

## Use of *Acidithiobacillus ferrooxidans* for Decontamination of Explosive Waste from Oil Refineries

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### ABSTRACT

Pyrophoric iron sulfides formed as a result of oil cracking, when in contact with air oxygen, have the ability to self-ignite, as a result of which they are highly explosive at oil refining enterprises. It is known that the oil refineries in Kazakhstan produce from 4 to 10 tons per year of this hazardous waste. The main idea of the study was to use the biochemical abilities of microorganisms, in particular the thionic bacteria *Acidithiobacillus ferrooxidans*, to change the physico-chemical properties of pyrophoric iron sulfides. In this regard, the aim of the study was to determine the possibility of using *A. ferrooxidans* for deactivation of pyrophoric iron sulfides at an oil refinery in the south of Kazakhstan. It was found that the cultivation of a strain of thionic bacteria *A. ferrooxidans* ThIO1 in solutions with pyrophoric iron sulfides as the only source of divalent iron and compliance with optimal conditions for their vital activity: +28 °C, pH 2.0–2.5, S:L=1:10±2, will decontaminate explosive waste of oil and gas industry enterprises. The method of biological decontamination of pyrophoric iron sulfides was introduced at the PetroKazakhstan Oil Products LLP refinery in Southern Kazakhstan in 2007. For the successful implementation of this method at other enterprises, it is necessary to develop a special adapted industrial installation for the biological decontamination of pyrophoric deposits with continuous (in the case of receiving waste from different enterprises of Kazakhstan) or periodic cultivation of microorganisms, and compliance with optimal parameters for the vital activity of microorganisms.

**Keywords:** pyrophoric iron sulfides, *Acidithiobacillus ferrooxidans*, explosion hazard, waste from oil refineries, cultivation of microorganisms.

### INTRODUCTION

It is known that a special type of hazardous waste is formed at many industrial enterprises, which, acquires the ability to self-ignite when in contact with air oxygen. In studies by Bertani et al. (2016), it was revealed that dried sludge obtained from the sewage of a tannery, under certain conditions, can lead to self-heating. In most cases, this leads to moderate heating (reaching 70–90 °C), but with a longer stay in the dryer, not provided for by the project, active

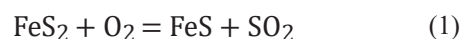
reactive solids can form in an atmosphere with a low oxygen content. Usually, leather production waste contains several chemicals, which mainly fall into the sediment during wastewater treatment. Unexpected and unpredictable self-heating can lead to fire and even environmental problems. The authors tried to formulate a mechanism for starting heating, where they found that the Fe/S/O system was involved in this process. It has been proven that the key factor of spontaneous combustion is the formation of small amounts of pyrophoric iron sulfides. They turn into sulfates as

a result of reaction with water and oxygen during exothermic processes. The production of this type of pyrite/pyrrhotite depends on the sludge drying process. Oxidation of sulfides to oxides and sulfates at exothermic stages, catalyzed by metals contained in the sediment, occurs preferably in a humid environment. The authors' hypothesis about the mechanism of spontaneous combustion of waste was proven by reproducing in the laboratory long-term heating in an oxygen-free/suboxic atmosphere.

Pyrophoric deposits, which are compounds formed as a result of the interaction of hydrogen sulfide corrosion products, resinous substances, organic products and mechanical impurities, are currently one of the serious sources of fire hazard in the oil and gas industry. These deposits in the presence of oxygen in the air can gradually warm up and self-ignite with an explosion of oil vapor. Emissions of harmful substances into the atmosphere cause not only environmental, but also great economic damage. Pyrophoric deposits can be formed during storage, transportation and processing of sulfurous oils and petroleum products on unprotected surfaces of tanks and pipelines; pyrophoric deposits have chemical heterogeneity and complexity of composition. In studies of fire hazard at oil refineries, unexpected ignition of deposits of pyrophoric iron sulfide in the fractionating device of a visbreaking plant was revealed (Plellis-Tsaltakis, 2015). At the same time, the distillation column was previously chemically disinfected. During the investigation of this event, conclusions were drawn about the limitations in the field of chemical decontamination on ships operated during coking. In this regard, a recommendation was made on the priority of work on manual cleaning of containers during coking.

