SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 8 – 12 RECEIVED 13. 2. 2008 ACCEPTED 4. 5. 2008

D. BARLOKOVÁ

NATURAL ZEOLITES IN THE WATER TREATMENT PROCESS

DANKA BARLOKOVÁ, PhD.
Assistant Professor at the Department of Sanitary and Environmental Engineering
e-mail: danka.barlokova@stuba.sk

Slovak University of Technology
Faculty of Civil Engineering
Radlinského 11
813 68 Bratislava

Research field: water treatment methods, natural materials in water treatments, groundwater pollution removal of iron and manganese

ABSTRACT

In many cases it is necessary to treat water intended for human consumption in order to meet the requirements under the Regulation of the Government of the Slovak Republic No. 354/2006 defining the requirements for water intended for human consumption and monitoring the quality of drinking water. When searching for appropriate water treatment technologiess emphasis is placed on the development of new, more efficient and cost-effective technologies and materials. The objective of the study was to compare the removal of dissolved iron and manganese from water by using the natural zeolite – clinoptilolite mined in the territory of Slovakia with imported filtration material – Birm. The results obtained from the experiments carried out at the Holíč Water Treatment Plant indicate that Klinopur-Mn can be used for the removal of iron and manganese in the water treatment process (contact manganese removal). This material is comparable with the imported Birm.

KEY WORDS

- *Drinking water*
- *Water treatment*
- *Natural zeolites*
- *Clinoptilolite and modified clinoptilolite*
- *Removal of manganese and iron from water*

1. NATURAL ZEOLITES – PROPERTIES AND OCCURRENCE

Despite the fact that water consumption has experienced a downward trend during recent years in Slovakia, the construction of water supply systems is still expanding. In 2005, more than 85 percent of the population was connected to the public water supply, which represents an increase of 0.7 percent compared to 2004. This means that municipalities still exist without any connection to a public water supply. Obviously, this is also related to suitable drinking water resources which are a part of a water supply system. In many cases, water meets the required quality standards, but there are also some cases where it has to be treated. In the abstraction of groundwater this mainly relates to the removal of iron and manganese. Since this technological process is very demanding with regard to investment and operational costs, it is important to search unceasingly for new ways to optimize the process. One alternative is to use distant resources and transport water by long-distance distribution systems instead of water resources of an inappropriate quality. Another option is to make the status quo ante more effective. In both cases it is necessary to carry out an economic analysis and compare the costs for water transport and treatment.
Using the natural material zeolite is one of the methods to make iron and manganese removal more effective.
Natural zeolites have been known for more than 200 years. Zeolites as mineral substances were discovered by the Swedish mineralogist Cronstedt in 1756. More than 35 types of zeolites have been discovered and described since then. However zeolites were not

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 8 — 12

applied in practice for a long time. New identification methods have contributed to the fact that in the last thirty years, over 1,000 significant cases of the occurrence of more than 50 types of zeolites in 40 countries have been recorded.

In the 1980s, a deposit of natural zeolite with a high content of zeolitic material – clinoptilolite – was found in Nižný Hrabovec in the region of the East Slovakia neovolcanites.

Natural zeolites were formed by the long-lasting effect of mineral alkaline solutions on various petrographic types of rocks of different ages at increased temperatures. It is not surprising that deposits of these aluminium silicates are located near hot mineral springs or volcanic craters. The environment in which they were formed reflects their structure and chemical composition. In a natural environment zeolites do not occur in a pure state but usually together with other minerals and rocks. Each deposit contains rocks with a specific mineralogical structure. This fact explains the importance of comprehensive research focused on the properties of natural zeolites and options for their use [1].

An octahedron is a basic structural unit of zeolite. It is a regular octahedron formed by atoms of silicon and aluminium with the tetrahedric coordination of oxygen atoms. The ratio of aluminium and manganese to oxygen is 1:2. In the crystal structure there are relatively large cavities interconnected by channels with effective diameters in a range from 0.2 to 0.7 nm. The volume of empty spaces in the structure ranges from 20 to 50 percent of the total volume of the zeolite. In these cavities mobile univalent and bivalent cations of alkali metals and alkaline earth metals (Ca, K, Na) are located and surrounded by water molecules that can be replaced with others from the surrounding solution.

A mineralogical analysis of the zeolitic mineral – clinoptilolite – is shown in Table 1. Table 2 includes a chemical analysis of clinoptlilolite from the deposit in Nižný Hrabovec and, for the sake of comparison, an analysis of samples from deposits in the Unites States – Oregon and Death Valley Junction, California [2].

