

## Kinetics of oxidation of sulfide ions in model solutions of sea water

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The possibility of catalytic oxidation of sulfide ions from model solutions of seawater is studied. ZrO<sub>2</sub> catalyst incorporated into a matrix of activated carbon is synthesized. The surface of the catalyst is characterized by iodine adsorption. The effect of the deposited catalyst is studied. Experiments at different initial concentrations of sulfide ions and temperatures are conducted in two regimes - continuous aeration or stirring at the same speed without aeration. The reaction products in the case of continuous aeration are 90% of sulfate ions relative to the initial quantity of sulfides. The reaction products at stirring without aeration at the same temperatures are stable reducers that should not be dumped into the sea water. The oxidation in the regime of continuous aeration follows the kinetics of a first order reaction with relatively low activation energy.

**Keywords:** kinetics, oxidation, sea water, sulfide ions, ZrO<sub>2</sub> - catalyst

### INTRODUCTION

Hydrogen sulfide is common in some geothermal springs and closed deep water basins. Deep Black Sea waters contain significant amount of hydrogen sulfide [1,2]. This is the reason for the lack of aquatic life below a certain depth. The latest data show that the level of the "dead zone" is constantly rising. Different methods are used for catalytic decomposition of hydrogen sulfide to harmless products [3-6]. In many of them the end product is elemental sulfur [3]. However, elemental sulfur is undesirable because it inhibits the catalytic oxidation by blocking the active sites of the catalyst. Moreover, sulfur is not of particular interest as a commercial product and its back return into the Black Sea water is inappropriate from an environmental point of view. In the present work no elemental sulfur is formed in all experiments. The sulfates are the desirable product because they are naturally present in the sea water.

It is known according to the literature [2, 7] that Me<sup>2+</sup> cations (Me: Mn, Co, Ni, Fe, Cu) catalyze the process of sulfide to sulfate oxidation. As the reaction between the metals and the sulfide produces precipitates it is not preferable to add them in the form of salts. On the other hand, it is not environmentally acceptable to use large quantities of catalyst and dumping it into the water. The research for stable catalysts that can be subsequently incorporated into electrodes working under these conditions imposed synthesis of metal oxides incorporated in matrices of activated carbon.

A further advantage is that the activated carbon is also a catalyst in this case [8]. The principle of obtaining such catalysts includes impregnation of the initial organic material with a salt of the given metal and subsequent pyrolysis with simultaneous activation [9].

This study is part of collaborated efforts to clean the waters of the Black Sea by oxidation of the sulfide anions of the seawater. The aim of this work is to study the catalytic oxidation of the sulfide ions to sulfite and sulfate with high enough concentrations and yields. This goal requires the selection of a suitable catalyst, its optimal amount, as well as establishing the optimum conditions for the process.

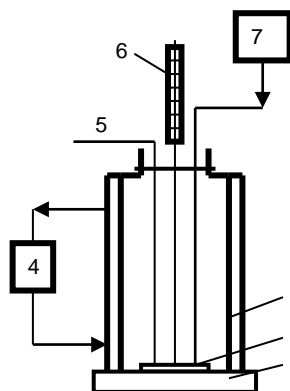
### EXPERIMENTAL PART

#### *Experimental conditions*

The kinetics of the oxidation process of sulfide ions was investigated. In order to select the proper catalyst the experiments were carried out at room temperature and constant stirring speed. After the proper catalyst and its amount were chosen two types of experiments were carried out for determination of the kinetic parameters – by continuous aeration and by stirring at the same speed without aeration. The flow rate of the air was 120 l.h<sup>-1</sup> corresponding to 10 vvm. The experiments were carried out in a stirred cell at different temperatures (20, 30 and 60°C) maintained by a thermostat. The volume of the solution in the cell was 200 ml. A sketch of the experimental set-up is shown in Fig. 1.

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**Fig. 1.** Scheme of the experimental set-up. 1- thermostated cell; 2,3- magnetic stirrer; 4- thermostat; 5- sampling outlet; 6- thermometer; 7- aerator.

The experiments were carried out in model solutions imitating sea water prepared by dissolving NaCl to attain a concentration of  $16.5 \text{ g dm}^{-3}$ , corresponding to the Black Sea salinity (i.e.  $15\text{-}17 \text{ g dm}^{-3}$ ) [10, 11]. Sulfide was added by dissolving sodium sulfide nonahydrate ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  reagent ACS  $\geq 98\%$ ) in the model sea water. The experiments were performed within the concentration range of sulfides  $25\text{-}120 \text{ mg dm}^{-3}$  which is 5-20 times higher than their actual concentration (i.e. between  $5$  and  $15 \text{ mg dm}^{-3}$ ) [2, 12].