Pyrophoric iron sulfides (FeS, FeS, FeS) are combustible substances that, at ambient temperature and atmospheric pressure, are capable of spontaneous combustion as a result of chemical interaction with oxygen in the air, especially during the extraction of sulfur-containing oil. Pyrophoric compounds are formed on the surface of metal equipment used in oil cracking, which is subjected to corrosion processes. The study of the composition of corrosive deposits showed that the components of the formed deposits are finely dispersed iron sulfides  $Fe_xS_u$  and elemental sulfur (up to 76% by weight) both in the form of pyrophoric compounds – sulfides and mercaptides – and in the free state (Beilin, 2007). Elemental

sulfur is formed in the reactions of iron sulfides and hydrogen sulfide with oxygen in the air. As a result, an exothermic reaction occurs, leading to the heating of pyrophoric deposits:



At the same time, the thermal effect of the reaction is 220 kJ/mol. When pyrophoric sulfides are heated to 180–220 °C, free sulfur self-ignites. This is the cause of fires in tanks both during oil storage and pumping.

Optical microscopy studies have shown that the composition of the initial deposits throughout their thickness contains multiple brilliant geometrically regular crystals of iron sulfides, such as pyrite or marcasite (Butovsky, 2010). The high rate of oxidation of pyrophoric iron sulfides is due to the large surface area of contact with air. However, the direct cause of pyrophoricity is not so much the total surface area as the distortion of the crystal lattice of particles in comparison with the structure stable for the corresponding metal. The composition of pyrophoric deposits is determined by the conditions of their formation, which, depending on the location in the reservoir, may differ markedly in their composition (Hughes et al., 1974). The porous structure of pyrophoric deposits and impurities of organic substances contributes to their rapid oxidation. Pyrophoric deposits saturated with heavy petroleum products and oils are particularly dangerous, since the latter can heat up themselves, contributing to the spontaneous combustion of pyrophoric deposits. The explosiveness of pyrophoric compounds increases along with ambient temperature, although their spontaneous combustion is possible at any, even the lowest temperature (Nolan, 2019). This is due to the fact that pyrophoric compounds do not conduct heat well, and the heat released at the initial stage of oxidation accumulates in the mass of the deposit, which leads to its heating up to a dangerous temperature. Especially these compounds are dangerous during the repair of equipment, when opening devices. Therefore, a mandatory safety requirement in order to avoid spontaneous combustion of structures is the constant humidification of pyrophoric deposits.

Depending on the composition and place of formation, the pyrophoric activity of deposits (the ability to self-ignite) can be different. Pyrophoric compounds formed under the action of crude distillates of light petroleum products containing elemental sulfur have the greatest activity.

The authors of the study (Payant et al., 2012) tested their hypothesis that galvanic interaction between some sulfides can promote self-heating. 4 variants were investigated: 1 – samples of sulfides and 2 – concentrates containing four sulfides: pyrite, chalcopyrite, sphalerite and galena. They were tested individually and in the form of mixtures by weight of 50:50. Individual samples and mixtures with a low resting potential difference were not subjected to self-heating, unlike mixtures with a high resting potential difference. In option 3, pyrite was mixed 50:50 with two materials that were self-heated independently, pyrrhotite and nickel concentrate, and self-heating was further increased. In option 4, pyrite–sphalerite mixtures were tested depending on the particle size. It was found that self-heating increased as the particle size decreased, and it was the fineness of pyrite (a mineral with a high resting potential or cathode) that determined the reaction. The authors found that an increase in self-heating with a high resting potential difference and an increase in the particle size of the cathode mineral confirm that galvanic interaction can contribute to the self-heating of sulfides. A possible mechanism based on the hydrogen sulfide hypothesis is proposed, in which the reduction reaction on the cathode surface of the mineral occurs from trivalent iron to divalent iron.

A method is known for removing hazardous, including pyrophoric deposits from pipelines, including injection of liquid nitrogen into pipelines. As a result of such treatment of pipelines, pyrophoric deposits are frozen and can then be extracted under controlled conditions (WO 8201408, 1982).

