JADWIGA KALETA*, ALICJA PUSZKAREWICZ*, DOROTA PAPCIAK*

REMOVAL OF IRON, MANGANESE AND NITROGEN COMPOUNDS FROM UNDERGROUND WATERS WITH DIVERSE PHYSICAL AND CHEMICAL CHARACTERISTICS

Technological testing of underground waters collected in four localities in the Podkarpackie province and characterized by various physicochemical and chemical parameters is presented. In order to determine the optimum methods of pollutant removal, a number of unit processes were tested. In addition to traditional methods (aeration and filtration through sand bed), the catalytic masses proved to be effective for removing iron and manganese. In the case of water of low hardness, its alkalization with calcium appears to be a favourable process. The water of excessive hardness was softened by means of sodium hydroxide and in ion exchange process. The process of ion exchange on nitrate-selective anion exchanger appeared to be an effective way of removing nitrate ions.

1. INTRODUCTION

Waters taken from underground reservoirs most often contain excessive levels of iron, manganese and ammonia nitrogen. Some of those waters have too low pH, low hardness and alkalinity, some are characterized by excessive hardness. Sometimes high concentration of iron is accompanied by more intense colour and high turbidity.

The methods which allow comprehensive removal of all contaminants from treated water are the best. Although we know many methods for removing water pollutants, new ones have still been sought and the existing improved. Most of them are based on biological and chemical oxidation [1].

The following methods deserve closer attention:
- water filtration through autogenously activated sand beds,
- filtration through active mass beds,

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* Faculty of Civil and Environmental Engineering, Department of Water Protection and Purification, Technical University of Rzeszów, aleja Powstańców Warszawy 6, 35-959 Rzeszów, Poland. E-mail: jkaleta@prz.rzeszow.pl

• application of trickling filters [4].

In some regions (the Podkarpackie province), nitrates contained in underground waters make them unfit for human consumption [2], [3], [5]. Ion exchange is considered to be the most efficient method of nitrate removal from water [6].

On the basis of research performed on natural underground waters, optimum technological methods for conditioning such waters were developed and presented. Moreover, the need to carry out full technological testing in each case is demonstrated. The designing of water conditioning stations based exclusively on physicochemical and chemical parameters of water frequently appears incorrect and conditioned water fails to meet sanitary requirements, while investors have to bear additional costs involved in subsequent modernizing steps for such stations.

2. MATERIALS AND METHODS

Water for technological tests was taken from four underground water intakes exploited in various localities in the Podkarpackie province. Basic physicochemical determinations were carried out in accordance with obligatory Polish Standards.

The following unit processes were applied during technological testing:

a) preliminary water aeration,

b) water alkalization with calcium hydroxide ($Ca(OH)_2$),

c) water alkalization with sodium hydroxide (NaOH),

d) filtration of water through beds of quartz sand, the MZ-10 (green-sand) catalytic mass, the Defeman manganese ore and the Birm mass [9],

e) the ion exchange on Wofatit KPS cation exchanger regenerated with 5% solution of NaCl (filtration column diameter, 12 mm; filling height, 220 mm; filtration rate, 8 m/h),

f) ion exchange on Purolite A520E nitrate-selective anion exchanger [8], regenerated with 5% NaCl solution (filtration column diameter, 12 mm; filling height, 220 mm; filtration rate, 8 m/h).

In filtration columns, 35 mm in diameter (the case d), the following layers can be itemized:

• a gravel (supporting) layer of 5–30 mm granulation, 0.2 m in height,

• a proper filtration layer, 0.7 m in height,

• surface anthracite layer of 1.4–2.5 mm granulation, 0.2 m in height and filtration rate of 8 m/h.

Due to highly differentiated physicochemical parameters of the waters tested, the above mentioned unit processes took place in technological process developed individually for each case.

3. DISCUSSION OF RESULTS

3.1. CHARACTERISTICS OF UNDERGROUND WATERS
FROM SELECTED INTAKES

The results of physicochemical tests (average value is based on the water samples taken in three consecutive weeks) are summarized and compared with the standards being obligatory in Poland (table 1) [11].