The metal containing catalysts incorporated in a matrix of activated carbon were obtained according to [9]. The principle of the preparation of the catalysts on the carbon matrix consists of impregnation of the initial organic material with a metal salt - precursor and subsequent pyrolysis with simultaneous activation. The metal ions are in the form of oxides. The obtained catalysts incorporated in a matrix of activated carbon were characterized by iodine adsorption. The obtained specific surface area of the  $\text{ZrO}_2$  - catalyst is  $780.66 \text{ m}^2 \text{ g}^{-1}$ . The cobalt and manganese catalysts are spinel type oxides with 30 % concentration of the active components. The specific surface area of the Co - catalyst is  $897.98 \text{ m}^2 \text{ g}^{-1}$ .

The annually averaged ion content in the natural Black Sea surface water close to the Bulgarian coast is shown in Table 1 [13, p. 44].

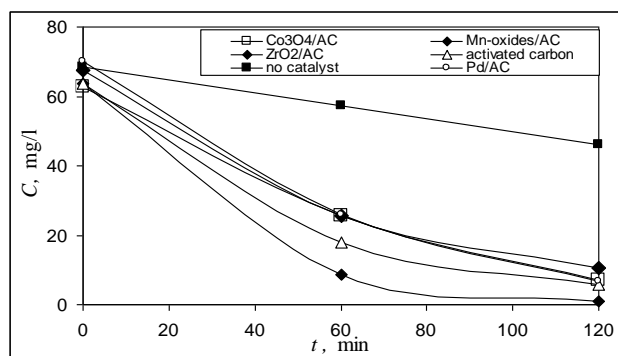
**Table 1.** Data for the concentrations of major ions in the seawater.

Components	Content, %
Chloride	9.96
Sulfate	1.39
Hydrocarbonate	0.16
Carbonate	0.0204
Sodium	5.49
Magnesium	0.68
Calcium	0.269
Potassium	0.200

Samples from the reacting solution were taken periodically. The concentration of the total sulfur containing reducing substances was determined iodometrically. The sulfide ( $\text{S}^{2-}$ ) content was determined photometrically [14] and the presence of sulfate ions was detected qualitatively by addition of barium chloride solution. Sulfates were determined quantitatively by addition of barium chloride and back-titration of the excess of  $\text{Ba}^{2+}$  ions with EDTA using Eriochrom Black T as indicator.

## RESULTS AND DISCUSSIONS

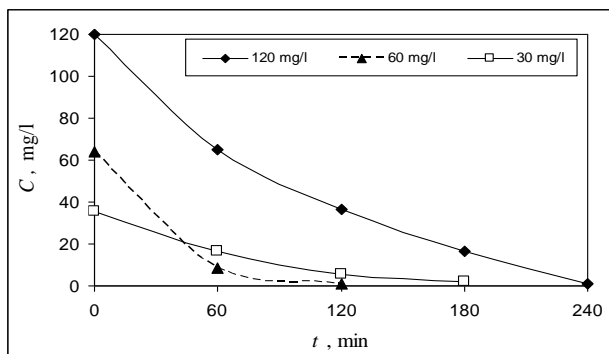
While screening for the proper catalyst four types of metal oxides incorporated into an activated carbon matrix were investigated. The use of the activated carbon from the same origin was also studied. The results are shown in Fig.2. The oxidation rate for the non-catalyzed process at the same conditions is given for comparison. The initial concentration was chosen to be  $65 \text{ mg l}^{-1}$  because at this concentration there is no retard of the oxidation rate due to parallel processes [8,12]. The amount of the catalyst was the same ( $0.5 \text{ g l}^{-1}$ ) for all experiments.



**Fig. 2.** Influence of the type of catalyst on the oxidation rate. AC means activated carbon.

Figure 2 shows that the oxidation of sulfide ions without catalyst is slow (about 10 % reduction of the sulfide ions in the first sixty minutes). The addition of the catalyst into the reactor volume leads to a considerable acceleration of the process (from 50 to 90% reduction of the sulfide ions in the first sixty min). The effect of the  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Pd}^{2+}$  catalysts was comparable and the activated carbon also had good catalytic activity. As a catalyst for the further experiments  $\text{ZrO}_2$  was used, because it provided the highest oxidation rate (by 40% higher than all other metal catalysts).