There are known methods involving the treatment of already formed deposits with various chemical reagents: inhibitor of INFX-1 (SU 825102, 30.04.1981), trilon B (SU 1404462, 23.06.1988) and others. The disadvantages of these methods are high cost due to the use of reagents as well as the need for mandatory emptying of pipelines and tanks before pumping inert liquids into them with constant irrigation of sediments. In addition, the method does not deactivate pyrophoric activity and is aimed only at preventing spontaneous combustion of deposits.

The disadvantages of these methods are the need to use additional equipment for installing membranes and obtaining nitrogen from the air, complicating the process of preservation of

pyrophoric deposits, unresolved problems of storage and decontamination of pyrophoric deposits.

On the other hand, it is known that in the biogeochemical cycle of iron and sulfur in nature, a number of microorganisms are known to participate in various redox reactions (Nuñez et al., 2017; Fariq et al., 2019).

The main idea of the study was to use the biochemical abilities of microorganisms, in particular the thionic bacteria *Acidithiobacillus ferrooxidans*, to change the physico-chemical properties of pyrophoric iron sulfides. In this regard, the aim of the study was to study the possibility of using *A. ferrooxidans* for deactivation of pyrophoric iron sulfides at an oil refinery in the south of Kazakhstan.

## MATERIALS AND METHODS

The object of the study consisted of pyrophoric iron sulfides formed at the cracking stage of an oil refinery “PetroKazakhstan Oil Products” in Shymkent. The strain *Acidithiobacillus ferrooxidans* ThIO1 isolated from a polymetallic waste storage site in the south of Kazakhstan was used in the work.

Isolation and cultivation of the thiobacterium *Acidithiobacillus ferrooxidans* ThIO1 used a medium of 9K, Silveman-Lundgren of the following composition (g/l): 1 solution – 700 ml of distilled water,  $(\text{NH}_4)_2\text{SO}_4$  – 3.0; KCl – 0.1;  $\text{K}_2\text{HPO}_4$  – 0.5;  $\text{MnSO}_4 \times 7\text{H}_2\text{O}$  – 0.5;  $\text{Ca}(\text{NO}_3)_2$  – 0.01; 2 solution: 300 ml of distilled water,  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$  – 44.2; pH 2 is adjusted using 10N  $\text{H}_2\text{SO}_4$ .

The content of  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$  was determined by using the complexometric method (Lurie, 1984). Microscopes “Tauda” and “Mikmed-5”, light microscopy methods were used during microscopic studies.

In the study of raw materials, a mass spectrometer with inductively coupled plasma was used, the determination of elements was carried out in accordance with ST RK ISO 17294-2-2006. Chemical analysis was carried out according to GOST 13685-84. Research conditions: temperature – 25 °C; humidity – 83.0%; pressure – 714 mm Hg.

Under the industrial conditions of the PetroKazakhstan Oil Products refinery, a concreted tank with a volume of 50.0 m<sup>3</sup> was selected for enlarged experiments, where an aqueous solution for the cultivation of thiobacteria was prepared, with pyrophoric deposits as a source of iron

and sulfur. The pH of the medium was brought to 2.0–2.5 with the help of sulfuric acid. The air supply was carried out using aerator pipes made of inert plastic material. Pyrophoric deposits were deposited in an amount of  $5.0 \pm 0.5$  tons. The flammability of the waste was checked daily with thermometers.

Statistical processing of the obtained results was carried out by calculating the arithmetic mean and the value of the standard deviation. All determinations were carried out in 3 and 5-fold repetition. The data was processed using an IBM Pentium personal computer based on Excel application software packages.

## RESULTS AND DISCUSSION

Analysis of the situation with the formation of pyrophoric deposits at oil refineries in Kazakhstan showed that 8–10 tons/year are formed at the Pavlodar plant, 6–7 tons/year at the Atyrau plant and 4–5 tons/year of these explosive wastes at the Shymkent plant. Up to 25–40 tons of pyrophoric deposits are formed annually at oil refineries in the post-Soviet countries with a similar technological scheme for producing petroleum products. Despite the small amount of waste generated, the consequences of their formation can lead to fires at an enterprise with a high explosive hazard. Currently, the problem with spontaneous combustion of these wastes is solved by wetting the waste.

