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Manganese removal from water by magnesium enriched kaolinite-bentonite ceramics

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ABSTRACT

Manganese is frequently present at elevated concentrations in both surface and groundwater. In addition, manganese is a health hazard, highly soluble over a wide pH range and difficult to remove from the contaminated waters. It was observed that during the interaction of Mg-enriched kaolinite-bentonite ceramics (2 wt% of Mg and Al surplus each) prepared in this work, with manganese aqueous solutions (530 μg L^{-1}–530 mg L^{-1} of Mn(II)) the manganese concentration decreases. It appears that these changes of metal concentration are on account of manganese deposition on the ceramics surface. The interaction of the ceramic samples prepared at 800°C with the manganese aqueous solutions for 24 h reduced manganese concentration up to 80%.

Keywords: Mg-enriched aluminium silicate ceramics; Manganese aqueous solution; Manganese removal from water

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1. Introduction

Intensive development of industry and agriculture causes a progressive deterioration of natural environment and a decrease in drinking water resources. The increase in concentration of different elements and compounds, which are dangerous for humans, in surface and underground waters was also observed. Among others there is manganese. Elevated concentration of manganese may also affect the appearance, taste or odour of the drinking water, leading to consumer complaints. Therefore, there is a need for drinking water treatment processes which remove manganese from natural waters in order to reduce its concentration below the recommended value for drinking water (50–400 μg L^{-1}) [1–3].

A number of methods for the removal of heavy metal and metalloid ions from waters and wastewaters have been investigated and reported: solvent extraction, ion exchange, electrochemical reduction, reverse osmosis, membrane filtration and adsorption [4].

The most common methods of manganese removal from water are oxidation, precipitation, adsorption and filtration [3,5–7]. However, soluble Mn cannot be removed by membrane filtration without being oxidized to manganese dioxide. Specifically, microfiltration after oxidation with potassium permanganate or hydrogen peroxide, and manganese sand filtration, as well as ultrafiltration with in-line prechlorination, have been applied to remove iron and/or manganese from waters [6].

Increased interest in removal of manganese from waters has prompted possible utilization of solid adsorbents: sand filters [8,9], physically and chemically

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activated carbons [5,10–13], lignite [14], fly ash [15], limestone and dolomite [16,17] instead of coagulants. Attempts to remove manganese from water by some other methods have also been reported: biological processes [18–21], water-soluble chelating polymers such as polycyclic acid [22] and electrolysis in a membrane electrolysis cell [23].

Recently, natural materials like clays, which are good and inexpensive sorbents, have received much attention in removal of heavy metals from contaminated water solutions. Due to their high cationic exchange capacity, clay minerals [24] such as montmorillonite [25], allophane [26], sepiolite [27], smectites [28], kaolinite [29], and bentonite [30] appear to be some of the most useful heavy metal adsorbents and ion exchange substances. The sorption of Ag^+, Cd^{2+}, Co^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} cations on natural and modified clays have been reported and choice of mechanisms proposed [31].

However, new, more efficient and low cost methods of drinking water treatment are searched for. The results obtained [32–35] in interaction of the Mg-enriched kaolinite-bentonite ceramics, with water solutions (with arsenic), showed favourable changes in drinking water parameters (increased rH, increased positive redox potential and substantially decreased concentration of As). Here, we report the results of manganese removal from water solutions in contact with the ceramics prepared.

2. Materials and methods

2.1. Preparation of magnesium enriched aluminium silicate ceramics

Natural kaolinite and bentonite clays were taken from the location near village Lece, south Serbia.

