PART THREE

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MAJOR APPLIED RESEARCH AND IMPLEMENTATIONS

PERSONAL INFORMATION

29th August 1955

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Kazimierz Darowicki – Wikipedia, the free encyclopedia

Corrosion is a naturally occurring phenomenon, commonly defined as the deterioration of devices, structures, objects, installations, and various usually metallic equipment. Due to the numerous forms, causes, and methods of prevention, corrosion science is a complex field that requires extensive expert knowledge and considerable resources. These issues were given importance by cost analyses for corrosion damage carried out in 2001 and financed by the US Federal Highway Administration. The program of these analyses was called: „Corrosion costs and preventive strategies in the United States". The annual direct cost of corrosion was found to be a staggering 276 billion dollars – or 3.1% of gross domestic product. These data were based on the analysis of direct costs in individual industrial sectors. Within this total, 121 billion dollars was accounted for by inspections and controls, research, corrosion education, and training. The financial analyses carried out indicated that between 25 and 30% of annual corrosion costs could be saved if optimal corrosion management practices were applied. This basic information on corrosion costs must be impressive. These data prove that anticorrosion protection is a transnational problem that is important from the point of view of the economy and finances.

The science of corrosion and its control is interdisciplinary and highly complex. Additionally, corrosion takes many different forms and depends on numerous external factors. The first step in effective anticorrosion protection is a thorough knowledge of the various forms of corrosion, their mechanisms, methods of detection, and causes. As part of my academic activities, I have created a wide didactic offer at the Gdańsk University of Technology in the field of corrosion and anticorrosion protection. It includes directions of study, postgraduate studies, and certified inspector courses.

Apart from basic research, I have been developing applied research in my professional career. In this field, I solved practical problems in cooperation with various enterprises and industrial partners, domestic and foreign. I have completed approximately 500 research works, scientific expert opinions, and implementations. To illustrate the nature of this work, I have selected representative, in my opinion, achievements, the general description of which I have presented in this chapter.

The main areas of my applied research are cathodic protection, coating protection, corrosion monitoring, and corrosion diagnostics. The contracted research work did not involve standard technical problems. These were serious research problems with a high cognitive load, and their solution was always important from the point of view of the production activities of individual enterprises and companies. When solving practical problems, I used basic achievements, such as time-frequency analysis methods or impedance measurements. The results of the applied research were often published in recognized scientific journals. The implemented solutions were effective and met the expectations of entities commissioning research work. The value of completed implementations is reflected in the recommendation letters from individual clients.

1. CATHODIC PROTECTION

Cathodic protection is one of the main technologies of anticorrosion protection. It has been developed by me and my colleagues for years. It is characterized by high protection effectiveness. However, its application is limited only to conductive corrosive environments. Below, I have presented three main works from this research area.

1.1	Cathodic protection of the Baltic Beta oil production platform
Research project ordering party	PETROBALTIC S.A.

At the location of the 'Baltic Beta' platform (Photo. 1.1.-1 A), the crude oil is at a depth of about 1450 metres below the bottom of the Baltic Sea. The platform tower structure includes three truss legs. Oil is extracted through twelve operating holes equipped with surface heads and underwater heads manufactured by Cooper-Cameron. In order to increase the reservoir pressure, a water injection system was installed on the 'Baltic Beta' platform. Water is injected into the B-3 bed through directional injection holes. Geoservices' separation devices installed on the 'Baltic Beta' platform separate the extracted oil from the gas. The installations and tanks of the water system are equipped with a corrosion monitoring system developed in my Department.

The oil production platform has been in operation for decades. Its foundation on the seabed, in a highly corrosive environment with high waves, required particularly effective, reliable protection technology. For this purpose, we designed an original electrochemical system of cathodic protection. This system consists of six sacrificial zinc anode sets (Photo. 1.1-1B). Two sets were placed near each of the three legs. Photo. 1.1-1D shows one of the sacrificial anode sets after five years of protection. Photo 1.1-1C presents the moment when the set is placed at the bottom of the sea.

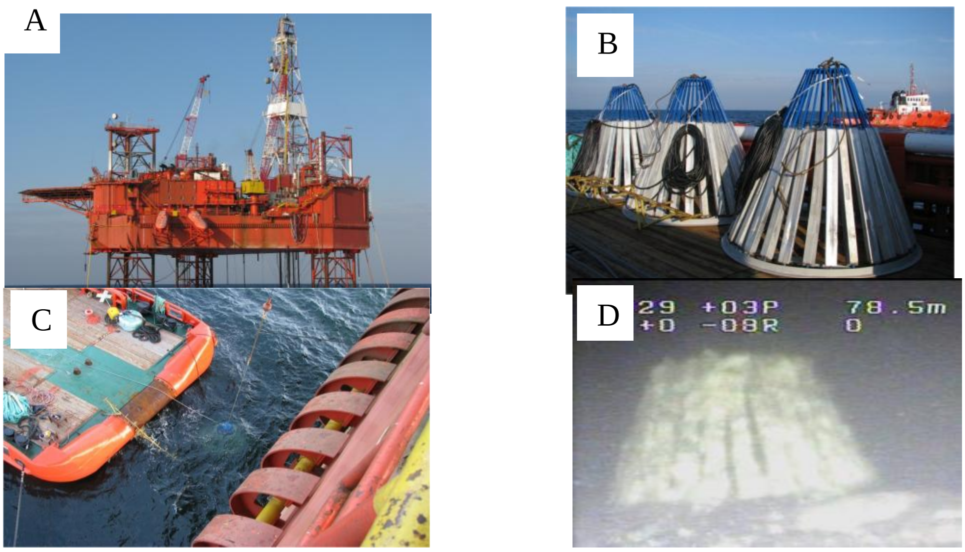

Photo. 1.1. A) Baltic Beta oil production platform, B) Sacrificial anode sets on board a tugboat, C) Placing the sacrificial anode set on the seabed, D) Image of sacrificial anode set on the seabed.

Pre-design laboratory tests were performed, and the optimal sacrificial anode alloy was selected. As part of the research work, a design was prepared, including the calculation of the mass of sacrificial anodes for the assumed 30-year protection period. The locations of the sacrificial anode sets and the anode connections were determined. After the cathodic protection system was activated, potential measurements were carried out. As a result of the sacrificial anode operation, the corrosion potential of the platform legs along their entire height was shifted by 170-190 mV in the cathodic direction. The water supply system has been subjected to inhibitor protection. The research and implementation works received a high rating from the client. Some aspects of this technological solution have been published:

K. Zakowski, P. Iglinski, J. Orlikowski, K, Darowicki, K. Domańska, Modernized cathodic protection system for legs of the production rig – Evaluation during ten years of service, Ocean Engineering, Volume 21815 December 2020 Article number 108074

J. Orlikowski,K. Zakowski, J, P. Iglinski, K, Darowicki, K. Domańska, Actual field corrosion rate of offshore structures in the Baltic Sea along depth profile from water surface to sea bed, Ocean Engineering, Volume 2651 December 2022 Article number 112545

M. Narozny. K. Zakowski, K. Darowicki,Time evolution of Electrochemical Impedance spectra of cathodically protected steel in artificial seawater, Construction and Building Materials, Volume 154, Pages 88 - 9415 November 2017

LOTOS Petrobaltic

Gdańsk, 02.07.2021

Współpraca LOTOS Petrobaltic z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej, Wydziału Chemicznego Politechniki Gdańskiej

LOTOS Petrobaltic od wielu lat współpracuje z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej, Wydziału Chemicznego Politechniki Gdańskiej. Współpraca dotyczy obszarów o strategicznym znaczeniu dla firmy.

Katedra w sposób ciągły nadzoruje stan korozyjny instalacji wody zatłaczającej wodę złożową do złoża ropy oraz stan korozyjny i integralność nóg konstrukcji nośnej wież platformy wydobywczej Baltic Beta. Prace te mają zasadnicze znaczenie dla utrzymania możliwości eksploatacyjnych wież wydobywczych i bezpieczeństwa pracy. Zaprojektowany oraz wdrożony system ochrony katodowej nóg platformy Baltic Beta, uzyskał akceptację Polskiego Rejestru Statków. Jego efektywność i funkcjonalność są monitorowane.

Podobnie zaprojektowano i wdrożono system monitorowania korozji zatłaczanej wody morskiej, który ze względu na strategiczne znaczenie, jest permanentnie nadzorowany przez pracowników katedry. Wdrożony monitoring pozwala wdrożyć środki zaradcze i tym samym utrzymać pożądaną jakość wody wtłaczanej do złoża ropy, w celu zwiększenia jej wydobycia. To z kolei zapewnia ochronę złoża oraz niezmienną, wysoką jakość naszego produktu końcowego jakim jest ropa.

BIURO EKSPLOATACJI I INŻYNIERII ZŁOŻOWEJ
WIODĄCY SPECJALISTA
Kinga Domańska

DYREKTOR
ds. WYDOBYCIA I WIERCEŃ
Krzysztof Kielas

1.2	Cathodic protection of slipways and locks of the Elbląg Canal
Research project ordering party	TOR-BUD Sp z o.o.

Five slipways are built (Photo. 1.2B) on the Elbląg Canal (Photo. 1.2A). Each slipway consists of two parallel rail tracks connecting the upper and lower stations. There are two bogies on the tracks. The rail tracks begin at the upper station (still underwater), pass through the ridge (top) of the slipway and descend to the lower station, ending underwater. Each track carries a bogie pulled by a wire rope between the upper and lower stations. The bogies are connected to each other by a rope. One end is connected to the bogie from the bottom water side, then the rope runs to the pillar of the rope wheels at the lower station and then, after passing through the turning wheel on the pillar, it is connected to the second bogie with the other end. On the upper water side, steel ropes were attached to the bogies and fed to a rope drum located in the engine room building. These ropes are wound on the drum counter-rotating, thanks to which, when the drum rotates, one rope is wound on the drum and the other is unwound. This allows simultaneous movement of the bogies on the slipway in opposite directions. Dragging one bogie from the lower to the upper station is performed simultaneously with pulling the other bogie from the upper to the lower station. Ropes, bogies, and rail tracks are periodically immersed in water and undergo destructive processes (Photo. 1.2C). Electrochemical anticorrosion protection systems have been designed to increase operating time between renovations. The research and design work were ordered by the TOR-BUD company, the general contractor of the renovation works.

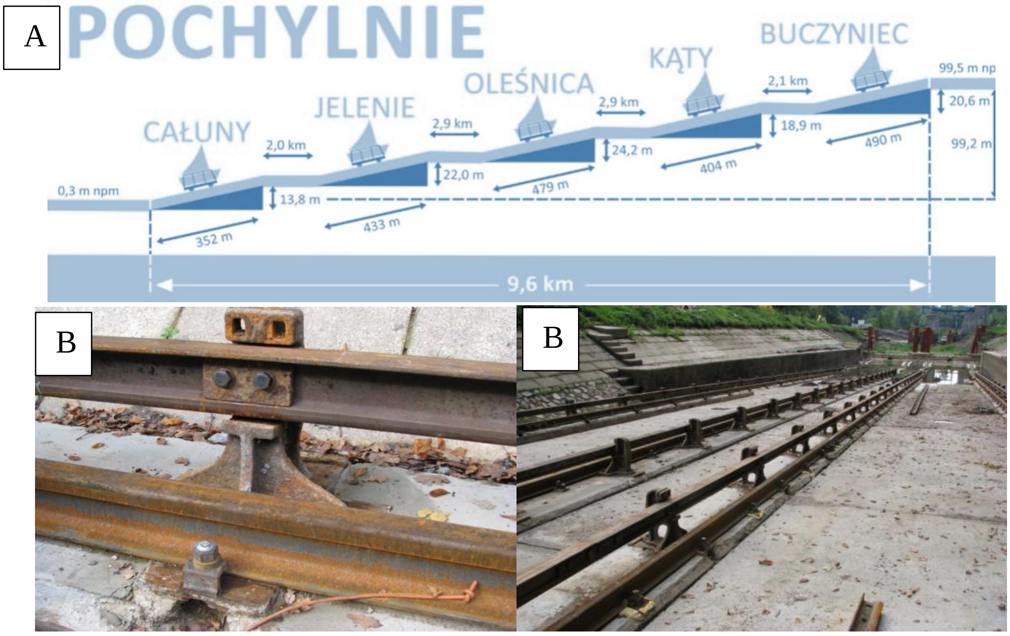

Photo. 1.2. (A) Profile of the Elbląg Canal slipway in Buczyniec, (B) Corroded running rails in Buczyniec

A pre-design study was conducted. The mass of sacrificial anodes required for 30 years of operation was determined. The corrosion rate of steel in the water of the Elbląg Canal was calculated. As part of the project, a sacrificial alloy was selected, the size of the sacrificial anodes and their distribution over the running tracks were determined. The cathodic protection system consists of segments composed of self-regulating zinc electrodes mounted directly on the rails.

M. Narozny, K. Zakowski, K. Darowicki. Method of sacrificial anode transistor-driving in cathodic protection system, Corrosion Science, Volume 88, Pages 275 – 279 November 2014

Such a system is maintenance-free. In the next stage, operational tests were carried out. The designed protection system ensured a reduction in the corrosion potential of protected rail tracks and other structural elements by 180-200 mV in cathodic direction. The protection system using sacrificial anodes has been implemented. The Department was included in the construction log as a unit designing and supervising the anticorrosion protection system.

1.3 Cathodic protection of the spiral classifiers

Research project ordering party	KGHM Polska Miedź S.A.

Rod mills grind ore to a gradation below 3 mm. Two-turn classifiers operating on the principle of gravimetric classification separate the feed into two streams (Photo 1.3A). The first stream is a coarse-grained one with a predominant share of the shale-carbonate fraction. The second, fine-grained stream is characterized by a large share of the sand fraction. The view of the working classifier is presented in the Photo. 1.3B. The classifiers operate continuously, carrying huge amounts of sand material and carbonate shale suspended in water. Therefore, classifier spirals are subject to simultaneous erosive and corrosive impact. These two destructive processes interact synergistically (Photo. 1.3C-D). This manifests in rapid destructive processes and the need for frequent spiral replacements. There are 29 parallel grinding and classifying systems in the Ore Enrichment Plant, which include 5 types of mills: first grinding, second grinding, and the so-called post-milling, and 3 types of spiral classifiers. A total of 86 mills and 29 classifiers work in the Ore Enrichment Plant, each of which is equipped with two spirals, giving a total of 58 pieces.

As part of the research work, an impressed current cathodic protection system was designed (Photo. 1.3F). The polarization anodes were arranged at the bottom of the classifier tub. The system is equipped with control electrodes ensuring the assumed protective potential. The polarization of the working part of the spiral and the tub was achieved using an external DC source.

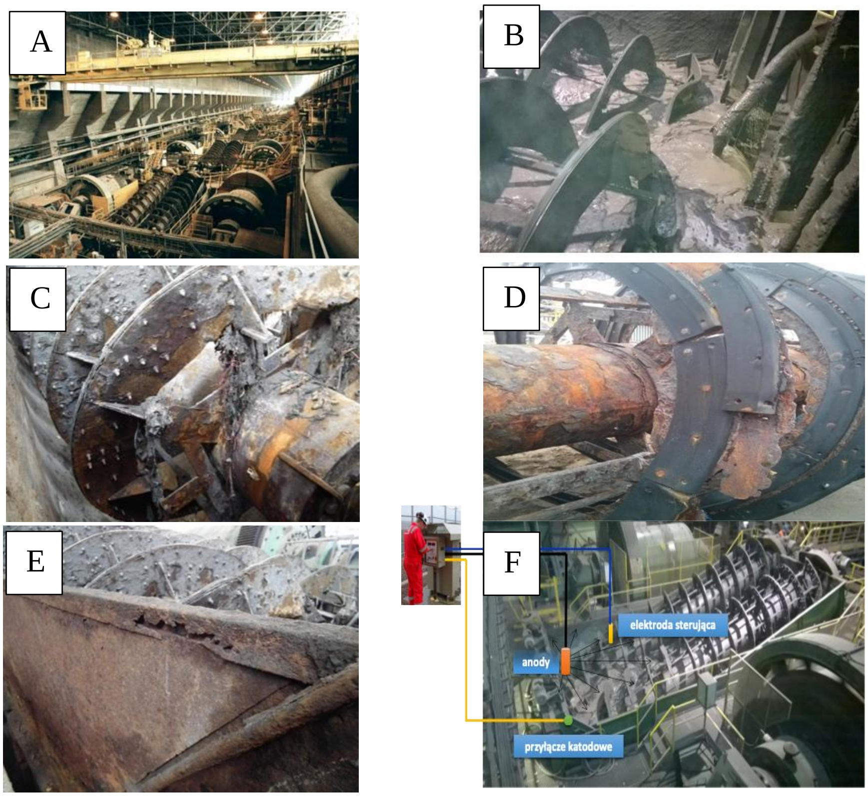

Photo. 1-3. (A) Classifiers in the Ore Enrichment Plant, (B) View of the classifier in operation, (C-D) Corrosion-erosion damage of the spiral, (E) Corrosion damage of the classifier tub, (F) Impressed current cathodic protection system

The research work consisted of material and structural analysis of the classifier. A power supply system and a cathodic protection system were designed, including an anode profile and anode arrangement. A laboratory-scale model of the classifier was prepared and the current conditions required to obtain the assumed degree of protection were determined. In the first stage, the implementation of cathodic protection consisted in the protection of one classifier. The advantages of using impressed current cathodic protection include:

- high effectiveness (correctly designed and properly supervised cathodic protection system provides full protection);
- ability to protect large metal surfaces without insulation or with defective insulation in environments with different resistivity;
- convenient adjustment of the polarizing current;
- maintenance of a given value of the structure's potential by changing the output voltage of the cathodic protection station and by application of an automation approach;

- relatively low operating costs.

Currently, all new classifiers are adapted to the installation of polarization anodes at the assembly stage. Regardless of the cathodic protection of the classifiers, corrosion risk assessment of the other facilities and installations of the Polkowice Ore Enrichment Plant and the Hydrological Plant of KGHM Polska Miedź S.A. with the Żelazny Most reservoir was carried out.

KGHM POLSKA MIEDŹ

Polkowice, 20 listopada 2020 r.

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Katedra Elektrochemii, Korozji i Inżynierii Materiałowej Politechniki Gdańskiej wykonała w latach 2014 – 2015 opracowanie dotyczące kompleksowej oceny zagrożeń korozyjnych pt. „Określenie możliwości zastosowania nowoczesnych metod ochrony antykorozyjnej obiektów technicznych i technologicznych w O/ZWR".

Opracowanie poprzedzone zostało stworzeniem kompleksowego atlasu zniszczeń korozyjnych z jednoczesnym wskazaniem ich potencjalnych przyczyn.

Wyniki uzyskane w trakcie realizacji pracy pozwoliły na wprowadzanie nowych rozwiązań związanych z ochroną przed korozją maszyn, urządzeń i instalacji użytkowanych w KGHM Polska Miedź S.A. Oddział Zakłady Wzbogacania Rud.

Z wyrazami szacunku

DYREKTOR
DS. TECHNICZNYCH
Jerzy Członka

2. ANTICORROSION COATING PROTECTION

Coatings are the most common anticorrosion protection technology. It appears to be simple to implement. Unfortunately, mistakes made in the surface preparation, the coating selection, and the coating application often lead to significant financial losses. Apart from polymer coatings, metal, conversion coatings, and anticorrosion linings are used to protect against corrosion.

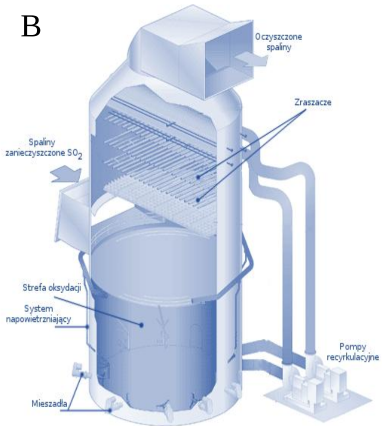
2.1.	Protection of flue gas desulphurization systems
Research project ordering party	**Bełchatów Power Plant, PGE Górnictwo i Energetyka Konwencjonalna S.A.**

Flue gas desulfurization in coal-fired power plants is traditionally conducted using the wet, lime-gypsum method, and its final product is gypsum with properties enabling its further industrial use. A side effect of the technological process in the absorber of the Flue Gas Desulfurization Plant (FGD) is the precipitation of deposits that are difficult to remove, which in turn results in a reduction in the efficiency of flue gas desulfurization and the occurrence of failures. Moreover, the mechanical method of removing these hard deposits significantly extends the FGD repair shutdown time and may cause damage to the equipment and protective coatings applied on the components of the FGD systems.

FGD installations are protected against corrosion using 304-316 steel claddings, glass flakes reinforced polymer linings, or foamed borane-silicate glass linings. In the case of the Bełchatów Power Plant, FGD installations (Photo. 2.1A) are protected from corrosion by rubber linings. This choice was determined by the economic factor, ease of application, ease of repairs, but above all, the flexibility of rubber systems.

