

ELECTROCHEMICAL BEHAVIOUR OF THE CATALYST WITH KAOLINITE-BENTONITE SUBSTRATE IN WATER

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Abstract. *Due to the fact that oxidation-reduction potential and rH_2 value of every water are its crucial features, numerous efforts have been made to use electrochemical means for water preparation. In this paper, we report the results of electrochemical influence research of magnesium-aluminium silicate catalyst, in the form of ceramics made of kaolinite and bentonite clays, on the rH_2 , pH and E_{OR} changes of the waters of particular characteristics in the wanted direction. Particularly, the possibility of changing "active water" characteristics was investigated. The composite made with microalloyed aluminium exhibits a very negative stationary potential and its interaction with water results in water reduction. Addition of some active components to the mixture of kaolin 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 surplus). Nonstoichiometric oxide mixtures and metallized amorphous ceramics regions show high electrochemical and chemical activities in contact with water. This leads to redox potential changes and appearance of Mg^{2+} ions in the magnesium aluminium silicate-water system.*

Key words: "active water", composite, electrochemical characteristics,
kaolinite- bentonite substrate, microalloyed aluminium, "passive water"

INTRODUCTION

Last twenty years it has become customary, in research as well as in industry, to use values of redox potential - E_{OR} , pH and rH_2 as the indicators for wanted and unwanted characteristics of water.

A water redox potential is defined as the potential measured in observed water against a reference electrode (usually normal hydrogen electrode, N.H.E.) and represents a com-

bined value due to numerous redox pairs, which can be found in the same water: cation pairs of dissolved mineral salts (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , Al^{3+} , Mn^{2+} etc.); anion pairs of dissolved mineral salts (SO_4^{2-} , CO_3^{2-} , Cl^- , HCO_3^- , F^- , SiO_3^{2-} etc.); cation and anion pairs of organic acids and their salts [1]; pairs of water, oxygen and hydrogen (H_2/H^+ , $\text{H}_2\text{O}/\text{H}_2$, H^+/H_2 , O_2/HO_2^- , $\text{HO}_2^-/\text{OH}^*$, $\text{O}_2^*/\text{HO}_2^*$, O_2/OH^- , $\text{HO}_2^-/\text{OH}^-$, $\text{HO}_2^*/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, OH^*/OH^- , $\text{OH}^*/\text{H}_2\text{O}$ etc.) and so on. In other words, at any chosen moment a water redox potential, E_{OR} , is a mixed potential of all in water present redox pairs and it directly dictates behaviour of the water towards any media it may get in contact with. The waters exhibiting high E_{OR} values (those positive to N.H.E.) are called highly oxidized waters (they contain high quantity of oxidized agents: Fe^{3+} , Mn^{4+} , sulphates, nitrates, inorganic carbon compounds etc. and small quantities of available electrons–high oxidation potential), and the waters exhibiting low E_{OR} values (slightly positive and/or negative to N.H.E.) are called highly reduced waters (they contain high quantities of reduced agents: Fe^{2+} , Mn^{2+} , sulphides, nitrides, organic carbon compounds etc. and high quantities of available electrons–high reduction potential). Therefore, the application of a particular water is defined by its redox potential value, E_{OR} [2]: for human consumption and health care (oxidized waters, $E_{\text{OR}} = + 700$ mV and more v.s. N.H.E., because they have high oxidizing potential suitable for drinking, cooking and hygiene maintenance; reduced waters, $E_{\text{OR}} = - 100$ mV and more negative v.s. N.H.E., because they have strong reduction potential suitable for pharmaceuticals and health care-free oxygen radicals neutralization); for industrial water processing; for water consumption in industry, etc. The degree of acidity or alkalinity of any water solution is defined by the activity/concentration of H^+ and OH^- ions present, or by the values of their negative logarithms:

$$\text{pH} = 1/\log[\text{H}^+] = -\log [\text{H}^+] \quad \text{pOH} = 1/\log[\text{OH}^-] = -\log [\text{OH}^-] \quad (1)$$

All living beings and chemical reactions (including those in industry), which include water are sensitive, or very sensitive, to pH. Organic world functions the best when it uses approximately neutral pH (pH = 6-8), or neutral water solutions (pH = 7). Blood plasma and other human body liquids surrounding the cells are pH = 7,2–7,3. Spring and drinking waters are approximately neutral, pH = 7, while reduced waters are pH \approx 8,5 and oxidized waters pH \approx 4. It is often very important to be able to adjust water or water solution pH for particular application.