The ceramics was prepared by chemical and thermal transformations of natural kaolinite-bentonite clay in the way described elsewhere [32–34]. The procedure included cleaning of natural clay from small stones and other unwanted ingridients (including humic metter): milling of the clay; washing of the clay with water and centrifugation. Obtained plastic clay was well homogenised and ''noodles'' (10 mm in diameter) were made. These ''noodles'' were dried at 200°C for 3–4 h and then crashed to powder in ceramic avon. The addition of Al and Mg to the powder was done by mixing the wanted mass of powder with the wanted quantity of sturated water solutions of salts ($Mg(NO_3)_2{\cdot}nH_2O$ and $Al(NO_3)_3{\cdot}nH_2O$). Water solution of $(NH_4)_2CO_3$ for aditional opening of the pores during sintering and aqueous sodium silicate to obtain a daw viscosity suitable for granulation, were added to the mixture. The clay mass was reworked into spheres or cylinders, 10 mm in diameter on average, dried at 200°C for 3–4 h, thermally treated for 30 min at 800°C and subsequently cooled. At the sintering temperature Mg and Al nitrates and amonium carbonate decomposed and left Al and Mg atoms in the form of thin films at grain boundaries and in the pores. Expiring gases opened macro, mezo and micro pores providing, in the same time, a protective atmosphere. Thus, during the sintering process polycrystalline materials with pronouncely amorphised grain and subgrain boundaries alloyed with Mg, microalloyed with Al and enriched in nonstoichiometric surplus of these metals are formed. Movement of the grain boundaries was hindered, grain growth stopped and macro, mezo, micro and submicro pores were formed. Cooled granules were kept in closed plastic container to avoid undesired adsorpion of chemicals or water. All chemicals used were Merck p.a..

2.2. Preparation of manganese water solutions

Water solutions of manganese (II) were prepared by dissolving $MnCl_2{\cdot}4H_2O$ (Lach-ner, Czech Republic, p. a.) in distilled water. The basic solution concentration was 530 mg L^{-1} of Mn (II). Other synthetic solutions were prepared by dilluting the basic solution to the wanted concentration of Mn(II). The experiments were done with water solution of the Mn(II) concentration: 530 μg L^{-1}; 53 mg L^{-1} and 530 mg L^{-1}.

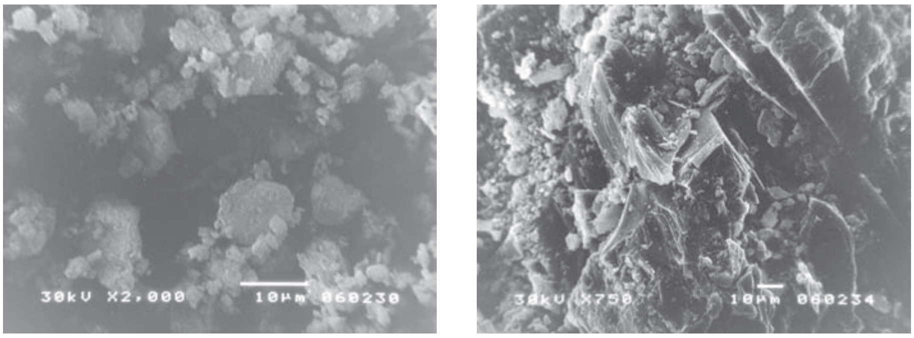
2.3. Manganese water solution in contact with Mg enriched aluminium silicate ceramics

Experimental procedures included:

(A) Randomly chosen sample among 13 ceramic spheres (a quantity used in each experiment) was taken to scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), infrared spectroscopy (IR) analysis before contact with manganese water solution.

(B) pH and E_{ROX} of a prepared manganese water solution of a chosen concentration were measured before contact of the ceramic sample with the manganese water solution.

(C) 13 spheres with total mass of 27–28 g were brought into contact with periodically stirred 250 ml of the manganese water solution (permanent stirring of all of the content in the glass beaker resulted in erosion and partial decomposition of the ceramic spheres).
  a. Concentration of Mn (II) 530 μg L^{-1} in a glass beaker for 30 min to 24 h.
  b. Concentration of Mn (II) 53 mg L^{-1} in a glass beaker for 30 min to 24 h.



(a) (b)

Fig. 1. SEM photographs of Mg-enriched aluminium silicate ceramics (2 wt% Mg and 2 wt.% Al added) obtained at 800°C: (a) magnification 2,000× and (b) magnification 750×.

   c. Concentration of Mn (II) 530 mg L^{-1} in a glass beaker for 30 min to 24 h periodically stirred with a glass stick (every 15 min for 1 min in experiments lasting one hour or less, and every 30 min for 2 min in experiments lasting more than one hour).