A

B



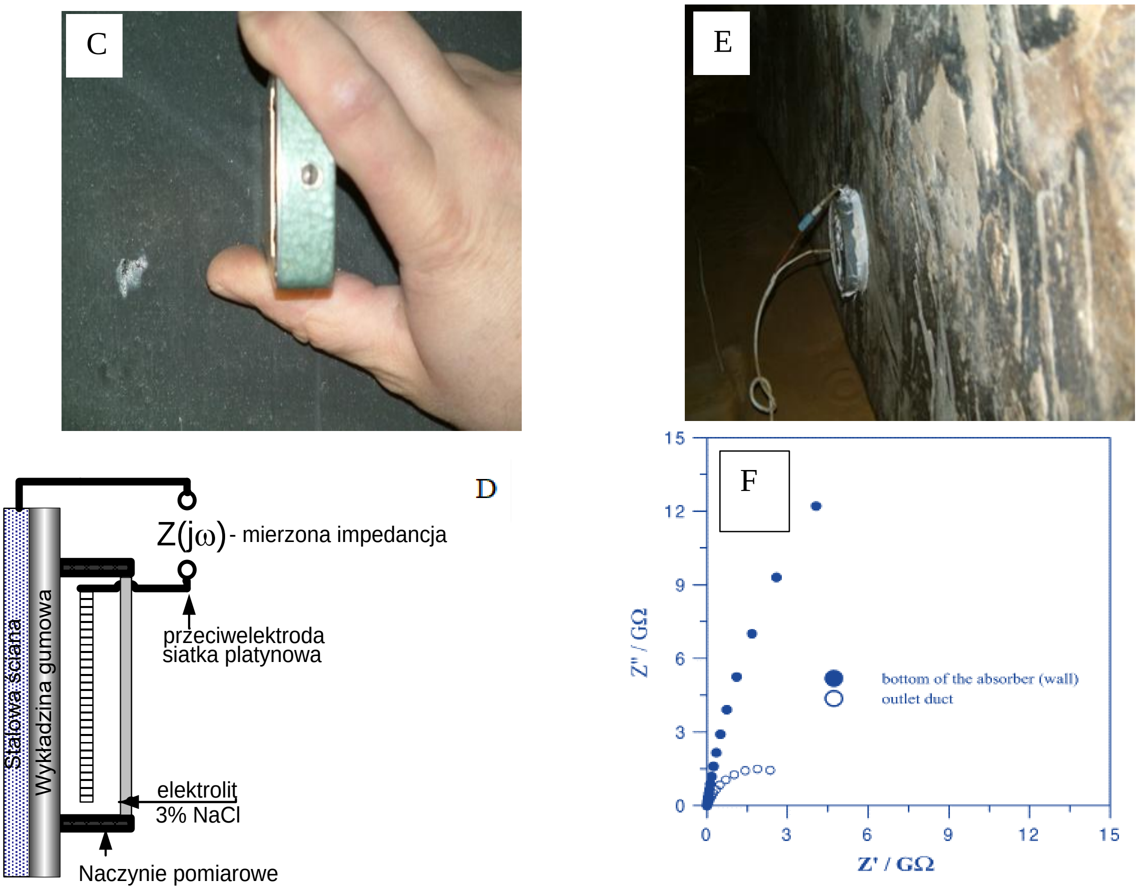


Photo. 2.1. (a) Absorber, (B) Scheme of absorber structure, (C) Hardness measurement of rubber lining, (D) Scheme of measurement cell, (E) Measurement cell on tested rubber lining, (F) Collected impedance spectra for penetrated lining (outlet duct) and unpenetrated lining (bottom part of absorber)

Flue gases contaminated with SO_2 are fed through the duct to the absorber and sprayed with limestone slurry (Photo. 2.1B). Air is introduced in the oxidizing zone of the absorber, and gypsum is produced. The absorber walls are lined with two layers of protective rubber (Photo. 2.1C). Unfortunately, after some time, the rubber lining is destroyed and loses its protective properties. Due to the different corrosion hazards in particular zones, the level of lining destruction varies.

The research determined the reasons for the limited durability of rubber linings. A non-destructive impedance method for assessing the condition of rubber liners has been developed. The idea of measuring the impedance of a rubber lining is presented in the Photo. 2.1D. Photo. 2.1E shows the operating measurement cell. By measuring impedance in selected locations, hydration profiles of rubber linings were obtained. Photo. 2.1F presents an impedance spectrum indicating good barrier properties of the lining and an impedance spectrum of the penetrated lining. Using an impedance method for assessing the condition of linings, a system of rational planning of renovation periods and the extent of individual absorbers was created. The described research methodology was one of the first field applications of electrochemical impedance spectroscopy in the world. The proposed solution was published and received a very high rating from the Bełchatów Power Plant and the company carrying out anticorrosion works.

S. Krakowiak, K. Darowicki, Inspection of rubber linings operating in flue gas desulphurisation units, Progress in Organic Coatings, *Volume 46, Issue 3 SPEC, Pages 211 - 215May 2003*
A. Miszczyk, K. Darowicki, Accelerated ageing of organic coating systems by thermal treatment, Corrosion Science, Volume 43, Issue 7, July 2001, Pages 1337-1343

S. Krakowiak, K. Darowicki, J. Orlikowski, R. Zuchowski, Assessment of protective properties of rubber lining in absorbers of flue gas desulphurization systems, Progress in Organic Coatings*, Volume 78, Pages 220 - 2241 January 2015*
A. Miszczyk, K. Darowicki, Water uptake in protective organic coatings and its reflection in measured coating impedance, Progress in Organic Coatings, Volume 124, November 2018, Pages 296-302
A. Miszczyk, K. Darowicki, Inspection of protective linings using microwave spectroscopy combined with chemometric methods, Corrosion Science, Volume 64, Pages 234 – 242 November 2012

PGE

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REKOMENDACJA

W Katedrze Elektrochemii, Korozji i Inżynierii Materiałowej Wydziału Chemicznego Politechniki Gdańskiej opracowano metodykę diagnostyki stanu wykładzin antykorozyjnych wielkogabarytowych instalacji i urządzeń. Metoda ta polega na wykorzystaniu elektrochemicznej spektroskopii impedancyjnej i z powodzeniem jest wykorzystywana w ocenie stanu wykładzin gumowych instalacji odsiarczania spalin Elektrowni Bełchatów.

Inspekcje stanu systemów antykorozyjnych przeprowadzane są przez pracowników Katedry Elektrochemii, Korozji i Inżynierii Materiałowej od ponad dziesięciu lat. W wyniku pomiarów inspekcyjnych identyfikowane są obszary absorberów o największym zagrożeniu korozyjnym. Ocena zawartości wody w wykładzinach gumowych w funkcji czasu pozwala racjonalnie planować prace remontowe absorberów oraz przewidywać bezpieczny czas eksploatacji wykładzin.

Wysoko oceniamy współpracę z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej.

W szczególności wysoko oceniamy opracowaną i wdrożoną w PGE GiEK SA Oddział Elektrownia Bełchatów metodykę monitorowania stanu wykładzin gumowych stosowanych do ochrony przed korozją instalacji odsiarczania spalin.

Z poważaniem

PGE Górnictwo i Energetyka Konwencjonalna S.A.
Oddział Elektrownia Bełchatów
Kierownik Zakładu Remontowego
Roman Szczęsny
Pełnomocnik

Ochrona środowiska
Kompleksowe zabezpieczenia antykorozyjne stali i betonu
Wykładziny i powłoki chemoodporne

KORCHEM

KORCHEM K & W Sp. z o.o., Biłgoraj k. Bełchatowa, 97-427 Rogowiec, tel./fax 44 735-30-35, 735-30-36, e-mail: korchem@korchem.pl, www.korchem.pl, NIP 769-10-65-016

REFERENCJE

Katedra Elektrochemii, Korozji i Inżynierii Materiałowej Politechniki Gdańskiej opracowała metodykę diagnostyki i monitorowania wykładzin antykorozyjnych w instalacjach odsiarczania spalin. Metodyka ta pozwala ocenić czas eksploatacji oraz obszary lokalnych napraw.

Firma KORCHEM K&W Sp. z o.o. współpracując z Katedrą z powodzeniem wykorzystuje te metodę na zabezpieczanych obiektach instalacji odsiarczania spalin.

Metoda ta jest bardzo przydatna firmie zarówno w trakcie jak i po realizacji prac chemoodpornych w kraju i za granicą.

Wysoko oceniamy współpracę z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej ze względu na terminową i profesjonalną obsługę.

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my chronimy niezawodnie

2.2.	Evaluation of the anticorrosion protection of the Eugeniusz Kwiatkowski Route
Research project ordering party	WARBUD S.A.

Implementation of the project 'Construction of the Kwiatkowski Route in Gdynia – III stage', consisted in building the missing transport connection on a supra-regional scale in the European transport corridor, which ensured: facilitating and securing international exchange, including transit; improving land-sea connections between important economic centres of Northern, Central and Eastern European countries, serving their economic integration; elimination of 'bottlenecks' of the European road network; accelerating the creation of a modern, port transport hub; development of industrial and storage functions in areas surrounding the port (Photo. 2.2A).

Photo. 2.2. (A) The course of the Kwiatkowski Route, (B) The view of the overpass over the ring highway, (C) Impedance measurements of the condition of the coating system, (D) Defects of the anticorrosion coating

The construction of the third stage of the Kwiatkowski Route in Gdynia was one of the basic conditions for the full use of the A-1 highway, the main road connection serving streams of international passenger and cargo traffic in the north-south system between the Scandinavian countries, Poland, and other countries of Central and Southern Europe. Photo. 2.2A shows a view of the overpass of the Kwiatkowski Route over the ring highway. Design aspects and the importance of this road solution required special anticorrosion protection.

We participated in selecting the optimal coating system. Bridge and road structures are subject to mechanical stress and vibration. Therefore, the selected system was characterized by appropriate flexibility. We carried out an original study of the influence of mechanical vibration and moisture impact on the durability of organic coatings. Our contribution to the protection design implied our participation in acceptance procedures. For this purpose, we employed the previously developed impedance method, which is non-invasive and allows objective determination of the barrier properties of the applied coating system at a given time and place (Photo. 2.2C). Not all areas met protective standards. For example, Photo 2.2.D clearly shows a defect in the protective coating caused by too low viscosity of the coating material.

K. Darowicki, M. Szocinski, P. Slepski, Application of the dynamic EIS to investigation of transport within organic coatings, Progress in Organic Coatings, Volume 52, Issue 4, 1 April 2005, Pages 306-310
M. Szociński, K. Darowicki, Performance of organic coatings upon cyclic mechanical load, Progress in Organic Coatings, *Volume 146 September 2020 Article number 105718.*
A. Miszczyk, K. Darowicki, Water uptake in protective organic coatings and its reflection in measured coating impedance, Progress in Organic Coatings, 2021, 124, pp. 296–302

2.3. Evaluation of protective coatings in the Narva Power Plant in Estonia

Research project ordering party	Monta Sp. z o.o.

Narva Power Plant (Photo. 2.3A) was built between 1969and1973. It is located approximately 25 km southwest of the city of Narva. The available capacity is 1610 MW of electricity and 77 MW of heat. Narva Power Plant initially had sixteen TP-101 boilers and eight 200 MW steam turbines. Fourteen boilers and seven turbines are currently in operation. Eight boilers have been fitted with new efficient electrofilters, and six boilers have old, less efficient electrofilters of Russian design. Bottom ash from boilers and dry ash from electrofilters are deposited next to the power plant. Cooling water is obtained from the Narva River. Bituminous shale is used to power the Narva Power Plant. In 2010-2015, modernization works were carried out at the Narva Power Plant.

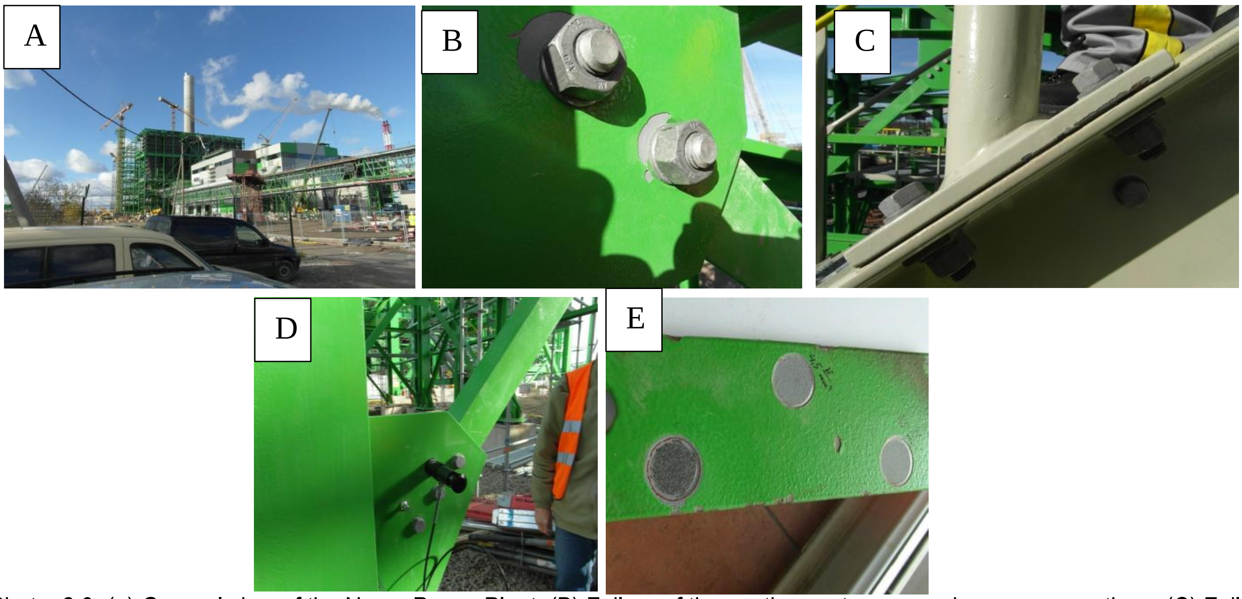

Photo. 2.3. (a) General view of the Narva Power Plant, (B) Failure of the coating system around screw connections, (C) Failure of the coating at the edges of the structure, (D) Measurement of adhesion with the pull-off method, execution of measurement (pull-off tester head visible), (E) View after the pull-off test

As part of the construction works, the elements painted in Poland by Konsbud company from Tarnów were used and transported to the construction site, where the structure was assembled using screw connections. A coating system from Fabryka Farb i Lakierów Malchem was used. The research work and local inspection showed that the contact surfaces in screw connections in such structures require special preparation, ensuring an appropriate coefficient of friction of the contacting materials (Photo. 2.3B), guaranteeing the durability of the screw connection with no possibility of loosening. conclude that these conditions are met only by the following surfaces:
(a) steel after abrasive blasting,
(b) steel galvanized with a layer of zinc or aluminium (or their alloys),
(c) steel surface after rolling (presence of mill scale on the surface),
(d) steel surface cleaned with flame and/or by a wire brush,
(e) surfaces painted with an alkyl silicate zinc paint having a thickness of 50µm to 80µm.
No other situations are accepted.

The use of a coating system at the points of friction contact does not meet the aforementioned requirements (Photo 2.3.B). The stresses generated in the tightening of the screws (and/or nuts) cause mechanical damage to the weakest layer. The slip generated in the final tightening stage causes the layers to crack and detach. This does not guarantee the durability of the connection and the appropriate friction coefficient. Another issue is the appropriate mechanical durability of the primer coating (Photo. 2.3C). In order to avoid an ambiguous situation, it was safer to exclude the use of coatings at the connection points. This is due to the fact that the mechanical strength of coating layers (Photo. 2.3D-E) may depend on a number of factors not always controllable in industrial and field conditions. In many cases, a primer layer was noticed on the surface after the pull-off test.

3. CORROSION MONITORING

Corrosion monitoring is a process that evaluates and monitors equipment components, structures, process units, and facilities for signs of corrosion. Monitoring programs aim to identify certain conditions to extend the lifetime and utility of assets, while increasing safety and reducing replacement costs. Corrosion monitoring covers all types of corrosion and materials.

The main advantage of implementing corrosion monitoring is the detection of early warning signs of corrosion and the determination of trends and processing parameters that can cause a corrosive environment. Processing parameters that may need to be changed include temperature, pressure, pH, etc. In addition, corrosion monitoring is used to measure the effectiveness of corrosion prevention methods to determine whether different inspection and/or monitoring techniques should be employed.

3.1.	Monitoring of the municipal water supply system in Gdańsk
Research project ordering party	Saur-Neptun Gdańsk S.A. (obecnie Gdanskie Wodociągi S.A.)

Before 2005, users of municipal water from the lower terrace of Gdańsk noticed the effect of „red water" (Photo. 3.1A). Water originated from an open intake, Lake Straszyn. Water from this reservoir exhibited low magnesium and calcium content. As a result, protective layers of calcium and magnesium oxides and carbonates were not deposited on the internal walls of the pipelines. Forming iron oxide (Photo. 3.1B) revealed no protective properties and dissolved in tap water, giving a specific brown-red colour.

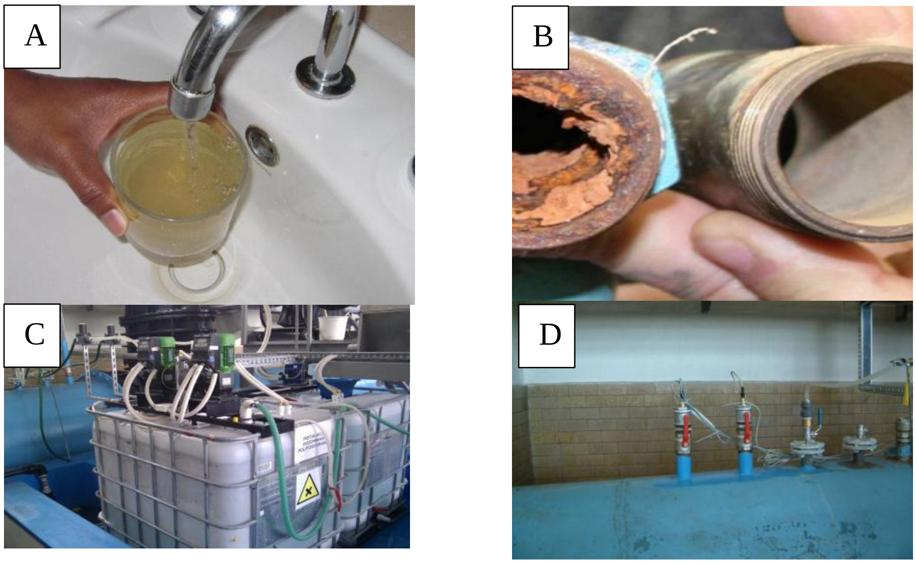

Photo. 3.1. (a) Red water effect, (B) Corrosion products deposited in the pipe and the desired condition of the pipe, (C) Tank and pump for milk of lime, (D) Mounted corrosion sensors of a maintenance-free corrosion monitoring system

The adopted solution was based on the introduction of calcium oxide into the water to increase its hardness (Photo. 3.1C). At the request of the Gdańsk City Hall and the Saur Neptun Gdańsk, we have developed a corrosion monitoring system. (Photo. 3.1D). The main purpose of this system was to control the dosed amount of calcium oxide so as to limit the corrosion rate on the one hand, and on the other hand, to limit the amount of dosed calcium oxide (Photo. 3.1C) to the necessary concentration to eliminate the red water effect. A maintenance-free corrosion monitoring system was designed and implemented in municipal water installations. In addition to assessing the corrosion rate, changes in water pH were also recorded. Our solution was innovative, has been published and accepted by the Saur Neptun Gdańsk.

J. Orlikowski, K. Darowicki, Multi-sensor monitoring of the corrosion rate and the assessment of the efficiency of a corrosion inhibitor in utility water installations, Sensors and Actuators, B: Chemical, Volume 181, Pages 22 – 282013, 2014

J. Orlikowski, K. Darowicki, Kazimierz, A. Jazdzewska, M. Jazynka, The protection and monitoring of a distribution piping network for potable water supply, Anti-Corrosion Methods and Materials, Volume 62, Issue 6, Pages 400 - 4062 November 2015
J. Orlikowski, A. Zielinski, K. Darowicki, S. Krakowiak, K. Zakowski, P. Slepski, Research on causes of corrosion in the municipal water supply system, Case Studies in Construction Materials, Open Access, Volume 4, Pages 108 - 115June 01, 2016
A. Jażdzewska K. Darowicki, J. Orlikowski, A. Zielinski, S. Krakowiak, K. Zakowski, P. Slepski, Critical analysis of laboratory measurements and monitoring system of water-pipe network corrosion-case study, Case Studies in Construction Materials, Open Access, Volume 4, Pages 102 - 107June 01, 2016

SNG

Gdańsk, 11 kwietnia 2006

List Referencyjny

Przedsiębiorstwo Saur Neptun Sp. z.o.o wdrożyła System Monitorowania Korozji zaprojektowany przez Katedrę Elektrochemii, Korozji i Inżynierii Materiałowej Politechniki Gdańskiej kierowanej przez prof. dr hab inż. Kazimierza Darowickiego. Stosowane są dwa rozwiązania systemu: automatyczny, bezobsługowy system monitorowania na ujęciu wodnym oraz system monitoringu okresowego na sieci wodociągowej. Wyniki szybkości korozji dostępne są bezpośrednio poprzez łącza internetowe. Wdrożony system pozwala w sposób ciągły monitorować szybkość korozji wody, w sieci wodociągowej oraz oceniać skuteczność technologii uzdatniania wody. Ponadto system ten pozwolił rozwiązać szereg problemów technicznych związanych z eksploatacją sieci wodociągowych. Biorąc pod uwagę uzyskane efekty oraz sposób realizacji zadania bardzo wysoko oceniamy system monitorowania korozji zaprojektowany i wdrożony przez Katedrę Elektrochemii, Korozji i Inżynierii Materiałowej.

DYREKTOR
ds. technicznych
Stanisław Mikołajski

Saur Neptun Gdańsk S.A.

wpisana do rejestru przedsiębiorców pod numerem KRS: 0000006553
Zarząd: Prezes Zbigniew Maksymiuk, Wiceprezes Jacek Kieloch, Członek Zarządu Philippe Toussaint
Wysokość kapitału akcyjnego: 7.755.100,00 zł
80-858 Gdańsk, ul. Wałowa 46, skrytka poczt. 375, tel. centrala (0 ... 58) 301 30 91, sekr. (0 ... 58) 301 20 18, fax (0 ... 58) 301 45 13
www.sng.com.pl e-mail: info@sng.com.pl

3.2.	Monitoring of the petroleum installations
Research project ordering party	ORLEN S.A., LOTOS S.A. i Rafineria Trzebinia S.A.

