

## INFLUENCE OF DIFFERENT FACTORS ON THE PROCESS OF BIOLOGICAL DECONTAMINATION OF PYROPHORIC IRON SULFIDE

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This article describes the use strains thiobacteria *Acidithiobacillus ferrooxidans* Achi1, Achi3 for decontamination pyrophoric deposits, which are a source of fires in refineries. It is found that the inhibitory factor is the intensity of insolation and organic impurities, and optima conditions for decontamination of hazardous waste are the temperature of  $30 \pm 35$  ° C, the use of hydrocarbon-oxidizing microorganisms and pH 2.0-2.5.

*Keywords: pyrophoric iron sulfides, microbiological oxidation, microorganisms.*

### Introduction

Pyrophoric iron sulfides are formed in the process equipment, storage tanks, oil wells by interaction with the hydrogen sulfide corrosion products contained in the sour crude [3]. The most dangerous formation of pyrophoric deposits of oil in storage tanks, where their self-ignition may ignite the vapor mixture and explosion [1]. Pyrophoric deposits on equipment surfaces are layered or porous solid education. On the surface deposits crystallized elemental sulfur, as a heat insulator and increasing the ability to spontaneous combustion [2, 4]. Activity pyrophoric deposits, i.e. propensity to spontaneous combustion, is determined by their chemical composition containing iron sulfides from FeS to FeS<sub>2</sub>, iron oxides FeO<sub>3</sub> and FeO<sub>4</sub>, petroleum products, and free sulfur. Accordingly, the idea of using different properties of autotrophic microorganisms to oxidize the sulfide minerals in the composition pyrophoric deposition. Currently known studies related to the study of microbiological processes, coupled with the oxidation of various sulfides in mineral and technogenic raw materials [5- 9].

**Objective:** To study the influence of various factors on the process optimization of microbiological decontamination of pyrophoric iron sulfides.

**Material and methods.** Research material pyrophoric deposits formed by the interaction of oil Kumkol field with technological equipment at the Shymkent refinery LLP "PetroKazakhstan Oil Products" (PKOP).

Kumkol oil is as follows: pour point 1000 C, the content of Silica Gel resins - 19.2%; carbo-karboides- 5.82%; asphaltenes -5.4%; paraffin - 7.5%; sulfur - 0.064%. At a temperature of 200 ° C has a density - 0.850 g / cm<sup>3</sup>.

The study used strains of *Acidithiobacillus ferrooxidans* Achi1, Achi3, isolated from field Taukent productive solutions that are grown on selective medium Silverman and Lyundgren. Composition g/l as ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 3.0, magnesium sulphate MgSO<sub>4</sub>·7H<sub>2</sub>O - 0.5, potassium hydrogen phosphate K<sub>2</sub>HPO<sub>4</sub> - 0.5, potassium chloride KCl - 0.1, calcium nitrate Ca (NO<sub>3</sub>)<sub>2</sub> - 0.01, ferrous sulphate FeSO<sub>4</sub>·7H<sub>2</sub>O - 21.00 [10]. The medium was autoclaved at 121 °C for 15 minutes to prevent interference of other microorganisms. Microscopy was performed using a microscopes "Biomed 5» and «Tayuda». The iron content was determined trilonometric method[7].

To maintain the aeration and temperature of the flask with 250 ml of microbial biomass were placed on a shaker (AVU 6) at different temperatures. When studying the influence of the illumination level used modes: without light - into opaque spot, under artificial light - racks scattered light- room, sun light- exposed to direct sunlight. The pH of the medium was adjusted to 1, 2, 3, 4, 5, 6, 7, and 8, with 10 N H<sub>2</sub>SO<sub>4</sub>.

**Results and discussion.** When studying the effect of different temperatures on the oxidation rate of pyrophoric iron sulfides thiobacteria *Acidithiobacillus ferrooxidans* Achi1 and *A. ferrooxidans* Achi3, it was found that the optimal temperature was 35 +30 °C, wherein this temperature corresponds to the maximum number of cells and bacteria per 1 ml of solution. On the effect of temperature on *A. ferrooxidans* in the oxidation was studied Fe<sup>2+</sup> range: 0 to + 5<sup>0</sup>C, 10 + 15<sup>0</sup>C, 20+25<sup>0</sup>C, 30 + 35<sup>0</sup>C, 40 + 45<sup>0</sup>C. When reducing the temperature to 15 °C regardless of the initial concentration Fe<sup>2+</sup> specific growth rate of the bacteria and the rate of oxidation Fe<sup>2+</sup> reduced approximately equally (2.0 ± 0.2 and 1.2 ± 0.1 fold respectively). By lowering the temperature from 15<sup>0</sup>C to 5,5 °C depending on the initial concentration of Fe<sup>2+</sup> specific growth rate is suppressed significantly greater (9,2 ± 0,2 times). At a temperature of 30 + 35<sup>0</sup> C - the region of optimal concentration when the amount of oxidized Fe<sup>2+</sup> is 8,9 ± 0,2 g / l per day.