(D) After the period of contact with the manganese water solution the ceramic samples were dried at room temperature on filter paper and SEM, EDS, XDR and IR analysis were performed.

(E) After the time period chosen (see C (a), (b) and (c)) pH, E_{ROX} of the manganese water solution were measured. After adding hydrochloric acid (to acquire pH = 3) the solutions obtained from starting 530 µg L^{-1} Mn(II) concentration were taken to atomic absorption spectrometry (AAS) or sent to authorized analytical laboratories for manganese concentration verification.

2.4. Analytic methodes used

All pH and E_{ROX} values were obtained with laboratory pH-meter (''HACH, sensION 3'', USA). Glass electrode ''HACH'' was used to measure pH and platinum redox electrode and Ag/AgCl reference electrode ''METROHM'' was used to estimate E_{ROX}.

SEM (''JEOL JSM-5300'', Japan) with XRD (XRD – SIEMENS INSTRUMENT OF THE TYPE D – 500) and EDS capabilities (''LINK QX-2000 Oxford Instruments-XR400'', U.K.) was used to establish appearance and perform compositional and semi-quantitative analysis of the ceramics before and after contact with synthetic manganese water solutions.

''Varian Spectra A-20'' AAS instrument and independent authorized analytical laboratories (''Scientific Institute Milan Jovanovic-Batut'', Beograd, Serbia, Independent analytical laboratory ''Anachem'' Beograd, Serbia) were used to obtain manganese concentration in water solutions used.

3. Results and discussion

3.1. Characteristics of the Mg-enriched aluminium silicate ceramics prior to the contact with manganese water solutions

Figs. 1(a) and (b) show SEM photographs of the surface of the aluminium silicate ceramics prepared at 800°C (magnification 2,000× and 750×, respectively). Very high surface area, complicated morphology, range of grain sizes and shapes and high porosity of the ceramic' surface can be observed. Figs. 2 and 3 exhibit EDS and XDR analysis of the same ceramics, respectively. Fig. 4 shows the IR analysis of the ceramics presented in Figs. 1(a) and (b).

3.2. Characteristics of Mg-enriched aluminium silicate ceramics after contact with manganese water solutions

3.2.1. Characteristics of Mg-enriched aluminium silicate ceramics after contact with low concentration manganese water solutions

The AAS analysis of the manganese water solution (starting concentration of Mn(II): 530 µg L^{-1}) in contact with the ceramics in a glass beaker for 30 min (15 experiments performed) to 24 h (9 experiments

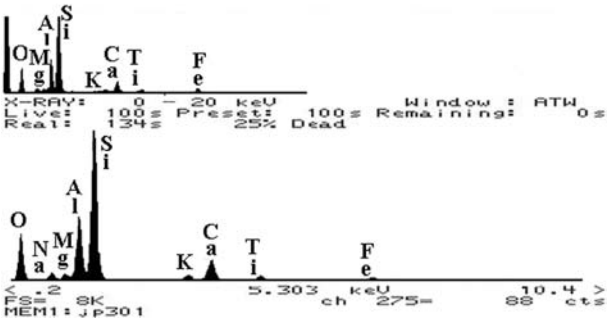


Fig. 2. EDS analysis of the ceramics presented in Figs. 1(a) and (b).

