CRADA Final Report
ANL/NE/C0001501- Amendment 2

"Studies on the Impact, Detection, and Control of Microbiologically Influenced Corrosion Related to Pitting Failures in the Russian Oil and Gas Industry"

This CRADA involved Argonne National Laboratory as the Contractor and overall Project Manager. The CRADA Industrial Participant was ONDEO Nalco Energy Services, LP located in Naperville, IL. The Project Subcontractors who did the majority of the work included the following parties:

State Research Center for Applied Microbiology and Biotechnology (SRCAMB) headquartered in Obolensk, Moscow region, Russia. SRCAMB served as the lead Russian subcontractor.

A.E. Arbuzov Institute of Organic and Physical Chemistry (AIOPC), Kazan Research Center, Russian Republic of Tatarstan, Russia.

Moscow State University located in Moscow Russia.

To improve logistics in contracting in the Russian Federation, an international not-for-profit organization, the International Science and Technology Center (ISTC) put in place the subcontract. The project number is 2245p. Argonne National Laboratory served as the technical manager of this contract under the NIS-IPP program.

The attached ISTC 2245p report serves as the CRADA Final Report.

Summary Final
Project Technical Report
of ISTC 2245p

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Studies On the Impact, Detection, and Control of Microbiologically Influenced Corrosion Related to Pitting Failures in the Russian Oil and Gas Industry

(From 1 February 2002 to 31 January 2006, 48 months)

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State Research Center for Applied Microbiology and Biotechnology (SRCAMB), Obolensk

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ISTC 2245p

Studies On the Impact, Detection, and Control of Microbiologically Influenced Corrosion Related to Pitting Failures in the Russian Oil and Gas Industry

(From 1 February 2002 to 31 January 2006, 48 months)

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Objectives of the Project:

- to design effective anti-corrosion preparations (biocides, inhibitors, penetrants and their combinations) for gas- and oil-exploration industries;
- to study a possibility of development of environmentally beneficial ("green") biocides and inhibitors of the new generation;
- to develop chemical and microbiological methods of monitoring of sites at risk of corrosion;
- to evaluate potentialities in terms of technology, raw materials and material and technical basis to set up a production of effective anti-corrosion preparations of new generation in Russia.

During the four years of the project 228 compounds and formulations were synthesized and studied in respect to their corrosion inhibiting activity. A series of compounds which were according to the Bubble tests more efficient (by a factor of 10-100) than the reference inhibitor SXT-1102, some possessing the similar activity or slightly better activity than new inhibitor EC-1154A (company ONDEO/Nalco). Two synthetic routes for the synthesis of mercaptopyrimidines as perspective corrosion inhibitors were developed. Mercaptopyrimidine derivatives can be obtained in one or two steps from cheap and easily available precursors. The cost for their synthesis is not high and can be further reduced after the optimization of the production processes. T

A new approach for lignin utilization was proposed. Water-soluble derivative of lignin can by transformed to corrosion protective layer by its electropolymerization on a steel surface. Varying lignosulfonates from different sources, as well as conditions of electrooxidation we proved, that drop in current at high anodic potentials is due to electropolymerization of lignin derivative at steel electrode surface. The electropolymerization potential can be sufficiently decreased by an increase in ionic strength of the growing solution. The lignosulfonate electropolymerization led to the considerable corrosion protection effect of carbon steel. More than three times decrease of corrosion rate on steel surface was observed after lignosulfonate electropolymerization, exceeding protective effect of standard commercially available corrosion inhibitor. Solikamsky lignin could be a promising candidate as a base for the development of the future green corrosion inhibitor.

A protective effect of isothiazolones in compositions with other biocides and inhibitors was investigated. Additionally to high biocidal properties, combination of kathon 893 and copper sulfate may also produce a strong anticorrosion effect depending on concentrations of the biocides. Based on its joint biocidal and anticorrosion properties, this combination can be recommended for protection of pipelines against carbon dioxide-induced corrosion. By means of linear polarization resistance test, corrosion

properties of biocides of different classes were studied. Isothiazolones can be recommended for treating oil-processing waters in Tatarstan to curb carbon dioxide – induced corrosion.