A direct relationship exists between pH and equilibrium potentials of redox pairs $\text{H}_2\text{O}/\text{H}^+$ and $\text{H}_2\text{O}/\text{OH}^-$:

$$E(\text{H}_2\text{O}/\text{H}^+) = E^0 + (\text{RT}/z\text{F}) \ln[\text{H}^+]/[\text{H}_2\text{O}] = -0,059 \text{ pH} \quad (2)$$

$$E(\text{H}_2\text{O}/\text{OH}^-) = E^0 + (\text{RT}/z\text{F}) \ln[\text{H}_2\text{O}]/[\text{OH}^-] = -0,059 \text{ pOH} = -0,059(14 - \text{pH}) \quad (3)$$

but the relationship between hydrogen gas, H_2 , and hydronium ion, H^+ (i.e. $\text{H}^+(\text{H}_2\text{O})_n$), in their redox reactions is not that simple, because it has to take into account the pressure of the gaseous hydrogen, H_2 , participating in the reaction:

in acidic media:



$$\begin{aligned} E(\text{H}^+/\text{H}_2) &= E^0(\text{H}^+/\text{H}_2) + (\text{RT}/2\text{F}) \ln [\text{H}^+]^2 - (\text{RT}/2\text{F}) \ln [p(\text{H}_2)] \\ &= E^0(\text{H}^+/\text{H}_2) - 0,059 \text{ pH} - 0,0285 \log [p(\text{H}_2)] \end{aligned} \quad (5)$$

in alkaline media:



$$\begin{aligned} E(\text{H}_2\text{O}/\text{H}_2) &= E^0(\text{H}^+/\text{H}_2) + (\text{RT}/2\text{F})\ln[\text{H}_2\text{O}]^2 - (\text{RT}/2\text{F})\ln[\text{p}(\text{H}_2)] - (\text{RT}/2\text{F})\ln[\text{OH}^-]^2 = \\ &= E^0(\text{H}^+/\text{H}_2) - 0,059(14 - \text{pH}) - 0,0285 \log [\text{p}(\text{H}_2)] \end{aligned} \quad (7)$$

It was one of the reasons, which led Clark and Cohen to propose the idea of $r\text{H}_2$ [3] defined as:

$$r\text{H}_2 = -\log [\text{p}(\text{H}_2)] \quad (8)$$

and for any particular water for which pH and $E(\text{H}^+/\text{H}_2)$ are known it is possible to calculate its $r\text{H}_2$ value using:

$$E(\text{H}^+/\text{H}_2) = 0,06 \log [\text{H}^+] - 0,03 \log [\text{p}(\text{H}_2)] \quad (9)$$

$$r\text{H}_2 = [E(\text{H}^+/\text{H}_2)] / 0,03 + 2\text{pH} \quad (10)$$

Experiments have shown that $r\text{H}_2 > 26-28$ and positive values of $E(\text{H}^+/\text{H}_2)$ are characteristic for oxidized waters, and that $r\text{H}_2 < 26-28$ and clearly negative values of $E(\text{H}^+/\text{H}_2)$ are characteristic for reduced waters [4,5].

Experiments have also demonstrated that pH contribution to water characteristics is exaggerated in comparison with E_{OR} and $r\text{H}_2$ contributions. In fact, when pH for electrolytically ionized waters (for reduced $\text{pH} \approx 8$, and for oxidized $\text{pH} \approx 4$) is deliberately increased or diminished, E_{OR} is not significantly changed.

Last thirty years have shown appreciable researches and industrial efforts directed to better understanding of water structure and characteristics in order to assure particular quality of water tailor made in advance for particular application. Due to the fact that oxidation-reduction potential and $r\text{H}_2$ value of every water are its crucial features, numerous efforts have been made to use electrochemical means for water preparation; mainly by specifically designed electrolysis.