However, when tested in "PKOP" LLP has been found that in spite of the temperature optimum of 30 + 35<sup>0</sup>C in the summer, there is inhibition of the biological processes of oxidation of ferrous iron. A possible reason for this may be the active surface insolation aqueous solutions with bactericidal direct sunlight. Study on the effect of light on the processes of biological oxidation of ferrous iron in the composition of pyrophoric deposits showed that artificial lighting regimes

significant influence on the oxidation rate of no effect. In contrast, direct sunlight has dramatically inhibitory effect (**Figure 1**).

In studies under LLP "PKOP" has been found that when cleaning the pipes of pyrophoric deposits with them fall petroleum residues, is a limiting factor for the development of autotrophic microorganisms thiobacteria. When making pyrophoric sulphide in an aqueous solution to the bacterial suspension and nutrients organic impurities form an oily film on the water surface. In laboratory conditions, the model has been found that the rate of biooxidation of pyrophoric iron sulfides is correlated with the amount present in the aqueous solution of organic impurities introduced in concentrations of 0.1; 1,0; 3,0; 5,0; 10.0%. (**Figure 2**).

The using of adapted to the organic pollutants thiobacteria culture coupled with hydrocarbon-oxidizing microorganisms allowed on the fifth day completely oxidize ferrous iron in the composition of pyrophoric deposits (**Figure 3**). Thus it is seen that if the control under the influence of physical and chemical factors, oxidation  $96,9 \pm 0,1\%$  ferrous iron, in the embodiment with the original strains of thiobacteria, this figure rises to 65.3%. Introduction solution adapted strains of thiobacteria reduces the content of ferrous iron to 39.7%. Using only hydrocarbon-oxidizing microorganisms reduces organic impurities in the aqueous solution, but significant changes in the concentration of divalent iron does not cause as oxidation leaves with only 4.1. Supplement composition hydrocarbon-oxidizing microorganisms adapted thiobacteria leads to the complete oxidation of ferrous iron and deactivation of pyrophoric iron sulfides.

In addition, the marked changes in pH values, so if in the control variant pH increased from 2.2 to 2.4, the version with the original batch culture thiobacteria pH increases by 2.04 times. Adapted culture pH increased 2.38 times, coupled with the hydrocarbon-oxidizing microorganisms - a 2.52-fold (Figure 4).

Furthermore, it was found that the dynamics of the oxidation of ferrous iron is significantly affected by the initial titer of the microorganisms used. Thus, in the case of using the biomass of microorganisms with a titer of  $10^3$  cells / ml in complete oxidation of divalent iron does not take place, an increase in titer of microorganisms to  $10^6$  cells / ml optimizes the process. Oxidation of ferrous iron occurs after 48 hours at pH 2.0 and 2.5, wherein the pH is 1.5 inhibitory factor on the rate of oxidation of ferrous iron.

### **Conclusion**

A study of the influence of various factors on the processes of biological decontamination of pyrophoric iron sulfides found that:

- limiting factors inhibiting microbiological processes associated with oxidation of ferrous iron in the composition pyrophoric deposits: insolation is intense and the presence of organic impurities;
- optimize the processes necessary to create and maintain the optimum conditions for life thiobacteria *Acidithiobacillus ferrooxidans* Achi1 and *A. ferrooxidans* Achi3: +30+ 35 °C solution temperature, pH 2.0 - 2.5, the introduction of hydrocarbon-oxidizing microorganisms to oxidize the organic impurities.