A wide range of corrosion monitoring methods is utilized in many branches of industry. In the petroleum and petrochemical industry, the number of measurement methods is limited. An important factor is the presence of explosive and flammable environments, which significantly complicates the construction of electronic measurement systems. The second significant difficulty is access to monitoring points. Petroleum installations are large-scale columns and tanks, which usually require the construction of completely autonomous online monitoring systems. In practice, gravimetric systems are most often used for refineries. Corrosion of metals is an oxidation process that involves changes in mass. Gravimetric techniques based on measurements of weight loss or weight gain of test samples using high-precision and sensitive analytical scales are effective means of assessing material degradation as a function of exposure time or temperature in corrosive environments.

The coupon method is one of the cheapest and oldest corrosion monitoring techniques. This method, combined with microscopic and NDT techniques, allows the determination of the corrosion mechanism. As part of the research work, gravimetric corrosion monitoring systems were modernized. In addition to mass coupon changes, corrosion types have been described. Photo. 3.2A. illustrates the surface of a coupon, which apart from mass loss also documents the cracking mechanism (aqueous H_2S environment). Photo. 3.2B shows a corrosion coupon documenting stress-oriented hydrogen-induced cracking (HIC/SOHIC) facilitated by moisture condensation with a significant amount of H_2S.

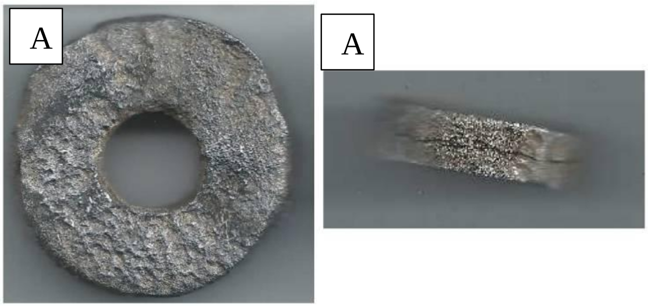

Photo. 3.2A. Coupon after 420 days of exposure to a H2S-saturated aqueous environment

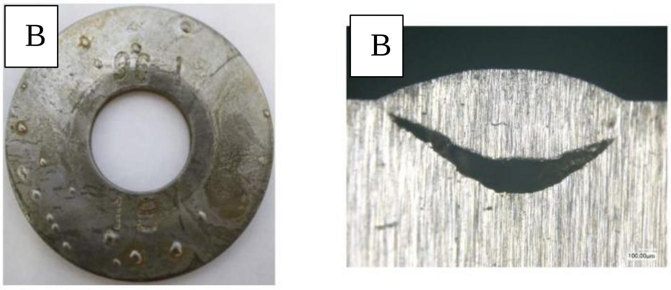

Photo. 3.2B. Coupon after 330 days of exposure to vapours from the second stage hydrodesulfurization (HDS) reaction

Another form of gravimetric measurement is resistance measurement. In this case, the measurement loop is exposed to a corrosive environment. The mass loss is related to the reduction of the loop cross-section, which affects the magnitude of resistance. Our achievements in the construction and supervision of coupon and resistometric monitoring systems in the petroleum and petrochemical industry has been published in: *A. Jazdzewska, S. Krakowiak, K. Darowicki, J. Orlikowski, Complex Corrosion Monitoring System for Crude Distillation Unit in Form of Neutral Network, Proceedings - 2018 Global Smart Industry Conference, GloSIC 20187 December 2018 Article number 85701292018 Global Smart Industry Conference, GloSIC 2018 Chelyabinsk13 November 2018 through 15 November 2018Code 143565*

J. Orlikowski, A. Jażdżewska, I. Luksa, M. Szociński K. Darowicki, Corrosion Monitoring in Petroleum Installations—Practical Analysis of the Methods, Materials, Open Access, Volume 17, Issue 11June 2024 Article number 2663

ORLEN

Piotr Chełmiński
Członek Zarządu ds. Rozwoju i Energetyki

Warszawa, 2017.02.15.
DR 23/2017/W

Politechnika Gdańska
Wydział Chemiczny
Katedra Elektrochemii,
Korozji i Inżynierii Materiałowej
ul. Narutowicza 11/12
80 - 233 Gdańsk

Dotyczy: opinia na temat współpracy

Szanowni Państwo,

zespół Pana Profesora Kazimierza Darowickiego, Kierownika Katedry Elektrochemii, Korozji i Inżynierii Materiałowej, stanowi wsparcie laboratoryjno-badawcze dla PKN ORLEN S.A. przy realizacji prac naukowo-rozwojowych i naukowo-przemysłowych, w obszarze korozji i monitorowania korozyjnego instalacji i obiektów rafineryjnych. Nasza współpraca jest bardzo efektywna i długotrwała.

Pan Profesor wspiera nasze działania w utrzymaniu i modernizacji systemów monitorowania korozji, które są nieodzownymi ogniwami zapewniającym zwiększenie bezpieczeństwa technicznego, procesowego i doskonałości operacyjnych aktywów PKN ORLEN S.A. Bardzo wysoko oceniamy także prace badawcze wyjaśniające przyczyny uszkodzeń korozyjnych lub intensyfikację korozji wielu naszych instalacji. Wykonane dla nas prace charakteryzują się wysokim poziomem naukowym i biznesowym.

Mając na uwadze dotychczasową współpracę PKN ORLEN S.A. oraz Katedry Elektrochemii, Korozji i Inżynierii Materiałowej Politechniki Gdańskiej jednoznacznie i mocno wspieramy kandydaturę Pana prof. Kazimierza Darowickiego do Nagrody Ministra Nauki i Szkolnictwa Wyższego za osiągnięcia badawcze na rzecz gospodarki, której PKN ORLEN S.A. jest istotnym ogniwem.

Z poważaniem

ORLEN

Płock, 18.11.2020r.
(miejscowość i data)

Kazimierz Darowicki
Politechnika Gdańska
Katedra Elektrochemii, Korozji
i Inżynierii Materiałowej
ul. G. Narutowicza 11/12
80-233 GDAŃSK

LIST REFEENCYJNY Nr 2/2020

Informujemy, że Politechnika Gdańska - Katedra Elektrochemii, Korozji i Inżynierii Materiałowej z siedzibą w Gdańsku była Wykonawcą:

a) Umów nr: 229/2015, 230/2015, 233/2015, których przedmiotem była kontrola zagrożenia korozyjno-osadowego instalacji Olefiny II, FKK II, HOG i HONH, w latach 2015-2017;
b) Umowy nr 1/213/2015, której przedmiotem było opracowanie systemu monitorowania korozji instalacji podstawowej Alkilacji HF w celu bieżącej oceny zagrożenia korozyjnego instalacji.

Wszystkie prace zostały zrealizowane zgodnie z Umowami, z zachowaniem należytej staranności i w uzgodnionym terminie.

Referencje wydaje się na wniosek Politechniki Gdańskiej - Katedra Elektrochemii, Korozji i Inżynierii Materiałowej, do przedłożenia w Grupie LOTOS S.A., ul. Elbląska 135, 80-718 Gdańsk, celem udokumentowania doświadczeń badawczych w obszarze monitorowania procesów korozyjnych.

List referencyjny nie uprawnia do upublicznienia faktu współpracy lub wykorzystania elementów wizualizacji ORLEN w celu innym niż wskazany powyżej.
List referencyjny może zostać anulowany w przypadku zaistnienia następujących warunków: Wykonawca zostanie obciążony karami umownymi, wejdzie w spór sądowy ze Spółkami GK ORLEN, podejmie działania, które bezpośrednio lub pośrednio mogą wpłynąć negatywnie na wizerunek PKN ORLEN.

Dyrektor Wykonawczy
ds. Rozwoju i Technologii
....
Janusz Bogdański

(podpis osoby uprawnionej)

Polski Koncern Naftowy ORLEN Spółka Akcyjna z siedzibą w Płocku
09-411 Płock, ul. Chemików 7, tel.: (+48 24) 256 00 00, fax: (+48 24) 367 70 00 wpisana do Krajowego Rejestru Sądowego prowadzonego przez Sąd Rejonowy dla Łodzi-Śródmieścia w Łodzi XX Wydział Gospodarczy pod numerem: 0000028860
NIP: 774-00-01-454, BDO: 000007103, kapitał zakładowy / kapitał wpłacony: 534.636.326,25 zł.
Biuro w Warszawie: 00-085 Warszawa, ul. Bielańska 12, tel.: (+48 22) 778 00 00, fax: (+48 22) 367 70 00
www.orlen.pl

3.3.	Monitoring system for general and hydrogen-induced corrosion
Research project ordering party	PKN ORLEN S.A.

The Fluid Catalytic Cracking II (FCC II) process is carried out in a reactor of a special design on a zeolite catalyst maintained in the so-called fluidized layer at a temperature of 526–543°C, under a pressure of 0.25-0.30 MPag. The process involves the breakdown of paraffinic, olefinic and aromatic hydrocarbons with side chains into lower molecular weight hydrocarbons. During the process, the catalyst is deactivated due to the deposition of coke on its surface. In order to regenerate it, the catalyst is separated from the cracking products and directed to regeneration. Catalyst regeneration involves firing coke from its surface in an apparatus with a special design, the so-called regenerator. The reaction products are separated by distillation.

FCC's main products are propylene, C4 light fraction, C4 heavy fraction, cracked gasoline, diesel oil, and clarified oil. In the catalytic cracking process, in addition to the normal hydrocarbon cracking process, organic sulphur and nitrogen compounds present in the raw material also disintegrate, as a result of which light compounds are released, such as hydrogen sulphide, ammonia, cyanides, and carbon dioxide. As a result of the catalytic cracking reaction, paraffinic hydrocarbon molecules are capable of disintegrating in several chain links, and the predominant decomposition products are hydrocarbons from C3 to C7.

One of the most corrosion-sensitive sections of the Fluid Catalytic Cracking installation is the condensation section of the main distillation column due to condensed water, which is obtained from the injection of stripping steam into the evaporation column. The presence of H_2S, NH_3, and HCN promotes an accelerated process of general corrosion caused by ammonium disulfide and hydrogen embrittlement, causing hydrogen blisters.

The investigation results of the Catalytic Cracking II installation indicated periodically elevated hydrogen content in the steel, even exceeding the level of 6 ppm per month. Blisters have been found, which are the result of hydrogen ingress into the microcrystalline lattice of steel.

Photo. 3.3-1. Image of hydrogen blisters

To increase safety and reduce the number of corrosion failures, it was decided to build a system for monitoring general and hydrogen-induced corrosion. The original elements of this system were dual corrosion sensors equipped with a measurement loop sensitive to hydrogen impact and a measurement loop sensitive to uniform corrosion. This monitoring system has the layered structure shown in Fig. 3.3-2.

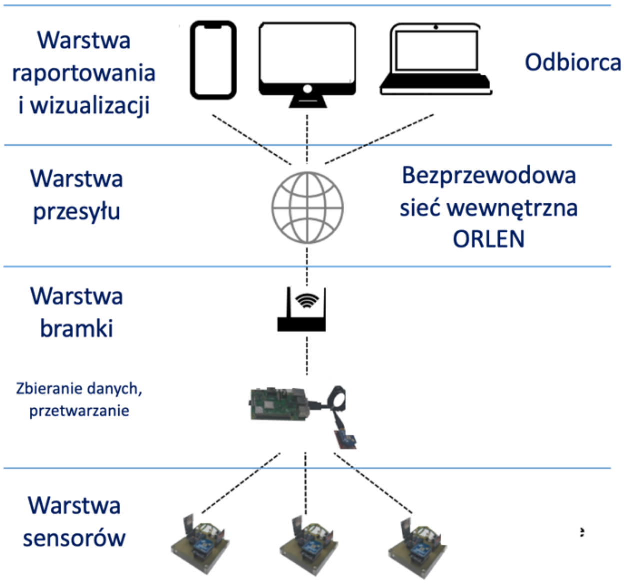

Fig. 3.3-2. Scheme of a layered wireless hydrogen and uniform corrosion monitoring system

The corrosion monitoring system built and implemented on the Catalytic Cracking installation is fully autonomous. The layer of corrosion sensors is our original solution. At the gate layer, data from the sensors is collected and sent to the internal ORLEN network. In the reporting module, measurement data is processed, and the report is sent to the control room or individual recipients.

The sensors are mounted on lances in specially designed locks. The mounting diagram is shown in Fig. 3.3-3.

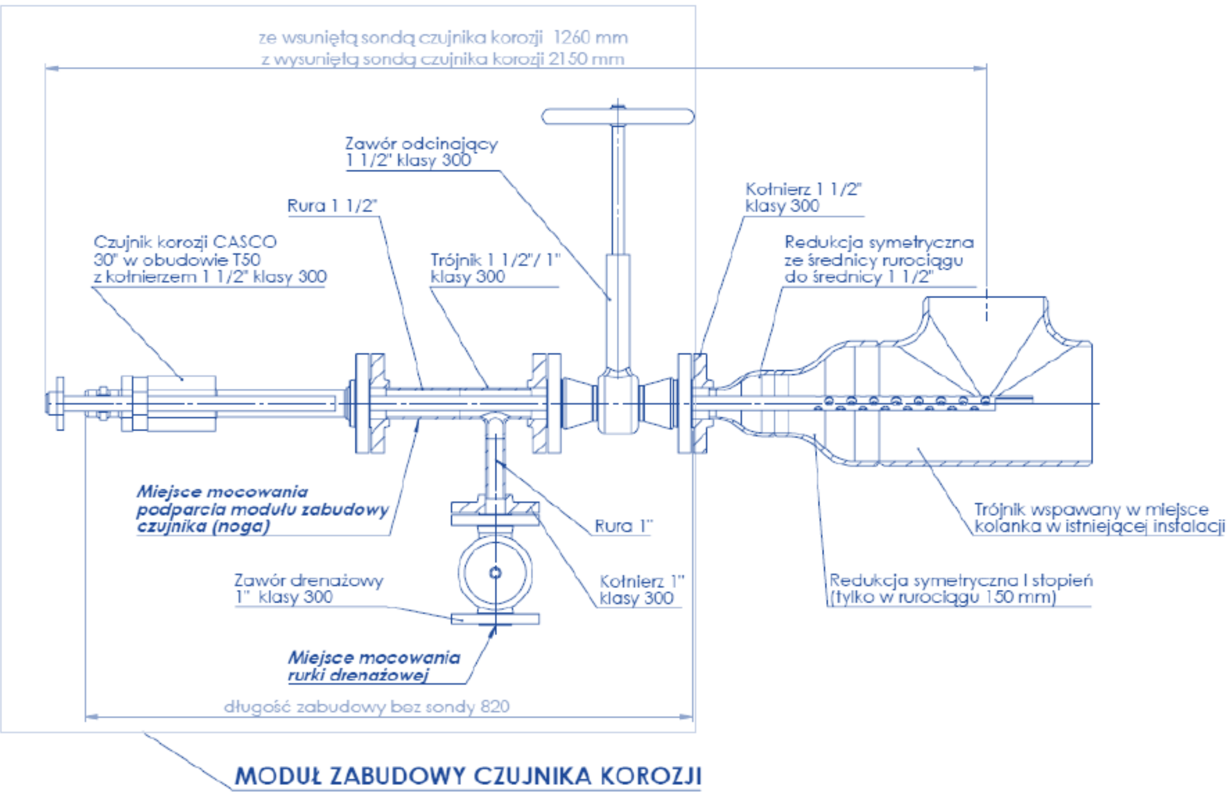

Fig. 3.3-3. A scheme showing the location of the corrosion sensor lance inside the lock

After corrosion analysis of the Catalytic Cracking II installation, the sensors were placed in selected, critical areas of the installation.

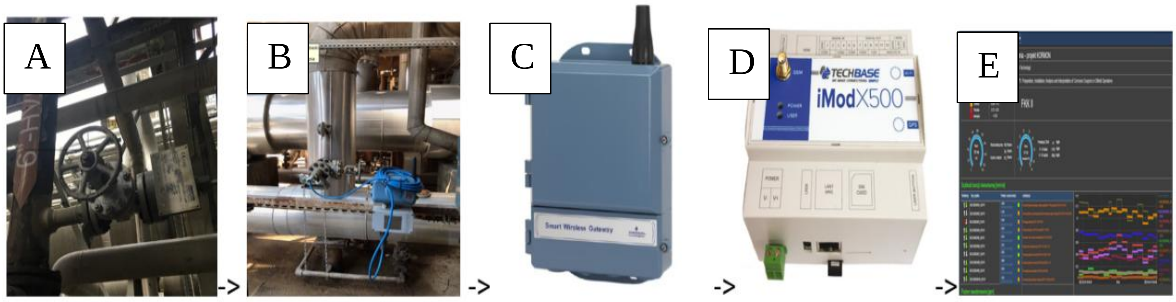

Photo. 3.3-4. Scheme of signal transmission from the corrosion sensor to the PI system. (A) Sensor in the process stream, (B) Measuring module to measure resistance, convert signal to electrical voltage and transmit signal wirelessly, (C) Wireless communication gateway, (D) Industrial microcomputer, (E) PKN ORLEN S.A. - control room

Real-time monitoring of uniform and hydrogen-induced corrosion can be used to assess the current corrosion situation. This approach ensures immediate response during process disruptions. The monitoring system is used to optimize process parameters, better assess the effectiveness of corrosion agents, and optimize their doses.

Due to the ability to monitor the corrosion rate at a given moment (online), dynamic changes in the corrosion hazard can be observed based on the adjustments made in the process, which significantly increases process safety. The solution has been submitted for patenting.

K. Darowicki, J. Orlikowski, G. Lentka, I. Łuksa, R. Gospoś, App. 18/282/234: „Corrosion rate measuring probe", Zgłoszenie patentowe: PCT/PL2022/050015, US Patent

The elaborated monitoring system earned the recognition of the client and the developed corrosion sensors received the main awards at the innovation fair.

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The President of International Jury
Prof. Krzysztof Biernat

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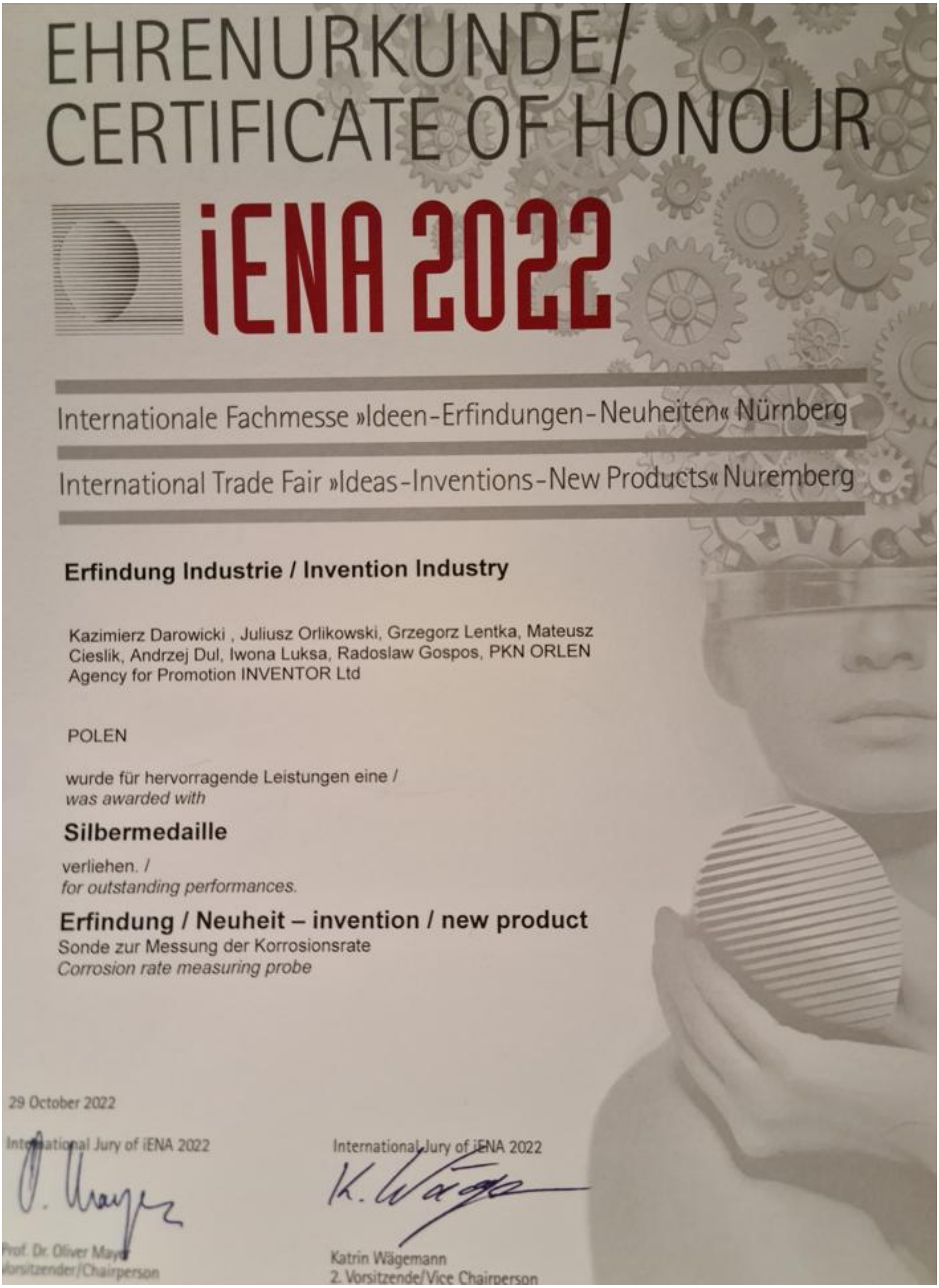

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Internationale Fachmesse »Ideen-Erfindungen-Neuheiten« Nürnberg

International Trade Fair »Ideas-Inventions-New Products« Nuremberg

Erfindung Industrie / Invention Industry

Kazimierz Darowicki , Juliusz Orlikowski, Grzegorz Lentka, Mateusz Cieslik, Andrzej Dul, Iwona Luksa, Radoslaw Gospos, PKN ORLEN Agency for Promotion INVENTOR Ltd

POLEN

wurde für hervorragende Leistungen eine /
was awarded with

Silbermedaille

verliehen. /
for outstanding performances.