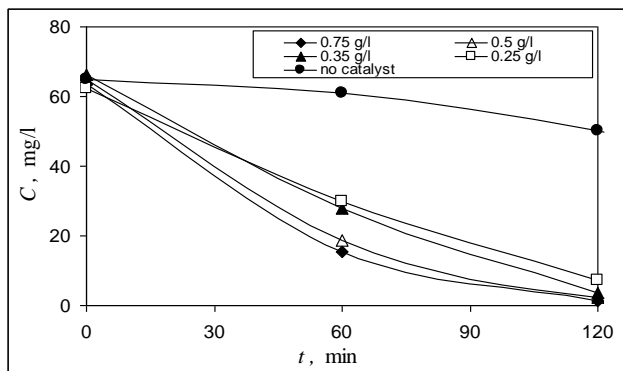
The influence of the initial concentration of sulfide at the same amount of catalyst was investigated and the results are shown in Fig. 3.



**Fig. 3.** Influence of the initial concentration of sulfide on the rate of oxidation at the same amount of  $ZrO_2$  catalyst.

It appears that at low and high concentrations, 50% of the sulfides are oxidized for 1 hour while at  $60\text{ mg l}^{-1}$  the oxidation rate is 90%. The reason for the low rate of oxidation is probably the accumulation of intermediates, competitive reaction or catalyst poisoning by the intermediates, e.g. elemental sulfur. Therefore a concentration of about  $60\text{--}70\text{ mg l}^{-1}$  was found suitable for conducting the process.

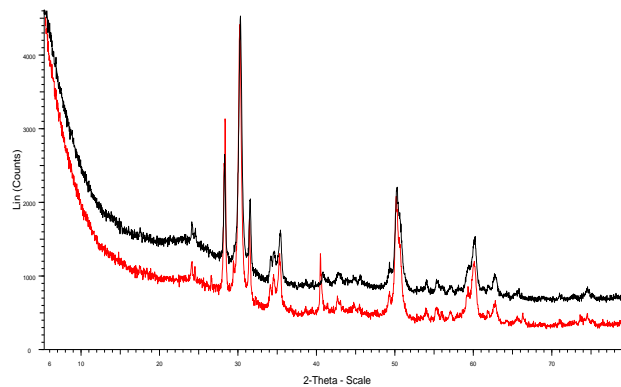
The influence of the  $ZrO_2$  catalyst on the rate of oxidation of sulfide ions at an initial concentration of  $65\text{ mg l}^{-1}$  was investigated (Fig.4).



**Fig. 4.** Influence of the amount of  $ZrO_2$  catalyst on the oxidation rate at initial concentration of  $60\text{ mg l}^{-1}$ .

The optimum amount of  $ZrO_2$  catalyst which provided a satisfactory rate of oxidation was  $0.75\text{ g l}^{-1}$  as shown in Figure 4. In the further experiments a catalyst amount of  $0.5\text{ g l}^{-1}$  was used which provided a rate of oxidation comparable to that of  $0.75\text{ g l}^{-1}$  of catalyst. The oxidation rate was low with a lower amount of catalyst and did not change significantly at a higher amount.

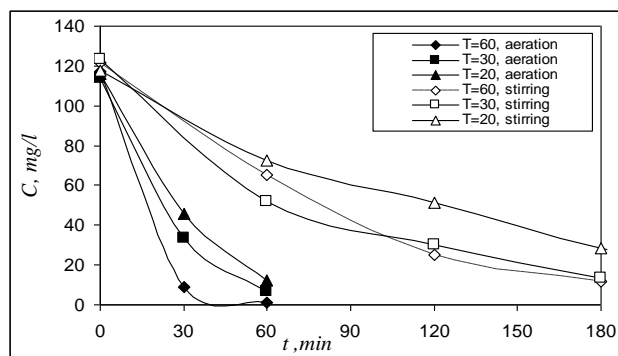
The catalyst was characterized by X-ray analysis in order to establish the proper crystallographic structure (Fig.5).



**Fig. 5.** XRD patterns of the  $ZrO_2$  catalyst before (upper X-ray gram, black) and after sulfide oxidation process (lower X-ray gram, red).

The  $ZrO_2$  is in monoclinic and tetragonal form. Comparison before and after conducting the oxidation process is also shown in Fig.5. As it can be seen, the structure and the composition of the catalyst are the same before and after performing sulfide oxidation. This means that there is no transformation of its surface.

