

MODIFIED CLINOPTILOLITE FOR THE REMOVAL OF MANGANESE AND IRON FROM ARTESIAN DRINKING WATER

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ABSTRACT

Drinking water was purified with respect to manganese and iron by treating it with a clinoptilolite-rich volcanic tuff, the surface of which had been coated with a thin layer of manganese dioxide. Industrial testing was performed using pilot equipment and real artesian water. A two-stage technology for the purification of the water was employed. In the first stage, most of the iron was removed by aeration and filtration through an industrial filter loaded with natural clinoptilolite-rich tuff (Cp). In the second stage, pilot equipment was employed, in which modified Cp was used to remove manganese and residual iron. Using 1 kg of modified Cp (i.e., manganese dioxide-coated zeolitic tuff), the Mn and Fe content of 800 dm³ of water containing 1.2-1.4 mg/dm³ Mn and 0.2-0.5 mg/dm³ Fe ions was reduced to <0.1 mg/dm³ and <0.03 mg/dm³, respectively, without regeneration. The optimum conditions for regenerating the "saturated" filter material, using potassium permanganate, was found to be 0.7-0.9 dm³ 0.1% KMnO₄ solution per kilogram of modified clinoptilolite.

The industrial implementation of the proposed complex technology is now being performed at water preparation plant at Beregove, Transcarpathian Ukraine.

INTRODUCTION

Underground water specific to some regions of Ukraine contains high levels of Fe²⁺ ions (≤ 10 mg/dm³) and Mn²⁺ ions (≤ 3 mg/dm³). The health standards approved in Ukraine (see Drinking Water, 1984) require a much lower content of these ions, i.e., 0.3 mg/dm³ and 0.1 mg/dm³, respectively. Although Fe²⁺ ions can be removed from artesian water using aeration at the filters containing granular materials (see Zolotova and Ass, 1975), the existing methods for the removal of Mn²⁺ ions summarized in Tarasevich (1991) are rather inefficient. For example, White *et al.* (1995) and Hosszu *et al.* (1985) proposed the use of clinoptilolite modified with Li⁺, Na⁺, or Mn²⁺ to remove Mn²⁺ from water by ion exchange. In fact, laboratory studies by White *et al.* (1995)

showed that clinoptilolite treated with lithium or sodium was the most efficient form for the removal of manganese. In cleaning artesian water having a high manganese concentration using this material, saturation of the exchange sites of the zeolite should take place quite rapidly. In addition, the presence of Ca²⁺ and Mg²⁺ cations, characteristic of actual artesian waters, leads to a decrease of the Cp selectivity with respect to Mn²⁺. Similarly, the Na⁺- or Mn-exchanged Cp (see Hosszu *et al.*, 1985), can be used to remove manganese from drinking water having a low Mn²⁺ content (<0.3 mg/dm³), but it should not be as useful in purifying artesian waters. The regeneration of these exchanged forms of Cp is commercially inefficient.

Special filtering materials for removing Mn²⁺ must be developed (see, e.g., Colella,

1995). At present, the most efficient method seems to be the removal of Mn^{2+} from water by oxidizing onto granular filtering materials modified with higher manganese oxides, see, e.g., Graveland and Heertjes (1975) and Polyak *et al.* (1985). The regeneration of these materials is also important. The presence of hydrochloric acid in the regeneration solution, as proposed by Polyak *et al.* (1985), in addition to the $KMnO_4$, can likely lead to the dissolution of the modifying film, resulting in the degradation of the purification quality. Also, both the concentrations of the reagents and the volume ratio of the regeneration solution to filtering material proposed by Polyak *et al.* (1985) are too high.

In the present publication, we discuss the optimum conditions for the modification of clinoptilolite-rich tuff with manganese dioxide to obtain the efficient material for use in the removal of Mn^{2+} from the artesian water. The commercially and technologically efficient process of the regeneration of modified MnO_2 -Cp is described. The aim of the studies is the commercial technological implementing of modified Cp for the removal of Mn^{2+} and Fe^{2+} ions from the artesian water. Preliminary results of the demanganation of artesian water with modified Cp in the actual conditions at a working water-preparation plant were briefly summarized in Polyakov *et al.* (1997); here, we present more extended and detailed discussion.

EXPERIMENTAL

The 1-3 mm fraction of the clinoptilolite-rich zeolitic tuff (Cp) from Sokirnitsa, Ukraine, containing about 60-70% clinoptilolite was used in the study. The impurities present in the tuff are quartz, mica and magnesite; the tuff contains no smectite that swells in water. The absence of clay minerals in the zeolitic tuff from Sokirnitsa makes this material suitable for the modification and subsequent application as the filtering material. The external surface of

Cp grains, measured from benzene adsorption, was 20 m^2/g . Chemical composition of the rock (wt.%) is as follows: SiO_2 , 67.29; TiO_2 , 0.26; Al_2O_3 , 12.32; Fe_2O_3 , 1.26; FeO , 0.25; MgO , 0.99; CaO , 3.01; Na_2O , 0.66; K_2O , 2.76; H_2O , 10.90; total 99.70; Si/Al ratio 4.63. The tuff has a cation-exchange capacity of 1.44 meq/g; the exchangeable cation composition (meq/g) is: Na^+ , 0.21; K^+ , 0.22; and Ca^{2+} , 1.01.