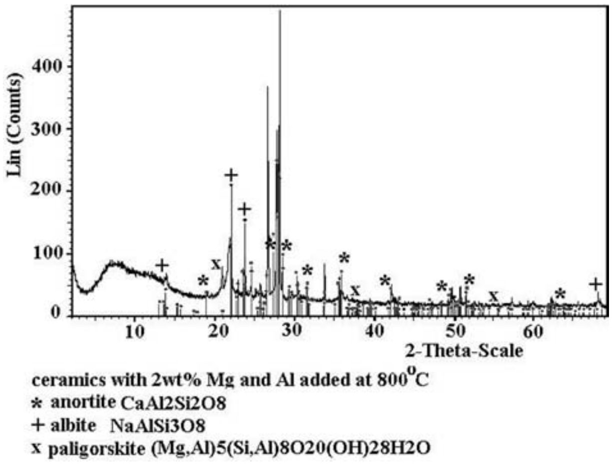


Fig. 3. XDR analysis of the ceramics presented in Fig. 1(a) and (b) revealing presence of: Anortite – $CaAl_2Si_2O_8$; Albite – $NaAlSi_3O_8$; and: Paligorskite – (Mg, Al)5(Si, Al)$8O_{20}$ (OH) $28H_2O$.

performed), showed that the Mn concentration decreased. Interaction period of 30 mins removed on average 75% of Mn, while during interaction period of 24 h Mn concentration was reduced on average for 81%. Manganese concentration decreases with the increasing interaction time, however, the largest concentration decrease was observed during initial thirty minutes to two hours of the interaction periods applied.

The average pH of the starting manganese solution was 5.42 and the average redox potential (E_{ROX}) was + 381.3 mV vs. normal hydrogen electrode (NHE). After 30 min to 24 h contact with the ceramics pH of manganese solution was 5.45 and 5.81 on average, respectively, and average redox potential was +385.2 and +390.2 mV vs. NHE, respectively

In spite of an appreciable reduction of Mn concentration in these manganese water solutions, SEM, EDS and IR analysis of the ceramics surface did not record the presence of manganese.

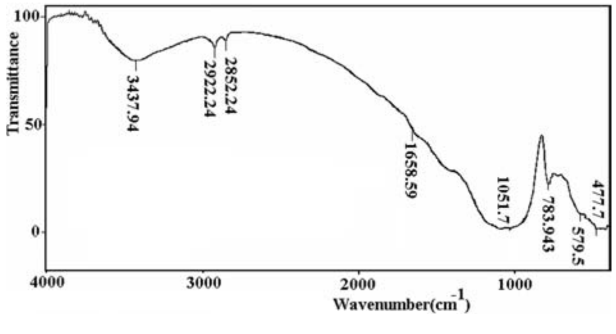


Fig. 4. IR analysis of the ceramics presented in Fig. 1(a) and 1(b).

3.2.2. Characteristics of the Mg-enriched aluminium silicate ceramics after contact with high concentration manganese water solutions

Mg-enriched aluminium silicate ceramics was brought (Section 2.3.C b) and c) into contact for 30 min to 24 h with ''high concentration'' manganese water solution (concentration of Mn (II): 53 and 530 mg L^{-1}). These experiments were performed only in order to increase the presence of manganese on the ceramics surface, if there was one, so that it could be visible on SEM and recordable by EDS. In these experiments manganese concentration in water was not measured.

The average pH of the starting manganese solution (concentration of Mn (II): 53 mg L^{-1}) was 5.75 and the average redox potential (E_{ROX}) was +400.16 mV vs. NHE.

After 30 min of interaction period pH of manganese solution was 5.87 and redox potential was +401.1 mV vs. NHE, on average and 24 h contact with the ceramics changed pH of manganese solution to 6.38 and redox potential to +420.7 mV vs. NHE, on average.

The presence of Mn at the ceramics' surface in contact with the water solution (concentration 53 mg L^{-1} of Mn (II)) for 24 h was barely visible on SEM at magnification of 7,500×, (Fig. 5a) and recorded by EDS (Fig. 5b).

