OXIDATION OF SULFIDE IONS IN MODEL SOLUTIONS OF SEA WATER USING OF METAL CATALYSTS BUILT IN CARBON MATRIX

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ABSTRACT

The possibility of catalytic oxidation of sulfide ions from model solutions of seawater in a lab-scale model of fuel cell is studied. Two types of metal-containing catalysts (Mn and Co) incorporated in a matrix of activated carbon are synthesized. The metals are in the form of spinel-type oxides containing about 35 % vol. of the activated carbon. The processes of oxidation occurring in the anode space are considered. Experiments with different initial concentrations of sulfide ions (25-125 mg/dm$^3$) are carried out. The quantity of catalyst added into the solution volume is varied. The experiments are performed at room temperature and with constant mixing rate. The sulfide ions are oxidized above 90 % in about 3 hours for all initial concentrations by the use of both types of catalysts whereas the process is much slower without a catalyst (40 % in about 3 hours).

Keywords: sea water, oxidation, sulfide ions, catalysts, spinel-type oxides, activated carbon, fuel cell.

INTRODUCTION

Hydrogen sulfide is common in some geothermal springs and closed deep water basins. Its presence in geothermal springs is due to volcanic gases, whereas that in closed deep water basins it is due to anaerobic sulfate reducing bacteria decomposition of sulfur-containing organic matter and sulfate reduction. Deep Black Sea waters contain significant amount of hydrogen sulfide [1, 2]. Because of the conditions in the Black Sea a lot of the produced hydrogen sulfide is stored in the deep water [2] and this is the reason why the depths of the Black Sea are practically dead.

Different methods are used for decomposition of hydrogen sulfide to harmless products [3-6]. In many of them the end product is elemental sulfur [3].

This study is part of the collaborated efforts to clean the waters of the Black Sea by oxidation of the sulfide anions of the seawater in a fuel cell (Fig. 1).

In this fuel cell, the following main anode and cathode reactions are intended to take place:

Anode: $S^{2-} + 6OH^- = SO_3^{2-} + 3H_2O + 6e^-$
$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-$

Total: $S^{2-} + 8OH^- = SO_4^{2-} + 4H_2O + 8e^-$

Cathode: $2O_2 + 8H^+ + 8e^- = 4H_2O$

Net reaction: $S^{2-} + 2O_2 = SO_4^{2-}$

Skipping the stage of producing elemental sulfur is an advantage, since no anode passivation will occur and the secondary pollution of the seawater will be avoided.

Since sulfate ions are naturally contained in seawater they can be returned to the sea without harming the environment, restoring the sulfur cycle. This process can be used as a base for creation of a fuel cell that combines purification of sea water with utilization of the energy of the hydrogen sulfide. The extraction of the energy in Black Sea waters is hindered by the low concentration of sulfide ions.

According to the literature [2, 7] it is known that metal cations $Me^{2+}$ ($Me$: Mn, Co, Ni, Fe, Cu) catalyze the process. As the reaction between the metals and the sulfide produces precipitate it is not preferable to add them in the form of salts. On the other hand it is not acceptable to use up large quantities of catalyst and dumping it into the water. The research for a stable catalyst led us to the synthesis of spinel-type metal oxides, which can be used for production of electrodes that are
useable in these conditions. The oxides are applied onto a matrix of activated carbon with the additional benefit of the activated carbon being a catalyst as well.

The aim of this work is to study the catalytic oxidation of the sulfide ions to sulfite and sulfate in the anode space of the fuel cell. Achieving this goal requires the selection of suitable catalyst and its optimal amount, as well as working with high enough concentrations of sulfides.

**EXPERIMENTAL**

Model solutions were prepared by dissolving sodium sulfide nonahydrate ($\text{Na}_2\text{S}.9\text{H}_2\text{O}$ reagent ACS $\geq 98\%$). The concentration of hydrogen sulfide in the Black Sea at depth of 200 m is $5\text{ mg/l}$ [2]. This concentration is poor for the effective work of the fuel cell. The experiments were performed with concentrations 25-110 mg/l, which is 5-20 times higher than the actual concentration of sulfides. The water in the Black Sea has relatively low salinity (15-17 g/l) [8, 9]. The model solutions of sea water were imitated by dissolving $\text{NaCl}$ ($C_{\text{NaCl}} = 16.5 \text{ g/l}$). Experiments with two types of model solutions of seawater were carried out: model solution 1: $\text{NaCl}$ (analytical grade) in distilled water; model solution 2: sea salt, dissolved in tap water. Initial experiments were carried out with model solution 1 for determination of the catalytic oxidation of sulfides with salinity simulating seawater. Work with model solution 2 is done for determination the influence of other ions on the oxidation process ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Cl}^-$, $\text{SO}_4^{2-}$, etc. contained within the actual sea water).

