but still meet the Russian as well as the EU guidelines. Oxygen is intensively used for the catalytic FeO(OH) film build-up in both filters as its remaining concentration at the outlet of the filters is low (0.1–1.2 mg/L). Between the two filters, water is enriched with pure oxygen from the oxygen generator.

## CONCLUSIONS

The adsorbent humic matter fraction separated from Kogalym groundwater by XAD-16 was homogeneous, with only one peak on the chromatogram with maximum  $Rt = 10.75$  min and corresponding molecular mass of about 2000. Thus, our investigation showed, differently from the soil scientists' statements, that the organic matter in this specific groundwater responsible for metals complexing is not of high molecular mass (>2000).

The problem of complexed iron removal from groundwater may be solved in two different ways: first, using almost all known and available current water treatment operations (aeration, coagulation, flocculation, clarification, oxidation, filtration), which involves treatment problems of a significant amount of waste sludge, or, secondly, using a new, modern non-reagent treatment technology (fast intensive aeration together with the selection of appropriate, new filtration media capable of separating iron–organics complexes). In this study the second solution was elaborated: intensive aeration in the GDT unit together with the sequent two-stage filtration through hydroanthracite and special anthracite Everzit. The elaborated technology does not include any strong oxidants other than the usual gaseous oxygen to keep the concentration of dissolved oxygen in water at an optimum level between the first- and second-stage filters.

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## REFERENCES

1. Sommerfeld, E. O. *Iron and Manganese Removal Handbook*. American Water Works Association, Denver, CO, USA, 1991.

2. Oldham, W. K. & Gloyna, E. F. Effect of colored organics on iron removal. In *Proc. Canadian Section Meeting*. Toronto, Ont., Canada, 1968, 88–98.
3. Jobin, R. & Ghosh, M. M. Effect of buffer intensity and organic matter on the oxygenation of ferrous iron. *J. AWWA*, 1972, **64**(9), 590–595.
4. Ghosh, M. M. Filtration as related to the removal of iron from groundwaters. *Sanitary Eng. Ser.*, (Univ. Illinois, Urbana, Ill., USA), 1965, 32, 260–280.
5. Stumm, W. *Aquatic Chemical Kinetics*. A Wiley-Interscience Publ., USA, 1990.
6. Knocke, W. R., Shorney, H. L. & Bellamy, J. Reactions between soluble iron, dissolved organic carbon, and alternative oxidants during conventional water treatment In *Proc. AWWA Annual Conference*, Denver, CO, USA, 1992, 315–331.
7. Cromley, J. T. & O'Connor, J. T. Effect of ozonation on the removal of iron from groundwater. *J. AWWA*, 1976, **68**(6), 315–319.
8. Reckhow, D. A., Knocke, W. R., Kearney, M. J. & Parks, C. A. Oxidation of iron and manganese by ozone. *Ozone: Sci. Eng.*, 1991, **13**(6), 675–695.
9. Voorinen, A. Chemical, mineralogical, and microbiological factors affecting the precipitation of Fe and Mn from groundwater. *Water Sci. Technol.*, 1988, **20**(3), 249–259.
10. Mouchet, P. From conventional to biological removal of iron and manganese in France. *J. AWWA*, 1992, **84**(4), 158–167.
11. Lepane, V. Characterization of aquatic humic substances by size exclusion chromatography and capillary electrophoresis. PhD Thesis. TTU Press, 2001.

## Rauakompleksid ja põhjavee töötlemise tehnoloogia

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On uuritud raua ja mangaani orgaanilisi komplekse Kogalõmi linna (Siber, Tjumeni oblast, Vene Föderatsioon) põhjavees. Selgus, et umbes 60% rauast ja 7% mangaanist olid seotud kompleksidesse orgaanilise ainega, mille üldine sisaldus põhjavees oli piirides 3,2–6,4 mg/L. Kasutades eksklusioonkromatograafiat, tuvastati, et humiinaine on homogeenne, esitatud üheainsa piigiga kromatogrammil ( $R_t = 10,75$  min) ja molekulmassiga ligikaudu 2000. Kompleksse raua kõrvaldamiseks võib kasutada kaht erinevat tehnoloogilist lähenemist: esimene, kus kasutatakse kõiki teadaolevaid vee töötlemise operatsioone (õhustamine, koagulatsioon, flokulatsioon, selitamine, oksüdatsioon, filtrimine), mis toob ühtlasi kaasa jääkmuda käitlemise probleemi, ja teine, kus kasutatakse nii uudset vee õhustamise tehnoloogiat kui ka uudseid filtrimaterjale orgaaniliste rauakomplekside eraldamiseks. Käesolevas artiklis on valitud viimati mainitud tehnoloogiline lähenemine. On välja töötatud efektiivne Kogalõmi põhjavee töötlemise tehnoloogia, millega praktiliselt ei kaasne jääkmuda ning mille järel puurkaevust tulev põhjavesi õhustatakse väga lühikese aja jooksul USA-s välja töötatud GDT-tüüpi õhustis ja suunatakse kohe esimese astme hüdroantratsiitfiltrile ning sealt teise astme Everzit-filtrile. Skeemis ei kasutata tugevaid oksüdeerijaid, välja arvatud puhta vee reservuaaridesse järeldesinfitseerimiseks antav kloor. Esimese ja teise astme filtri vahel annustatakse vette piisava oksüdatsiooni-reduktsiooni potentsiaali (ORP) säilitamiseks puhast hapnikku.