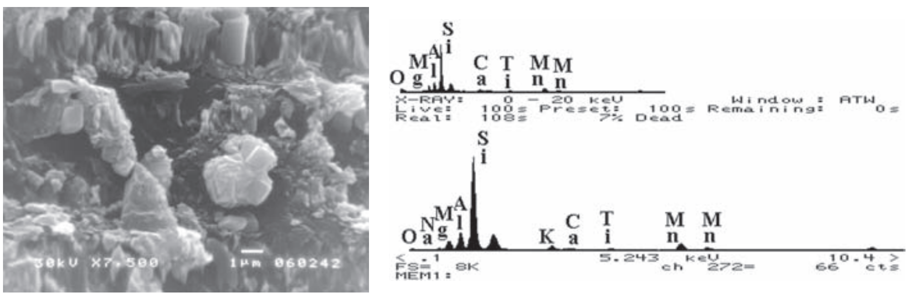
However, in the case of the most concentrated Mn water solution (530 mg L^{-1} of Mn (II)) in contact with the ceramics prepared in this work for 24 h, the results were more convincing (see Figs. 6(a) and (b)). In this case pH of the starting manganese solution was 5.90 and redox potential (E_{ROX}) was +409.6 mV vs. NHE. After 30 min of interaction period pH of manganese solution was 5.95 and redox potential was +410.5 mV vs. NHE, on average and after 24 h contact with the ceramics pH of manganese solution was 6.76 and redox potential was +431.2 mV vs. NHE.

3.3. Discussion

The aim of this work was to examine a possibility for a new process of manganese removal from water solutions, using earlier results [32–35] with magnesium-enriched aluminium silicate ceramics made from kaolinite-bentonite clay mixtures, from Blace, Serbia.

This included defining the composition (wt% of Mg and Al added) and the conditions of the thermal treatment of the ceramics preparation and its influence on the possible manganese removal from synthetic water solutions with different manganese concentration.

As it can be seen from SEM photographs, Figs. 1(a) and (b) chosen treatment of the kaolinite-bentonite clay mixture sample (2 wt% of Mg and 2 wt% Al added and



(a) (b)

Fig. 5. (a) SEM image and (b) EDS spectrum of a ceramic sample obtained at 800°C (added Mg and Al was 2 wt.% each) and treated for 24 h in 250 ml manganese water solution (concentration 53 mg L^{-1} of Mn (II)).

thermal treatment at 800°C) indicated that the ceramics is composed primarily of the highly porous and non-uniform ceramic structures, and well-developed surface. Individual metal grains of Mg and Al surplus (2 wt% of each added) could be seen on the ceramics' surface under SEM.

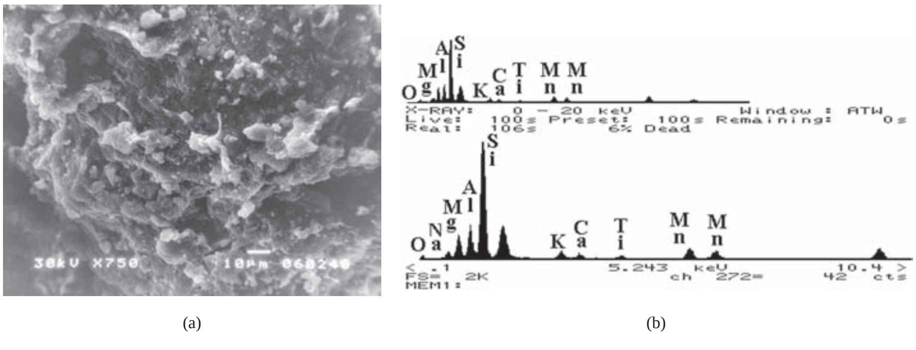
The EDS spectrum of this ceramics is presented in Fig. 2. showing Mg, Al, Ca, Na, Si and Fe, peaks which have been known to be the principal metal elements of the kaolinite- bentonite clays. EDS spectra observed difference in the element's peak intensities for different surface areas, that lead to the conclusion that the ceramics specimens are composed of individual phases that differ in amount and ratio of the oxides and elements present [35].

XDR analysis revealed more about chemical composition of the ceramics prepared in this work, Fig. 3, namely anortite ($CaAl_2Si_2O_8$), albite ($NaAlSi_3O_8$) and palygorskite ($(Mg, Al)5(Si, Al)8O_{20}(OH)28H_2O$); surplus of magnesium and aluminium and nonstoichiometric compounds-phases formed due to Mg and Al surplus apart from kaolinite and bentonite.

IR spectra of the ceramics prepared in this work, Fig. 4, were very much in accordance with published data concerning kaolinite-bentonite clay mixtures [36].