Table 1

Physicochemical and chemical characteristics of the waters tested

Index	Unit	The standard content	Pysznica	Hawłuszowice	Radymno	Lubzina
pH	–	6.5–9.5	5.91	6.9	6.6	7.1
Colour	Mg Pt/dm^3	15	4,0	14	49	5
Turbidity	NTU	1	5.0	5.0	48	1
Odour/flavor	–	acceptable	natural	hydrogen sulfide	natural	natural
Total hardness	mval/dm^3	1.2–10	1.26	6.80	14.60	8.5
	mg CaCO$_3$/dm^3	60–500	61.5	340	730	425
Alkalinity	mval/dm^3	–	0,15	7.20	8.7	5.1
Iron	mg Fe/dm^3	0.2	0.40	1.36	13.30	0.22
Manganese	mg Mn/dm^3	0.05	0.13	0.80	1.90	0.1
Ammonia	mg NH$_3$/dm^3	1.5	0.05	0.30	3.21	n.w.
Nitrate	mg NO$_3^-$/dm^3	50	n.w.	n.w.	n.w.	58.0
Chloride	mg Cl$^-$/dm^3	250	–	–	–	52.0
Sulfate	mg SO$_4^{2-}$/dm^3	250	–	–	–	79.1

The waters analyzed did not meet the requirements imposed on water for human consumption in the following respects:

• **Pysznica**: too low pH, too high turbidity, too high concentration of iron and manganese, low total hardness (threshold value), very low alkalinity. Although the alkalinity of water is not covered by standard, it is generally accepted that waters with alkalinity lower than 1.36 mval/dm^3 are aggressive, independently of the values of their other parameters.

• **Hawłuszowice**: inappropriate colour, turbidity, content of iron and manganese, as well as specific smell of hydrogen sulfide.

• **Radymno**: inappropriate colour, turbidity, content of iron, manganese and ammonia. Hardness of this water exceeds the upper permissible limit.

• **Lubzina**: too high concentration of iron, manganese and nitrates.

3.2. TECHNOLOGICAL TESTING OF WATER FROM THE WELL IN PYSZNICA

The tests were conducted to search for optimum methods for reducing water turbidity, excessive levels of iron and manganese, adjusting pH, raising water hardness and, in particular, the alkalinity. The technological tests were performed based on two alternative methods (table 2):

Method A. Initial aeration + alkalization with calcium hydroxide to pH 8.5, 9.0, 9.2 + filtration through sand bed.

Method B. Initial aeration + alkalization with calcium hydroxide to pH 8.5 + filtration through the MZ-10 bed.

T a b l e 2

Quality of treated water from the water intake in Pysznica

Index	Unit	Standard characteristics	Method A			Method B
			pH 8.5	pH 9	pH 9.2	
pH	–	6.5–9.5	8.2	8.9	9.2	8.2
Colour	mg Pt/dm^3	15	0	0	0	0
Turbidity	NTU	1	0	0	0	0
Odour	–	acceptable (A)	A	A	A	A
Total hardness	mval/dm^3	1.2–10	1.82	2.05	2.12	1.95
	mg CaCO$_3$/dm^3	60–500	91	102.5	106	97.5
Alkalinity	mval/dm^3	–	1.2	1.4	1.5	1.3
Iron	mg Fe/dm^3	0.2	0.01	0.00	0.00	0.00
Manganese	mg Mn/dm^3	0.05	0.08	0.07	0.00	0.00

In the method A, iron reached a standard content as early as at pH 8.5, whereas manganese compounds were removed when pH was increased to 9.2.

The method B permitted the water standards to be met at pH as low as 8.5.

Decision on an increase in alkalinity, e.g., to pH 9.0, through adding a higher dose of calcium hydroxide, ought to be taken by manager of plant.

3.3. TECHNOLOGICAL TESTING OF WATER FROM THE WELL IN HAWŁUSZOWICE

The research was aimed at searching for the methods allowing optimal removal of water odour, turbidity, colour as well as excessive level of iron and manganese. The technological tests were performed based on three alternative methods (table 3):

Method A. Aeration and filtration through sand bed.

Method B. Aeration, alkalization with NaOH to pH 9.4 + filtration through sand bed.

Method C. Filtration through the MZ-10 catalytic mass.

Quality of treated water from the water intake in Hawłuszowice

Index	Unit	Standard characteristics	Method A	Method B	Method C
pH	–	6.5–9.5	7.30	9.20	7.5
Colour	mg Pt/dm^3	15	4	0	0
Turbidity	mg SiO$_2$/dm^3	1	1	0	0
Odour	–	acceptable (A)	A	A	A
Total hardness	mval/dm^3	1.2–10	–	–	4.2
Alkalinity	mval/dm^3	–	–	–	6.5
Iron	mg Fe/dm^3	0.2	0.13	0.00	0.00
Manganese	mg Mn/dm^3	0.05	0.71	0.02	0.02

Water conditioned with method A did not allow the standards to be met because of high content of manganese. After being alkalized and filtered (method B) it reached permissible standards.