A wide range of options for using natural zeolites in various industries is predetermined by their structure and physical-chemical properties. The ability to exchange cations and adsorb inorganic and organic molecules of certain sizes and catalytic properties are among the most significant features of zeolites. Moreover, the high content of Si results in the chemical and thermal stability of the mineral structure.

Table 1 *Mineralogical analysis of zeolite from the Nižný Hrabovec deposit*

Mineral	Content [%]
Clinoptilolite	84
Cristobalite	8
Feldspar	3 - 4
Illite	4
Crystal	traces
Carbonate minerals	traces (<0.5 %)

Table 2 Chemical analysis of clinoptilolite from various deposits

Compound	Content [%]		
	Nižný Hrabovec	Oregon	California
SiO_2	66.4	67.3	66.8
Al_2O_3	12.2	11.2	11.3
K_2O	3.33	5.05	3.74
CaO	3.04	0.99	0.79
Fe_2O_3	1.45	1.38	0.97
MgO	0.56	<0.30	0.33
Na_2O	0.29	1.01	3.60
MnO	0.02	0.01	0.03
TiO_2	0.15	0.25	0.10
P_2O_5	0.02	0.03	0.02t
Annealing losses	12.2	12.0	13.3

In recent decades the zeolitic mineral – clinoptilolite – has been used in the drinking water treatment process. Their sufficient mechanical strength, chemical stability and abrasion values allow natural zeolites to be used as a filtration material [3].

2. IRON AND MANGANESE – OCCURRENCE IN WATER AND METHODS OF REMOVAL FROM WATER

Iron and manganese compounds in water give rise to technological problems, failures of water supply systems and deterioration of water quality with respect to sensory properties. If these waters are slightly over-oxidized, unfavourable incrustations are formed. Iron and manganese constitute a natural part of surface water and groundwater. In natural waters without oxygen they occur only as bivalent in dissolved form. The occurrence of manganese without the presence of iron is very rare in groundwater; therefore, the technological methods for the removal of manganese are closely connected with the removal techniques for iron. The principle of the removal of iron and manganese is based on the oxidation of iron and manganese compounds to a higher valency, where they form suspended floc, which can be removed through a one-stage or two-stage separation.

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 8 — 12

Table 3 *Filtration materials and some of their parameters*

Material	Clinoptilolite	Birm	Filtration sand	Activated carbon
Grain size [mm]	0.3 – 2.5	0.42 – 2.0	0.3 – 1.0	0.3 – 1.5
Specific weight [g.cm^{-3}]	2.20 – 2.44	2.0	2.66	2.19
Apparent density [g.cm^{-3}]	0.84	0.64 – 0.72	1.55	0.40
Porosity [%]	24 – 32	–	41.7	81.7
Abrasion [%]	8.2	–	0.57	39.08

One of the methods of dissolved removing manganese is a technique using oxidized film on the grains of a filtration medium. A film is formed on the surface of filtration medium by adding potassium permanganate (and also other strong oxidizing agents). This film serves as a catalyst of the oxidation. Grains of the filtration medium are covered by higher metal oxides. In such a case it can be said that it is a special filtration – a so-called "contact filtration" – filtration on manganese filters. The oxidation state of the $MnO_{x(s)}$ medium film plays a significant role in removing dissolved manganese. The efficiency of manganese removal is a direct function of the $MnO_{x(s)}$ concentration and its oxidation state. Different filtration media result in different degrees of the efficiency of the film in removing dissolved manganese from water [4-8].

3. EXPERIMENTAL PART

Based on the current knowledge about this natural material and on studies dealing with the removal of dissolved manganese from water using oxidation films formed on the surface of different filtration materials, we performed experiments with the zeolite from Nižný Hrabovec and natural material based on natural zeolite, where the surface is also activated by black manganese. The surface of zeolite from Nižný Hrabovec is activated industrially, and its trade name is Klinopur. The second material is imported from abroad under the trade name of Birm. The costs of Birm are almost threetimes higher than that of Klinopur. Birm is used for the removal of dissolved manganese and iron from water at small water treatment plants that treat water from local resources.
The parameters of the selected filtration materials are shown in Table 3.