When analysed in the ways presented above, the ceramic spheres brought into contact for 30 min to 24 h with ''low concentrated'' manganese water solutions (starting Mn(II) concentration: 530 Mn(II) µg L^{-1}), no visible difference in SEM, IR, XDR or EDS results could be observed. Very small difference in amplitude, but not in the wave length, between IR spectra of a ceramic sample before and after contact with manganese water solution could be seen. In other words, no presence of manganese on the ceramics examined was recorded by SEM, IR or EDS techniques for these samples. However, the AAS analysis of the manganese water solution concentration prior to contact with the ceramics and after 30 min to 24 h long contact have shown 75–81% reduction in manganese presence in the manganese water solution used.

It seemed logical to conclude that manganese ions concentration in the solutions was lowered by the ceramics it was brought in contact with, although SEM, IR and EDS examinations of the same ceramics did not show the presence of manganese. However, the concentrations smaller than 1 wt.% in the ceramics surface could not be detected by EDS attached to SEM, unless a pronounced inhomogeneous distribution or segregation of elements was present.



(a) (b)

Fig. 6. (a) SEM image and (b) EDS spectrum of a ceramic sample obtained at 800°C (added Mg and Al was 2 wt.% each) and treated for 24 h in 250 ml manganese water solution (concentration 530 mg L^{-1} of Mn (II)).

When SEM and EDS results obtained from the ceramics brought into contact for 24 h with the solutions whose starting Mn (II) concentrations was 53 and 530 mg L^{-1} were compared with those for the same ceramics before the contact, very convincing visible difference in SEM and EDS results could be observed (compare Fig. 1. and Fig. 2 with Fig. 5 and Fig. 6). SEM photographs in Figs. 5(a) and 6(a), exhibit manganese deposit in the form of small metal boulders on the ceramics surface.

In the same time Mn concentration in manganese aqueous solution (starting concentration 530 μg L^{-1}) brought into contact with the ceramics made in this work, according to AAS analysis, decreases with increasing time of contact up to 83%.

It seems that Mg, Al, Ca, K and Na metal surplus from the ceramics surface dissolves when in contact with manganese water solution due to the metal's negative electrode potentials. It appears that by dissolution of the said metals in the aqueous solution electrons are produced which reduce Mn (II) to atomic manganese. Having in mind standard electrode potentials of Mg (−2,372 V vs. NHE), K (−2,931 V vs. NHE), Al (−1,662 V vs. NHE), Na (−2,71 V vs. NHE), Ca (−2,868 V vs. NHE) and Mn (−11,857 V vs. NHE) [37] and pH changes of the manganese aqueous solution, the offered explanation seems reasonable.

It is well known that aluminium in contact with water, although having rather negative standard electrode potential, easily builds passive oxide layer. However, in the presented case the presence of magnesium and some other deposited metals in the ceramics surface (in ppm quantities compared to aluminium) keep aluminium dissolving very slowly at the corrosion potential 0.2–0.4 V more positive than the aluminium standard electrode potential. In the same time magnesium dissolves much faster under the same conditions.

The role of aluminium in this ceramics seems to be to act as a principal receptor for mobile oxygen ions because it builds the most stable oxides of all metals present. At the same time, all of the metals with electrode potentials more negative than aluminium dissolve in contact with water.

The electrons produced on the ceramics' surface in contact with water (or aqueous solution) induce reduction of Mn cations and their deposition on the ceramics' surface in the form of adsorption, separate clasters, occlusion and clathrate type deposits. Most probably, this deposition takes place, on the surface of nonstoichiometric phases and amorphous structures which cover almost every grain of the ceramics exposed to the water solution. Deposited manganese is probably initially in the form of adatoms and very thin adsorbed layers. These reduction–adsorption processes continue as long as magnesium and aluminium dissolve into metal ions and enter water solution. It should be expected that the removal of manganese from aqueous solution would cease when a manganese bulk phase is formed, or magnesium and aluminium dissolution in water terminates. Figs. 5(a) and 6(a) show rhomboid formed small grains of deposited manganese.