Erfindung / Neuheit – invention / new product
Sonde zur Messung der Korrosionsrate
Corrosion rate measuring probe

29 October 2022

International Jury of iENA 2022
Prof. Dr. Oliver Mayer
Vorsitzender/Chairperson

International Jury of iENA 2022
Katrin Wägemann
2. Vorsitzende/Vice Chairperson

ORLEN

Szanowny Pan Profesor Kazimierz Darowicki
Politechnika Gdańska
Gabriela Narutowicza 11/12, 80-233 Gdańsk

Warszawa, 2021-06-16 r.

Stanowisko PKN ORLEN

PKN ORLEN S.A. wspólnie z Politechniką Gdańską, Wydział Chemiczny zrealizował projekt „Monitoring korozji ogólnej i nawodorowania z wykorzystaniem zintegrowanego systemu dualnych czujników korozji". Celem projektu było opracowanie, budowa i wdrożenie nowatorskich czujników korozji będących elementem zintegrowanego systemu monitorowania korozji on-line, który zapewnia ocenę intensywności korozji równomiernej (ogólnej), podatności na pękanie korozyjne i kruchość wodorową poprzez ciągły pomiar stężenia wodoru (korozja wodorowa) jako pilotaż na instalacji przemysłowej PKN ORLEN.

Monitoring opracowanych sensorów korozji jest prototypem, który w pierwszej kolejności został zainstalowany na instalacji Kraking Katalityczny II w Zakładzie Produkcyjnym PKN ORLEN w Płocku. Obecnie nie istnieją komercyjne systemy dualnych czujników korozji, które łączyłyby funkcje monitoringu intensywności korozji równomiernej (ogólnej) oraz podatności na pękanie korozyjne i kruchość wodorową poprzez ciągły pomiar stężenia wodoru (korozja wodorowa). Projekt obejmował fazę laboratoryjną, zaprojektowanie i budowę prototypu oraz wdrożenie na instalacji przemysłowej.
Wdrożenie projektu nastąpiło w maju 2021

System dualnych czujników korozji umożliwia monitorowanie w trybie online korozję urządzeń, aparatów i systemów przesyłowych na instalacjach produkcyjnych, co w konsekwencji przyczyni się do zwiększenia bezpieczeństwa procesowego, minimalizacji zdarzeń awaryjnych i wydłużenia żywotności instalacji przemysłowych.

Zastosowanie w praktyce niniejszej technologii przyczyni się również do optymalizacji ilości dozowanych środków antykorozyjnych i parametrów procesowych oraz lepszej oceny efektywności stosowanych inhibitorów korozji.

PKN ORLEN bardzo dobrze ocenia współpracę z Politechniką Gdańską., Przedstawiciele Uczelni są wybitnymi ekspertami w dziedzinie ochrony antykorozyjnej, co przełożyło się na wdrożenie z sukcesem rezultatów w/w projektu badawczego, który uznawany jest jako innowacyjne na skalę światową rozwiązanie technologiczne.

Z wyrazami szacunku,

p.o. Z-ca Dyrektora
Obszaru Strategii Innowacji
oraz Relacji Inwestorskich
Patrycja Panasiuk

Polski Koncern Naftowy ORLEN Spółka Akcyjna z siedzibą w Płocku
Biuro w Warszawie: 00-085 Warszawa, ul. Bielańska 12, tel. (+48 22) 778 00 00, fax (+48 22) 367 70 00

4. CORROSION DIAGNOSTICS

Corrosion processes can cause major failures that lead to large economic losses, sometimes in combination with environmental pollution or the risk of injury to personnel. The most important steps to eliminate or limit the scope of such failures are early detection, proper diagnosis, and effective preventive measures.

4.1. Corrosion diagnostics of the ballast tanks of the 'INNOVATION' vessel

Research project ordering party	**Shipyard CRIST S.A.**

INNOVATION DP2 is a specialist vessel built at the CRIST Gdynia Shipyard (Photo. 4.1A). Its basic function is to lay the foundations for offshore wind farm turbines. With a lifting capacity of 1,500 tons and a load capacity of 8,000 tons, INNOVATION DP2 can transport and install 6MW wind turbines. The length of the wind turbine is limited to 120 m. The design of this vessel allows laying foundations at a depth of 65 m.

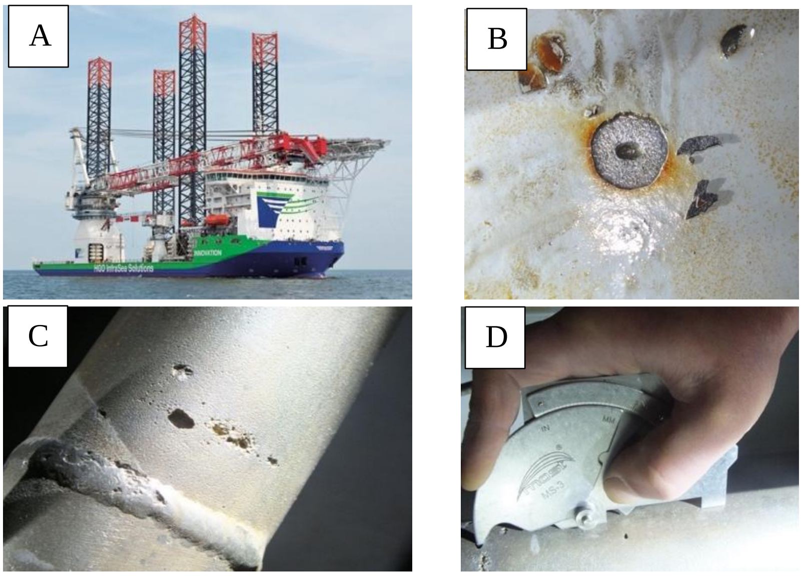


Photo. 4.1. (A) 'Innovation' vessel in the North Sea, (B) Open blister of anticorrosion coating at the bottom of a ballast tank with a deep crater caused by undercoating corrosion, (C) Pitting corrosion of 304 steel coils, (D) Measurement of pit depth.

The 'INNOVATION' vessel is equipped with ballast tanks that are filled with water for stabilization. The support legs allow lifting the vessel above the waterline. In this arrangement, 'INNOVATION' operates as a production platform. The lifting operation requires water to be removed from the ballast tanks. When operating below O°C temperature, the water in the ballast tanks freezes. The problem of water freezing was solved by installing heating coils inside the ballast tanks. After one season of service, serious damage to coils made of 304 steel was observed. Moreover, blisters of paint coating and corrosion craters were noticed at the bottom of the tanks, which were made of carbon steel. Photo. 4.1A shows deep damage to the coil tubes. Measurement of the size of corrosion craters indicated depth damage of 3 mm (Photo. 4.1C). X-ray analysis revealed that the coil was made of 304 steel. Regardless of the coil damage, degradation of the paint coating in the form of blisters was observed on the ship's plating. The removal of the blisters revealed deep corrosion in the hull plating made of carbon steel.

Electrical analysis of the tested structure showed that the hull is shorted to the coil. The formed corrosion cell changes the potential of the 304 steel in the cathodic direction. It destroys the passive state on 304 steel, causing pitting. On the other hand, the potential of carbon steel increases, causing accelerated corrosion processes in places where the protective coating is not tight, i.e., causing undercoating corrosion. In this way, both carbon steel and 304 stainless steel are damaged. The simplest solution to so diagnosed corrosion problem was to electrically isolate the heating coil from the hull.

4.2. Diagnostics of corrosion failure of the furnace in the column distillation installation

In atmospheric distillation, desalinated crude oil is heated in a furnace (Photo. 4.2A) to about 400°C and then fed to a vertical distillation column.

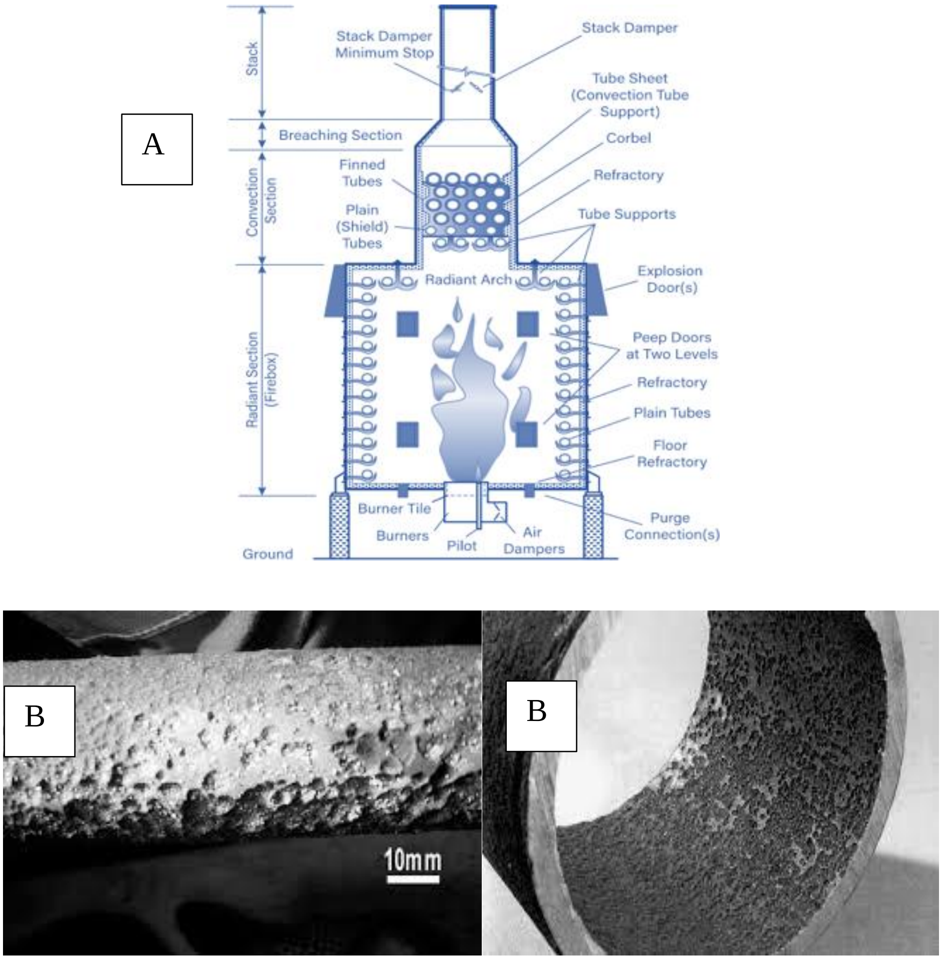


Photo. 4.2. (a) Furnace scheme, (B) Form of corrosion damage caused by metal dusting

The design of the furnace is intended to provide the most efficient heating process, so raw crude oil flows through a system of pipes that are heated in the furnace.

At a temperature of 300-850°C, the phenomenon of metal dusting is observed in gas environments saturated with carbon. Fe, Ni, and Co, as well as alloys based on these metals, are susceptible to this type of degradation. Metal dusting manifests itself in decomposition into metal powder - hence the term metal dusting.

The cause of this process is the formation of metastable iron carbide on the surface as a result of supersaturation with carbon. The next step is the dissociation of iron carbide triggered by interfacial graphite. Intercalation and diffusion of iron atoms in graphite is the mechanism that explains the lifting of iron particles from the corrosively active region. The form of damage is very characteristic and has the shape of scales and spherical defects. The identification of this corrosion process resulted in the furnace operating temperature being limited to a safe range. In the case of Ni and Co, where metastable carbides do not form over the entire temperature range, the mechanism of dusting these metals involves direct intercalation into graphite.

J. Orlikowski, A. Jażdżewska, K. Darowicki, J. Dampc, Metal dusting phenomena of 501 AISI furnace tubes in refinery fractional distillation unit, Engineering Failure Analysis, Volume 91, Pages 108 – 114 September 2018

4.3. Diagnostics of failures in heat exchangers

Research project ordering party	LOTOS S.A.

Heat exchangers are systems that exchange heat between two or more process fluids. It is difficult to imagine refining processes without heat exchangers, the design of which depends on technological conditions. The efficiency of production and process safety often depend on the proper operation of the tubular heat exchanger. Photo. 4.3A shows the insert of shell-and-tube heat exchanger. The most common cause of damage to exchangers of this type is galvanic corrosion and/or crevice corrosion formed in the gap between the outer surface of the pipe and the sieve plate, followed by cracking. Material and corrosion diagnostics of the exchanger presented in the Photo. 4.3A excluded the possibility of this type of corrosion. Corrosion damage took the form shown in the Photo. 4.3B.

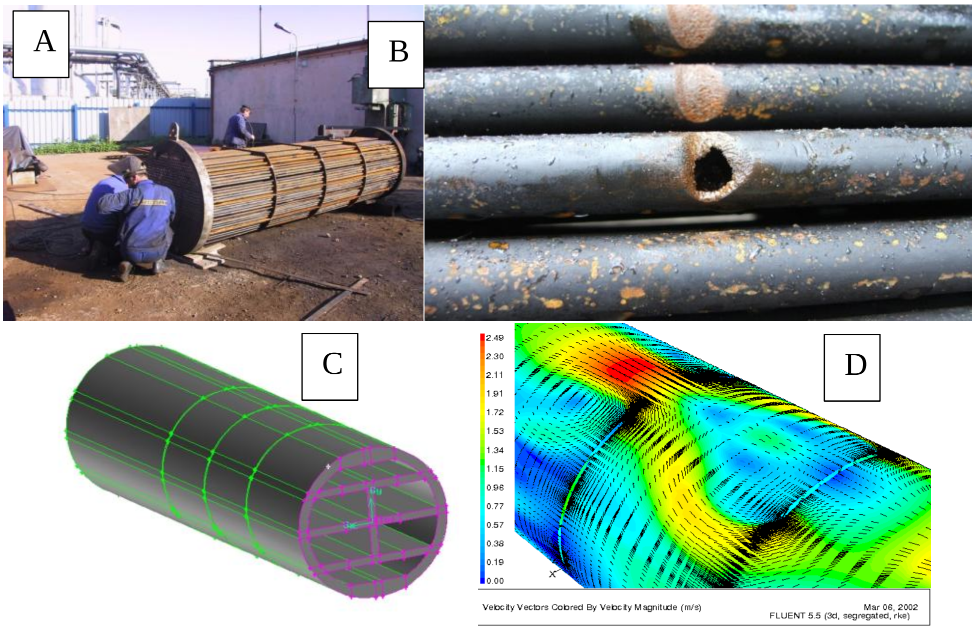


Photo. 4.3. (A) Tube insert of heat exchanger, (B) Unusual form of damage to tubes, (C) Digital model of heat exchanger, (D) Image of changes in vector field of the medium flow in the intertube space.

The problem was solved by digital analysis of the exchanger's operation. A digital model of a shell-and-tube heat exchanger was created (Photo. 4.3C). The flow of the cooling medium was simulated using the finite element method. The vector field $\overrightarrow{W}$ of the medium flow was determined, and then the rotation $rot(\overrightarrow{W})$was determined at each point of the field, which is the vector spatial derivative of this field with the opposite sign (Photo. 4.3D).

The coherence between the location of corrosion damage in heat exchanger tubes with a vector field, or rather with the rotation of this field, was demonstrated.

In the analysed case, damage to the heat exchanger was not standard in character. The damage was caused by erosion and corrosion factors.

Experience with corrosion problems of heat exchangers has been published:

Z. Klenowicz, K. Darowicki, S. Krakowiak, Corrosion-erosion damage of heat exchanger tubes by desalted crude oil flowing at shell side, Materials and Corrosion, Volume 54, Issue 3, Pages 181 – 187 March 2003

Z. Klenowicz, K. Darowicki, Waste incinerators: Corrosion problems and construction materials - A review, Corrosion Reviews, Volume 19, Issue 5-6, Pages 467 - 4912001

4.4.	Pipeline failures due to stray currents
Research project ordering party	Mazowiecka Spółka Gazownicza Sp. z o.o.

Let us assume that the source of stray currents is railway or tram electric traction. The reason for the current leakage may be high electrical resistance on the rails. Improper installation of rails on the ground or widely spaced substations that cause voltage drops on the rails. The leakage pattern of currents is shown in Fig. 4.4A. The form of damage is presented in the Photo. 4.4B. Mazowiecka Spółka Gazownicza (Białystok, Warsaw, Łódź Voivodeships) undertook an action to assess the stray currents risk. Unfortunately, conventional detection and evaluation methods did not always provide correct results in assessing the corrosion hazard of gas pipelines due to stray currents. There was a need to develop a more unequivocal method.

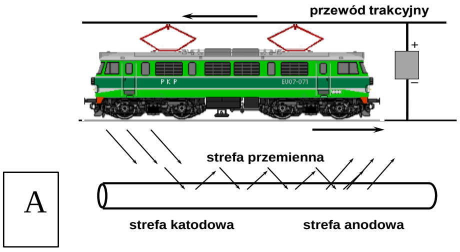
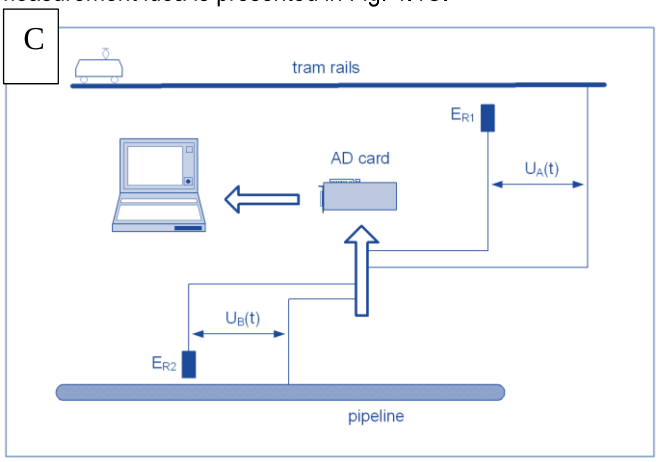


Fig. 4.4. (a) Scheme of stray currents leakage from railway traction, (B) Typical corrosion damage caused by stray currents

Stray currents can be evaluated and recorded using advanced metrological technology. However, the interpretation of measurement data is often ambiguous. In order to assess the stray currents risk, it is necessary to identify the source of currents and the place of their leakage. For this purpose, a digital method based on time-frequency analysis was developed. The measurement idea is presented in Fig. 4.4C.



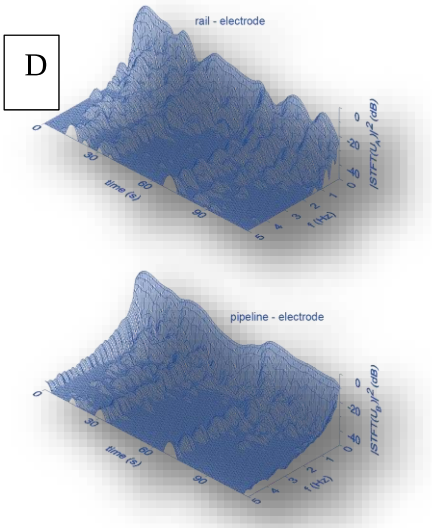


Fig. 4.4. (C) Scheme for simultaneous recording of current interactions, (D) STFT spectrograms of the rail potential change register and the gas pipeline potential change register.

Changes in the potential of the stray current generator (railway traction) were measured along with changes in the potential of the endangered structure. Two registers were subjected to the STFT transformation. This situation is presented in Fig. 4.4D. Corrosion caused by stray current is limited by using a galvanic insulator, reducing the electrical resistance of the rail return circuit, drain connections between pipelines and railway systems, which enable galvanic recycling of stray currents, the so-called drainage.

K. Darowicki, K. Żakowski A new time-frequency detection method of stray current field interference on metal structures, Corrosion Science, Volume 46, Issue 5, Pages 1061 – 1070 May 2004M.
Narożny. K. Darowicki, K. Żakowski, Method of sacrificial anode dual transistor-driving in stray current field, Corrosion Science, Volume 98, Pages 605 - 6091 September 2015
K. Zakowski, K. Darowicki, J. Orlikowski, A. Jazdzewska, S. Krakowiak, M. J. Gruszka, J. Banas, Electrolytic corrosion of water pipeline system in the remote distance from stray currents-Case study, Case Studies in Construction Materials, Open Access, Volume 4, Pages 116 - 124June 01, 2016

4.5.	Corrosion diagnostics of the facilities of the former concentration camp 'Auschwitz'
Research project ordering party	Memorial and Museum Auschwitz-Birkenau

The former Auschwitz extermination camp is constantly being degraded as a result of groundwater, precipitation, and polluted atmosphere impact. In order to counteract these processes, the management of the Auschwitz Memorial and Museum proposed a detailed damage analysis and the development of preventive methods. The following photographs show the extent of degradation.

Photo. 4-5. (a) Exposed reinforcing bars of the ruins of crematorium no. 2 in Auschwitz II-Birkenau, (B) Ceiling of the gas chamber of this crematorium, (C) Typical forms of damage to concrete structures, (D) Recording a map of electrochemical potential on a reinforced concrete ceiling beam inside the ruins of crematorium no. 2 in Auschwitz II-Birkenau

Based on the results of corrosion investigations conducted in the former Auschwitz extermination camp, five main conclusions were formulated:

- The corrosivity of the atmosphere, as determined during the one-year exposure of steel samples according to the EN ISO 12944-2 (1998) standard, was determined at the boundary between low C2 and medium C3.
- The corrosion rate of steel under these conditions was in the range of 14–34 μm/year at an average rate of 27 μm/year.
- The layer of corrosion products formed on bare steel reinforcing bars during approximately 70 years of atmospheric exposure was examined for its protective properties. It has been estimated that this layer reduces the corrosion rate of the steel by about five times. This discovery allows for more precise determination of the corrosion rate of steel structures of the former Auschwitz camp and enables more accurate prediction of their lifetime and identification of appropriate potential protective measures.
- It can be inferred that the corrosion rate of the original steel elements under the corrosion products layer should not exceed 7 μm/year.
- The corrosion products layer on rebar is composed primarily of magnetite (Fe_2O_3) and lepidocrocite (γ-FeOOH) with a minor addition of calcium carbonate ($CaCO_3$) and calcium oxide (CaO).