4. RESULTS AND EVALUATION

The measurements were carried out in a laboratory at first and later at the Holíč water treatment plant. In the water treatment plant the dissolved iron, manganese and carbon dioxide were removed from the raw water. The treatment technology included aeration of the water, the addition of $Ca(OH)_2$ to the water, slow and rapid mixing, settling tanks and contact filters. The technological scheme of the Holíč water treatment plant together with the marked location of the experimental measurements is shown in Figure 1. The experimental equipment – filtration columns – was placed behind the settling tanks (before the water inlet to the filters).
During the technological tests at the Holíč water treatment plant, the individual filtration materials and their effects on the monitored parameters and the efficiency of the removal were compared.
The diameter of the column was 5.0 cm, the height of the column was 2 m, the surface of the column covered 19.635 cm^2, and the

Table 4 *Filtration conditions*

Parameter	KLINOPUR-Mn	BIRM
Grain size [mm]	1 - 2	1 - 2
Medium weight [g]	1610	1640
Mean flow rate through the column [ml/min]	180	190
Mean filtration velocity [m/hour]	5.51	5.80
Total filtration time [hours]	1312	1312

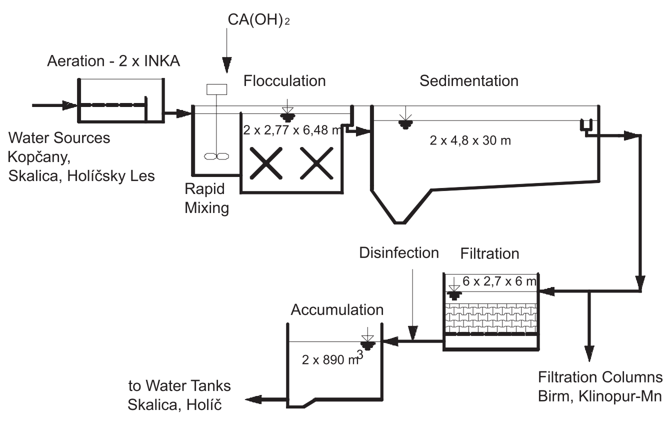

Figure 1 *Holíč Water treatment plant scheme*

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 8 – 12

height of the medium was 110.0 cm, which represented a volume of 2159.85 cm^3. The filtration material used was sieved through the sieves, and the grain size was in a range from 1 to 2 mm. The filtration conditions are shown in Table 4.

Based on the results of the "treated water" analyses, the iron concentrations after aeration and sedimentation moved in a range from 0.37 to 0.85 mg/l (mean concentration = 0.56 mg/l), and the manganese concentrations were in a range from 0.57 to 0.88 mg/l (mean concentration = 0.70 mg/l). The pH value was in a range from 8.26 to 8.38 (mean value = 8.3).

The filtration device was in operation for several months. The Charts 1 – 2, which demonstrate the removal of iron and manganese from the water were prepared based on the measured values.

It was necessary to backwash the filtration media by return flow every second day. After some time, as can be seen in charts 3 and 4, the concentration of manganese increased in the treated water over 0.05 mg/l. Both media were regenerated by 0,5 % potassium permanganate solution at that time. After the regeneration the values of the dissolved manganese in the treated water met the limits set under the Regulation of the National Council of the Slovak Republic No. 354/2006.