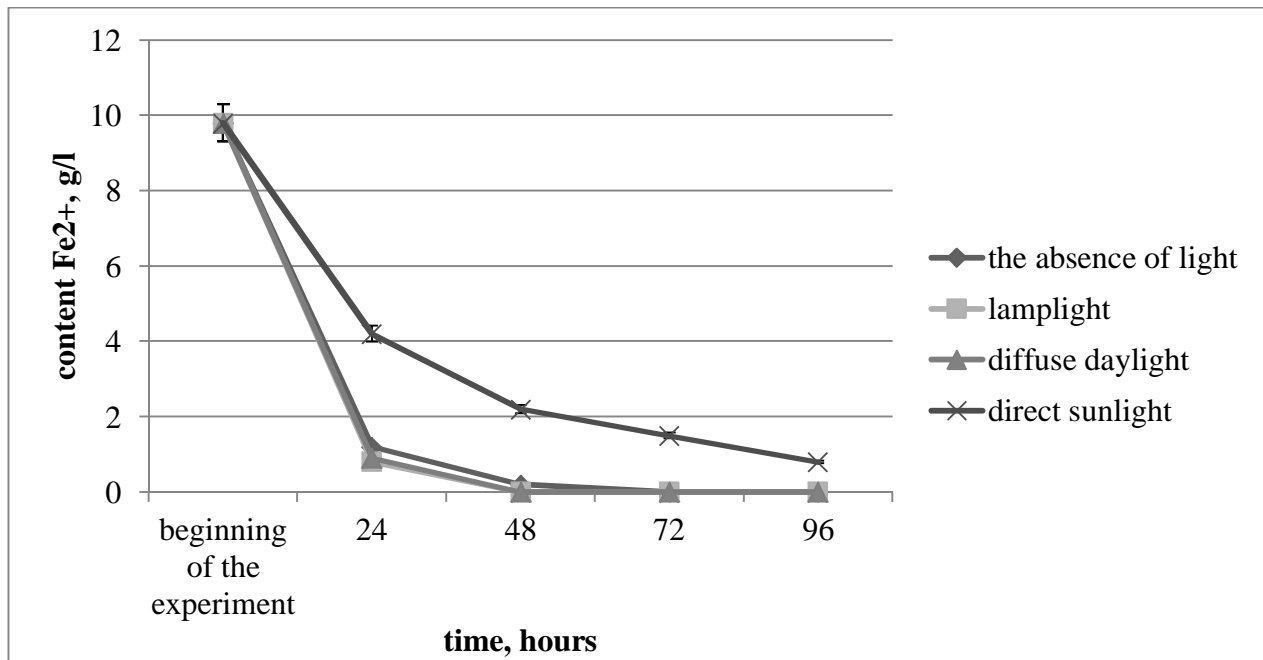


Figure 1- Effect lighting modes on biological oxidation of ferrous iron pyrophoric deposits