A laboratory research on evaluation of the efficiency of biocides, inhibitors and penetrants by biological and physical-and-chemical methods has been carried out. It was shown that action of corrosion inhibitors and biocides strongly depends on character of their interaction with mineral substances available in waters on oil-exploration sites. It was found that one of approaches to designing environmentally safe ("green") antimicrobial formulations may be the use of synergetic combinations, which allow one to significantly decrease concentrations of biocides. It was shown that the efficacy of biocides and inhibitors depends on physicochemical characteristics of the environment. Anticorrosion and antimicrobial effects of biocides and inhibitors depended in much on the type of medium and aeration regimen. Effects of different biocides, corrosion inhibitors. penetrants and their combinations on the biofilm were investigated. It has been shown that minimal inhibiting concentrations of the reagents for the biofilm are much higher than those for aquatic microorganisms. Results obtained from the research in stationary conditions have been confirmed with data from experiments carried out in hydrodynamic conditions.

New approaches to the investigation of biocorrosive processes on the basis of bioluminescent method of intracellular ATP determination have been developed. Approaches and methods developed on the basis of bioluminescent method could significantly simplify the analysis of biocorrosion processes and allow to conduct the analysis directly under the field conditions *in situ*. An express method to assess biogenic sulfate reduction in soil and water samples has been elaborated. The method intends for field application and allows one to no-problem assess action of such harmful and corrosion provoking microorganisms, as sulfate-reducing bacteria.

Keywords: Carbonic acid-induced corrosion, corrosion inhibitors, "green" inhibitors, inhibitor production, electro-polymerization of lignins and lignosulphonates, microbially induced corrosion, sulfate-reducing bacteria, biofilms, biocides, synergestic combinations, monitoring of sites at risk of corrosion.

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Summary of the project

Objectives of the Project:

- to design effective anti-corrosion preparations (biocides, inhibitors, penetrants and their combinations) for gas- and oil-exploration industries;
- to study a possibility of development of environmentally beneficial ("green") biocides and inhibitors of the new generation;
- to develop chemical and microbiological methods of monitoring of sites at risk of corrosion;
- to evaluate potentialities in terms of technology, raw materials and material and technical basis to set up a production of effective anti-corrosion preparations of new generation in Russia.

One of the tasks to be solved in the frames of the project 2245p was the search of promising corrosion inhibitors for protection of oil-production equipment. It was necessary to find a compound outperforming the reference inhibitor SXT-1002 and possessing similar or better activity than a new inhibitor EC-1154A. Test methods to estimate anticorrosion activity (Bubble test) and experimental conditions were agreed with "Nalco". The Arbuzov group formulated the working hypothesis to make the search of inhibitors efficient**.** We have supposed that the potential inhibitor should form stable complex with iron(0), insoluble in water and oil, and should reduce the electron density on iron. The studies performed during four years of the project proved the validity of the hypothesis and its efficiency. It allowed choosing perspective classes of compounds *a priori.* During 4 years a total number of 228 compounds belonging to various chemical classes and formulations were synthesized and tested on corrosion inhibition activity in the A.E.Arbuzov Institute.

As a result 60 compounds were found which significantly outperform SXT-1002 (by a factor of 10-100), and 10 samples have activity comparable or even better than EC-1154A. A series of active compounds was passed on to "Nalco", which confirmed their high efficiency in the conditions of Bubble test both on experimental brines and field waters. It was shown that the addition of 1-2% of surfactants to found inhibitors increases their activity by a factor of 1.5-2.

Mass-spectrometry, potentiodynamic and impedance studies of the activity mechanism of inhibitors 26 and 43 and their hydrochlorides 55 and 138 were carried out. The compounds were shown to form stable complexes on the metal surface, their dissociation being observed in high vacuum at temperatures of 280-470°C. The formation of the complex is accompanied by sharp increase (by a factor of 300) of the charge transfer energy from the metal surface. Inhibitors influence both the cathode and anode reactions, their neutral forms being preferable for adsorption on the metal surface. Cationic forms are adsorbed in smaller amounts and form less stable complexes.