Filtration through the MZ-10 catalytic mass (method C) appeared to be most effective.

3.4. TECHNOLOGICAL TESTING OF WATER FROM THE WELL IN RADYMNO

Due to very high level of iron, a two-stage filtration was applied in water conditioning. In the first stage, water was passed through a sand filter, while the Defeman catalytic mass was applied in the second stage. Additionally the treated water had to be subjected to sodium-hydroxide softening or ion-exchange softening.

The following methods were tested:

Method A. Initial aeration + filtration through sand bed + alkalization to pH 8.7 (NaOH dose of 150 mg/dm^3) + filtration through the Defeman mass.

Method B. Initial aeration + filtration through sand bed + filtration through the Defeman mass + cation-exchanger softening.

The results obtained in each method tested are summarized in table 4.

Filtration of water through sand bed proved to be sufficient for obtaining a permissible content of iron. Trace quantities of manganese could be removed only in the second stage of filtration through both of chemically active masses. Water alkalization led to its partial softening. The alternative method of removing excessive water hardness was the ion-exchange process. Over a whole filtration cycle (time between regenerations) water with no hardness was obtained. Since such a water did not meet sanitary and health standards as well as for economic reasons it was mixed with deironed and demanganized water in suitable proportions. The water of an average hardness, well within standard, was obtained when its small volume (25%) was treated on cation exchanger. Accurate value of hardness must be determined during trial run of plant. A

significant hardness reduction at a high per cent share of water from ion exchanger is justified only in the case of claims of water consumers.

Quality of treated water from the water intake in Radymno

| Index	Unit	Standard characteristics	Filtration through sand bed	Method A	Method B
pH	–	6.5–9.5	7.06	7.41	7.18
Colour	mg Pt/dm^3	15	2	1	1
Turbidity	NTU	1	2	1	1
Odour/flavor	–	acceptable (A)	A	A	A
Total hardness	mval/dm^3	1.2–10	13.85	8.92	0.00
	mg CaCO$_3$/dm^3	60–500	692	446	0.0
Alkalinity	mval/dm^3	–	7.9	6.1	6.5
Iron	mg Fe/dm^3	0.2	0.11	0.05	0.05
Manganese	mg Mn/dm^3	0.05	0.64	0.00	0.01
Ammonia	mg NH$_3$/dm^3	1.5	1.12	0.45	0.00

3.5. TECHNOLOGICAL TESTING OF WATER FROM THE WELL IN LUBZINA

Because of excessive level of nitrates in the water taken, highly alkaline anion exchangers, working in chloride cycle, were chosen as the optimum method of its conditioning. Considering the permissible levels of impurities in water to be treated on ion exchangers, being determined by ion-exchanger manufacturers, an initial treatment was applied. It consisted in complete removal of iron and manganese compounds as a result of water filtration through the chemically-active Birm mass. The water to be conditioned was characterized by quite high total hardness, wherein the contribution of carbonate hardness to total hardness was substantial (over 60%). In order to eliminate the risk of precipitation of sediments on anion-exchanger bed, some volume of raw water was softened on sodium-cation exchanger. The selection of anion-exchanger for nitrate removal depends on the content of sulfates in water. If the ratio of sulfate ion concentration to nitrate ion concentration in conditioned water is higher than or equal to unity ($SO_4^{2-}/NO_3^- \geq 1$, the concentration expressed in mval/dm^3), the nitrate-selective anion-exchangers are applied. If this ratio is lower than unity, a regular resin may be used [7], [10]. Since the ratio of sulfates to nitrates in water from water intake no. 1 was 1.65, the Purolite A520E nitrate-selective anion-exchangers are applied in further technological tests.

On the basis of the tests performed, the changes in the quality of conditioned water during the whole cycle of ion-exchanger operation were determined, and the breakthrough-curve i.e., isoplane, was plotted. It represents the dependence of C/C_0