In our laboratory water treatment (purification, pH and E_{OR} adjustment) without direct classic water electrolysis has been a subject of research for more than a decade. Particular attention is given to low energy electrochemical processes induced by the interaction of aluminium microalloys (microgalvanic cells inherent to its surface; catalytic reactions with them and their products) with water and their influence on water structure and composition.

In this paper, we report the results of recent electrochemical influence research of magnesium-aluminium silicate catalyst, in the form of ceramics made of kaolinite and bentonite clays, on the $r\text{H}_2$, pH and E_{OR} changes of the waters of particular characteristics in the wanted direction. Particularly, the possibility of changing "active water" (produced by electrochemical destruction of distilled water structure by aluminium microalloyed composite) characteristics was investigated. The composite made with microalloyed aluminium exhibits a very negative stationary potential (-1,5 V to -1,7 V v.s. SCE) and its interaction with water results in water reduction (hydrogen evolution, increase in OH^- concentration etc.) [6]. However, apart from the overall reaction this process of "active water" production includes other parallel and sequential multistep reactions leading to ionic intermediates and radicals (OH^* , HO_2^* , O_2^* , H^*). Thus, the stability of original water has been disturbed and treated water had no more known stability constant and

respective pH value, minimum electroconductivity and enough positive value of the redox potential [7].

The aim of this work was to "passivate" the "active water" using magnesium-aluminium silicate catalyst to oxidize radicals present and perform a partial ion exchange.

EXPERIMENT

The experiments were performed included following steps:

- preparation of the composite made of microalloyed aluminium, which was used for "active water" production;
- measurement of physicochemical characteristics of "active water" (pH and E_{OR}) (the distilled water treated by the above-mentioned composite made of micro-alloyed aluminium);
- preparation of magnesium-aluminium silicate catalyst, which was used to "passivate" "active water";
- treatment of "active water" with magnesium-aluminium silicate catalyst (the process of "passive water" production);
- measurement of physicochemical characteristics (pH and E_{OR}) of "passive water" samples during treatment with magnesium-aluminium silicate catalyst (during "passivation") after 1, 2, 3, 4, 5, 22 and 24 hours of treatment;
- treatment of distilled water with magnesium-aluminium silicate catalyst;
- measurement of physicochemical characteristics (pH and E_{OR}) of "passive distilled water" samples during treatment with magnesium-aluminium silicate catalyst (during "passivation") after 1, 2, 3, 4, 5, 22 and 24 hours of treatment;
- FTIR, SEM and EDS analyses of magnesium-aluminium silicate catalyst ceramic spheres were done before and after they were used in "passivation" process.

The microalloyed aluminium was prepared by alloying 99,8 % pure aluminium with Sn, Ga and Bi. Flame atomic spectrophotometry on "Varian AAS Spectra A-20" has shown that final product contained: 0,105 % Sn; 0,098 % Ga and 0,040 % Bi apart from aluminium. Then the steel wires (1,2 x 1,2 mm) were plated with the microalloyed aluminium (in a molten metal metallizing process) taking care to obtain well-developed amorphous surface with very high specific area [8]. The nets made of this plated wire were activated in NaCl solution (30–60 min), before being used in the process of "water activation".

Bentonite and kaolin are natural colloidal, hydrated aluminium silicates, which depending on the chemical content and purity can improve quality of water and influence the participation of minerals in it [9]. Therefore, this particular kind of clay was chosen to act, in its ceramic form, the support substrate for magnesium aluminium silicate catalyst for water "passivation". The process of this catalyst preparing included:

- clay mechanical purification;
- homogeneization of the clay with water;
- centrifugation ("Tehtnica Zelezniki");
- plastic formation of clay;
- addition of $Mg(NO_3)_2$ ("Merck", *p.a.*) mixture with Na_2SiO_3 ("Merck", *p.a.*) to the plastic clay;

- granulation of the plastic mixture to spheres (5 mm in diameter);
- drying of the spheres (at 120-200 °C for 90 min);
- backing of the dried spheres (at 800-900 °C) to obtain the ceramic catalyst.