The presented research was used to check the condition of steel elements located in the former Auschwitz camp and to select possible methods of their preservation and protection. Determining the corrosivity of the atmosphere was a necessary step because it was the starting point for corrosion risk assessment.

The research and analysis of concrete and reinforced concrete structures in the former Auschwitz I and Auschwitz II-Birkenau camps allowed for the following conclusions:

- The utilization of a method to measure the electrochemical potential of reinforcement, in accordance with the standard procedure described in ASTM-C 876-91, enables non-destructive assessment of the condition and corrosion risk of rebars in selected reinforced concrete structures;
- The results of electrochemical potential measurements are consistent with the results of laboratory analyses of reinforced concrete artifacts, proving that this method is reliable and well-suited for the non-destructive evaluation of objects of high historical value;
- The main threat is the carbonation process, since a significant proportion of concrete elements exhibit complete carbonation; in the case of reinforced concrete structures, it causes corrosion of the reinforcement, giving corrosion products, the volume of which is greater than the volume of the original steel, causing cracking and chipping of the concrete;
- Elements with larger dimensions and thicker concrete cover, as well as higher quality of workmanship, show better mechanical properties and provide better protection of the reinforcement;
- The presence of chloride and sulphate ions has little effect on the durability of concrete due to their relatively low concentration;
- Carbonation depth can reach up to 5–10 cm into the concrete cover.

The research results and proposed preservation methods have been published in the following journals:

M. Szociński, A, Miszczyk,K. Darowicki, Corrosivity of environment and the current state of the steel elements at the former Auschwitz concentration camp, Studies in Conservation, Volume 62, Issue 8, Pages 456 - 46417 November 201

M. Szociński, A, Miszczyk,K. Darowicki, Condition of Reinforced Concrete Structures and Their Degradation Mechanism at the Former Auschwitz Concentration and Extermination Camp, Studies in Conservation, Volume 64, Issue 3, Pages 174 - 1863 April 2019

M. Szociński, A, Miszczyk,K. Darowicki, Restoration and preservation of the reinforced concrete poles of fence at the former Auschwitz concentration and extermination camp, Case Studies in Construction Materials, Open Access, Volume 4, Pages 42 - 48June 01, 2016

4.6.	Corrosion diagnostics of fermentation tanks
Research project ordering party	Kompania Piwowarska S.A.

Fermentation tanks are made of 4307 (304 L) and 4404 (316 L) austenitic stainless steel, with the choice of grade depending on the level of chloride and chlorine in the water. LDX 2404® and 2205 duplex grades perform very well in all tested chlorinated environments and are attractive alternatives, with a more attractive price and a higher level of corrosion resistance. Unfortunately, there is little data available on their use in brewing. The fermentation process produces large amounts of protein, hop resin, polysaccharides, and yeast. Calcium oxalates and other inorganic compounds are formed. Fermentation tanks are covered with brown sediment. Tank washing is carried out using caustic soda solutions, which remove organic matter. After the process, the passivation is carried out using dilute nitric acid. Cleaning and passivation are conducted using aqueous solutions. The European Drinking Water Directive sets a maximum limit of 250 ppm (mg/l) of chlorides in water, but does not provide guidelines on chlorine. Potable water is usually treated to obtain a residual level of 0.2 to 0.5 ppm chlorine to remove bacteria, but the actual added concentrations are usually higher. For disinfection to be more effective, the residual amount of free chlorine should exceed 0.5 ppm after at least 30 minutes of contact at pH 8 or lower.

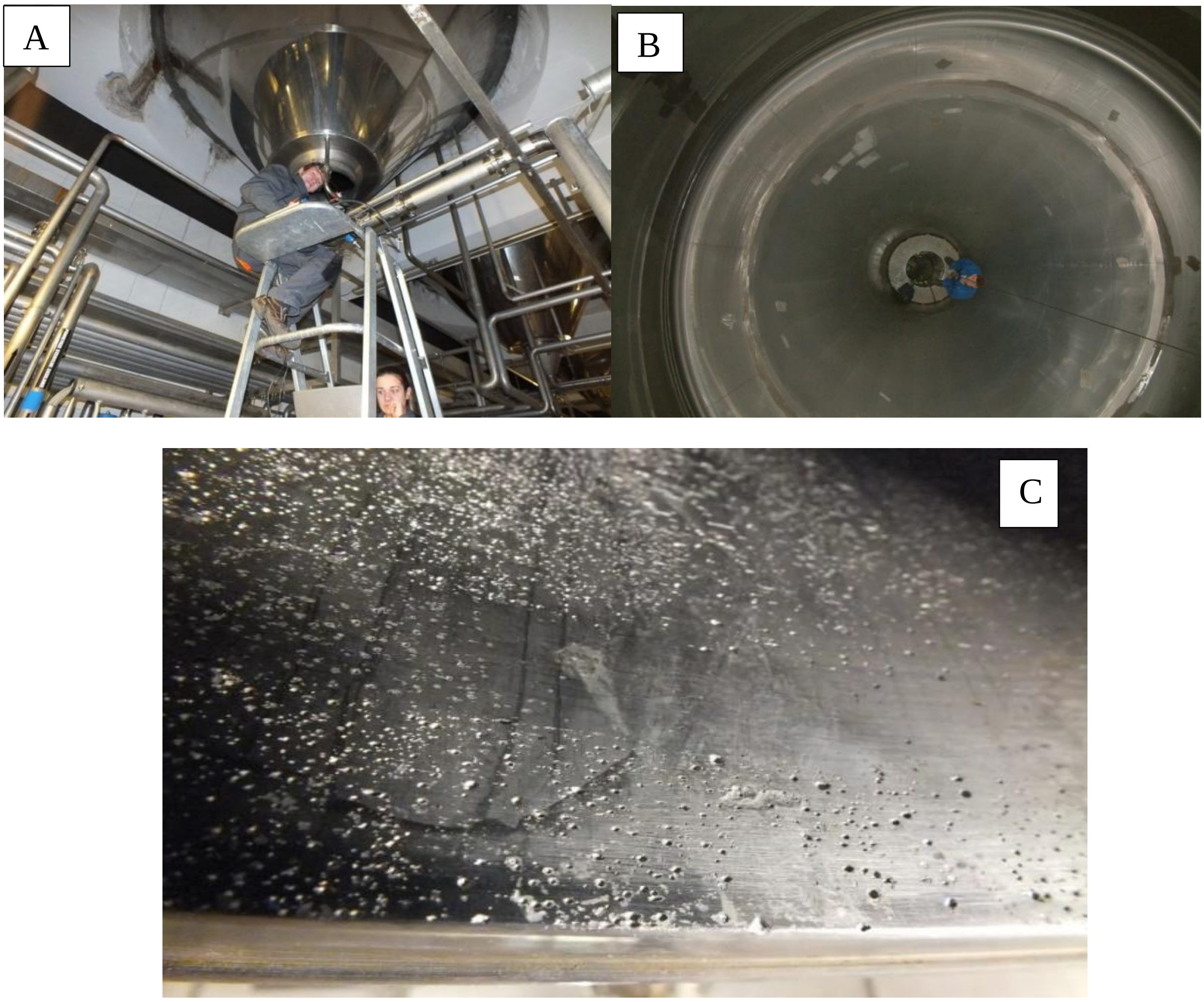


Photo. 4.6. (A) View of the fermentation tank cone, (B) Worker analysing the extent of corrosion damage, (C) Pitting corrosion of tanks.

Fermentation tanks are made of 4307 (304 L) and 4404 (316 L) austenitic stainless steel, with the choice of grade depending on the level of chloride and chlorine in the water.

Our research has shown that the use of washing agents containing chlorine or even residual chlorine has a significant impact on the corrosion behaviour of stainless steels. Chlorine has a disinfecting effect and, on the other hand, causes corrosion risk. This oxidizing effect of chlorine has harmful consequences because stainless steels undergo pitting corrosion (Photo. 4.6C). The anticorrosion properties of stainless steels result from the formation of a layer of chromium (III) oxide on their surface. Under washing conditions at elevated temperature with chlorine-containing agents, local chromium (VI) oxychloride moieties are formed in the passive layer:

$$Cr_2O_3 + 2Cl_2 + \frac{1}{2}O_2 = 2CrCl_2O_2$$

$$CrCl_2O_2 + H_2O = CrO_3 + 2H^+ + 2Cl^-$$

The influence of the aqueous environment causes acidification at the places where $2CrCl_2O_2$ was produced and the formation of a very strong oxidant CrO_3, which initiates pitting corrosion. A dissolution process occurs inside formed micro-pit:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

In the presence of chloride ions, iron (II) dichloride is formed inside the pit. Hydrogen cations are produced in the hydrolysis reaction inside the pit:

$$FeCl_2 + H_2O = Fe(OH)_2 + 2H^+ + 2Cl^-$$

The hydrogen cations produced undergo electrochemical reduction inside the pit. In this case, the depolarization process is about 3 orders of magnitude faster than that of the oxygen reaction. The corrosion process is intensified and exemplified by numerous and deep pits. The described process is an autocatalytic loop. Producing a new portion of Fe^ (2+) results in the production of an equivalent amount of hydrogen cations. In this way, hydrogen cations are not depleted. The proposed autocatalytic corrosion mechanism explains the dramatic development of corrosion damage to tanks. The elimination of chlorine and/or chlorine suboxide stopped the pitting corrosion of stainless steels.

The research work was carried out for the Poznań Brewery Company, the Białystok Brewery Company, and the Tychy Brewery Company.

J. Ryl, J. Wysocka, K. Darowicki, Determination of causes of accelerated local corrosion of austenitic steels, Construction and Building Materials, Volume 64, 14 August 2014, Pages 246-252

4.7.	Corrosion diagnostics of the amine washing installation
Research project ordering party	LOTOS S.A.

Amine/ammonia acid gas washing installations are an inherent part of petroleum and petrochemical plants around the world. The main purpose of the installation is to remove acid gases such as hydrogen sulphide and carbon dioxide from dry process gases. This operation allows hydrogen sulphide to be processed in Claus units and to use purified gases as fuel in the plant furnaces.

The amine installations consist of an absorber for removing CO_2 and H_2S from the acid gas stream and a regenerator for the purification of the amine. Therefore, the amine operates in an almost closed circuit in which it is constantly recycled and reused. The added amine and water compensate for losses from the top of the regenerator. Common causes of failures in amine systems are related to the complexity of amine washing installations. These installations are subject to various types of attacks. Photo. 4.7 presents the images of corrosion damage.

Photo. 4.7. Forms of damage to amine washing installations

Based on literature analysis and conducted research, it was shown that the main types of corrosion are:

A) Local corrosion on rich amine lines. The cause of this corrosion is the premature release of CO_2 and H_2S before reaching the desorber.

B) Stress corrosion cracking is observed in carbon steel pipelines where no post-welding heat treatment has been carried out.

C) Amine degradation. Lean amine contains less than 1% of the heat-stable salts that accumulate over time in the recycling process. Amounts of stable salts of 2 to 3% and higher can lead to corrosion of the lean amine line. Other causes of amine degradation are high temperatures and the ingress of impurities.

D) High flow rates or turbulence of the liquid phase cause erosion-corrosion of pipelines and equipment. (This process condition may occur downstream of the feedline control valve or in the desorber return lines).

E) The regeneration gases leaving the column contain a significant amount of water vapor. Under these conditions, intense corrosion processes called wet H_2S corrosion. Wet H_2S corrosion is revealed in various forms of cracking and blistering.

Corrosion prevention mainly involves the use of more corrosion-resistant materials, such as stainless steels, which have much higher corrosion resistance in aqueous environments containing amines, as well as in acid gases.

J. Orlikowski, M. Kalinowski, I. Lasota, P. Maruszewski, M. Szocinski, K. Darowicki, Wet H_2S corrosion and degradation of pipeline in amine regeneration system, Materials and Corrosion, Volume 75, Issue 6, Pages 778 – 785 June 2024

J. Orlikowski, A. Jazdzewska, U. Ilyas, R. Gospos, T. Olczak, K. Darowicki, Effect of wet Hydrogen Sulfide on Carbon Steels Degradation in Refinery Based on Case Study, Arabian Journal for Science and Engineering, Open Access, Volume 48, Issue 7, Pages 9171 - 9178July 2023

4.8.	Corrosion diagnostics of the 'NAFTOPORT' facilities
Research project ordering party	**NAFTOPORT Sp. z o.o.**

NAFTOPORT is an important element of the logistics of crude oil supplies for domestic refineries, export and import transit of this raw material, as well as land-sea transhipment of petroleum products. The Terminal's infrastructure includes five stations enabling the reloading of 36 million tons of crude oil and 4 million tons of petroleum products annually.

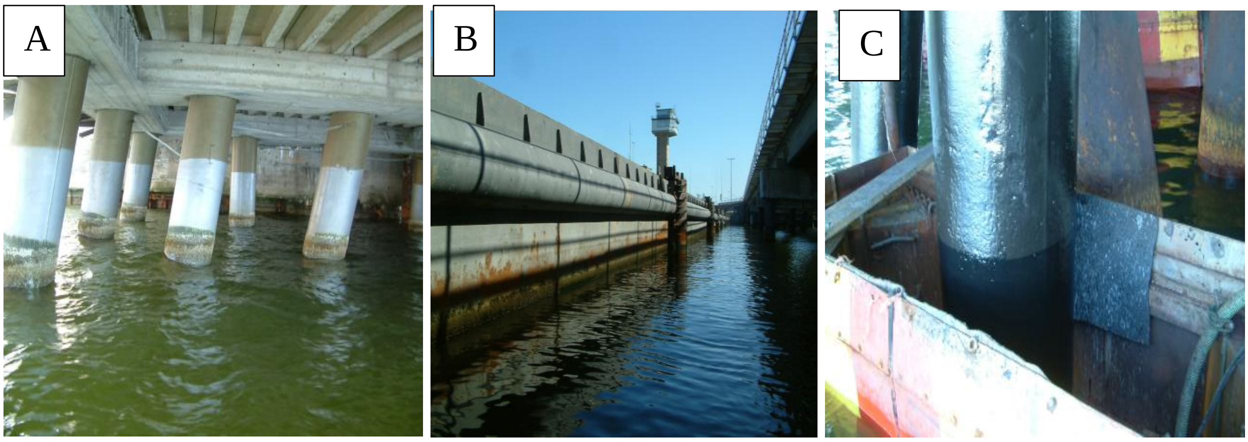


Photo. 4.8. (A) View of corrosion damage to piles at the waterline, (B) View of corrosion damage to the pier structure, C). Caisson structure for anticorrosion work

Waterline corrosion is a type of oxidation process that can occur in materials that come into contact with water. Waterline corrosion occurs when one part of the material is immersed in water and the other is in contact with air. This causes a difference in the amount of oxygen in contact with the surface of the material above and below the waterline and leads to a corrosion reaction.

Waterline corrosion occurs due to the difference in oxygen concentration between the atmosphere and water. This is because the part of the substrate exposed to more oxygen (area exposed to air) becomes a cathode, while the part of the substrate exposed to less oxygen (area in contact with water) becomes an anode. The formation of an anode and a cathode allows oxidation. This ultimately causes oxidation and corrosion of the area of the substrate immersed in water.

Waterline corrosion is a problem in several different industries. Tanks that are used to store liquids such as water are often susceptible to waterline corrosion. Marine structures can also suffer from waterline corrosion, which can lead to complete structural failure. Ships left in water for extended periods may also be exposed to waterline corrosion.

Waterline corrosion can be combated in several different ways. One way is to coat the material placed in water. The coating maintains the exposure of the substrate to oxygen in an even amount and at a minimum level. Another method is to use materials that are not as susceptible to oxidation as steel. Stainless steels and aluminium may be better alternatives for preventing waterline corrosion. Correctly conducted anticorrosion works required the use of caisson structures to dry the protected surfaces (Fig. 4.8C).

K. Zakowski, M. Narozny, M. Szocinski, K. Darowicki, Influence of water salinity on corrosion risk - The case of the southern Baltic Sea coast. Envionmental Monitoring and Assessment, Open Access, Volume 186, Issue 8, Pages 4871-4879 August 2014

Przedsiębiorstwo Przeładunku Paliw Płynnych
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Kapitał zakładowy: 45.942.000,00 PLN

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NFP/853 /2006 Gdańsk, dn. 12 .11 .2006

LIST REFERENCYJNY

Katedra Èlektrochemii, Korozji i Inżynierii Materiałowej Politechniki Gdańskiej wykonała badania i dokonała oceny zagrożeń niszczenia korozyjnego konstrukcji hydrotechnicznych oraz oceny stanu i efektywności istniejących zabezpieczeń przeciwkorozyjnych obiektów będących własnością Przedsiębiorstwa Przeładunku Paliw Płynnych NAFTOPORT Sp. z o.o. w bazie paliw w Porcie Północnym w Gdańsku.

Wysoko oceniamy prace wykonane przez Katedrę. Uzyskane wyniki będą wykorzystane w działaniach NAFTOPORTu mających na celu utrzymanie odpowiedniego stanu zabezpieczeń przeciwkorozyjnych konstrukcji hydrotechnicznych.

Na podstawie naszej współpracy możemy zarekomendować Katedrę Elektrochemii, Korozji i Inżynierii Materiałowej jako rzetelnego i fachowego partnera wywiązującego się z przyjętych terminów i umów.

CZŁONEK ZARZĄDU
Z-ca DYREKTORA
mgr inż. Andrzej Radzikowski

PREZES ZARZĄDU
DYREKTOR
mgr inż. Tadeusz Zakrzewski

4.9. Failure diagnostics and anticorrosion protection of electrofilters

Research project ordering party	**Kozienice Power Plant, PGE Górnictwo i Energetyka Konwencjonalna S.A.**

Electrofilters are environmental protection objects designed to reduce dust caused by the combustion of solid fuel in boilers. The dust-laden exhaust gas from the boiler enters the electrofilters, which contain the collecting and discharge electrode sections. A very high-intensity electric field is generated between the discharge electrodes sandwiched between the collecting electrodes. Dust particles passing in the space between the electrodes are electrically charged. While traveling through an electric field, electrically charged particles are transported to the electrodes in the direction of the electric field generated. At the collecting electrodes, they agglomerate with already separated dust particles and are dumped by drop hammers. The process of removing dust from collecting electrodes is intensified by the shaker system. The dumped dust layer falls into the filter hopper and is discharged to the outside, while the purified gas leaves the electrofilter with a duct connected to the chimney. Under operating conditions, electrofilters do not undergo significant corrosion processes, and their operation is failure-free. The situation is different during periods of renovation downtime or during periods of shutdown. During these periods, electrofilters undergo serious corrosion processes.

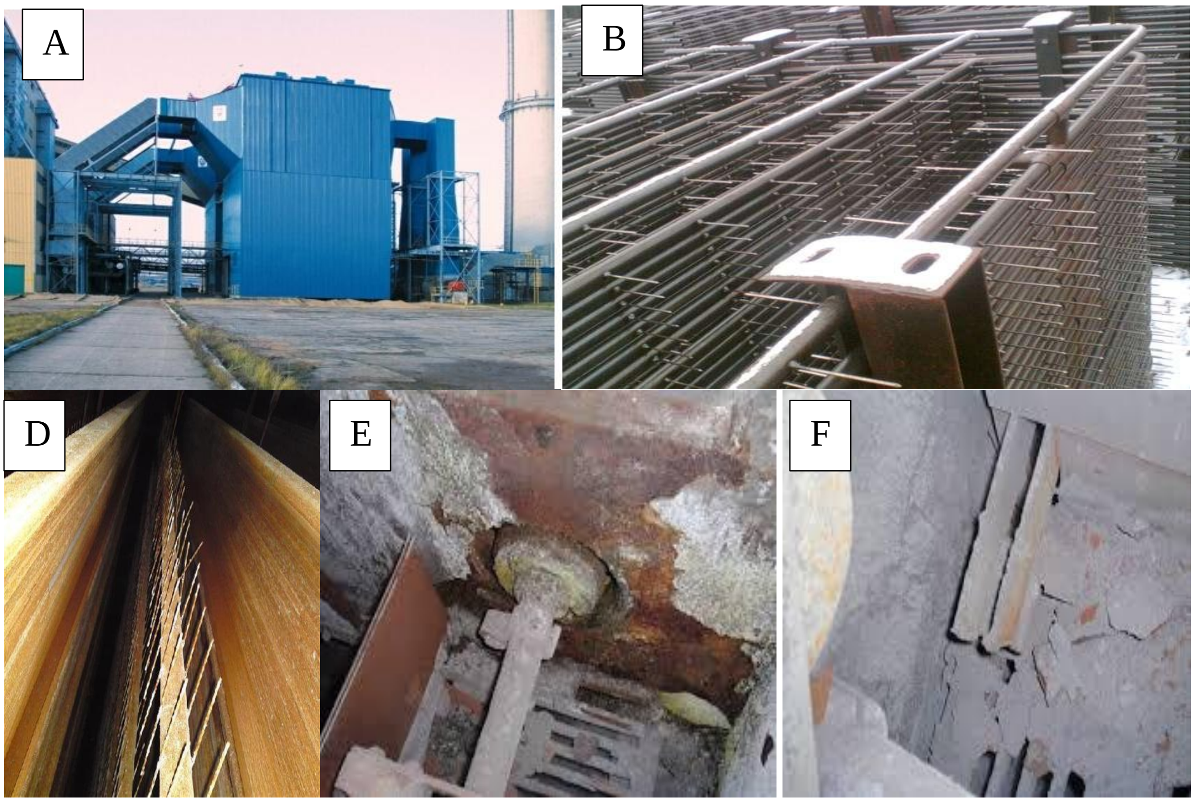


Fig. 4.9. (A) View of electrofilter, (B) Discharge and collecting electrode section, (C) Discharge and collecting electrode section after a week of downtime, (D) Shaker damage, (E) Fragment of filter hopper.