Studied compounds are synthesized in one or two steps using available market compounds, the laboratory yields being equal to 60-90% respective to theoretically calculated. Synthetic methods were not optimized and do not have experiment regulations. The price for synthesis of studied compounds is not high and can be further reduced after the optimization of the production processes.

Quantum chemistry studies of structure-activity relationships for 2-mercaptopyrimidines were carried out. The aim of these studies was theoretical modeling of compounds possessing the highest inhibition activity. For this purpose it was necessary to reveal molecular parameters which determine the corrosion rate, and select the "best" molecule by variation of chemical composition and by investigation structure-activity

relationship. We have chosen electronic structure of inhibitor as such parameter, in particular the boundary orbitals being analized – LUMO (lowest unoccupied molecular orbital), able of accepting electrons and HOMO (highest occupied molecular orbital), able of donating electrons. On the basis of our results we derived two important conclusions. First, one of the promising class of compounds is small monocyclic molecules with small gap containing a substituent of the size 500-600 $Å^3$. Second, the decrease of the gap might be achieved not only by the introduction of electron donor or electron acceptor substituents into the thiopyrimidine ring but also via binding two thiopryrimidine rings together. Thus, the research carried out allows to conclude , that quantum chemistry studies and QSAR analysis are useful methods to correlate the activity of compounds with their molecular parameters. The dependence of activity on the energy gap between the boundary molecular orbitals, molecular volume and lipophilicity was derived. This dependence allows to predict the structure of promising inhibitors, including those which possess the activity about 300.

Investigation of possibilities for surface and electrochemical polymerization on steel surface for corrosion protection has been carried out**.** a new approach for lignin utilization was proposed. Water-soluble derivative of lignin can by transformed to corrosion protective layer by its electropolymerization on a steel surface. Varying lignosulfonates from different sources, as well as conditions of electrooxidation we proved, that drop in current at high anodic potentials is due to electropolymerization of lignin derivative at steel electrode surface. The electropolymerization potential can be sufficiently decreased by an increase in ionic strength of the growing solution. The lignosulfonate electropolymerization led to the considerable corrosion protection effect of carbon steel. More than three times decrease of corrosion rate on steel surface was observed after lignosulfonate electropolymerization, exceeding protective effect of standard commercially available corrosion inhibitor. The fraction of Solikamsky lignin with molecular weight higher then 10 kDa does not posses any anticorrosive effect, nevertheless the contribution of this part to the total weight is 75%. The fraction of Solikamsky lignin with molecular weight lower then 10 kDa poses all anticorrosion properties as the original lignin. The energy of adhesion of lignosulphonate to metal surface is higher then for the typical corrosion inhibitor SXT –1003. A new ‘green’ corrosion inhibitor based on low molecular weight fraction of lignosulphonate was created. It was shown that inhibiting properties of lignosulphonate can be enhanced by ammonia. Moreover, experiments in flow system showed that the energy of adhesion of lignosulphonate to metal surface is higher then for the typical corrosion inhibitor SXT –1003 produced by NALCO Corporation. Future experiments could enhance inhibiting properties of lignosulphonate by screening of new additives.

By means of linear polarization resistance (LPR) test, corrosion properties of biocides of different classes were studied. They were: hexahydro-1,3,5,-tris(2-hydroxy-ethyl) sym triazine - formaldehyde–releasing biocide, quaternary ammonium compounds (QAC), mix of heterocyclic nitrogen-containing compounds, isothiazolones and Russian manufactured biocides: karbamol, katamine, baccide. Of all tested biocides, only QACs and isothiazolones nearly fully protected steel against carbon dioxide –induced corrosion. Unlike QACs, anticorrosion properties of isothiazolones have not been known. Kathon 893F - 2-octyl-4-isothiasolin-3-on; kathon LXE - mix of 5-chloro-2-methyl-4-isothiazolin-3-on (1.15%) and 2-methyl-4-isothiazolin-3-on (0.35%); Rozon 2000 - 4.5-dichloro-N-octyl-4-isothiazolin-3-on were used as

isothiazolones. In the absence of hydrocarbon phase, isothiazolones have several orders of magnitude higher protection than by Corexites and close to inhibitors designed in IOPC (Kazan).