Catalytic treatment of the chosen water samples (distilled water or "active water") was performed through direct contact of the water with the catalyst in a 50 cm long glass tube filled in with 76 ceramic spheres of magnesium-aluminium silicate. After 1, 2, 3, 4, 5, 22 and 24 hours period all treated water (50 cm³) would be drained into an appropriate glass vessel where pH and E_{OR} would be measured (pH meter "sensION 3", Hach Comp. USA with Ag/AgCl reference electrode and Pt working electrode), and then the water would be returned back to the tube for further treatment with the catalyst.

FTIR spectrophotometer ("Win-Bomem 100") was used to analyse magnesium-aluminium silicate catalyst ceramic spheres before and after their use in the process of "passivation". The samples for the analysis were prepared by standard KBr technique for solid probes. Obtained data were processed by Win Bomem-Easy software with 1 cm⁻¹ accuracy. The ceramic catalyst spheres were also subjected to SEM ("JEOL JSM-5300") and EDS ("LINK QX-2000 ANALITICAL") analyses prior to their use and after.

RESULTS

Measured pH value for the distilled water treated with microalloyed aluminium composite net (so called "active water") was pH = 4,14 and measured redox potential of the same "active water" was $E_{OR} = 0,435$ V v.s. Ag/AgCl.

The pH change of "active water" as a function of the "passivation time" (time spent in contact with magnesium-aluminium silicate catalyst) is shown in Fig. 1., and the redox potential change, E_{OR} , for the same samples in Fig. 2.

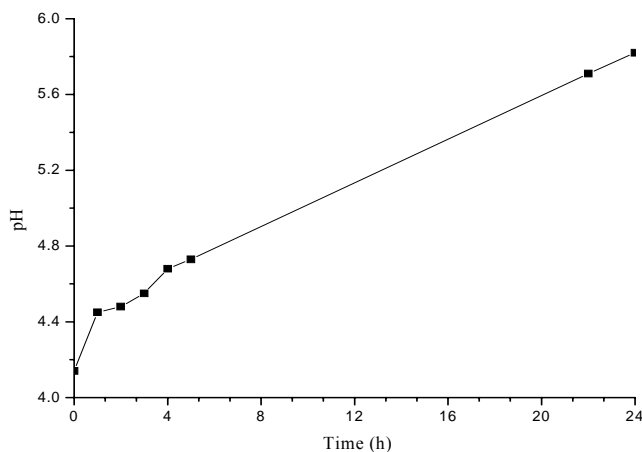


Fig. 1. The change of "active water" pH as a function of "passivation time"

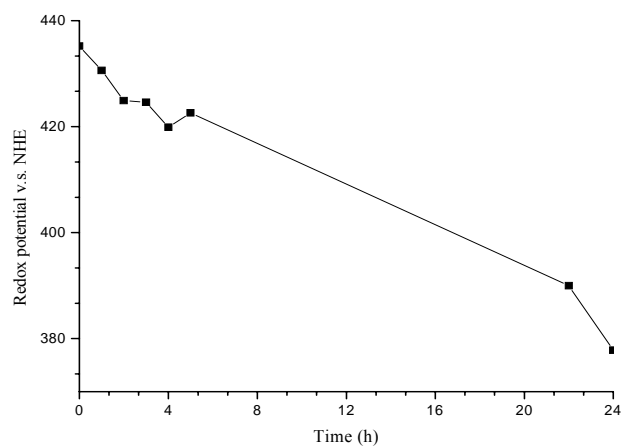


Fig. 2. The change of "active water" redox potential, E_{OR} , as a function of "passivation time"

The changes of pH of the distilled water treated with magnesium-aluminium silicate catalyst with treatment time and measured values of the redox potentials of the same samples are presented in Fig. 3. and Fig. 4., respectively.