To form the oxidant MnO_2 film on the surface of the Cp filtering material the tuff was mixed with a solution of manganese nitrate salt; Mn^{2+} introduced into the zeolite by cation exchange was then oxidized by treating it with potassium permanganate. To determine the maximum amount of the MnO_2 film that had been bonded tightly to the surface of the grains, samples containing different quantity of Mn^{2+} introduced into the exchange complex (0.02 to 0.16 meq/g) were treated with 0.5% $KMnO_4$ solution in the presence of 1% NaCl solution. The excess potassium permanganate and unbonded MnO_2 were then washed out and measured.

To evaluate the amount of manganese dioxide bonded tightly to the zeolite, the MnO_2 film was removed from the Cp surface by treating the samples with a mixture of sulfuric acid and sodium sulfite and, subsequently, with KNO_3 solution. The quantity sought was calculated from the concentration of Mn^{2+} ions in the resulting solution.

Special experiments were performed to find the optimum condition for modification of the Cp by MnO_2 . To optimize the production of MnO_2 -modified Cp the zeolitic tuff was processed using a 1% solution of $Mn(NO_3)_2$; the amount of the solution used was 0.7 dm^3/kg of zeolite. To prepare Cp, containing a surface film of MnO_2 , a 0.3% solution of $KMnO_4$ was passed through the layer of Mn-exchanged Cp at the rate of 2 m/hr; the consumption of the solution was 1.1-1.2 dm^3 per 1 kilogram of zeolite.

The methods of preparation and

application of modified Cp were tested both in the laboratory and on a pilot-plant scale at a working water-preparation plant. For the pilot plant studies artesian water of the Beregove region, Transcarpathian Ukraine, was used, the characteristics of which are listed in Table 1. Almost all of the iron was first removed using the technology of artesian water de-ironing accepted at the station. After aeration, the water was passed through the industrial filters loaded with unmodified Cp. This resulted in the decrease of iron content from 4.8-7.0 mg/dm^3 to 0.2-0.5 mg/dm^3 . To remove Mn^{2+} ions and residual iron from the water, the pilot plant was equipped with a 65-mm filter; a 2-m load height was employed and the feed flow rate was from 6 to 7 m/hr. The weight of the filtering material was 6.6 kg; the mean diameter of loaded grains ranged from 1 to 3 mm.

RESULTS

Preliminary experiments showed that to produce an acceptable quality of modified Cp the amount of Mn^{2+} ions introduced into its exchange complex should be ≤ 0.1 meq/g. The

introduction of Mn^{2+} ions into the Cp exchange complex in an amount that exceeded 0.1 meq/g did not increase the mass of MnO_2 film on the surface of the filtering material. The maximum amount of this mass, bonded tightly to the Cp surface, was shown to be about 0.4% by mass. The introduction of the amount of Mn^{2+} that exceeded that necessary to form MnO_2 film led only to the increase of the portion of weakly bonded manganese (i.e., easily removed from the zeolite surface). As applied to the industrial conditions, the prepared filtering material must be thoroughly washed to remove the MnO_2 precipitate not bounded with the zeolite; otherwise the pollution of the purified water with manganese dioxide will take place. In addition, optimizing the degree of substitution of zeolite exchange complex by Mn^{2+} ions minimized the consumption of the reagents used for the modification. The relative amount of the weakly bonded MnO_2 increased sharply if the amount (e) of Mn^{2+} introduced into the Cp exchange complex was >0.05 meq/g. For $e = 0.1$ meq/g, the amount of weakly bonded MnO_2 was 0.1% by mass. Therefore, to produce the acceptable quality of modified clinoptilolite, the amount of Mn^{2+} ions introduced into its exchange complex should be ≤ 0.1 meq/g. These ions are exchanged mainly on the external surface of the zeolite grains.

Table 2 shows the results of pilot studies for removing Fe and Mn from water using MnO_2 -modified Cp. Thus, modified Cp containing highly disperse manganese dioxide bonded tightly to the grains surface was effective in the removal of residual Fe ions and in the complete demanganation of artesian water. A calculation based on experimental results confirmed that 1 kg of modified Cp is capable of purifying 800 dm^3 of water containing 1.2-1.4 mg/dm^3 manganese and 0.2-0.5 mg/dm^3 iron ions. The Mn and Fe content was reduced to <0.1 mg/dm^3 and <0.03 mg/dm^3 , respectively, without regeneration. The capacity of the "saturated"

Table 1. Composition of artesian water of the Beregove region, Transcarpathian Ukraine, prior to cleaning with MnO_2 -modified clinoptilolite-rich tuff.

