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Alumosilicate ceramics based composite microalloyed by Sn: An interaction with ionic and colloidal forms of Mn in synthetic water

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This paper presents a procedure for the removal of manganese in ionic (Mn^{2+}) and colloidal (MnO_2) forms from synthetic waters, by reduction and adsorption processes on electrochemically active alumosilicate ceramics based composite material. Synthesis procedure of the composite material consists of two phases. Firstly, composite particles were synthesized by applying Al/Sn oxide coating on the bentonite particles in an aqueous suspension. In the second phase, aluminum powder was added to the previously obtained plastic mass and after shaping in the form of spheres 1 cm in diameter and drying, sintering was performed at 900 °C. Elemental tin, resulting from the reduction of Sn^{2+} ion, comes into contact with liquid aluminum in the pores of the matrix performing aluminum microalloying and activation. Moreover, due to a low partial pressure of oxygen, nonstoichiometric oxides with metal excess are obtained, and they play an important role in the electrochemical activity of composite material. In accordance with this, a redox potential of water is changed in contact with composite. The detailed characterization of the composite was carried out by SEM, FTIR and XRD techniques and the influence of pH values on the removal of ionic form of manganese from water was investigated as well.

1. Introduction

The presence of heavy metals in water exhibits a variety of harmful effects on the living organisms in polluted ecosystems. The removal of heavy metals from water includes the following procedures: chemical precipitation, coagulation/flocculation, membrane processes, ion exchange, adsorption, electrochemical precipitation, etc. [1,2]. Great influence on the removal processes has the following experimental conditions: pH, temperature, presence of foreign ions and organic matter. Usually, manganese does not present a health hazard in the household water supply. However, it can affect the flavor and color of water because it typically causes brownish-black staining of laundry, dishes and glassware [2]. Although manganese is one of the elements that are at least toxic, concentrations of manganese much higher than the maximum allowed concentration during long-term exposure can cause health damage. A number of known procedures for the manganese removal are not suitable for an elimination of its all chemical species due to reversible release of manganese into water systems. Therefore, these used procedures are at the edge of techno-economical viability.

Due to the series of good properties, such as high-temperature resistance and hardness, resistance to corrosion and degradation and high chemical stability, ceramic materials attract particular attention in science today [3]. Moreover, the application of these materials in controlling of pollutants in the environment and drinking water is significant [4,5].

Coated particles are composed of solid phase covered with thinner or thicker layer of another material [6]. These coating-layers on the surface are important for several reasons. In such way, the surface characteristics of the initial solid phase are modified and sintering conditions can be better controlled. Composite particles can be obtained in several ways, and in this paper, the procedure of Al^{3+}/Sn^{2+} co-precipitation onto dispersed particles of bentonite was applied.

An important factor in achieving the desired microstructure of ceramics is sintering procedure that includes very complex processes. An important influence on sintering has been exhibited by an addition of microalloying components, which significantly determined a microstructure and properties of ceramics [7]. The presence of small amounts of impurities in the starting material can vastly influence their mechanical, optical, electrical, color, diffusivity, electrical conductivity, and dielectric properties of alumosilicate matrix [1]. In summary, the process of diffusion mass transport in ceramic crystal regions is affected by temperature, oxygen partial pressure and concentration of impurities.

Composites based on the $Al–Al_2O_3$ system can be obtained by Reactive Metal Penetration (RMP) method which is based on infiltration

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of ceramic preforms by a liquid metal, generally aluminum or aluminum alloys [8,9]. During the process, a liquid metal simultaneously reacts and penetrates the ceramic preform, usually silica or a silicate, resulting in a metal/ceramic composite characterized by two phases that are interpenetrated. A modification of this synthesis procedure of composite based material was presented in this work. It comprises a synthesis of Sn-microalloyed Al–Al_2O_3 system incorporated in the structure of alumosilicate matrix by exposures to high temperatures treatments, and following rapid quenching process.

The detailed characterization of material was carried out by SEM, FTIR and XRD techniques. A microalloying of composite by Sn causes crystal grain surface layer amorphization and a creation of non-stoichiometric phases of Al_2O_3 with a metal excess [10,11]. In this way, microalloying causes electrochemical activity, which manifests itself in contact with the aqueous solutions of electrolytes and harmful substances in water. Therefore, the ceramics is unstable in contact with water and susceptible to corrosion because of surface electrochemical processes. In addition to the synthesis of Sn-microalloyed alumosilicate ceramic based composite, its influence on redox properties of water and interaction of ceramics with ionic and colloid forms of manganese in synthetic water systems was presented. The influence of pH on the removal of manganese from water was examined as well.