A comparison of the oxidation rates for both regimes at  $120\text{ mg l}^{-1}$ , and different temperatures is presented in Fig.6.



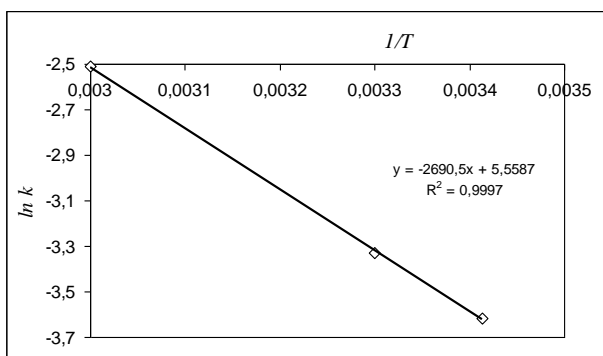
**Fig. 6.** Oxidation rates at different aeration rates and stirring.

It shows that the process at constant stirring is about 2 times slower than that with aeration. For this reason the kinetic parameters for aeration were derived for concentrations  $120\text{ mg l}^{-1}$ ,  $200\text{ mg l}^{-1}$ , and those with stirring - at  $60\text{ mg l}^{-1}$  and  $120\text{ mg l}^{-1}$  and temperatures  $20, 30, 60\text{ }^\circ\text{C}$ .

The oxidation with aeration follows the kinetics of first order reaction with rate constants  $k = 0.0269\text{ min}^{-1}$  for  $20\text{ }^\circ\text{C}$ ,  $k = 0.0358\text{ min}^{-1}$  for  $30\text{ }^\circ\text{C}$ ,  $k = 0.0813\text{ min}^{-1}$  for  $60\text{ }^\circ\text{C}$ .

$$\frac{dC}{dt} = kC$$

The Arrhenius plot for the studied reaction is presented on Fig.7.



**Fig. 7.** Arrhenius plot for the reaction with zirconia containing catalyst.

The reaction products are 90% of sulfate ions relative to the initial quantity of sulfides. Since sulfate ions are naturally present in seawater they can be fed back into it without harming the environment, restoring the sulfur cycle. Based on the experimental data obtained from the kinetic curves, the apparent activation energy of the reaction was calculated as 22 kJ mol<sup>-1</sup>.

In the second case with continuous stirring at constant speed for the same temperatures the reaction products were stable reducers which were determined iodometrically and should not be dumped into the sea water. The obtained rate constants are not alike for the different concentrations, i.e. the process is limited by the amount of dissolved oxygen in the cell. Therefore, in this case the Arrhenius dependence does not fit the experimental data properly.

### CONCLUSION

Best results for sulfide to sulfate oxidation were obtained when using ZrO<sub>2</sub> as a catalyst embedded into charcoal.

The optimum amount of ZrO<sub>2</sub> catalyst which provides a satisfactory oxidation rate is 0.5 g l<sup>-1</sup>. The oxidation rate of the sulfide ion is relatively high up to a concentration of 60-70 mg l<sup>-1</sup>.

In all experiments no elemental sulfur was observed. In the case of continuous aeration the sulfide conversion into sulfate was over 90% according to the initial sulfide concentration, whereas at continuous stirring without aeration the products of the reaction were stable reducers but no sulfate was obtained.

The oxidation follows the kinetics of a first

order reaction with relatively small activation energy – 22 kJ mol<sup>-1</sup>.

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## КИНЕТИКА НА ОКИСЛЕНИЕТО НА СУЛФИДНИ ЙОНИ ОТ МОДЕЛНИ РАЗТВОРИ НА МОРСКА ВОДА

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(Резюме)

Изследвано е каталитичното окисление на сулфидни йони от моделни разтвори на морска вода. Синтезиран е  $ZrO_2$  катализатор, инкорпориран в матрица от активен въглен. Повърхността на катализатора се охарактеризира чрез адсорбция по йод. Експериментите са проведени при различни начални концентрации на сулфидните йони и температури. Работено е при два режима на работа – непрекъсната аерация и разбъркване при едни и същи обороти без аерация. Продуктите на реакцията при процес с непрекъснато аериране са 90 % сулфатни йони, стехиометрично изчислени спрямо първоначалното количество сулфиди. Реакционните продукти при същите условия, но при процес с разбъркване, без аерация, са стабилни редуктори и са неприемливи от екологична гледна точка като крайни продукти. Окислението на сулфидни йони в режим на непрекъснато аериране следва кинетика на реакция от първи порядък с относително малка активизираща енергия.