Fe (total)	4.8 - 7.2 mg/dm^3
Fe^{2+}	0.15 - 0.20 mg/dm^3
Mn^{2+}	1.1 - 1.4 mg/dm^3
Hardness	2.4 meq/ dm^3
Alkalinity	2.4 meq/ dm^3
Chlorides	14.0 mg/dm^3
Sulfates	7 mg/dm^3
Ammonia	0.2 mg/dm^3
Nitrates	not detected
Nitrites	trace
SiO_3^{2-}	15.5 mg/dm^3
Oxidizability (permanganate)	1.44 $mg O_2/dm^3$
pH	6.9 - 7.1

filtering material with respect to Mn and Fe ions can be restored by regeneration with weak potassium permanganate solution. The consumption of 0.1% KMnO₄ solution for the regeneration of catalytic and oxidizing ability MnO₂-coated Cp was 0.7-0.9 dm³/kg. The linear regeneration rate was 2 m/hr, and wash-off water consumption was 1.0-1.5 dm³/kg of regenerated material.

DISCUSSION

Compared with data reported by other authors (White *et al.*, 1995; Polyak *et al.*, 1985; Hosszu *et al.*, 1985) the process described in the present report offers essential advantages. The method ensures the efficient removal of Mn²⁺ and residual Fe²⁺ from the artesian water, provides for the prolonged operation of the filter without the regeneration, and decreases the expenditure of the reagents used for the modification and regeneration of Cp. The method can be employed under industrial conditions, and requires only minor modifications of the apparatuses used in the cleaning process.

It is interesting to consider the mechanisms of the take up of Mn²⁺ ions by

MnO₂-modified Cp in more detail. The MnO₂ film bonded tightly to the grains acted both as a catalyst for Mn²⁺ oxidation by oxygen (Graveland and Heertjes, 1975) and as an efficient oxidant. Both factors led to the transfer of dissolved Mn²⁺ ions into insoluble compounds of Mn³⁺. Active MnO₂ deposited at the surface of Cp formed an intermediate complex MnO₂·O₂ with oxygen dissolved in water. The oxidation by sorbed O₂ can be schematically presented by the following chemical reaction:



The deposited manganese dioxide acts also as oxidant, transferring Mn²⁺ ions to insoluble manganese oxide:



General chemical considerations suggest that catalytic oxidation of Mn²⁺ by air oxygen resulted in the formation of several insoluble manganese compounds, such as MnO₂, Mn₃O₄, and Mn₂O₃. Graveland and Heertjes (1975) showed that this oxidation is an autocatalytic process, in which Mn₃O₄ and

Fe₂O₃ oxides act as catalysts together with MnO₂. When tightly bonded MnO₂ acts as oxidant, Mn₃O₄ forms along with Mn₂O₃. This mechanism of the MnO₂ film action seems to be realistic (see, e.g., Nekrasov, 1980), although the detailed studies of catalytic and oxidizing action of MnO₂ tightly bonded to the surface of Cp and the mechanism of its fixing at the surface of Cp grains must still be performed.

Generally speaking, the mechanisms of the removal of Mn²⁺ from water using Cp modified with MnO₂ are based on the extended studies in the chemistry of manganese with different oxidation degree. The detailed studies of the Mn²⁺ catalytic oxidation mechanism (see, e.g., Graveland and Heertjes, 1975) lead to more precise understanding of the processes involved; however, the basics of the reactions considered above remains the same.

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Table 2. Results of pilot studies for removing Fe and Mn from water using MnO₂-modified clinoptilolite-rich tuff.

Filtration Time (hr)	Fe (total) (mg/dm ³)			Mn ²⁺ (mg/dm ³)		
	Initial water	Filtrate after removal of Fe on natural Cp	Filtrate after removal of Fe on MnO ₂ -modified Cp	Initial water	Filtrate after removal of Fe on natural Cp	Filtrate after removal of Mn on MnO ₂ -modified Cp
1	4.9	0.22	0.02	1.25	1.05	not detected
24	4.9	0.17	trace	1.16	1.06	not detected
48	5.1	0.30	trace	1.34	1.21	not detected
97	5.2	0.19	trace	1.37	1.22	not detected
121	5.0	0.12	trace	1.18	1.12	not detected
142	5.2	0.45	0.03	1.42	1.37	0.02
162	5.1	0.28	0.13	1.44	1.38	0.05
168	5.0	0.25	0.25	1.42	1.35	0.10