In highly concentrated saline systems whose compositions are similar to those of oil-processing waters (Tatarstan), isothiazolones possessed as high protective properties as in sea water. Isothiazolones get loosing their protective properties in case of carbon steel corrosion, i.e. in the absence of oxygen at pH of about 3-3,5. But in the presence of oxygen they are highly protective toward carbon steel in strong acidic medium (10% HCl). In tested oil-processing water samples (Tatarstan), the value of pH did not decrease as low as 4.4. Therefore, isothiazolones can be recommended for treating oil-processing waters in Tatarstan to curb carbon dioxide – induced corrosion. A protective effect of isothiazolones in compositions with other biocides and inhibitors was also investigated. Kathon is so strong protector, that only equally high concentrations of copper sulfate are needed to decrease this protection. Therefore, additionally to high biocidal properties, combination of kathon 893 and copper sulfate may also produce a strong anticorrosion effect depending on concentrations of the biocides. Based on its joint biocidal and anticorrosion properties, the combination can be recommended for protection of pipelines against carbon dioxide-induced corrosion. The research has led to patenting the method of protection of steel construction against corrosion by means of isothiazoline compounds.

The ability of microbes to acclimate to biocides has been studied. Microorganisms were found to be able to acclimate to biocides when they were regularly exposed to sub-lethal biocidal concentrations. As a result, 3 or 4 months later the microorganisms acquired resistance to previously effective concentrations of biocides. Results conclude that while applying biocides to control undesirable microbiota, one should change biocides on a regular basis.

It is known that action of corrosion inhibitors strongly depends on character of their interaction with mineral substances available in waters on oil-exploration sites. In this connection, we have evaluated anti-microbial effects of biocide 7320 and inhibitor SXT 1003 using artesian water (oil-exploration site Romashkino; «Almetjevskneft»). In case of the biocide, the 2.5-fold stimulation of biocidal properties was observed, whereas properties of the inhibitor worsened by 5 times. According to our observation, influence of chemical compositions of waters on the efficacy of corrosion inhibitors and biocides should not be neglected. While developing corrosion inhibitors and biocides, one should take into account environmental conditions, which are specific for any particular oil-exploration.

Besides mineral substances dissolved in water, biocides can also react with corrosion inhibitors preliminary introduced into a system. We have studied the compatibility of biocides and corrosion inhibitors. Five biocides and corrosion inhibitors (company ONDEO/Nalco), as well as inhibitor #55 (IOPhC), have been tested. In most cases we observed either an additive effect or antagonistic one. The combination kathon 893 F +inhibitor SXT 1002A gave a synergetic effect. Owing to this effect, one could reduce biocidal concentrations 5-6-fold. We also assessed corrosive activity of this combination toward natural microbial association TAT. It has been found that corrosion losses reduce approximately 10-fold *vs* control, if the mix and microbes is simultaneously introduced into glucose-mineral medium. But antimicrobial and anticorrosion effects of this combination were not confirmed by making experiments with the use of mature biofilm TAT. The synergistic combination of kathon 893 F and inhibitor SXT 1002A is recommended for controlling aquatic microorganisms. The patent application for the combination has been submitted.

One of approaches to designing environmentally safe ("green") antimicrobial formulations implies the use of synergetic combinations, which allow one to significantly decrease concentrations of biocides. We have tested 8 biocides belonging to different classes of chemical compounds and assessed their joint action. Of 36 compounds, the antagonistic effect was registered in 8 cases. Additive and synergistic effects took place in 11 and 17 cases, respectively. The combination of 893 F and copper sulfate produced a strong synergistic effect. In case of *Ps. putida* we could reduce concentrations of copper sulfate by 8 times. Concentrations of kathon 893 F were reduced by 72 time. In our experiment on influence of this combination on the biofilm TAT, we confirmed synergism of the combination either. Concentrations of copper sulfate and kathon were reduced by 16 times and 2 time, respectively. Nevertheless, a rather high net concentration (400ppm) of the biocides is needed. The combination is a subject for a patent application.

We have had a series of experiments to assess the efficacy of biocides and inhibitors depending on physicochemical characteristics of the environment. We assessed antimicrobial and anticorrosion action of isothiasolines (kathon 893 F, Rozon 2000) and inhibitor SXT 1003 by changing media and aeration regimen. Anticorrosion and antimicrobial properties of the compounds depended in much on the type of medium and aeration regimen.