Corrosion processes are caused by the smoke dust remaining on the electrodes and in the hoppers. As a result of moisture absorption, an aggressive corrosive environment is created in the electrofilters. The presence of sulphur and nitrogen oxides in the dust causes the formation of strong acids and, consequently, intense corrosion processes. As part of our research work, we proposed a technology for anticorrosion protection of electrofilters. It consisted, in the first stage, of removing the smoke dust with a stream of water. In the second stage, an anticorrosion water-oil emulsion containing a set of corrosion inhibitors was applied to collection electrodes, shakers, and discharge electrodes. In this way, a number of electrofilters were protected at the Kawęczyn Heat and Power Plant, the Zabrze Heat and Power Plant, the Siekierki Heat and Power Plant, the Kozienice Power Plant, and many others. This type of temporary protection secured electrofilters for up to 4 months.

A patent has been obtained for the preparation of the water-oil emulsion:

J. Bordziłowski, K. Darowick, Patent krajowy PL 163545 B1: „Antykorozyjna wodna emulsja węglowodorowa do ochrony maszyn i urządzeń”.

4.10.	Implementation of the RBI programme
Research project ordering party	PKN ORLEN S.A., LOTOS S.A.

Risk-based inspection (RBI) was introduced by the American Petroleum Institute (API) as a risk management system. It is now a widely recognized global standard covering the petroleum and petrochemical industry and beyond. The system defines the risk level and ranks the risk of failure of process equipment and installations. Safety risks are reviewed. The probability of failure is reduced by creating an inspection system based on legal regulations:

- **Publ 941** Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants
- **Publ 942** Controlling Weld Hardness of Carbon Steel Refinery Equipment to Prevent Environmental Cracking
- **API 510** Pressure Vessel Inspection Code: Maintenance Inspection, Rating, Repair, and Alteration
- **API 570** Piping Inspection Code: In-service Inspection, Rating, Repair, and Alteration of Piping Systems
- **API RP 571** Damage Mechanisms Affecting Fixed Equipment in the Refining Industry
- **API RP 572** Inspection of Pressure Vessels
- **API RP 573** Inspection of Fired Boilers and Heaters
- **API RP 574** Inspection Practices for Piping System Components
- **API RP 575** Inspection of Atmospheric & Low-Pressure Storage Tanks
- **API RP 577** Welding Inspection and Metallurgy
- **API Std 579-**1/ASME FFS-1 Fitness-For-Service
- **API RP 580** Risk-Based Inspection
- **API RP 581** Risk-Based Inspection Technology
- **API RP 582** Recommended Practice Welding Guidelines for the Chemical, Oil, and Gas Industries
- **API Std 653** Tank Inspection, Repair, Alteration, and Reconstruction

The above-mentioned standards create a system presented in the form of a diagram.

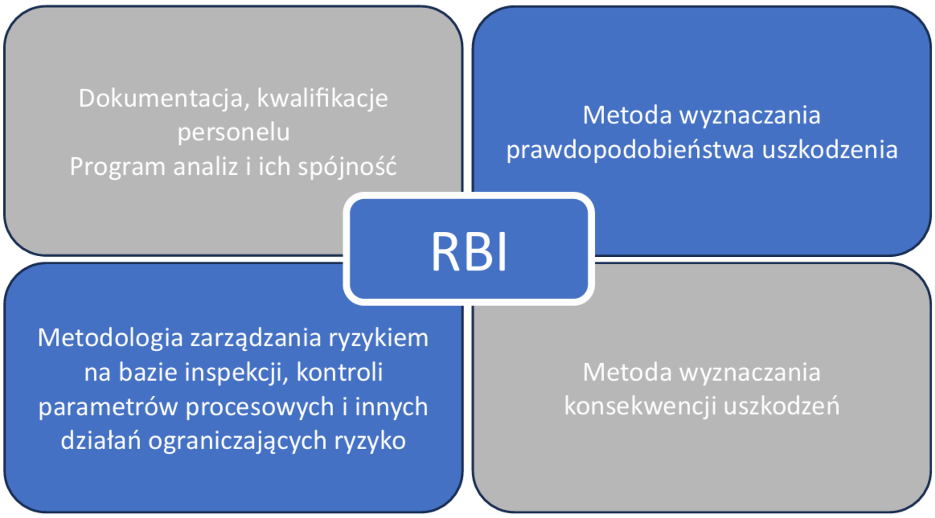


Fig. 4-10. A diagram illustrating dependencies and relationships in the created RBI system

The RBI system in Poland is gradually being introduced by PKN ORLEN. In recognition of our achievements and extensive experience, employees of the Department of Electrochemistry, Corrosion and Materials Engineering were invited to cooperate with inspectors of the Office of Technical Inspection in Gdańsk and Płock, as well as employees of corrosion teams from LOTOS and PKN ORLEN. The implementation of the RBI program was preceded by an RBI audit aimed at determining the level of preparation of the operator for the implementation of the program based on the API RP 580 and API RP 581 standards. We assessed existing management systems, staff, and their qualifications. The design of the RBI system included interdependencies between documentation and staff qualifications, reliable risk management methodology, risk probability assessment, and determination of damage consequences.

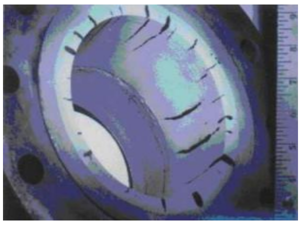
Professor Kazimierz Darowicki

Risk-based inspection (RBI) is an analysis method and process that, unlike condition control, requires a qualitative or quantitative assessment of the probability of failure (POF) and consequence of failure (COF) associated with individual elements of facilities and installations.

- A properly implemented RBI program classifies individual items of equipment in terms of failure probability, damage risk, and control priorities based on this categorization.
- The RBI system is used to identify and understand risks and risk factors.
- The RBI system makes it possible to determine whether control is necessary or not. However, this decision requires additional data to reduce uncertainty related to current threats.
- The RBI system should not be used to recommend an inspection that does not improve the level of knowledge about the condition of damage. In those cases where POF determines risk, the RBI system should lead to the replacement of critical equipment, repairs, or other activities that reduce risk.
- RBI can be used to prioritize inspection activities (usually through non-destructive testing) to reduce uncertainty about the true damage condition of equipment.
- The resulting control plan should specify the type and timing of controls with respect to the facility concerned. Other activities may include structural changes, material changes, applications of anticorrosion linings, changes in operating mode, injection of corrosion inhibitors, etc.
- Consistency and reproducibility of analyses are essential for producing an effective RBI program. The RBI system is based on relative risk. In creating the system, one should rely on international engineering standards and practices: API RP 580 and 581, ASME PCC-3, and RIMAP. The API RP 580 standard defines basic guidelines for implementing an effective and reliable RBI program. The API RP 581 standard specifies details of RBI procedures and methodologies.

The RBI system determined the mechanisms of corrosion processes, their intensity, and preventive measures:

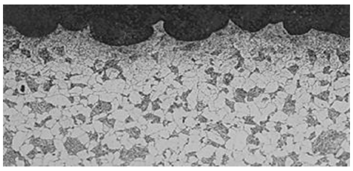
Metal dusting. Furnace pipe made of 304 steel



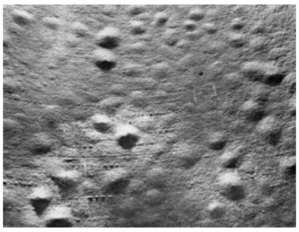
Dye penetrant, stub pipe inspection. 304 steel pipe discharging the catalyst

Carbonate cracking in a vicinity of weld

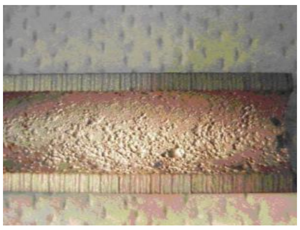
Craters at the bottom of the raw crude oil tank



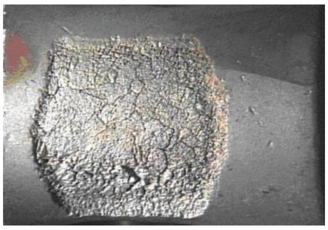
Classic carburizing-induced profile. Carbon steel, heater separator plate



Extensive hydrogen blisters on steel surface



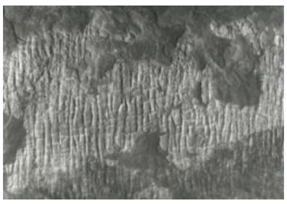
Heat exchanger tube on the cooling water side. Temperature 30°C



Selective dissolution of nickel from Monel. Presence of oxygen in hot HF

Erosion-corrosion damage to the elbow of the 5Cr alloy. Heater outlet

Titanium tube of heat exchanger . Hydrogen cracking of titanium in water



Alligator skin morphology with liquid carbon dust

Ammonia-induced cracking of the 5 Cr-0.5 Mo alloy

Within the cooperation with Lotos S.A., an RBI analysis of a number of installations was carried out. Individual selected areas of the installation were analysed from the material standpoint. The nature of the medium, the number of phases, temperature, pressure, and flow rate were defined. On this basis, the types of corrosion in individual plant nodes and their intensity were determined. The number, frequency, and types of inspection were proposed.

LOTOS

TD / w / 124 / 20 / JD

Gdańsk, 19.11.2020

Referencje

Grupa LOTOS S.A. udziela referencji Katedrze Elektrochemii, Korozji i Inżynierii Materiałowej Politechniki Gdańskiej za realizowane prace pt. „Analiza mechanizmów degradacji wraz z opracowaniem Kart Mechanizmów Degradacji dla urządzeń objętych Programem RBI na terenie Grupy LOTOS S.A. w Gdańsku". Prace realizowane były w terminie od 21.03.2016 do 30.12.2016 roku oraz w dalszym ciągu realizowane od 01.10.2018 roku.

W zakres prac wchodziły:

- analiza zagrożenia korozyjnego,
- wytypowanie mechanizmów degradacji,
- oszacowanie szybkości korozji
- opracowanie szczególnie zagrożonych obszarów.

Zlecane prace wykonywane są terminowo oraz z należytą starannością. Jakościowo spełniają wskazane w zamówieniu wymagania. Zadowolenie ze współpracy z firmą pozwala nam stwierdzić, że jest to rzetelny kontrahent.

DYREKTOR ds. TECHNIKI
Tomasz Branicki

Grupa LOTOS S.A., ul. Elbląska 135, PL 80-718 Gdańsk
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Sąd Rejonowy Gdańsk Północ w Gdańsku, VII Wydział Gospodarczy KRS, Nr KRS: 0000106150; NIP 583-000-09-60; REGON 190541636; BDO 000019759
Kapitał zakładowy 184 873 362 PLN wpłacony w całości

ORLEN

Pismo nr RT/ 01 61 /2021

Płock, 09.06.2021 r.

Szanowny Pan
Prof. Kazimierz Darowicki
Wydział Chemiczny
Politechnika Gdańska

Szanowny Panie Profesorze,

Biuro Techniki jako obszar odpowiedzialny w PKN Orlen S.A. za stan i sprawność infrastruktury technicznej Zakładu, bardzo ceni współpracę z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej Politechniki Gdańskiej.

W ramach współpracy na podstawie dotychczas zawartych umów, realizowano m.in. analizy technologiczno-korozyjne. Uzyskane wyniki pozwalały identyfikować nieprawidłowości w procesach technologicznych oraz wyjaśniać przyczyny przyśpieszonej degradacji korozyjnej w newralgicznych punktach analizowanych instalacji. Na wybranych obiektach realizujemy wspólnie analizę mechanizmów degradacji procesów korozyjnych w ramach wdrażanej w PKN Orlen S.A. analizy Risk Based Inspection na podstawie API RP 580 i 581. Współpraca ma na celu oszacowanie ryzyka występowania awarii wraz z planowaniem niezbędnych przeglądów technicznych i badań nieniszczących dla objętych nią urządzeń ciśnieniowych. Działania te przyczynią się do optymalizacji czasookresów prowadzenia remontów i przeglądów instalacji co przełoży się na zmniejszenie liczby postojów poszczególnych instalacji i znacząco wpłynie na bilans finansowy przedsiębiorstwa.

Zważywszy powyższe, wysoko oceniamy współpracę z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej - uwzględniając terminowość i poziom merytoryczny realizowanych prac.

Z poważaniem

Albert Kołodziejski
Dyrektor Wykonawczy ds. Techniki
PKN ORLEN S.A.

Tomasz Dobrowolski
Dyrektor Biura Techniki
PKN ORLEN S.A.

Polski Koncern Naftowy ORLEN Spółka Akcyjna z siedzibą w Płocku
09-411 Płock, ul. Chemików 7, tel: (+48 24) 256 00 00, fax: (+48 24) 367 70 00, www.orlen.pl
wpisana do Krajowego Rejestru Sądowego prowadzonego przez Sąd Rejonowy XIV Wydział Gospodarczy w Warszawie pod numerem: 0000028860
NIP: 774-00-01-454, kapitał zakładowy / kapitał wpłacony: 534.636.326,25 zł

4.11.	Control algorithm and controller for the fuel cell system
Research project ordering party	Ministry of Science and Higher Education, Federal Ministry of Research, Technology and Space (Bundesministerium fur Bildung und Forschung, Germany)

The research and development work engulfed a controller and control algorithms for a hybrid system, including a power reserve storage, which was a package of supercapacitors, and a stack of hydrogen cells with a polymer membrane (PEMFC), along with the entire flow and operating temperature management system. The developed solution ensured an increase in energy efficiency by 3.7% while reducing the mass of the system. This work was carried out in cooperation with the Zentrum fur Sonnenenergie- und Wasserstoff Forschung Baden-Württemberg (ZSW) Germany, the Deutsches Zentrum fur Luft- und Raumfahrt eV (DLR) Germany, the PowerCell Germany GmbH. Poland was represented by the IMPACT Clean Technology and the Faculty of Chemistry, which coordinated research on the Polish side. Renewable energy systems have been extensively studied in the last decade to reduce fossil fuel-based energy supplies and reduce CO_2 emissions. Research focused on improving the efficiency, reliability, and energy density of these systems. Fuel cells are widely promoted in the energy conversion system due to their high efficiency, low or zero emissions, and high power density. One of the factors implying the development of fuel cell technology is their efficiency, which reaches 60% while the efficiency of internal combustion engines is 30%. Unfortunately, the operational dynamics of the cell stack is unsatisfactory. PEMFC fuel cells are the most promising candidate due to their high flexibility and highest dynamics among fuel cells. Nevertheless, the transient response of PEMFC is limited by the rate of electrochemical reaction and the dynamics of reactant supply. In practical applications, PEMFC fuel cell systems are used as the primary source of energy conversion, with peak power demands being met by additional energy storage systems such as batteries or capacitors. The hybrid system's response to transition states is a major challenge for automotive and mobile applications. The capacitor-based energy storage system offers a number of advantages, such as higher energy density, power density, and dynamics compared to battery solutions. A lithium-ion capacitor (LiC) is the most modern supercapacitor that has very high energy density and very little leakage compared to other capacitors. The application of LiC allows the use of PEMFC covering only average power demand, not peak one. This results in a higher power density of the hybrid system. The operation of such a fuel cell-based hybrid system requires coordinated control of the energy generation subsystems and energy storage by the control unit. This unit provides rapid response to variable power demand and avoids destructive and suboptimal operating conditions. The developed and implemented control algorithm ensured the coordination and cooperation of particular components. Independently, a system has been created to monitor and control the operation of the controller in accordance with the diagram:

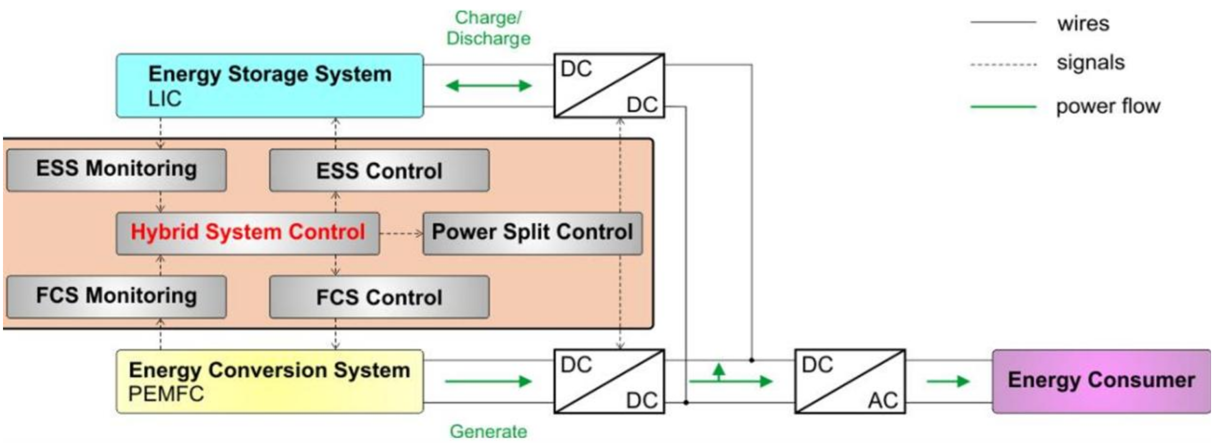

Fig. 4.11A. PEMFC-LiC hybrid system and its control

Load power division and energy management algorithms were key to achieving high performance and reliability of the hybrid system. The focus was also on innovative methods of optimizing operation for various operating modes and charge states, such as Dynamic Electrochemical Impedance Spectroscopy. A predictive control methodology was also developed. The fuel cell system controller was a key achievement of the international research team. Advanced monitoring and control of hybrid fuel cell power systems is a new field and very few solutions are available at the moment. One example is the diagnostic solution available at AVL LIST GmbH – THDA box23. As part of collaborative work, a prototype of a controller for a hybrid fuel cell system was developed. It took advantage of the SAE J1939 industrial automotive protocol, which uses a physical CAN bus. In this way, fuel cell systems intended for a specific application can be transferred to other applications. Stack condition was monitored with DEIS. A quick analysis of the complex response of the system allows determination of the impedance of the system at different frequencies of perturbation signals that make up the pack. This method saves the acquisition time of the impedance spectrum. For this reason, this original measurement method gave excellent results in monitoring systems subject to dynamic changes. This innovative and proprietary technique has proven itself in monitoring PEMFC stacks while working in a real system.

Photo. 4.11B. Digital Dynamic Electrochemical Impedance Spectroscopy measurement system based on National Instruments measurement cards coupled to a hydrogen fuel cell test bench.

The DEIS technique has been implemented in the controller hardware and software. Thanks to the application of very fast, dynamic impedance spectroscopy and spatially resolved, segmented measurement technology, it was possible to monitor the behaviour inside the fuel cell and, if necessary, optimize operating conditions using the developed algorithm. It has been shown that the efficiency of a fuel cell can be increased by up to 3.7%. The developed monitoring technology and various algorithms were implemented in a specially developed control unit. Further work plans to extend these achievements to other applications, in particular heavy transport. Dynamic Electrochemical Impedance Spectroscopy, developed by a team from the Gdańsk University of Technology, was implemented in the created controller. The DEIS method has proven to be an effective tool in the diagnostics of individual cells and the entire stack. The use of this innovative technique allows the determination of optimal operating conditions online depending on the load. The implemented DEIS method allowed demonstration of the reversible or irreversible character of the reduction in electrocatalytic efficiency, and also provides an assessment of the degree of deactivation. The application of the DEIS method for control allows avoiding the operation of cells in critical conditions, which translates into an extension of their service life. The developed and implemented DEIS system has no global equivalents. The development and implementation of the DEIS system is groundbreaking in the field of online fuel cell diagnostics and monitoring.

Institute of Engineering Thermodynamics /
Electrochemical Energy Technology

Deutsches Zentrum
für Luft- und Raumfahrt
German Aerospace Center

DLR e. V. Institute of Engineering Thermodynamics
Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

To:
Department of Electrochemistry, Corrosion and
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Narutowicza 11/12, 80-233 Gdańsk

Your correspondent Dr. Mitzel

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14 July 2021

The German Aerospace Center (DLR) cooperates with the Department of Electrochemistry, Corrosion and Materials Engineering in the field of fuel cells research.

As part of our collaboration, a research and development project entitled Control algorithm and controller for increasing the efficiency of hybrid PEMFC systems in different application (COALA) under the Polish-German sustainability research program STAIR funded by NCBR and BMBF was successfully realized. The Department of Electrochemistry, Corrosion and Materials Science took an important part in the project by implementing novel Dynamic Electrochemical Impedance Spectroscopy the main tool for monitoring and diagnostic module of the controller. Developed controller was implemented for a fuel cell system at DLR. The developed methodology is very promising for further development of the fuel cell testing area. Within the project it was proven that efficiency and lifetime of fuel cells can be extended with the proposed hybrid system controller.

We assess the importance of cooperation with Department of Electrochemistry, Corrosion and Materials Engineering very highly, and we are seeking opportunities to continue our collaboration in future projects.

Sincerely

Dr. Jens Mitzel

Zentrum für
Sonnenenergie- und Wasserstoff-Forschung
Baden-Württemberg
Gemeinnützige Stiftung

ZSW • Helmholtzstraße 8 • 89081 Ulm • Deutschland

Zertifiziert nach DIN EN ISO 9001:2008

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c/o Prof. Dr. Kazimierz Darowicki
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Jör-210715-01
KTr.

15. Juli 202116. Juli 2021

Confirmation of cooperation

Dear Prof. Darowicki,

Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW) cooperates with the Department of Electrochemistry, Corrosion and Materials Engineering in the field of fuel cells research.