When performing the operation of extracting the cut-out element from the disconnected section of the gas pipeline, atmospheric air enters the depressurized gas pipeline. Under these conditions, in order to prevent spontaneous combustion of pyrophoric deposits, their phlegmatization is carried out by wetting with water. However, the experience of such works shows that this operation can be started only after some time necessary to remove the cut pipe element from the pit. During this period, usually not exceeding 10–15 minutes, atmospheric air freely fills the depressurized gas pipeline and, interacting with pyrophoric deposits, causes their intense oxidation.

The operation of wetting pyrophoric deposits, carried out after removing the cut-out pipe element from the pit, also does not prevent their contact with air, since pyrophoric deposits moistened during the transport of gas by its condensate vapors are poorly wetted with water, and it is not possible to control the quality of wetting during

work. In addition, during the production of fireworks under the conditions of negative temperatures, the use of water as a phlegmatizer is impractical, since icing occurs on the inner surface of the gas pipeline and the formation of ice jams in it is possible.

Visually, the procedure is as follows: metal columns are removed from the oil cracking unit, which are covered with a layer of corroded metal with yellow sulfur-containing layers. Next, several workers clean the columns from formations on the concreted surface using metal scrapers. One of the workers continuously pours waste from a hose with water. The collected waste with pyrophoric deposits is placed in 200 liter barrels and filled with water, hermetically sealed with lids and sent to the burial grounds of hazardous waste. The difference in the methods used to combat the ignition of pyrophoric deposits at different oil refineries in Kazakhstan and Russia is only in the use of the type of liquid: from water to different solutions.

However, in general, the measures aimed at preventing spontaneous combustion of pyrophoric deposits by wetting them with water cannot be considered effective.

Currently, a bacterial-chemical method using the biomass of the bacterial strain *Acidithiobacillus ferrooxidans* ThIO1 is considered as one of the optimal and most promising ways to deactivate pyrophoric deposits. These bacteria can use as an energy substrate almost all sulfide minerals, reduced sulfur compounds ( $\text{SO}$ ,  $\text{SO}_3^{2-}$ , etc.) and other nitrous elements in solution, in particular, iron (Zhang et al., 2018). Gram-negative, rod-shaped cells,  $0.3\text{--}0.4 \times 0.7\text{--}1.7$  microns in size, move with the help of a polar flagellum.

The main idea of solving the problem was the ability of thiobacteria to oxidize divalent iron into trivalent, while elemental sulfur is converted into sulfate form. As a consequence of changes in the chemical and physical structure of pyrophoric iron sulfides, their ability to actively oxidize with oxygen in the air should also change, which will lead to deactivation of spontaneous combustion of waste.

To confirm the scientific guess, an express experiment was conducted, where pyrophoric iron sulfide was included instead of  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$  in the Silverman-Lundgren medium used for the cultivation of *Acidithiobacillus ferrooxidans* ThIO1. It was found that the bacteria *A. ferrooxidans* ThIO1, oxidize divalent iron and sulfur, which



are part of pyrophoric deposits for 5–6 days. The solid waste formed completely loses the ability to self-ignite. In the control variant, without introducing microorganisms into the modified Silverman-Lundgren medium, spontaneous combustion of pyrophoric iron sulfides was preserved. It was found that there are no fundamental differences in the cultivation of *A. ferrooxidans* ThIO1 bacteria grown on a traditional Silverman-Lundgren medium and a medium containing pyrophoric iron sulfides as the only source of iron. Thiobacteria retained their viability and oxidative activity.

The ability to self-ignite pyrophoric deposits was measured using a thermometer, which was placed in the waste center. When in contact with air, pyrophoric deposits begin to gradually heat up. At a temperature of  $+65 \pm 5$  °C, smoke appears, with a further increase in temperature, sparks begin to appear inside the waste and, in the future, the waste ignites. In the case of the use of thiobacteria, no increase in the temperature of the waste was detected; in the control variant, the temperature of the waste began to rise at 9–10 minutes.