(C – the concentration of the outflow from column, C_0 – initial concentration) on the time of ion-exchanger operation (figure).
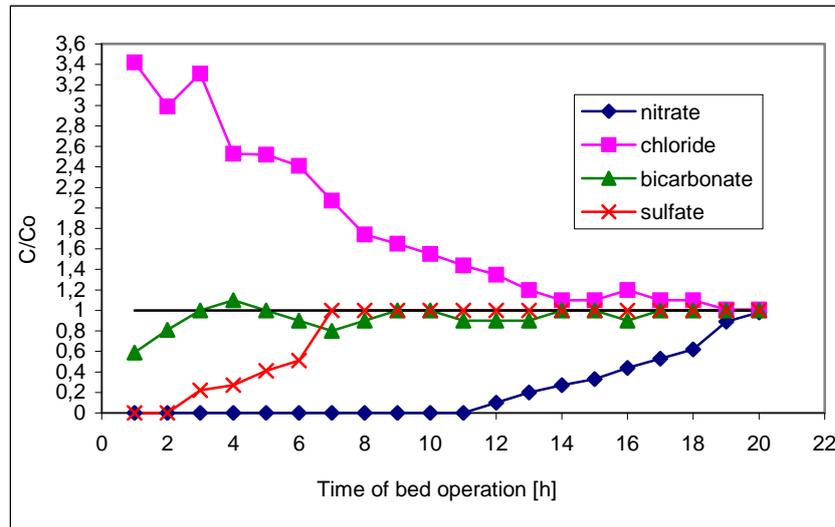
Isoplane of ion exchange on Purolite A 520 E

A very high efficiency of removing both nitrates and sulfates was observed in the initial period of ion-exchanger operation. The per cent of their reduction was 99.95% and 100%, respectively. An increase in the concentration of sulfate ions in the outflow was recorded as early as after 4 hours of ion-exchanger operation ($V_{cond.\ water}/V_{ion\ exchr.}$ = 170), while after 8 hours of operation ($V_{cond.\ water}/V_{ion\ exchr.}$ = 340) the exchange of sulfate ions stopped. Once the sulfate ion exchange capacity of anion exchangers was exhausted, nitrates continued to be exchanged with satisfactory effectiveness. The breakthrough point was observed as late as after 12 hours of bed operation ($V_{cond.\ water}/V_{ion\ exchr.}$ = 510), and the entire ion-exchange cycle lasted 24 hours ($V_{cond.\ water}/V_{ion\ exchr.}$ = 891). This confirms that the anion exchanger applied is highly selective in nitrate retention, thus it is advisable to use such an exchanger for conditioning the water containing competitive sulfate ions in high concentration. The practical/working capability of Purolit A520E in relation to nitrates was 0.40 val/dm³.

4. SUMMARY AND CONCLUSIONS

Conventional methods of underground water conditioning, i.e., aeration and filtration through sand beds, appear to be ineffective in the case of high concentration of iron and manganese, accompanied by high levels of ammonia nitrogen and hy-

drogen sulfide. Although many types of oxidative beds are available on Polish market, their capabilities of catalytic oxidation of iron, manganese and ammonia nitrogen vary widely from one to another, depending on the composition of water to be conditioned.

In the case of waters with low pH, filtration should be preceded by alkalization. Waters of low hardness should be alkalized with calcium, whereas NaOH alkalization is recommended for waters of excessive hardness. The ion exchange on cation exchanger regenerated with brine appeared to be a good alternative to hardness reduction.

Deironing and demanganizing processes, carried out with the use of catalytic masses, proved to be effective in removing ammonia nitrogen.

The conditioning system becomes more and more complicated when water contains considerable amounts of nitrates. This contaminant occurring in the water studied and tested was removed through ion exchange on highly alkaline nitrate-selective anion exchanger. The water to be treated on anion exchanger should be preconditioned in order to remove iron and manganese compounds as well as an excessive hardness.

Ion exchange has many advantages such as great process rate, simple operation of a conditioning station and the potential for its automation. However, ion exchange suffers from some drawbacks, i.e., the dependence of conditioning effects on the composition of water to be conditioned as well as secondary contamination of environment with post-regeneration outflows.

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USUWANIE ŻELAZA, MANGANU I ZWIĄZKÓW AZOTU Z WÓD WGŁĘBNYCH
O ZRÓŻNICOWANYCH CHARAKTERYSTYKACH FIZYKOCHEMICZNYCH I CHEMICZNYCH

Przedstawiono badania technologiczne czterech wód wgłębnych o zróżnicowanych charakterystykach fizykochemicznych i chemicznych. Pochodziły one z różnych miejscowości województwa podkarpackiego. Aby określić optymalne metody ich oczyszczania, przetestowano różne procesy jednostkowe. Do usuwania żelaza i manganu oprócz tradycyjnego napowietrzania i filtracji przez złoże piaskowe skuteczne okazały się masy katalityczne. W przypadku wody o małej twardości korzystnym procesem była alkalizacja wapnem. Wodę z ponadnormatywną twardością zmiękczano wodorotlenkiem sodu i w procesie wymiany jonowej. W usuwaniu jonów azotanowych skuteczny okazał się proces wymiany jonowej na anionicie azotanoselektywnym.