As part of the cooperation, a research and development project entitled *Control algorithm and controller for increasing the efficiency of hybrid PEMFC systems in different application* under the Polish-German sustainability research program was realized. As part of the project, the Department of Electrochemistry, Corrosion and Materials Science implemented Dynamic Electrochemical Impedance Spectroscopy as a monitoring and diagnostic tool of a fuel cell and supercapacitors hybrid system. The proposed methodology has a high application character and further cooperation of ZSW and Gdańsk University of Technology in this field is planned in the next research projects, which are currently undergoing evaluation by funding agencies. Joint research activities initiated the invention of a new methodology for local dynamic impedance measurements, which is in the phase of further development.

We assess very highly the importance of cooperation with the Department of Electrochemistry, Corrosion and Materials Engineering.

Mit freundlichen Grüßen

Prof. Dr. Markus Hölzle
(Member of the Board)

i.V.

Dr. Ludwig Jörissen
(Head of Department ECG)

IMPACT
CLEAN POWER TECHNOLOGY

Pruszków, 25 czerwca 2021

Do:
Katedra Elektrochemii, Korozji i Inżynierii Materiałowej
Wydział Chemiczny, Politechnika Gdańska
Narutowicza 11/12, 80-233 Gdańsk

Oświadczenie o współpracy

Firma Impact Clean Power Technology współpracuje z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej w obszarze badań elektrochemicznych źródeł energii. W ramach współpracy zrealizowany został projekt badawczo – rozwojowy pt. *Algorytm sterowania i sterownik do podnoszenia sprawności hybrydowych systemów zasilania opartych na ogniwach paliwowych z elektrolitem polimerowym w różnych zastosowaniach* w ramach Polsko-Niemieckiego Programu na Rzecz Zrównoważonego Rozwoju (STAIR). W ramach projektu Katedra Elektrochemii, Korozji i Inżynierii Materiałowej zaimplementowała Dynamiczną Elektrochemiczną Spektroskopie Impedancyjną do kontrolera systemu hybrydowego składającego się z ogniw paliwowych zasilanych wodorem oraz superkondensatorów litowo-jonowych. Metoda ta okazała się idealnym narzędziem do diagnostyki i monitorowania elektrochemicznych źródeł energii. Realizowana w ramach naszej współpracy tematyka jest kluczowa do dalszego rozwoju nowoczesnej energetyki w Polsce. Rezultaty badań zrealizowanych w ramach naszej współpracy mają wymiar praktyczny i są wykorzystywane w dalszej działalność Impact Clean Power Technology. Współpracę z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej oceniamy bardzo wysoko i zamierzamy kontynuować dalsze działania badawcze.

Bartłomiej Kraś
Prezes Zarządu

4.12.	Corrosion failures of stack ducts
Research project ordering party	**Rybnik Power Plant, PGE Górnictwo i Energetyka Konwencjonalna S.A.**

Stacks are an indispensable element of the industrial landscape and are important elements of processes taking place in power plants, stabilizing the production system, and releasing exhaust gases at the appropriate height into the atmosphere. The stack can operate as a single element in a rectilinear system, as well as support a larger number of system units as a collective element. The primary role of the chimney is to transport as much air as possible to stimulate the combustion process by creating a draft and removing exhaust gases. There are many stack structures. However, from a corrosion standpoint, they share the form of the observed damage and its location. Corrosion processes were observed after the construction of the exhaust gas treatment installations. Photo 4.12 shows the forms of damage to the stack of the Rybnik Power Plant S.A.

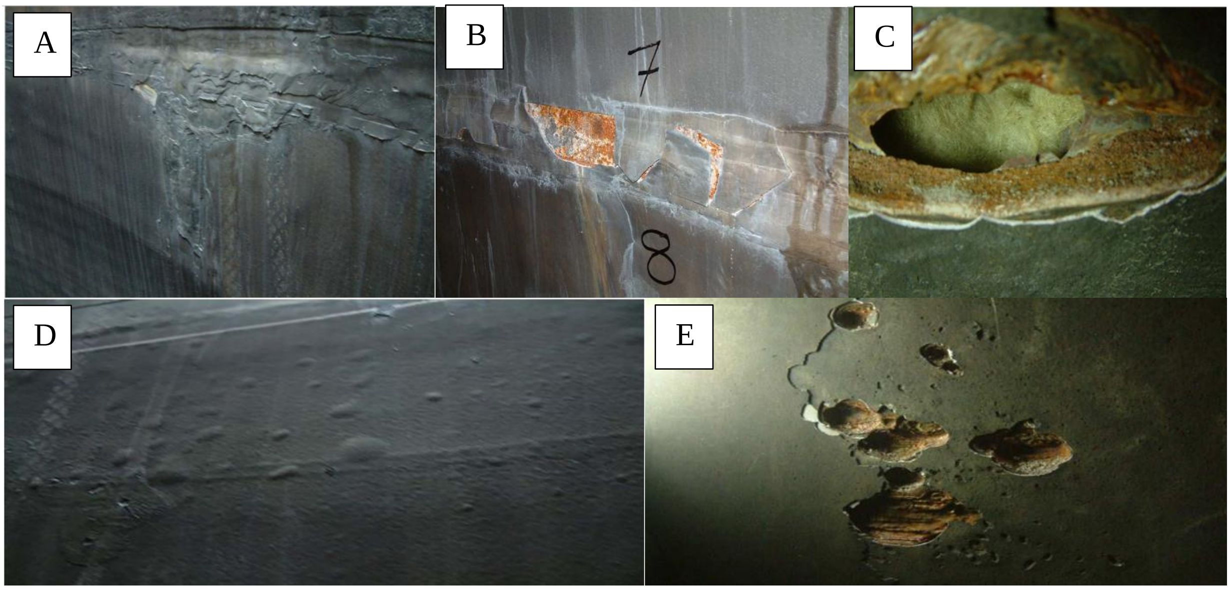

Photo. 4-12. (A) Coating protection at the connection of the two stack segments, (B) Disbonding of the protective coating on the stack walls, (C) Perforation of the internal stack wall, (D) Blistering of the coating on the stack duct walls, (E) Damage to the stack lining

Damage to the coatings began with the formation of blisters. Disbonding of anticorrosion coatings was observed. Places of stack ducts without protection suffered from serious corrosion damage. The importance of environmental protection made it necessary to introduce new technological solutions that reduced exhaust gas emissions into the atmosphere by the energy sector. To reduce emissions of such compounds as SO_2, HCl, HF, HBr, or nitrogen oxides, flue gas desulfurization installations were introduced, thanks to which it was possible to reduce the temperature of gases in the stack. Such exhaust gases are more aggressive to the structure than hot coal combustion exhaust gases. In addition to lower temperatures, the corrosivity of these exhaust gases is due to the higher moisture content and, in the case of desulphurized coal combustion exhaust gases, from the chlorine and fluorine content in the form of ions or HCl and HF acids. Within our research work, we selected new generation polymer linings for the protection of channels and ducts. We paid particular attention to the comparison of the values of the thermal expansion coefficients of the stack and duct structural material and the lining used. A decisive role in the selection of coating material was played not only by the chemical resistance of the resin, but also by the geometry of pigments and fillers. The flakes in the coating were arranged horizontally, overlapping so that almost impermeable layers were formed. The possibility of stress relief by using a flake filler, e.g., glass or hematite, was an important feature of the selected lining.

S. Krakowiak, K. Darowicki, Degradation of protective coatings in steel chimneys of flue gas desulfurisation systems, Progress in Organic Coatings, Volume 117, Pages 141 – 145 April 2018;

J. Bordzilowski, K. Darowicki, Anti-corrosion protection of chimneys and flue gas ducts, Anti-Corrosion Methods and Materials, Volume 45, Issue 6, Pages 388 – 396, 1998,
A.Miszczyk, K. Darowicki, Reliability of Flue Gas Desulphurisation Installations - The Essential Condition of Efficient Air Pollution Control, Polish Journal of Environmental Studies, Volume 11, Issue 3, Pages 205 – 2092002

4.13.	Diagnostics of brine-transporting pipelines
Research project ordering party	Research and Development Company 'HYDRO-POMP' Sp. z o.o.

The rock salt from the underground excavation is transported as a saturated aqueous solution through pipelines. In the opposite direction, water is forced into the excavation. The total length of both pipelines is approximately 30 kilometres. The transport pipeline routes are equipped with a system of inspection chambers visible in the photos and pumping stations. Ultimately, the caverns formed were to serve as underground locations for strategic reserves of energy carriers. Research has shown that storing crude oil in a salt environment for many years does not affect its properties, and in particular, does not reduce its quality. Such a raw material is as suitable for refinery processing as the raw material coming directly from the well.

Photo. 4-13. (A) Condition of exemplary inspection chamber, (B) Corrosion condition of the fittings (gate valve), (C) View of the surface parts of the transport pipelines

Due to the purpose of the caverns, we carried out a comprehensive, in-depth assessment of the condition of transmission installations and fittings intended for servicing the SOLINO ORLEN salt caverns. The client was the HYDRO-POMP company. The corrosive condition and functionality of the tested pipelines and fittings were assessed.

Corrosion processes were caused by brine leakage, high humidity in the inspection chambers, and insufficient anticorrosion protection. We have developed a digital map of the condition and progress of corrosion processes. The level of corrosion losses has been determined. Pipeline sections and inspection chambers particularly exposed to corrosion damage and brine leaks were identified. The selected parts of the installation were tested for the mechanical strength and expected lifetime. Construction material changes and appropriate anticorrosion protection technologies in the form of reinforced drainage and sacrificial anode protection were proposed. Permissible medium flow rates have been specified.

4.14. Diagnostics of cathodic protection systems on vessels of the Polish Navy

Research project ordering party	**Centre of Maritime Military Technologies** **Ośrodek Badawczo-Rozwojowy Centrum Techniki Morskiej S.A.** **(Research and Development Unit of the Maritime Technology Centre)**

Cathodic protection systems are implemented based on sacrificial anodes and/or impressed current installations. The cathodic protection system should provide sufficient and well-distributed currents on the steel surfaces of the ship's hull so that the surfaces can be polarized to potential within the limits specified by the protection criteria. The potential should be as uniform as possible so that the resulting field is homogeneous. In this way, the electromagnetic image of the immersed surface is minimized. This goal can only be achieved by appropriately distributing the protective current on the structure under normal operating conditions. Particular issues should be taken into account in areas such as water inlets and propellers.

The design of hull cathodic protection systems should take into account expected operating conditions, such as seawater characteristics (e.g., brackish/sweet water, temperature), expected average and maximum speeds, and service life associated with static (mooring) and dynamic (sailing) conditions. Exemplary photographs show vessels in dry dock during evaluation of the condition of electrochemical protection systems and one vessel mooring at the quay during test polarizations. An important work was the team's participation in the design of the cathodic protection system and electric field minimization system of the KORMORAN II special-purpose vessel. Field shaping consisted of an electrode array equalizing electrochemical potentials. At the same time, these electrodes were anodes in the cathodic protection system.

Photo. 4.14. (A) Submarine propeller, (B) Ship in dry dock; on the ship hull, there is a visible screen including the anode, (C) Warship at the quay during polarization tests.

A corrosion inspection of a number of Navy vessels was conducted at the order of the Centre of Maritime Military Technologies. The condition of electrochemical protection systems was assessed. An analysis of the effectiveness of cathodic protection was carried out, identifying failures of polarizing stations, damage to anodes, and reference electrodes. Damage to the cathodic protection stations resulted from improper use, and damage to the anodes was of an operational nature. Technologies were developed to repair screens in which anodes were embedded. The distribution of the electric field on the tested vessels was assessed. The electric field was optimized in accordance with the requirements and procedures of the Polish Navy and the Polish Register of Shipping.

Szanowny Panie Profesorze

Serdecznie dziękuję za wspólną współpracę przy realizacji elementów systemu ochrony katodowej na pierwszą jednostkę okrętu Kormoran II. Pracownicy Katedry Elektrochemii, Korozji i Inżynierii Materiałowej pod kierownictwem Pana Profesora Kazimierza Darowickiego przeprowadzili i przygotowali analizę przyśpieszonego zużycia anod pokrytych tlenkami mieszanymi tzw. MMO na podłożu tytanowym w celu określenia ich żywotności. Wysoko oceniam jakość przeprowadzonej analizy i jej wkład w prognozowanie żywotności elementów systemu ochrony katodowej oraz w badania jakościowe wyrobów OBR CTM S.A. Wieloletnia weryfikacja anod w warunkach rzeczywistych na okrętach potwierdziła poprawność i rzetelność wykonanej analizy przez Pana Profesora.

Łączę wyrazy szacunku,

Z poważaniem | Regards

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4.15.	Diagnostics and anticorrosion protection of fermentation chambers
Research project ordering party	**Gdańska Infrastruktura Wodno-Kanalizacyjna Sp. z o.o. (Gdańsk Water and Sewage Infrastructure)**

At the Gdańsk-Wschód sewage treatment plant, two types of sewage sludge are generated during the treatment process: pre-sludge and excess sludge. The sludge is subjected to processing, which results in a reduction in its volume, a change in composition, including a decrease in the content of organic substances, and biological stabilization. The pre-sludge is concentrated in the settling tank hoppers to a dry matter content of 4% and directed periodically to the pumping station and then to the mixed sludge tank. Excess sludge is directed to the wet well of the mixed sludge pumping station. Mixing with the pre-sludge takes place there. The mixed sludge is fed using screw pumps to Closed Fermentation Chambers, where the anaerobic mesophilic fermentation process occurs at temperature 37°C. The obtained biogas is used in a cogeneration installation (production of electricity and heat).

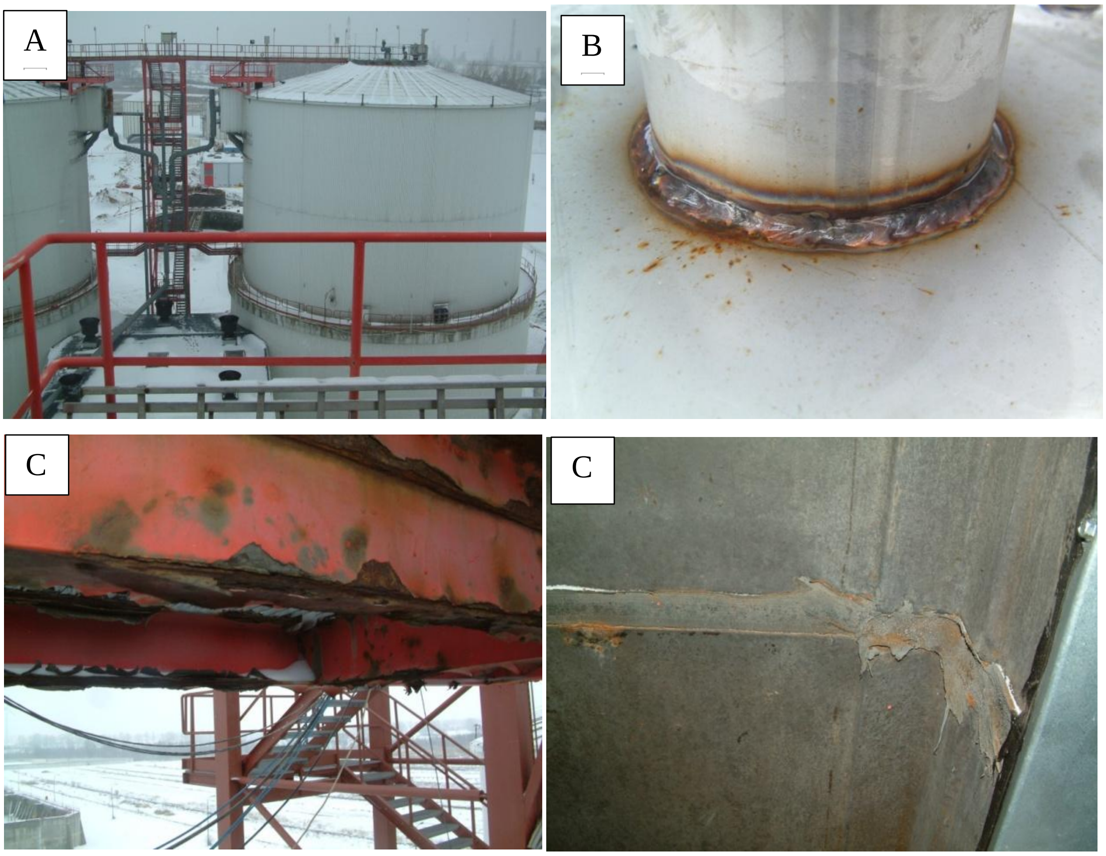

Photo. 4-15. (a) Fermentation tank, (B) View of weld cracking, (C) Corrosion damage to external parts of the installation

We found that as a result of technological processes taking place inside the tanks, anticorrosion coatings made of cobalt glass were degraded. At the same time, roof damage and tank leaks occurred.

The lack of experience with this type of protection has resulted in the need for detailed research.

Within the research project 'ANTICORROSION PROTECTION AND ELIMINATION OF GAS LEAKS OF CLOSED FERMENTATION CHAMBERS OF FACILITIES NO. 15.2, 15.3, AND 15.4 AT THE 'WSCHÓD' SEWAGE TREATMENT PLANT IN GDAŃSK' ordered by the Gdańsk Water and Sewage Infrastructure company, we have developed a technology for repairing mechanical damages. An anticorrosion protection method and technologies for repairing degraded cobalt glass linings have been developed. Repair and renovation works were conducted under the supervision of the Department's employees.

4.16.	Corrosion diagnostics of stainless steels in ozonation installation
Research project ordering party	**Miejskie Przedsiębiorstwo Wodno-Kanalizacyjne w WARSZAWIE Sp. z o.o. (Municipal Water and Sewage Company in Warsaw)**

The construction of an indirect ozonation station by the Municipal Water and Sewage Company in Warsaw consisted in the expansion of the existing technological line with two new systems, i.e., an indirect ozonation system and an activated carbon filtration system. After passing through the indirect aeration process, quick filtration, and coagulation, water is directed to the ozonation station. The ozonation process causes oxidation of organic substances, accompanied by their fragmentation. In this way, chlorine gas was completely eliminated, improving the taste of water. 316 L steel was used to build the ozonation station. It is a steel with very good anticorrosion properties, especially resistant to pitting corrosion. After half a year of operation, the user found many corrosion spots on the pipelines made of such highly corrosion-resistant steel. As a result, the Municipal Water and Sewage Company in Warsaw contracted us to conduct research aimed at 'DETERMINATION OF THE CAUSES OF CORROSION OF 316L STAINLESS STEEL IN OZONATION INSTALLATION'.

Photo. 4-16. Examples of corrosion damage to 316L steel localized in the vicinity of the welds in an ozonation station

After conducting laboratory corrosion tests of 316 steel in conditions simulating the operation of the ozonation installation, no susceptibility to corrosion was found. When evaluating the chromium concentration profiles in the projection perpendicular to the welds, a reduction in the content of this element was found in the areas adjacent to the weld. At the same time, electrochemical potential measurements were performed, which confirmed previous observations. This observation was also confirmed by metallographic and microscopic examinations. Investigations revealed the presence of chromium carbide $Cr_{23}C_6$ in the weld-neighbouring zones.

Reaction of carbon with chromium to form chromium carbide

$$23Cr + 6C = Cr_{23}C_6$$

leads to the depletion of the weld-neighbouring zone in free chromium, below 13%. As a consequence, this area undergoes depassivation and is subject to rapid corrosion processes as a result of a passive-active cell operation.

We have proven that the damage is the result of intergranular corrosion of 316L steel. We have shown that corrosion processes were caused by welding operations. The observed and documented damage resulted from sensitization of 316 L steel to intergranular corrosion. A very high rating of the research work has been granted by the client.

4.17.	Diagnostics and anticorrosion protection of discharge pipelines
Research project ordering party	Bełchatów Power Plant, PGE Górnictwo i Energetyka Konwencjonalna S.A.

Discharge pipelines evacuate water and steam from the power unit to the cooling tower. From this point of view, it is a critical element of the operation of the power plant. Previous tests and long-term service life indicated the risk of pipeline failures. Management of the Bełchatów Power Plant, in order to anticipate the potential threats of shutting down two power units, took the initiative to determine the actual condition and the risk of failures. Due to the potential serious hazard, research work involved significant responsibility.

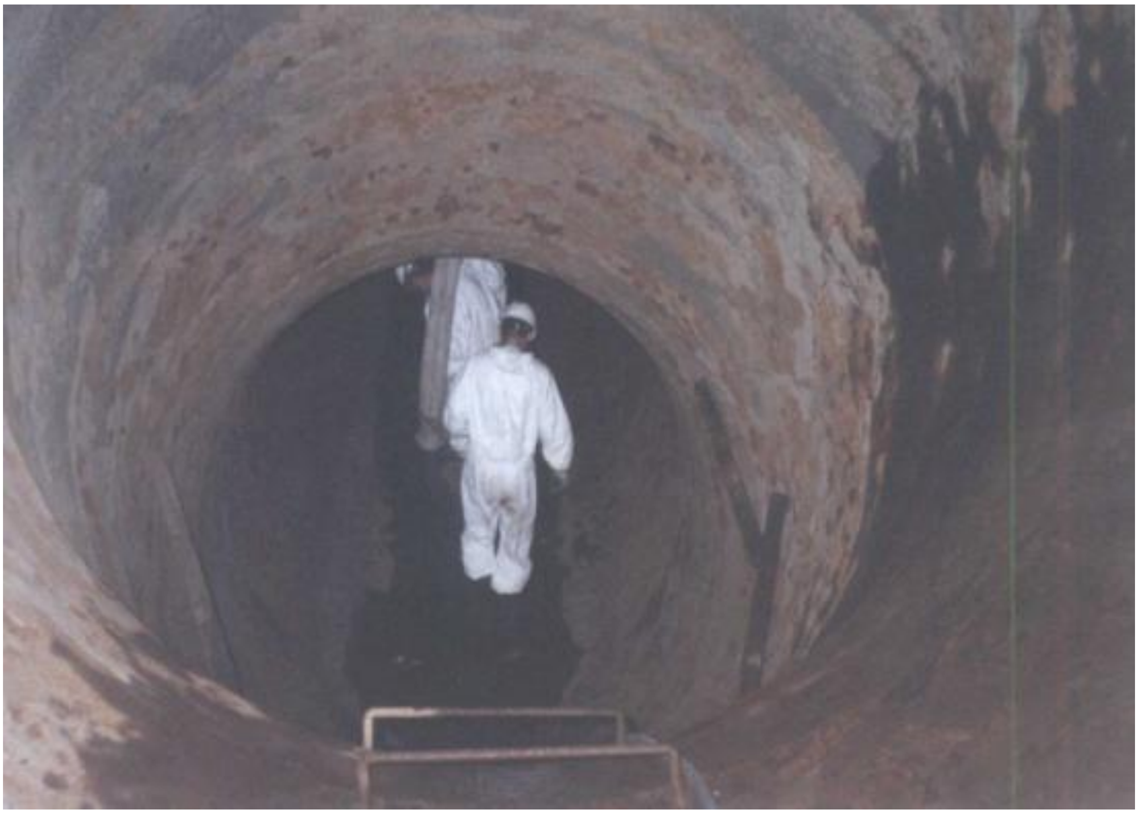

Fig. 4-17. Bełchatów Power Plant discharge pipeline and employees of the Department during corrosion inspection

Excluding the discharge pipeline from operation for the period of anticorrosion work would result in huge losses.