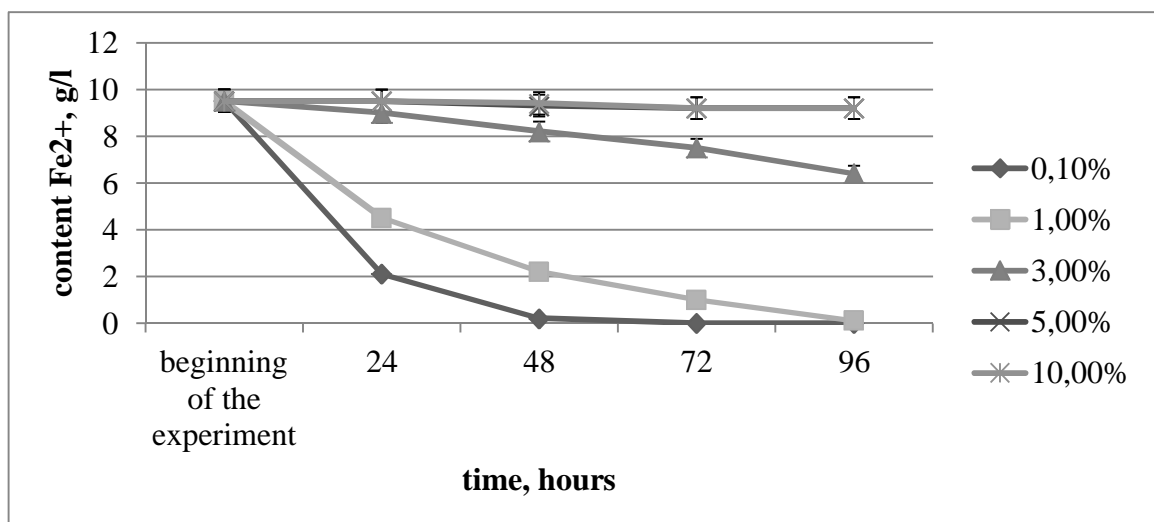
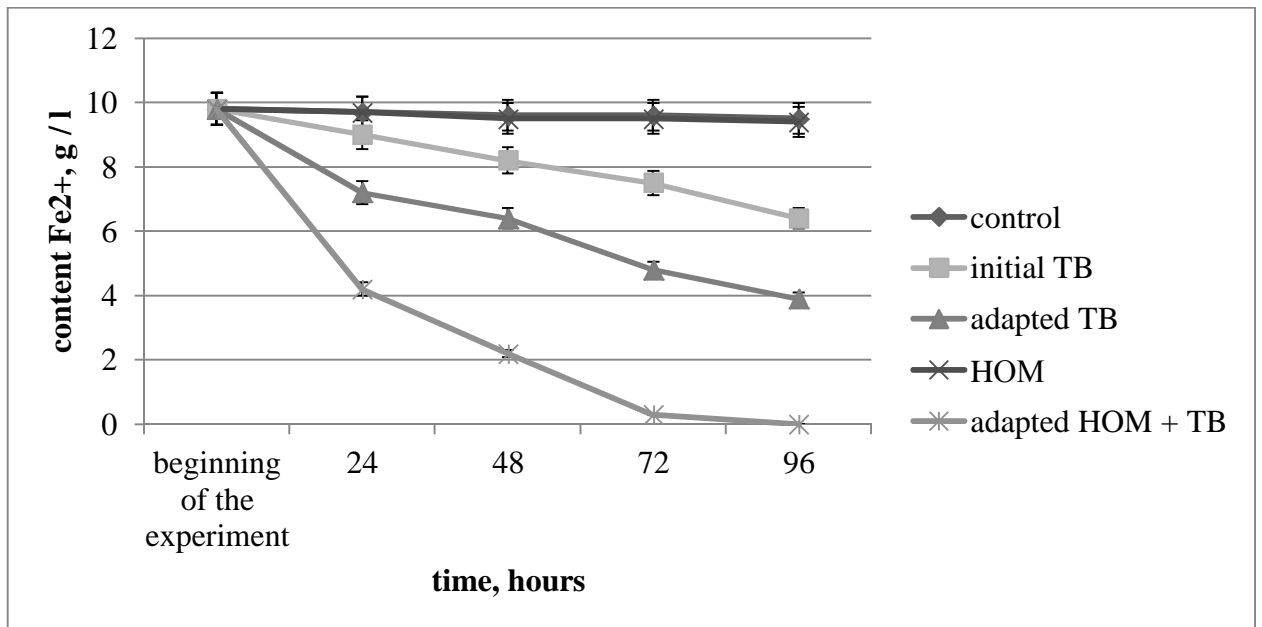
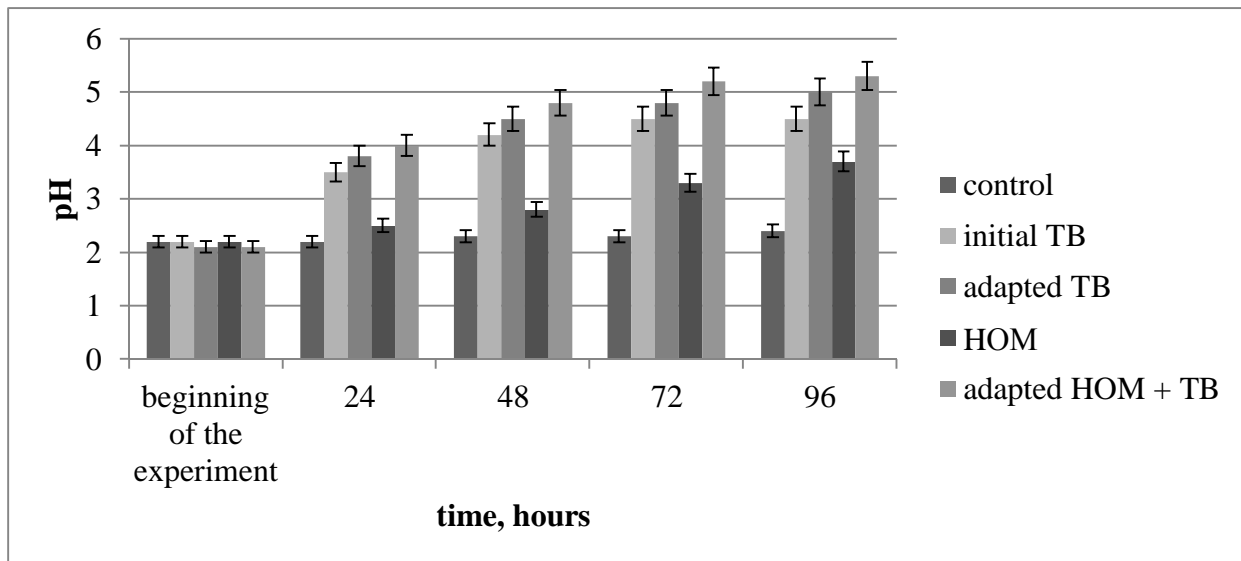


Figure 2- Effect of organic impurities on the rate of oxidation of ferrous iron thiobacteria



TB –thiobacteria Acidithiobacillus ferrooxidans Achi1, Achi3, HOM –hydrocarbon-oxidizing microorganisms

**Figure 3. The dynamics of changes in the content of ferrous iron in solution using different cultures of microorganisms**



TB –thiobacteria Acidithiobacillus ferrooxidans Achi1, Achi3, HOM –hydrocarbon-oxidizing microorganisms

**Figure 4. Dynamics of change of pH during the oxidation of pyrophoric iron sulfides different compositions of microorganisms**

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