

The Application of Microalloyed Alumo-Silicate Ceramics, as a Multifunctional Agent for Distilled Water Passivation and H₂O₂ Aqueous Solution Decomposition

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Abstract: *Modified porous alumo-silicate ceramics, alloyed with manganese and microalloyed with aluminum, belongs to modern multifunctional ceramic materials. Microalloyed element represents the corresponding nano-phases layered at the grain boundaries that act as functional groups in different valent manganese states. Significant electrochemical and electrophysical activity of this structurally modified material makes it an excellent agent for decomposition of H₂O₂ via spontaneous redox processes, providing active oxygen and hydrogen and small local changes in pH value. This unique material with amorphous-crystalline structure can be used in technological processes of removing large concentrations of organic phase from waste water. All of these changes are reflected in the change of redox water potential, which plays a very important role in the use of drinking water.*

Keywords: *ceramics; microalloying; water passivation; decomposition; redox processes.*

1. INTRODUCTION

Microalloying is most commonly used procedure in microelectronic technology, especially in thin film technologies, where microalloying is performed by ion implantation, chemical deposition from the gas phase and plasma chemical processes. Microalloyed and structurally modified multifunctional materials have a remarkable electrochemical and electrophysical activity. There is a primary modification of the microstructure, induced by synthesis and the sintering process, and secondary, due to the development of numerous physical-chemical interactions in a heterogeneous multiphase system solid-solid and heterogeneous system solid-liquid [1].

Alumo-silicate ceramics modified with manganese and microalloyed with aluminum has such a microstructure that provides an amorphous-crystalline structure with two electrochemical active metals (Mn and Al) and a modified matrix, with respect to the non-stoichiometric composition of alumo-silicate and manganese-silicate amorphous and crystalline layers. In terms of this type of ceramics, amorphous metal layers on the matrix are expressed, which provide high porosity,

developed surface and non-equipotential surface. Priority application of the new and unique material is directed to the use in technological processes of removing large concentrations of organic phase from fecal and other waste water by active oxygen and hydrogen, obtained by extremely rapid decomposition of H₂O₂ via redox processes on the granules of multifunctional ceramics. A very serious problem of all modern biological water treatment technologies is aeration and aerators with complex technical and technological supply systems [1, 2].

In this paper, the procedure is based on a completely new principle of providing active oxygen and hydrogen from H₂O₂, by spontaneous redox processes. The principle is based on the fact that with a small change in the local pH value, for example for one unit, hydrogen peroxide can be an oxidation or reduction agent. The oxidative decomposition of H₂O₂ in the acidic environment is defined by the relation: H₂O₂ → H₂O + O, and the reduction decomposition with a slight displacement of the pH value in the alkaline region is defined by the relation: H₂O₂ → O₂ + H₂. Thus small local changes in pH value is provided by multifunctional alumo-silicate ceramics microalloyed with

manganese, with highly expressed spontaneous redox properties. These properties are related to the transition of valence electrons by changing the valency state of manganese, which enters by microalloying into the non-stoichiometric optically active solid phase, with F and V optical centers. Thus, the microalloying element is not an ordinary mixture with the Al-Si-O lattice, but it represents the corresponding nano-phases layered at the grain boundaries that act as functional groups in different valent manganese states starting from Mn^{2+} , Mn^{3+} , Mn^{4+} to Mn^{7+} , in addition to the natural elements Al, Si, Mg, Na and K from bentonite clays. When granules of multifunctional ceramics come into contact with H_2O_2 aqueous solution, from 3% to concentrated H_2O_2 , H_2O_2 is completely decomposed in a short time. Regardless of the participation in the process, microalloyed ceramics retains its activity in redox properties, thanks to very pronounced changes related to the transition of valence electrons of redox pairs, which are included in the solid phase [3-5].

2. EXPERIMENTAL

Experiments with the separation of diluted and concentrated H_2O_2 solutions showed an extremely rapid decomposition at high pressure. With only one kilogram of multifunctional ceramic granules, it is possible to decompose 700-1000 kg of H_2O_2 , with retaining its redox and catalytic activity. By decomposing H_2O_2 , oxygen is obtained as an active element for all oxidation processes and changes in the redox potential of the aqueous medium. Reduction decomposition produces hydrogen in two possible states, such as atomic and molecular hydrogen, which participates in the processes of removing hydroxyl, peroxide, organic and other radicals in fecal and other waste waters. Interesting and scientifically based results were obtained by the influence of Mn-alumo-silicate ceramics on distilled water, where local changes in pH and redox potential of distilled water were found, as an example of active waters. Otherwise, water hardly "tolerates" the removal of any harmful or other ingredient from water, by electrochemical and redox processes, electrophoresis or membrane separation. All of these changes are reflected in the change of redox water potential, which plays a very important role in the use of drinking water.