Production of spinel-type oxides from organic compounds is done according to [10] and includes their impregnation with a solution of pre-determined salt and followed by pyrolysis and simultaneous activation. The catalytic effect is determined by adding them in the volume of the solution. As a catalyst is tested activated carbon with the same organic origin.

The experiments were accomplished in a lab-scale fuel cell, shown in Fig. 1. The anodic space was charged with a model solution of sulfide with 200 ml volume. During the runs the solution was stirred by magnetic stirrer with 300 rpm. The caticodic space was charged with the same salt solution being aerated by atmospheric air with a flow rate 100 dm$^3$/h. The anodic and caticodic spaces are coupled by salt bridge. The catalyst was added to the solution in the anodic compartment as a powder.

During the runs samples from anodic space were taken and analyzed for sulfide, sulfur-containing reducing compounds (e.g. sulfites) and sulfates. The concentration of all sulfur reducing substances was determined iodometrically. The sulfide ($\text{S}^{2-}$) content was determined photometrically [11] and the presence of sulfate ions was determined by barium chloride. The concentration of the dissolved oxygen in the cathode compartment of the fuel cell was determined by means of dissolved oxygen probe coupled to $\text{pO}_2$-analyzer. It was established that its concentration was close to the equilibrium one for the experimental conditions (about $95\%$ vol. of the equilibrium one).

**RESULTS AND DISCUSSION**

The process of oxidation of sulfide ions without catalyst was slow (about $10\%$ reduction of sulfide ions for the first 60 minutes).

The influence of the initial concentration of sulfides without catalyst has been studied (Fig. 2) and it was decided that it was not relevant to the rate of oxidation. In all investigated cases there was a $50\%$ decrease at the second hour, $80\%$ at the third hour, $90\%$ at the forth hour.

Introduction of catalyst in the volume of the reactor significantly increased the process (about $90\%$ reduction of sulfide ions for the first 60 minutes). Fig. 3 shows the influence of the type of the catalyst on the rate of oxidation with initial concentration of sulfides of $65 \text{ mg/l}$. 

![Fig. 1. Scheme of a fuel cell.](image-url)
Parallel experiments were conducted with equal amount of the two spinel-type oxides and activated carbon. For comparison the oxidation with the same concentration without catalyst is shown.

The rate of the process is few times higher with the addition of catalyst. The effect of the different catalysts is comparable. It is also notable that the activated carbon shows good results as a catalyst.

For future studies a Co$^{2+}$-impregnated activated carbon is prepared, because the increase of the oxidation rate of sulfide is a little-bit higher during the first hour. The influence of the initial concentration of sulfides with the same amount of catalyst was studied too (Fig. 4).

In the presence of catalyst the oxidation rate is dependant of the initial concentration (Fig. 4). At low concentrations, 75-80 % of the sulfides are oxidized during the first hour, while at higher ones the oxidation is 50 % for the same time. Experiments show that at low sulfide concentrations 75-80 % of the sulfides are oxidized in one hour, whereas at high concentrations the oxidation is 50 %. The cause for the lower rate of oxidation is most likely accumulation of intermediate compounds and realization of competitive reactions. Due to these causes concentration of about 70 mg/l are suitable for conduction of the process.

Experiments for determination of the amount of Co$^{2+}$ catalyst (Fig. 5) show the process rate does not depend with 30 % reduction of the catalyst.

Fig. 6 shows comparison between oxidation of sulfide ions in model solution 1 and model solution 2. The presence of additional ions, different from Na$^+$ and Cl$^-$ in model solution 2 decreases the rate of oxidation (Fig. 6). Similar results are published in [12].

In all experimental cases there no elemental sulfur was derived and the presence of sulfate ions was proved.
CONCLUSIONS

The process of oxidation of sulfide ions is slow (about 10 % reduction of sulfide ions for the first 60 minutes) without catalyst. In this case the rate of the process does not depend on the initial concentration.

Introduction of catalyst in the volume of the reactor significantly increases the process (about 90 % reduction of sulfide ions for the first 60 minutes). Mn and Co spinel-type catalysts show nearly identical properties. Activated carbon shows good catalytic properties as well.

In the cases of introduction of catalyst the oxidation rate depends on the initial concentration. At low concentrations, 75-80 % of the sulfides are oxidized during the first hour, while at higher ones the oxidation is 50 %.

The amount of catalyst does not significantly influence the rate of the reaction (Fig. 5).

The presence of additional ions (Ca, Mg, SO$_4^{-2}$, etc.), different from Na and Cl in the model system decreases the oxidation rate of the sulfide ions.

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