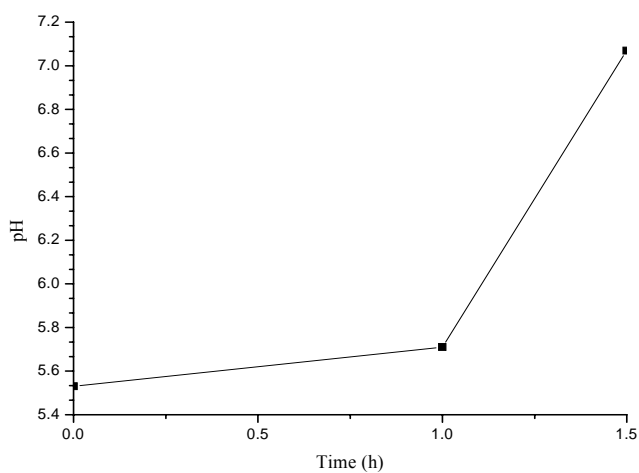


Fig. 3. The change of distilled water pH as a function of treatment time with magnesium-aluminium silicate catalyst

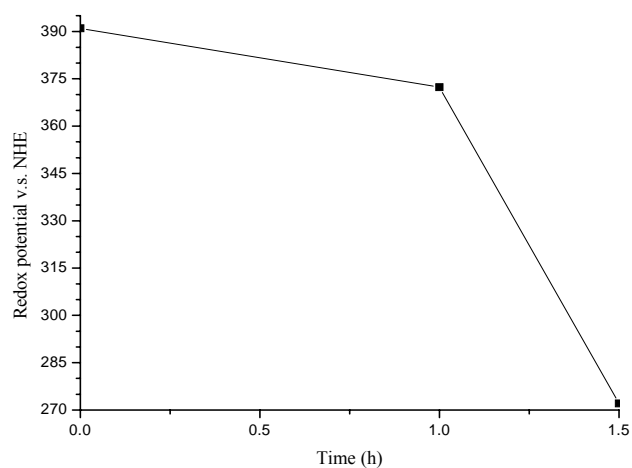


Fig. 4. The change of distilled water redox potential, E_{OR} , as a function of treatment time with magnesium-aluminium silicate catalyst

The IR spectrum of the magnesium-aluminium silicate catalyst before its use in the "passivation" process is presented in Fig. 5, and the IR spectrum of the same sample after 24 hours contact with "active water" in "passivation" process in Fig. 6.

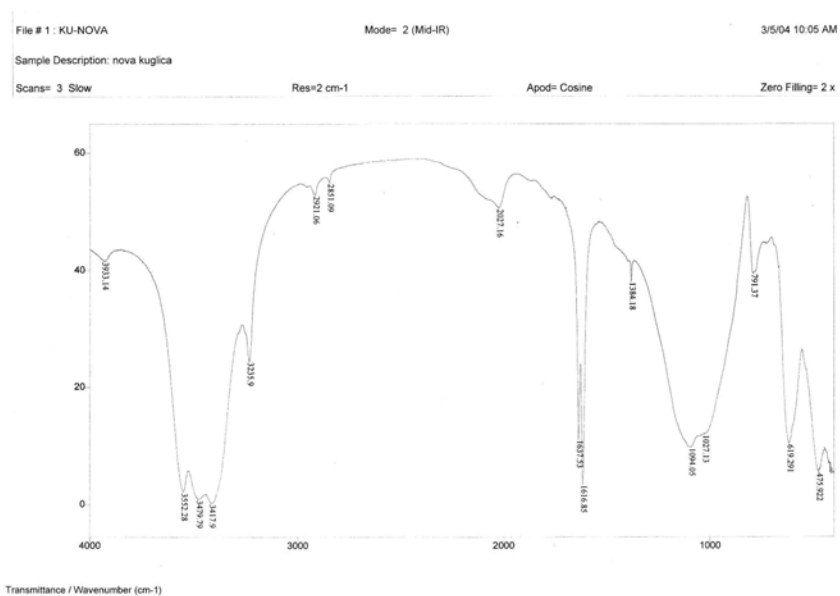


Fig. 5. The IR spectrum of a ceramic magnesium-aluminium silicate catalyst sample