3. RESULTS AND DISCUSSION

The changes of redox potential and pH value of distilled water after the treatment with Mn-alumo-silicate catalyst are given in Fig. 1-7.

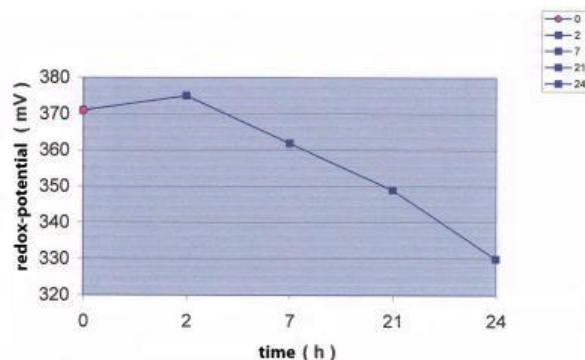


Figure 1. Change of redox potential with time during contact of distilled water with Mn-alumo-silicate catalyst, where the circle shows the value before and the square after the treatment.

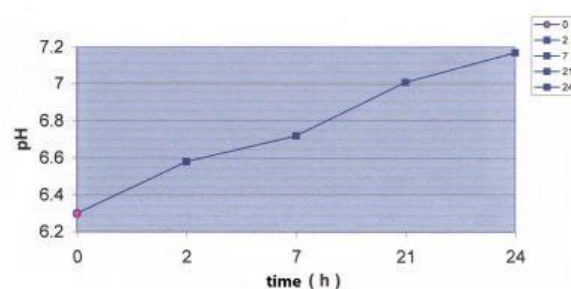


Figure 2. Change of pH value with time during contact with distilled water with Mn-alumo-silicate catalyst, where the circle shows the value before and the square after the treatment.

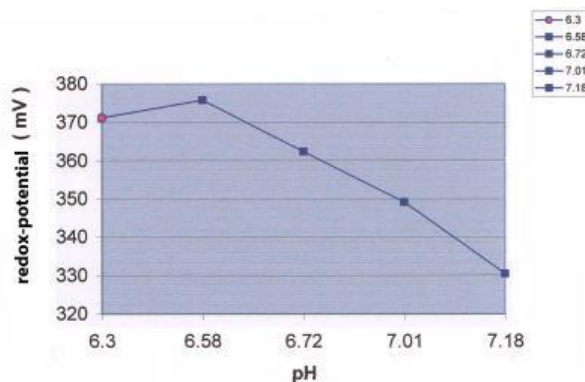


Figure 3. Change of redox potential with pH during contact of distilled water with Mn-alumo-silicate catalyst, where the circle shows the value before and the square after the treatment. (Ag/AgCl as reference electrode).

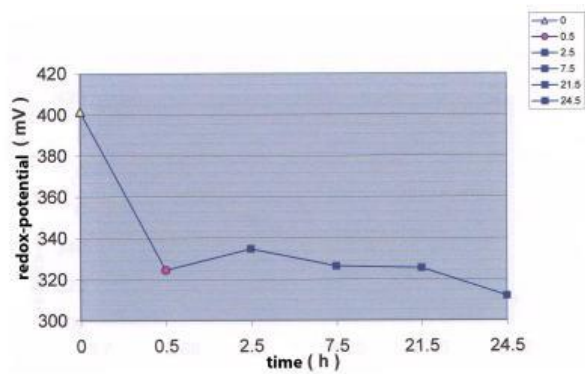


Figure 4. Change of redox potential of distilled water with time, where the triangle shows the value before aeration, the circle before the treatment and after aeration and the square after the treatment with Mn-alumo-silicate catalyst.

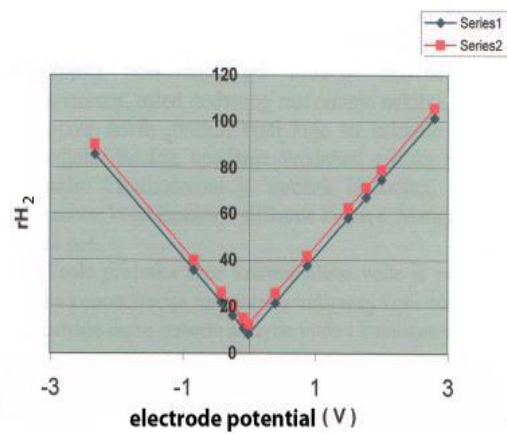


Figure 7. Change of r_{H_2} factor with electrode potential of distilled water before (series 1) and after the treatment (series 2) with Mn-alumo-silicate catalyst (H_2 as reference electrode).