Parameters characterizing quantitatively and qualitatively a biofilm, have been determined. Procedure to measure these parameters have been selected. Methods for culturing the biofilm on the basis of natural microbial communities (TAT) in different media and aeration regimen in stationary and hydrodynamics conditions are developed. Curves of the dynamics of the growth of the biofilm, as well as curves describing a related process of biocorrosion depending on media, are plotted. A relationship between a composition of the medium, aeration regimen and orientation of vector of influence of the biofilm on the process of biocorrosion is established. Effects of different biocides ($CuSO_4$; baccide; Glokill-80; Nalco 7320; some isothiosolones: Kathon 893F, LXE; CG and Rozon 2000), corrosion inhibitors (SXT 1002; SXT 1002A; SXT 1003), and surface active substances (CTAB, propanol, butanol) and their combinations on the biofilm are investigated. It has been shown that minimal inhibiting concentrations (MICs) of the reagents for the biofilm are much higher than those for aquatic microorganisms. It has been also found that inhibition of the growth of the mature biofilm by biocides and their combinations with corrosion inhibitors and penetrants significantly increases the level of corrosion losses. Whereas the reagents applied at initial stages of the growth of the biofilm produce anti-corrosion effects. The maximum reduction of corrosion underneath the mature biofilm (80% to 100%) is observed for corexytes and alcohols, with the vital ability of the biofilm being partially retained. Results obtained from the research in stationary conditions have been confirmed with data from experiments carried out in hydrodynamic conditions.

Biological activity of potential inhibitors synthesized in IOPCh was studied. Acute nonspecific toxicity was tested on mice and Daphnia. According to ecotoxicological classification potential inhibitors can be attributed to the following classes of toxicity: "moderately toxic", "slightly toxic" and "practically non-toxic". The ability of most active compounds (55 and 80) to fast biodegradation was estimated using "Closed Bottle" test. The test is based on the determination of compounds to biodegradation in aerobic conditions via measuring the oxygen concentration. It was shown that compounds 55 and 80 can not be regarded as ready biodegradable.

The integral toxicity of some biocides and corrosion inhibitors was assessed by some bioassays. They were a photobacteria-based bioluminescence assay, microbial reducing activity assay, electroorientation spectroscopy, and the plant growth assay. The first three assays are shown to be suitable to determine ecological safety of biocides, corrosion inhibitors and their compositions. By using the growth test it is possible to assess phytotoxicity of biocides and corrosion inhibitors for the flora available in the region of oil deposits.

New approaches to the investigation of biocorrosive processes on the basis of bioluminescent method of intracellular ATP determination have been developed. The main results of these investigations are the following. The possible estimation of total quantity of bacterial cells in the real samples of wastewaters taken from various oilfields was established; minimal cell concentration detectable with this method is 10^2 cell/ml. The higher sensibility of bioluminescent method compared to the microbial method was shown and it was established that bioluminescent method enables more effective determination of biocide activity of various compounds that microbial one. The method of differentiated quantification of bacteria, representing main taxonomic groups of cells provoking the biocorrosion and presented in the cell mixtures in the form of planktonic culture or biofilm, was elaborated. The method determining the total concentration of cells composing the content of corrosion biofilms was developed using bioluminescent method. The possible express screening of potential biocides among the corrosion biofilms and the determination of minimal inhibiting concentrations for the compounds was demonstrated by the use of bioluminescent method. Significant acceleration of biofilm growth was established by bioluminescent method in the flow systems. The exponential growth of sulphide concentration in the content of biofilm at its steady state of growth was revealed. The effectiveness of treatment of metal surfaces with corrosion inhibitors taken in MIC concentrations before their contact with planktonic cells in the flow system appeared to be effective to delay the formation of corrosive biofilms.

An express method to assess biogenic sulfate reduction in soil and water samples has been elaborated. The method intends for field application and allows one to no-problem assess action of such harmful and corrosion provoking microorganisms, as sulfate-reducing bacteria (SRB).

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SIGNATURES

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