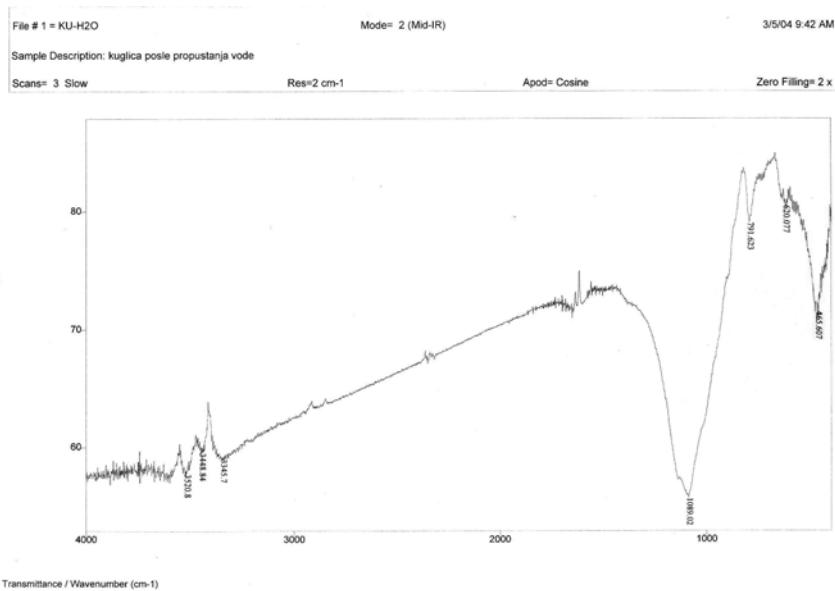


Fig. 6. The IR spectrum of the same sample (as in Fig. 5.) after being in contact with "active water" for 24 hours during "passivation" process

The surface of the ceramic magnesium-aluminium silicate catalyst obtained at 900 °C as seen by scanning electron microscope is shown in Fig. 7. and the EDS results of the same location in Fig. 8.

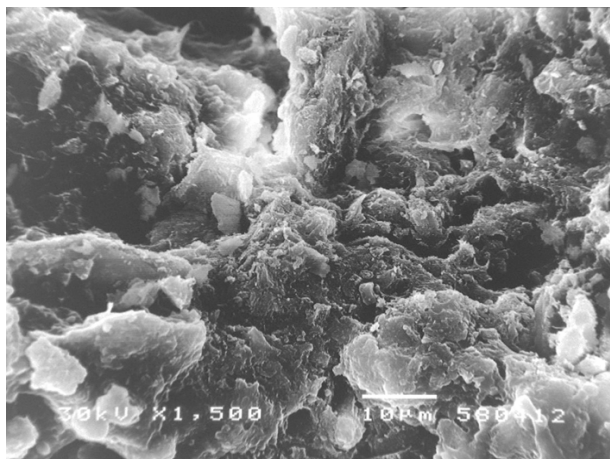


Fig. 7. The surface of the magnesium-aluminium silicate ceramic catalyst obtained at 900 °C (SEM used)

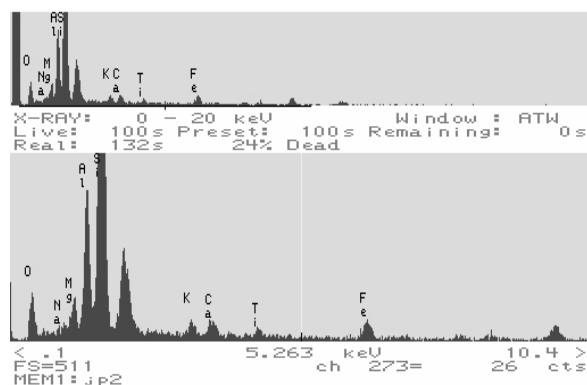


Fig. 8. The EDS results for the same location of the catalyst (as given in Fig. 7)

DISCUSSION

The rH_2 value for "active water", after completed "activation" process was calculated to be $rH_2 = 30,76$ for the redox potential measured $E_{OR} = 0,657$ V v.s. N.H.E. It appears, therefore, that the microalloyed aluminium (with very negative mixed stationary potential in water), during prolonged process of distilled water "activation", induces crucial changes in the formation of numerous ionic types and degraded water molecules, i.e. serious water molecules ionization. In such an "active water", it seems that previous equilibrium between dissolved oxygen and subsequently dissolved hydrogen has been disturbed, due to the reduction of the present oxygen (the most probably to OH^- ions, or OH^* and even HO_2^* radicals).