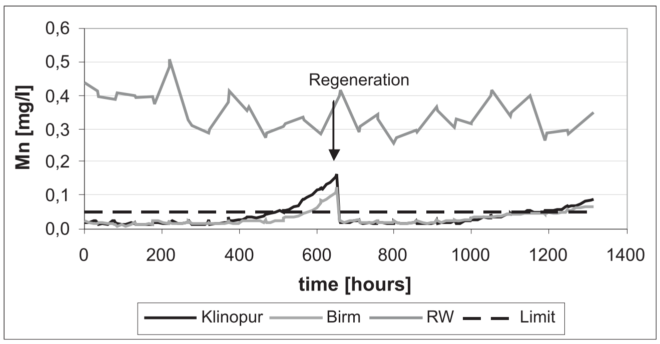

Chart 1 *Process of manganese removal at Holíč Water treatment plant*

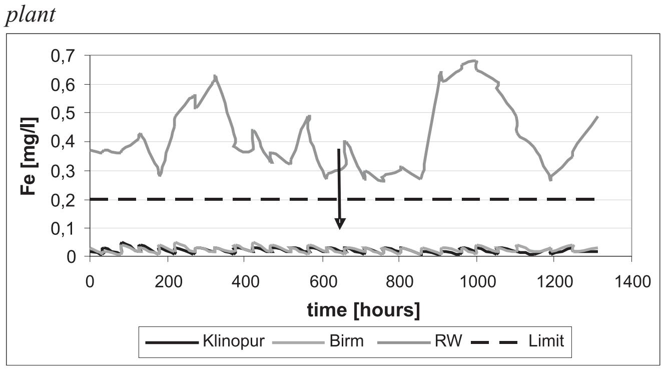

Chart 2 *Process of iron removal at Holíč Water treatment plant*

The limit value for manganese (0.05 mg/l) was exceeded after 485 hours' operation of the first filtration device filled with Klinopur-Mn and in the case of the Birm, after 576 hours. The total filtration time for the first filtration period was 651 hours. In the second filtration period the limit value for manganese was exceeded after 492 hours in the case of Klinopur-Mn and 576 hours for the Birm. The second filtration period lasted 661 hours.

The total amount of water passed through the filtration column with the Klinopur filtration material was 14.13 m^3. The volume of water flowing through the filtration device under the limit of 0.05 mg/l of Mn was 5.24 m^3 in the first filtration period; in the second filtration period, the volume of water passing through the Klinopur-Mn filtration column under the limit 0.05 mg/l Mn was 5.31 m^3.

In the case of the removal of iron from the water, Klinopur-Mn is comparable with the Birm. The limit value for iron (0.2 mg/l) was not exceeded during the whole time of the measurement (1312 hours) in the treated water.

5. CONCLUSION

The results obtained in this research stage show the possibility of using Klinopur-Mn in the removal of iron and manganese in water treatment processes (contact manganese removal). This material is comparable to the imported filtration material Birm. In this respect it is important to continue with the research aimed at identifying the length of the filtration cycle for water low and moderately contaminated by iron and manganese. Moreover, it is necessary to prepare a proposal for the optimum method of regeneration of the medium.

The same attention should be paid to knowledge about the properties of the active preparation layer, i.e., the layer's thickness or the ratio of its weight to the total weight of the material as well as its chemical composition. For future research it is recommended to carry out an evaluation of the chemical composition of the preparation and its activity based on the weight ratio of manganese to oxygen in the preparation. Based on the results of the following research, it will be possible to economically assess the whole technological process and give a clear opinion on the use of Klinopur-Mn in water treatment processes.

The technological tests were done within the VEGA1/4208/07 Grant Project.

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 8 — 12

REFERENCES

[1] **Šamajová, E., Kraus, I.(1984):** Prognózne oblasti slovenských zeolitov a možnosti ich využitia. Prediction of areas of Slovak Zeolites and the possibilities of utilizing them. In: Slovzeo"84, Vysoké Tatry, 1984, pp. 6-10.

[2] **Reháková, M., Čuvanová, S., Gavaľová, Z., Rimár, J.(2003):** Využitie prírodného zeolitu typu klinoptilolitu v agrochémii a poľnohospodárstve. Utilization of the Clinoptilolite Type of Natural Zeolite in Agrochemistry and Agriculture. Chem. listy 97, 2003, pp. 260-264.

[3] **Horváthová, E.(1989):** Výskum vlastností a eliminácie amónnych iónov z vôd prírodným zeolitom. Research of Properties and Elimination of Ammonium Ions from Water with Natural Zeolites. Vodní hospodářství 7/1989-rada B, pp.173-178.

[4] **Knocke,W.R., et al.(1991)**: Kinetics of Manganese and Iron Oxidation by Potassium Permanganate and Chlorine Dioxide. Jour. AWWA 6/1991, pp. 80 - 87.

[5] **Knocke,W.R., Hungate,R., Occiano,S.(1991)**: Removal of Soluble Manganese by Oxide-Coated Filter Media: Sorption Rate and Removal Mechanism Issues. Jour. AWWA 8/1991, pp. 64 - 69.

[6] **Knocke,W.R., Hamon,J.R., Thompson,C.P.(1988)**: Removal of Soluble Manganese on Oxide-Coated Filter Media. Jour. AWWA, 12/1988, pp. 65 - 70.

[7] **Merkle, P.B., Knocke,W.R, Gallagher (1996)**: Characterizing Filter Media Mineral Coatings, Jour.AWWA, 12/1996, pp. 62-73.

[8] **Doula, Maria, K.(2006)**: Removal of Mn^{2+} Ions from Drinking Water Using Clinoptilolite and a Clinoptilolite–Fe Oxide System. Water Research, Volume 40, Issue 17, October 2006, pp. 3167-3176.