2. Materials and methods

2.1. Synthesis of composite material

The alumosilicate matrix used in this work was bentonite clay because of its specific properties such as swelling, hydrophilicity, developed surface area, layered structure, natural abundance and low cost. Firstly, it was transferred into Na^+-bentonite by ion exchange reaction in 1 M NaCl solution, in order to remove other exchangeable cations naturally present in bentonite. After filtering and rinsing with deionized water (until free of Cl^- ions), clay was dried at 105 °C. In 50 cm^3 of vigorously stirred 0.1 mol/dm^3 $Al(NO_3)_3 \times 9H_2O$ solution, 0.5 mmol of Sn was added dropwisely from $SnCl_2 \times 2H_2O$ solution. Thus, such prepared solution and 50 cm^3 of 30 g/dm^3 urea solution were added to the suspension of 20 g Na-bentonite in 300 cm^3 of deionized water. Suspension was intensively and continuously stirred and heated at the temperature of 90 °C during 5 h under nitrogen atmosphere. After cooling, a precise adjustment of pH to 6.5 was done by adding ammonia. The suspension was left for 24 h, then filtered in a vacuum, and the residue flushed with a plenty of deionized water. The resulting plastic mass was mixed with 0.2 g of aluminum metalic powder (Merck) and well homogenized. The spheres of 1 cm in diameter were made and dried in oven at the temperature of 40 °C. Then, the temperature was gradually increased to 120 °C and drying was continued in the next 2 h.

Sintering was conducted in a furnace under an inert atmosphere with nitrogen flow of 100 cm^3/min according to the following temperature regime. The heating rate from 120 °C to 700 °C was 10 °C/min, and from 700 to 900 °C sintering was continued with the rate of 5 °C/min. At temperature of 900 °C heating was carried out for 30 min. Then, the composite material was rapidly cooled in protective atmosphere of N_2 and grinded in achat mortar. After seeding of crushed composite through appropriate sieves two particle size fractions were collected. One fraction was in the range 0.5–0.7 mm and other $<$0.125 mm. Each of them was stored in an appropriate plastic container with hermetic lid.

2.2. The influence of active ceramic composite on the redox properties of deoxygenated water

The experiment was conducted by bringing into contact 0.6 g of composite ceramics, particle size ranging from 0.5 to 0.7 mm with 100 cm^3 of distilled water, which was purged with nitrogen until establishing a stable redox potential. After addition of ceramics into water, nitrogen purging was continued during the next 20 min, and redox potential as well as pH values were measured simultaneously after each 2.5 min. Finally, a suspension was centrifuged and a value of total dissolved solids (TDS) was determined.

All pH and E (redox potential of water) values were measured by pH-meter HACH, sensION 3, USA equipped with a HACH glass electrode, platinum redox electrode and METROHM Ag/AgCl as a reference electrode.

2.3. Removal of ionic and colloidal forms of Mn

All experiments were carried out under an ambient condition (20 °C) bringing into contact 0.1 g of composite material (fraction$<$0.125 mm) with 50 cm^3 of synthetic water containing a certain concentration of colloidal or ionic form of manganese. For these purposes, two types of synthetic waters were made, as follows. Synthetic water means water that contains a certain concentration of chemical ingredients in the ionic or colloidal form. Water which contains Mn^{2+} was obtained by a dissolution of $MnCl_2 \times 4H_2O$ in deionized water. Colloidal manganese synthetic water was prepared by a reduction of $KMnO_4$ with $Na_2S_2O_3$ as described elsewhere [12,13]. The colloidal MnO_2 was characterized by recording a UV–vis spectrum on Lambda 15 UV/vis Spectrophotometer.

The pH values of the solution were adjusted by adding negligible volumes of HCl or NaOH. Contact period of liquid and solid phases of 20 min was the same in all experiments. Separation was performed by filtration. Concentration of manganese and other cations was determined by ICP-OES method using ICP — OES SPECTROMETAR iCAP 6000, Thermo Electron Corporation, Great Britain.

2.4. XRD, SEM and FTIR characterization of composite material

XRD measurements were conducted on a Siemens D500 diffractometer with a Ni filter using Cu Ka radiation ($\lambda = 0.154$ nm) and the step-scan mode with a step width of 0.02° and 1 s/step. Scanning electron microscopy (SEM) was performed on a JEOL JSM-5300. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was carried out using ATR-FTIR spectrometer Bruker tensor-27 in conjunction with a FTIR Bruker Hyperion-1000/2000 microscopy attachment equipped with a 15× objective and a 250-lm liquid-nitrogen cooled, narrow-band mercury–cadmium–telluride (MCT) detector (ATR objective GMBH, Germany) with the range of the IR spectrum from 4000 to 400 cm^{-1} was used in this work. The single-pass transmission FTIR spectra of the composite material prior and after interaction with synthetic waters and drying at 105 °C were also recorded by means of BOMEM MB-100 FTIR spectrometer (Hartmann & Braun, Canada) using KBr pellets containing 1 mg of the sample in 150 mg KBr. Instrument is equipped with a standard DTGS/KBr detector in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1} by the Win–Bomem Easy software.

3. Results and discussion

3.1. Characteristics of the composite material

Fig. 1. shows the ATR-FTIR spectrum and a corresponding photograph of the composite surface.

The very strong adsorption band in the spectrum (Fig. 1) at 1309 cm^{-1} is due to Si–O bending vibration on the surface of composite. The absence of broad absorption band at around 3630 and 3435 cm^{-1} indicates that during thermal treatment the irreversible dehydroxilation and surface reconstruction of alumosilicate matrix occurred. The single-pass transmission FTIR spectra of composite are shown in Fig. 2 (A, B and C) and it is observed that there are no significant shifts of bands prior to and after composite interaction with synthetic waters. The spectra were analyzed in details as follows. A broad bend at 3463 cm^{-1}