During 24 hours treatment of the "active water" with the magnesium-aluminium silicate catalyst, the rH_2 value changed in the way presented in Table 1. and Fig. 9., while the rH_2 values for the distilled water subjected to the same treatment can be seen in Table 2.

Table 1. The redox potential, E_{OR} , and rH_2 values as a function of the "passivation treatment time" for "active water"

Redox potential E_{OR} (V v.s. N.H.E.)	"Passivation time" (h)	rH_2
0,657	0	30,76
0,653	1	31,42
0,647	2	31,27
0,647	3	31,41
0,642	4	31,50
0,645	5	31,70
0,612	22	32,52
0,600	24	32,33

Table 2. The change of the redox potential, E_{OR} , and the rH_2 value with the "passivation treatment time" for the distilled water

Redox potential E_{OR} (V v.s. N.H.E.)	Time (h)	rH_2
0,613	0	31,49
0,594	1,0	31,22
0,494	1,5	30,60

It seems obviously that "passivation treatment", due to dominating oxydation processes, pushes the redox potentials to more negative values.

The position of the $rH_2 = f(E_{OR})$ function (from Table 1) in the theoretical $rH_2 = f[E(H^+/H_2)]$ diagram is presented in Fig. 10.

As expected, during the contact of "active water" with magnesium-aluminium silicate catalyst, due to additional dissolution of the catalyst's components, new ionic types provoked additional pH and E_{OR} changes. The reason for the E_{OR} becoming more negative during the "passivation" process can be probably found in the oxygen consumption reaction with magnesium (Mg dissolves from the catalyst spheres).

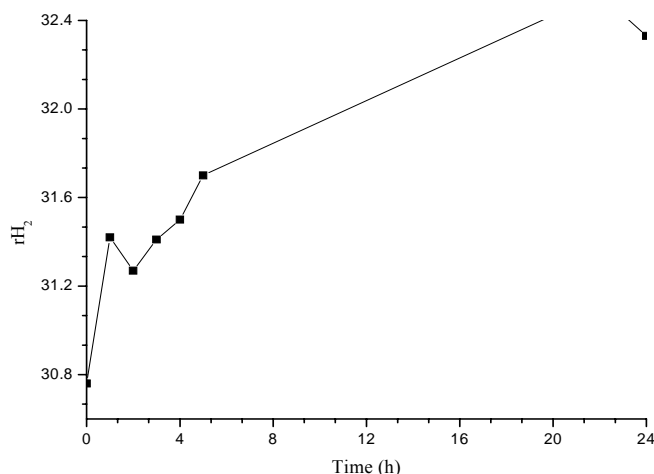
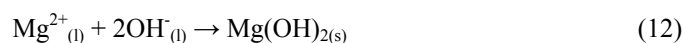
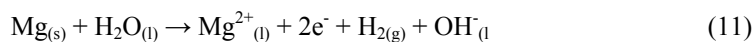


Fig. 9. The rH_2 dependence on "passivation treatment time" for the "active water" treated (data from Table 1)

The surplus of metal magnesium and the magnesium from nonstoichiometric oxides presents at the surface of the catalyst is dissolved in water due to:



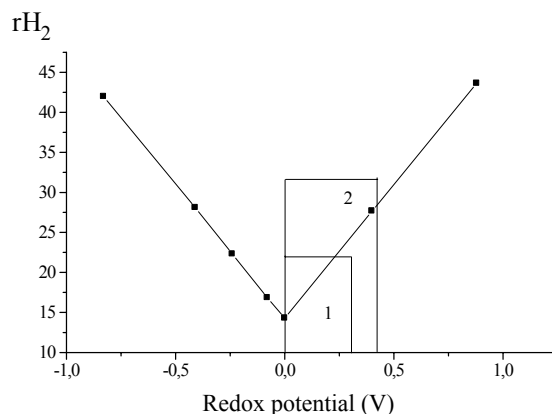


Fig. 10. (▪) the theoretical rH_2 dependence on $E(H^+/H_2)$; (●) the rH_2 and E_{OR} values obtained for the "passivation" treatment of the "active water" (given in Table 1)

Bearing in mind Fig. 7, which shows a very porous structure of the magnesium-aluminium silicate catalyst surface, it is easy to envisage $Mg(OH)_2$ being precipitated into that surface structure and reentering catalysis reactions with water.