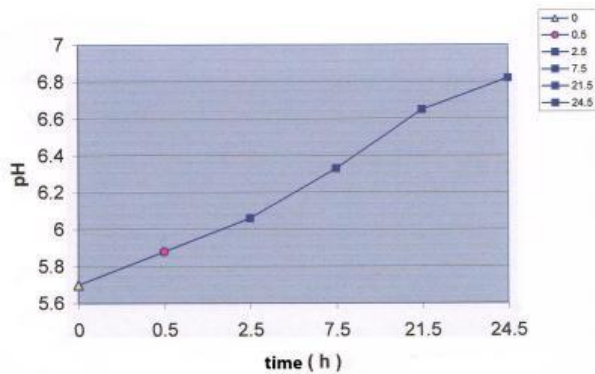


Figure 5. Change of pH value of distilled water with time, where the triangle shows the value before aeration, the circle before the treatment and after aeration and the square after the treatment with Mn-alumo-silicate catalyst.

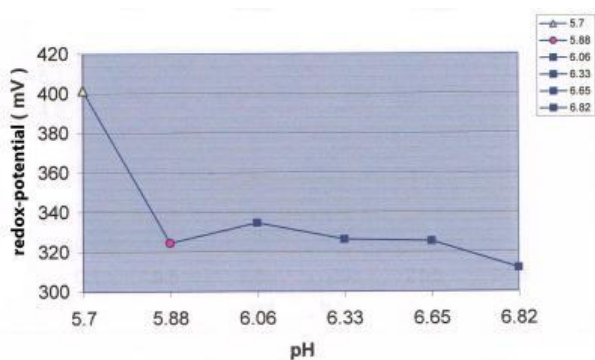


Figure 6. Change of redox potential with pH during contact of distilled water with Mn-alumo-silicate catalyst and aeration, where the triangle shows the value before aeration, the circle before the treatment and after aeration and the square after the treatment with Mn-alumo-silicate catalyst (Ag/AgCl as reference electrode).

3.1. Redox reactions

$1/2 H_2 + e^- \rightleftharpoons H^-$	(E= -2,33) V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	(E= -0,83) V
$2H^+ + 2e^- \rightleftharpoons H_2$	(E= -0, 414) V
$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	(E= -0,076) V
$HO_2^- + H_2O + e^- \rightleftharpoons OH^- + 2OH^-$	(E= -0,24) V
$2H^+ + 2e^- \rightleftharpoons H_2$	(E= -0,00) V
$O_2 + H_2O + e^- \rightleftharpoons OH^- + HO_2^{\cdot}$	(E= 0,4) V
$O_2 + H_2O + 4e^- \rightleftharpoons 4OH^-$	(E= 0,401) V
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	(E= 0,88) V
$HO_2^{\cdot} + H^+ + e^- \rightleftharpoons H_2O_2$	(E= 1,5) V
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	(E= 1,77) V
$OH^{\cdot} + e^- \rightleftharpoons OH^-$	(E= 2,0) V
$OH^{\cdot} + H^+ + e^- \rightleftharpoons H_2O$	(E= 2,8) V

$$r_{H_2} = E_h/0.03 + 2pH \text{ (V)}$$

r_{H_2} factor indicates whether the medium is oxidative or reductive, depending on the redox potential.

The microalloyed aluminum composite was destructively acting on water molecules and water-dissolved oxygen, which essentially displaced the balance of hydronium and hydroxyl ions. r_{H_2} factor has a very important role in water electrochemistry and its redox potentials. The main ionic species produced by water and water-dissolved oxygen reduction is peroxide ion or peroxide radical (HO_2^- , HO_2^{\cdot}). Reduction of this ions, or radicals, is carried out only in the acidic environment and on very positive potentials, with the formation of hydrogen peroxide. Water aeration is necessary in order to return the dissolved oxygen, but first it is necessary to adjust the pH to 6.5 - 7.0 [6, 7].

4. CONCLUSION

Mn-alumo-silicate ceramics has unique amorphous-crystalline microstructure, modified by synthesis and the sintering process and due to the development of numerous physical-chemical interactions. Amorphous metal layers on the matrix provide high porosity, developed surface and non-equipotential surface.

Microalloyed alumo-silicate ceramics, as electrochemical and electrophysical active multifunctional material can be used for decomposition of H₂O₂ via redox processes, providing active oxygen and hydrogen and small local changes in pH value. Therefore, this unique material can be used as agent in technological processes of removing large concentrations of organic phase from waste water.

Distilled water passivation can be carried out by multifunctional microalloyed ceramics. Changes of redox water potential, pH value and rH₂ factor are noticed during the contact of distilled water with Mn-alumo-catalyst.

ACKNOWLEDGEMENTS

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