Studies conducted by Kong et al. (2016) have shown that the process of spontaneous combustion of pyrophoric iron sulfides has its risks. In order to evaluate the thermal characteristics of the sulfide concentrate sample, thermogravimetry and differential scanning calorimetry (TG-DSC) methods were used. Samples of pyrophoric iron sulfides were heated from ambient temperature to 1000 °C with four heating speeds. On the basis of the Semenov model, the authors calculated the oxidation temperature during self-accelerating decomposition (SADT) and the temperature of no return (TNR). Assuming that the sulfide reserves are in a quasi-adiabatic state, the authors predicted the self-ignition delay time (AIDT) of the sulfide reserves. In general, the results showed that the oxidation of samples of pyrophoric deposits at different heating rates undergoes a similar process: the initial stage of physical absorption, the subsequent stage of chemical absorption and the subsequent stage of thermal oxidation. It is found that the thermal behavior of a sulfide mineral at different heating rates indicates that the higher the heating rate, the higher the initial and peak temperature. As the heating rate increases, the holding time decreases from about 20 to 12 days under a given set of conditions. The information obtained in this study is useful for reducing the risks associated with spontaneous combustion of pyrophoric waste in their storage areas, which is

especially important for the conditions of Southern Kazakhstan with extreme summer temperatures above +50 °C.

In addition, the influence of various factors (temperature, solid-to-liquid ratio, pH of the medium) on the rate of oxidation of pyrophoric iron sulfides was studied. It was found that there are no fundamental differences in the cultivation of *A. ferrooxidans* ThIO 1 bacteria grown on a traditional Silverman-Lundgren medium and a medium containing pyrophoric iron sulfides as the only source of iron.

When studying the effect of different temperatures on the oxidation rate of pyrophoric iron sulfides, laboratory tests were carried out in the temperature range of 5–28 °C. It was found that the optimum temperature is 28 °C, and the maximum number of cells of *A. ferrooxidans* ThIO1 bacteria per 1 ml of solution corresponded to this temperature. When the temperature decreases to 15 °C, regardless of the initial concentration of  $Fe^{2+}$ , the specific growth rate of bacteria and the rate of oxidation of  $Fe^{2+}$  decrease approximately equally (1.5–2.5 and 1.1–2.3 times, respectively). When the temperature drops to 5.5 °C, depending on the initial concentration of  $Fe^{2+}$ , the specific growth rate is suppressed significantly more (4.2–14.3 times).

The study of the influence of different pH values on the rate of oxidation of pyrophoric iron sulfides showed that the optimum pH for this process is in the range of 2.0–2.5. The results of production tests confirmed the results of laboratory studies and showed that the use of the oxidizing ability of thionic bacteria allows the complete deactivation of pyrophoric compounds.

Study of the influence of the ratio of solid to liquid (S:L) showed that the optimum is at  $1:10 \pm 2$ , in the mode of active bubbling to increase the area of contact of pyrophoric iron sulfides with the nutrient liquid medium. An increase in the content of the solid component in the reacting liquid leads to an increase in the decontamination time.

The verification of the authors' idea of the possibility of using microbiological processes in the deactivation of pyrophoric iron sulfides in the production conditions of an oil refinery has shown its viability. Under the conditions of pilot tests, a number of measures necessary for the further use of the proposed idea of processing pyrophoric iron sulfides have been established. The method of biological decontamination of pyrophoric iron sulfides was introduced at the PetroKazakhstan

Oil Products LLP refinery on the Southern Kazakhstan in 2007. For the successful implementation of this method at other enterprises, it is necessary to develop a special adapted industrial installation for the biological decontamination of pyrophoric deposits with continuous (in the case of receiving waste from different enterprises) or periodic cultivation of microorganisms, compliance with optimal parameters for the vital activity of microorganisms.

## CONCLUSIONS

As a result of the conducted studies, it was found that the cultivation of a strain of thionic bacteria *A. ferrooxidans* ThIO1 in solutions with pyrophoric iron sulfides as the only source of divalent iron and compliance with optimal conditions for their vital activity: +28 °C, pH 2.0–2.5, S:L= 1:10±2 will allow decontamination of explosive waste of oil and gas industry enterprises. To implement the idea of biological decontamination of pyrophoric deposits on a production scale, it is necessary to develop a special industrial plant for the cultivation of microorganisms with the maintenance of optimal living conditions.

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