Fig. 5. exhibits the IR spectrum typical for combination of several crystalline and amorphous aluminium silicates, the most of them probably: feldspar (albite like structure: 428–650; 720–790 and 992–1155 cm^{-1}); kaolin (magnesium-aluminium silicate with characteristic Mg-oxide peak around 790 cm^{-1}); strongly adsorbed waters (1625–1635 and 3200–3280 cm^{-1}) and crystalline water (around 3200 cm^{-1}) [10, 11]. After prolonged contact of the catalyst with water, the IR spectrum of the same surface changes (Fig. 6.). Loss of the fine spectrum structure seen in Fig. 5. is obvious, particularly from 1089 cm^{-1} towards high wave numbers, the most probably as a consequence of the chemical changes induced to the ceramic surface and stronger bonds of the water molecules and OH^- groups with Al, Mg, Ca, K, Si and Fe cations [10, 11].

It appears possible, from Fig. 7, that the ceramics made of the used ingredients exhibit crystalline areas, the most probably of zeolite structure, but the most of the ceramics bulks are made of amorphous oxides.

The peaks observed in Fig. 8. reflect the elements present in the clay used (O_2 , Na, Mg, Al, Si, K, Ti, Fe) and the difference in their intensities leads to the conclusion that they are present in very different amounts and as such contribute to nonstoichiometric structure of the individual phases of the ceramics. It is important to note that some portions (however small) of so developed surface are covered permanently or temporarily with the metals present, predominantly Mg and Al, presumably.

CONCLUSION

Addition of some active components to the mixture of kaolin and bentonite can provide clay mixtures, which after sintering at high temperatures produce very porous ceramics with microcrystalline and amorphous regions of stoichiometric and non-stoichiometric new oxides and some metallized surface (in our case-mainly with magne-

sium surplus). Nonstoichiometric oxide mixtures and metallized amorphous ceramics regions show high electrochemical and chemical activities in contact with water. This leads to redox potential changes and appearance of Mg^{2+} ions in the magnesium aluminium silicate–water system.

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 processing of drinking water and sewage disposal or waste waters. 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 come in contact with.

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ELEKTROHEMIJSKO PONAŠANJE KATALIZATORA SA KAOLINITNO-BENTONITNIM SUPSTRATOM U VODI

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Usled činjenice da oksido-redukcioni potencijal i rH_2 vrednosti vode jesu njene presudne odlike, brojni naporu su učinjeni u smislu korišćenja elektrohemijskih sredstava za pripremu vode. U ovom radu, saopštavamo rezultate ispitivanja elektrohemijskog uticaja magnezijum-aluminijum silikatnog katalizatora, u obliku keramike sačinjene od kaolinitne i bentonitne gline, na promene rH_2 , pH i E_{OR} voda sa posebnim karakteristikama u željenom pravcu. Posebno je ispitivana mogućnost promene karakteristika "aktivne vode". Kompozit sačinjen sa mikrolegiranim aluminijumom pokazuje veoma negativni stacionarni potencijal, a njegova interakcija sa vodom rezultira redukcijom vode. Dodatak pojedinih aktivnih komponenata smeši kaolina i bentonita, može obezbediti smeše gline, koje posle sinterovanja na visokim temperaturama, daju veoma porozne keramike sa mikrokristalnim i amorfim površinama novih stehiometrijskih i nestehiometrijskih oksida i izvesnu metaliziranu površinu (u našem slučaju-uglavnom sa viškom magnezijuma). Nestehiometrijske oksidne smeše i površine metaliziranih amorfnih keramika pokazuju visoke elektrohemijske i hemijske aktivnosti u kontaktu sa vodom. Ovo vodi promenama redoks potencijala i pojavi Mg^{2+} jona u magnezijum-aluminijum silikat-vodenom sistemu.