Additionally, electrophoretic deposition of Mn particles into macro, mezo, micro and sub micro pores of the ceramics, due to high surface charge density (positive and negative) therein, is very probable.

Redeposited metals make microgalvanic cells with magnesium and aluminium on the ceramics surfaces, whereby electrons are produced by magnesium and aluminium oxidation for further reduction processes in the adjacent water.

Evidence of magnesium and some aluminium hydroxides in the form of gelatinous sediment; and contribution of sodium, potassium and calcium changes pH of the solution from $pH = 5.75$ to the values $pH = 6.76$, also support the proposition.

All the material taken from the water by the reduction processes, induced in contact with the ceramics, becomes part of the ceramics complex structure and being electrochemically more positive than Na, K, Ca, Mg and Al cannot dissolve in water again. This makes used ceramics ecologically safe. Therefore, the used ceramics can be mixed with cement and used for concrete block production, for example.

On the other hand, it is obvious that magnesium-enriched aluminium silicate ceramics can improve the quality of treated waters, Table 1.

The possibility to choose from a great number of processes (adsorption, electrochemical, partial ion exchange and other redox processes) engaging heavy metal cations present in water, makes this ceramic a very powerful tool for treatment of drinking waters.

4. Conclusions

Addition of some active components ($Al(NO_3)_3$, $Mg(NO_3)_2$ and $(NH_4)_2CO_3$) to the mixture of kaolinite and bentonite can provide clay mixtures, which after sintering at high temperatures produce very porous ceramics with microcrystalline and amorphous regions of stoichiometric and nonstoichiometric new oxides and some metallized surface (in our case-mainly with magnesium and aluminium surplus). Nonstoichiometric oxide mixtures and metallized amorphous ceramics regions show high electrochemical and chemical activities in contact with water. It seems that the surplus of Mg and Al in plastic clay mixture before and change of stoichiometric contents during the thermal treatment results in amorphization of grain boundaries

Table 1
The change of the pH, E_{Rox} and rH of manganese water solution before and after contact with magnesium enriched aluminium silicate ceramics

	The pH, E_{Rox} and rH of manganese water solution before contact with magnesium enriched aluminium silicate ceramics			The pH, E_{Rox} and rH of manganese water solution after contact with magnesium enriched aluminium silicate ceramics			
	pH	E_{Rox} (mV) vs. NHE	rH	Time (h)	pH	E_{Rox} (mV) vs. NHE	rH
Manganese water solution conc. 530 μg L^{-1}	5.42	+381.3	23.55	0.5	5.45	+385.2	23.74
				24	5.81	+390.2	24.62
Manganese water solution conc. 53 mg L^{-1}	5.75	+400.16	24.83	0.5	5.81	+401.1	24.99
				24	6.38	+420.7	26.78
Manganese water solution conc. 530 mg L^{-1}	5.90	+409.6	25.45	0.5	5.95	+410.5	25.58
				24	6.76	+431.2	27.89

of all present phases, i.e., in an effect of metallization of the ceramics. This metallization offers substantially greater mobility of ions present (Mg^{2+}, Al^{3+}, K^{+}, Na^{+}, Ca^{2+}, SiO_3^{2-}).

It appears that magnesium-enriched aluminium silicate ceramics prepared in this work substantially decreases manganese concentration in the manganese water solutions they were brought into contact with.

During the interaction of the ceramics with manganese aqueous solution the decrease of Mn concentration in the solution was due to electrochemical reduction and incorporation of Mn from the solution into ceramics' surface. With the ceramic samples prepared at 800°C up to 83% of manganese was removed from manganese aqueous solution (starting concentration 530 μg L^{-1}). It has taken only 30 min to reduce manganese concentration for 75% in the manganese aqueous solution of this starting concentration.

In fact, by careful planning and right choice of active components of the magnesium–aluminium silicate ceramics, it is possible to program in advance the tailor made electrochemical activity and capacity of their influence on the structure and the content of the waters it comes in contact with.

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