As part of the project ordered by the BOT Bełchatów Power Plant, we performed comprehensive laboratory corrosion tests in water collected from the Bełchatów Power Plant. Corrosion rate measurements were conducted using polarization methods. Additionally, we analysed the condition of the welds. We measured wall thickness along and around the perimeter of the pipeline.

We obtained a measurement grid for the thickness of the tested pipeline. We found uniform corrosion loss over the entire internal surface of the pipeline. We did not find areas particularly susceptible to corrosion.

One of the concepts of anticorrosion protection was the installation of a cathodic protection system. This solution implemented at the Łaziska Power Plant by the Department ensured the elimination of corrosion processes. We carried out a preliminary technical analysis of the cathodic protection system, thus verifying the validity of cathodic protection of the interior of the pipeline at the Bełchatów Power Plant. The corrosion condition of the pipeline, global and local mass losses, and the condition of the welds indicated the possibility of departure from the need to install a cathodic protection system. The corrosion rate of pipeline walls is limited by the rate of cathodic process, i.e., the oxygen reduction rate. Increasing the temperature limited the solubility of oxygen in water. The corrosion condition of the pipeline was assessed as satisfactory. This case was completely different from the situation at the Łaziska Power Plant. In the latter case, a cathodic protection system based on rope anodes has been developed. The design and implementation received a number of awards and medals.

4.18.	Corrosion diagnostics of the water tank on the Baltic Beta oil production platform
Research project ordering party	**Petrobaltic S.A.**

The Baltic Beta oil production platform extracts crude oil, natural gas, and water from the accumulation under the bottom of the Baltic Sea. At the initial stage, all three fluids are separated, and each of them is directed to a separate technological process. The installation responsible for the separation process is called GEOSERVICE. Crude oil is sent by underwater pipeline to a tanker moored near the oil production platform. Natural gas separated from crude oil is used on board Baltic Beta, among others, to produce electricity that powers the platform. The remaining gas is dried, filtered, and compressed, then sent via underwater pipeline to the power plant in Władysławowo. The formation water is treated and purified in the OIL PLUS installation and then reinjected into the oil accumulation.

There is also a seawater treatment and injection plant (BHPS) on board the platform, which is the subject of research and implementation. Water injection into an accumulation is a technological process that has been used in the exploitation of oil accumulations for years. During the exploitation of the accumulation, the reservoir pressure gradually decreases as the oil volume decreases. The effect of water injection is an increase in this pressure, so more oil can be extracted. In order to protect the environment of the Baltic Sea and meet stricter environmental requirements regarding a complete ban on dumping oily waters (including purified formation waters) directly into the sea, Lotos Petrobaltic decided to inject the extracted water back into the accumulation after appropriate treatment. This solution does not affect the marine environment and the accumulation layers from which oil is extracted. However, it affects the technical condition of the water injection installation. Fig. 4.18 A shows a scheme of the organization of oil extraction and transport.

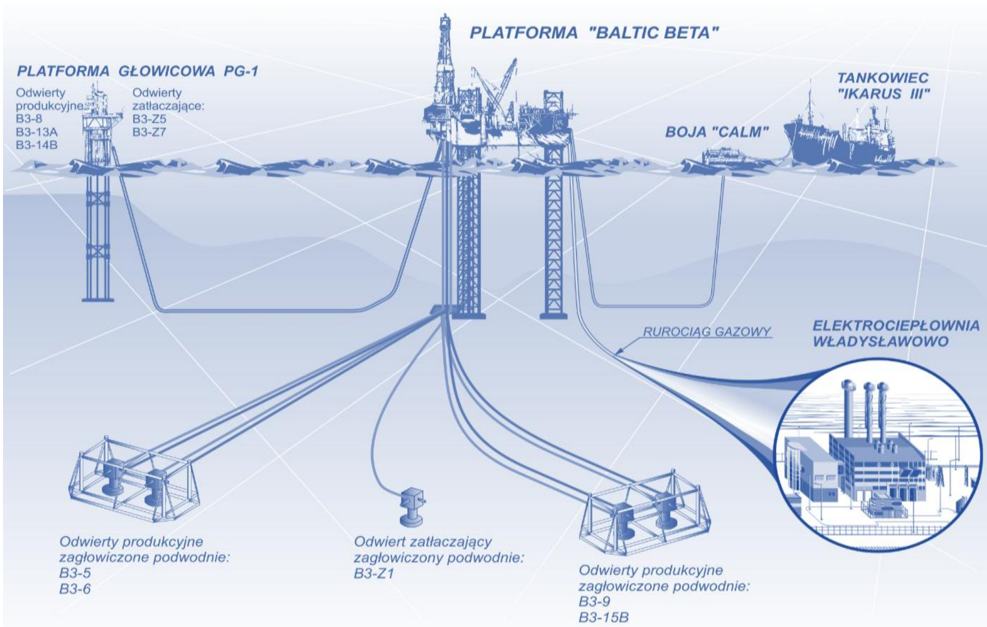

Fig. 4-18A. Illustrative production scheme of the Baltic Beta oil production platform

The water injection installation is one of the critical installations. Unfortunately, corrosion processes in the water injection installation result in the need for frequent replacement of pipeline sections, high repair costs, and, above all, deterioration of the quality of water injected into the accumulation. As part of the research work ordered by Petrobaltic, an inhibitor protection system and a coupled corrosion monitoring system were designed and implemented. Laboratory research allowed the development of optimal corrosion sensors.

Photo 4-18B presents a corrosion sensor installed through the lock into the tank. Photo 4-18C shows the installed data transmission system.

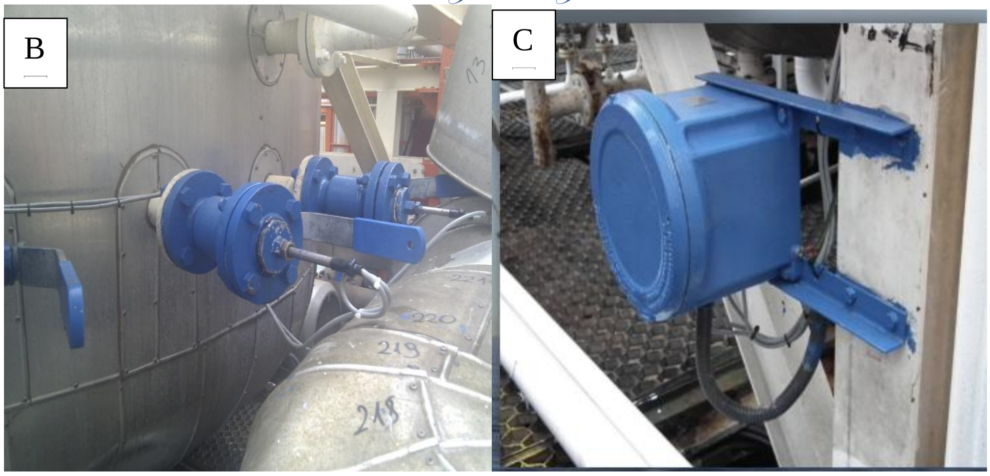

Photo. 4-18. (B) View of the mounted corrosion sensor (C) Measurement module

The effectiveness of the inhibitor is documented in Photos 4-18D-E.

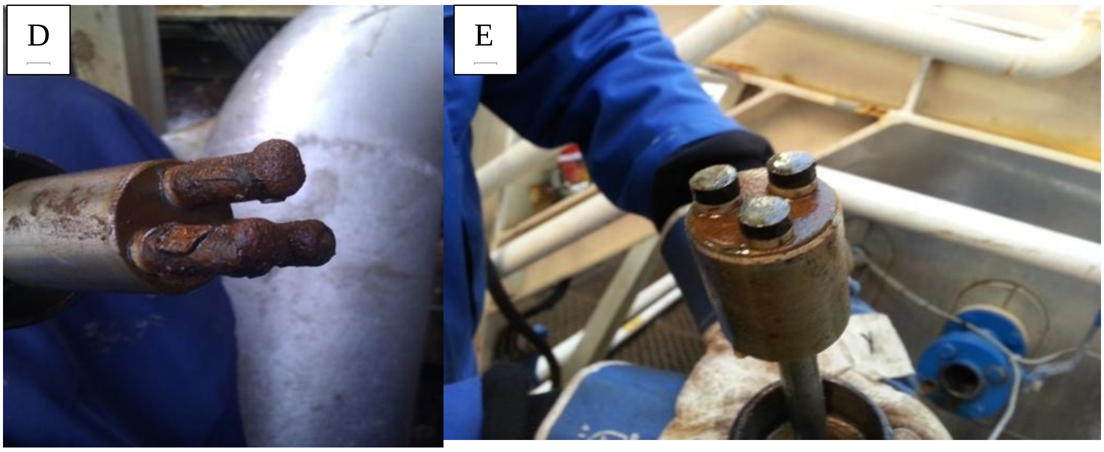

Photo. 4-18. (D) Corrosion sensor after one month of exposure in injected water without inhibitor, (E) Corrosion sensor after a three-month exposure in injected water with the addition of inhibitor

As part of the implementation, optimal, original corrosion sensors intended for particularly aggressive corrosive environments were designed, manufactured, and installed. The developed monitoring system is an automatic one operating in a continuous regime.

- The monitoring system allows online corrosion rate evaluation
- Corrosion rate measurements provide an unequivocal assessment of the effectiveness of the applied corrosion inhibitors
- Corrosion rate measurements ensure inhibitor dose optimization

The monitoring system is supervised by the Department staff.

The originality of this corrosion monitoring system, coupled with corrosion inhibitor protection technology, has been documented in the publication:

K. Domańska, P. Igliński, J. Orlikowski, K. Żakowski, K. Darowicki, Corrosion hazards and inhibitor protection in the seawater injection system on the Baltic sea rig, International Journal of Corrosion and Scale Inhibition, Volume 9, 2020 Pages:941-952

The proposed solution received a high rating from Petrobaltic S.A.

LOTOS Petrobaltic

Gdańsk, 02.07.2021

Współpraca LOTOS Petrobaltic z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej, Wydziału Chemicznego Politechniki Gdańskiej

LOTOS Petrobaltic od wielu lat współpracuje z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej, Wydziału Chemicznego Politechniki Gdańskiej. Współpraca dotyczy obszarów o strategicznym znaczeniu dla firmy.

Katedra w sposób ciągły nadzoruje stan korozyjny instalacji wody zatłaczającej wodę złożową do złoża ropy oraz stan korozyjny i integralność nóg konstrukcji nośnej wież platformy wydobywczej Baltic Beta. Prace te mają zasadnicze znaczenie dla utrzymania możliwości eksploatacyjnych wież wydobywczych i bezpieczeństwa pracy. Zaprojektowany oraz wdrożony system ochrony katodowej nóg platformy Baltic Beta, uzyskał akceptację Polskiego Rejestru Statków. Jego efektywność i funkcjonalność są monitorowane.

Podobnie zaprojektowano i wdrożono system monitorowania korozji zatłaczanej wody morskiej, który ze względu na strategiczne znaczenie, jest permanentnie nadzorowany przez pracowników katedry. Wdrożony monitoring pozwala wdrożyć środki zaradcze i tym samym utrzymać pożądaną jakość wody wtłaczanej do złoża ropy, w celu zwiększenia jej wydobycia. To z kolei zapewnia ochronę złoża oraz niezmienną, wysoką jakość naszego produktu końcowego jakim jest ropa.

BIURO EKSPLOATACJI I INŻYNIERII ZŁOŻOWEJ
WIODĄCY SPECJALISTA
Kinga Domańska

DYREKTOR
ds. WYDOBYCIA I WIERCEŃ
Krzysztof Kielas

4.19. Diagnostics and anticorrosion protection of fuel terminals and stations

Research project ordering party	KB Building Company Sp. z o.o. KOREKO Sp. z o.o., ORLEN Paliwa

Anticorrosion protection and monitoring of fuel stations is not only a matter of care for the environment, but also a matter of safety for people using these facilities. The rules of anticorrosion protection were collected in the regulation of the Minister of Economy on the technical conditions to be met by liquid fuel terminals, stations, and transmission pipelines. Journal of Laws 2014.0.1853

SECTION IV. Liquid fuel stations and container stations, Chapter 4. Storage tanks, technological equipment, and pipelines of liquid fuel stations
§ 113 Anticorrosion protection of underground tanks and technological pipelines of fuel stations

1. The external surfaces of underground steel tanks and technological pipelines of liquid fuel stations are protected against corrosion by using appropriate protective coatings.
2. If the tank or pipeline referred to in point 1, is exposed to an increased risk of corrosion due to the occurrence of stray currents or the presence of sulphate-reducing bacteria, appropriate cathodic protection systems should be used to eliminate this type of corrosion hazard.
3. The internal surfaces of the steel tank can be protected with a protective coating, which should meet the requirements specified in Polish Standards regarding the ability to discharge electrostatic charges.
4. Cathodic protection is not required to protect an underground steel tank or technological pipeline if the outer surface of the tank in contact with the soil has a coating, the tightness of which is monitored during operation.
5. A technological steel pipeline for which cathodic protection is used should have electrical continuity and be electrically isolated from objects that do not require protection and from all structures and elements with low resistance to the ground.

The effective operation of cathodic protection of steel surfaces of underground tanks at fuel stations, guaranteeing sufficiently long and reliable anticorrosion protection of steel walls of tanks contacting the ground, depends not only on the corrosion hazard from the soil (including soil resistivity, the presence of sulfate-reducing bacteria or the impact of stray currents), but also, and often primarily, on the proper installation of tanks and technological installations connected to them.

Photo. 4.19. (A) Fuel tank laid on plastic foil, (B) View of installed tanks of a fuel terminal

At the request of the Building Company S.A., cathodic protection design for two LOTOS fuel terminals was developed. In the first stage, the corrosion risk for the tanks was assessed. The need to replace the soil and install tanks on the polymer foil was determined. An analysis of the interactions of electromagnetic fields was carried out. Novel cathodic protection designs have been developed. Technological supervision of proper implementation was conducted. A pre-service assessment was performed, checking compliance with the cathodic protection criterion. Maintenance was carried out on the devices and installations of the cathodic protection system for the routes of underground product pipelines, as well as the devices and installations of the CP system of the Fuel Terminal No. 21 in Dębogórze.

Cathodic protection is a recommended method of anticorrosion protection of fuel tanks. So far, over 30 cathodic protection systems for fuel station tanks have been developed, mainly for ORLEN and LOTOS. Due to different locations, geological and corrosive conditions, each case was treated individually. However, it was not always technically justified to install cathodic protection systems. The photographs show fuel tanks protected by a 500 µm coating system placed in low corrosion-aggressiveness soil in a plastic foil insulation. We made decisions about the potential necessity of cathodic protection system installation based on tests of the corrosion aggressiveness of the soil and on the basis of measurements of the stray current hazard and the biocorrosion hazard. Additionally, we assessed the degradation resistance of coating systems used to protect tanks. In justified cases, due to the very low corrosion risk, we recommended waiving the installation of cathodic protection systems. However, in the case of the fuel terminal, a cathodic protection system was designed and implemented.

KB POMORZE

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Gdańsk, 14.04.2025r.

List referencyjny

KB Pomorze Sp. z o.o. potwierdza, że współpracowała z Katedrą Elektrochemii, Korozji i Inżynierii Materiałowej kierowaną przez prof. Kazimierza Darowickiego w zakresie ochrony przed korozją przy realizacji następujących projektów:

- Modernizacja i rozbudowa Bazy Paliw w Poznaniu - zadanie "pod klucz"
- Rozbudowa i modernizacja Terminala Paliw w Piotrkowie Trybunalskim – zadanie „pod klucz".

W ramach współpracy opracowano projekty ochrony katodowej, które zostały ocenione bardzo wysoko i w pełni wdrożone. Prace budowlane związane z instalacją systemów ochrony katodowej były nadzorowane przez pracowników Katedry.

Współpracę z zespołem prof. Kazimierza Darowickiego cenimy na najwyższym poziomie, szczególnie pod względem nowatorstwa, profesjonalizmu oraz zaangażowania.

WICEPREZES ZARZĄDU
Artur Woronko

KB POMORZE Sp. z o.o.
[illegible]

4.20.	Corrosion risk assessment due to high-voltage lines
Research project ordering party	Polskie Sieci Elektroenergetyczne S.A. ELTEL Networks Energetyka S.A.

Buried metal pipelines are used to transfer natural gas and petroleum products to residents. Sometimes these pipelines are built on the same path as overhead transmission lines. Interactions between pipelines and high-voltage transmission lines depend on several factors. This impact depends on the length of parallel sections of the transmission line and the pipeline. It also depends on the voltage and current of the transmission line and the distance between the pipelines and the transmission lines. The impacts depend on the type of coating covering the pipeline, its technical condition, and dielectric characteristics. Interactions between high-voltage transmission lines and underground structures are divided into three types: conductive coupling (during failure conditions), capacitive coupling, and inductive coupling.

Conductive coupling (resistive). Conductive coupling occurs when a short circuit occurs. When a short circuit takes place, the current from the power line flows to the ground. The short-circuit current must return to the source using available flow paths. This current flow increases the earth's potential near the structure, often to thousands of volts relative to the potential of distant earth. High voltage impact is destructive to coatings or other structures. This high voltage impacts the coating of neighbouring pipelines and can cause an electric arc that damages the coating or the structure itself. In addition, this large voltage difference may pose a risk of electric shock.

Electrostatic coupling (capacitive). Any two conductors separated by a dielectric material can be considered a capacitor. In our case, capacitive coupling occurs due to the presence of a ground pipeline located on an insulated base under an overhead transmission line. This case is common when a series of newly built pipes are laid and wait for welding. In this case, we have two capacitors connected in series. The first one is between the overhead power line and the pipeline, and the air acts as a dielectric material. The second capacitor is located between the pipeline and the ground. This situation is illustrated in Fig. 4-20A.

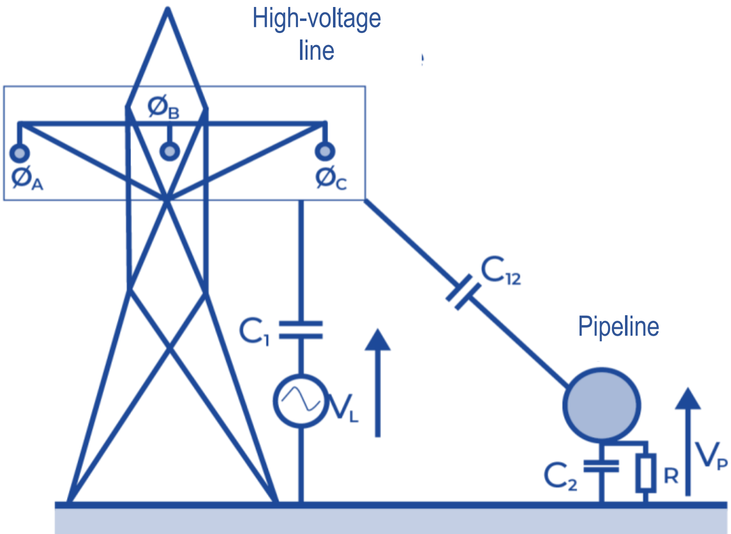


Fig. 4.20A. Capacitive coupling between the high-voltage line and the ground pipeline.

Inductive coupling. The stationary electrical conductor is a buried pipeline. A rotating magnetic field is generated by a power line. The presence of a rotating magnetic field induces a voltage in the pipeline. The magnitude of the induced voltage depends on several factors. The most important of them are: distance between the pipeline and the power line, exposure length (parallelism) between the pipeline and the power line, current magnitude of the power line, coating resistance of the buried pipeline, pipeline grounding, and soil resistivity. It should be noted that significant power is transferred to pipelines due to inductive coupling. The transmitted power can cause a current flow of tens or hundreds of amperes in a nearby area of the pipeline during peak operating conditions. It can even reach thousands of amperes in failure conditions. Potential peaks occur in places where sudden changes in parameters occur; this is the case in areas where pipelines and power lines deflect or intersect.

Inductive interaction is the most significant mechanism of AC current impact due to the risk of pipeline corrosion. The flow of alternating current in the power leads generates a variable magnetic field around these leads, which in turn induces a variable electric field in adjacent structures. Changes in the intensity of the electric field constitute an electric current. Its flow from the structure results in a characteristic form of damage.

Photo 4.20B. Image of damage as a result of the inductive interaction of a high-voltage line

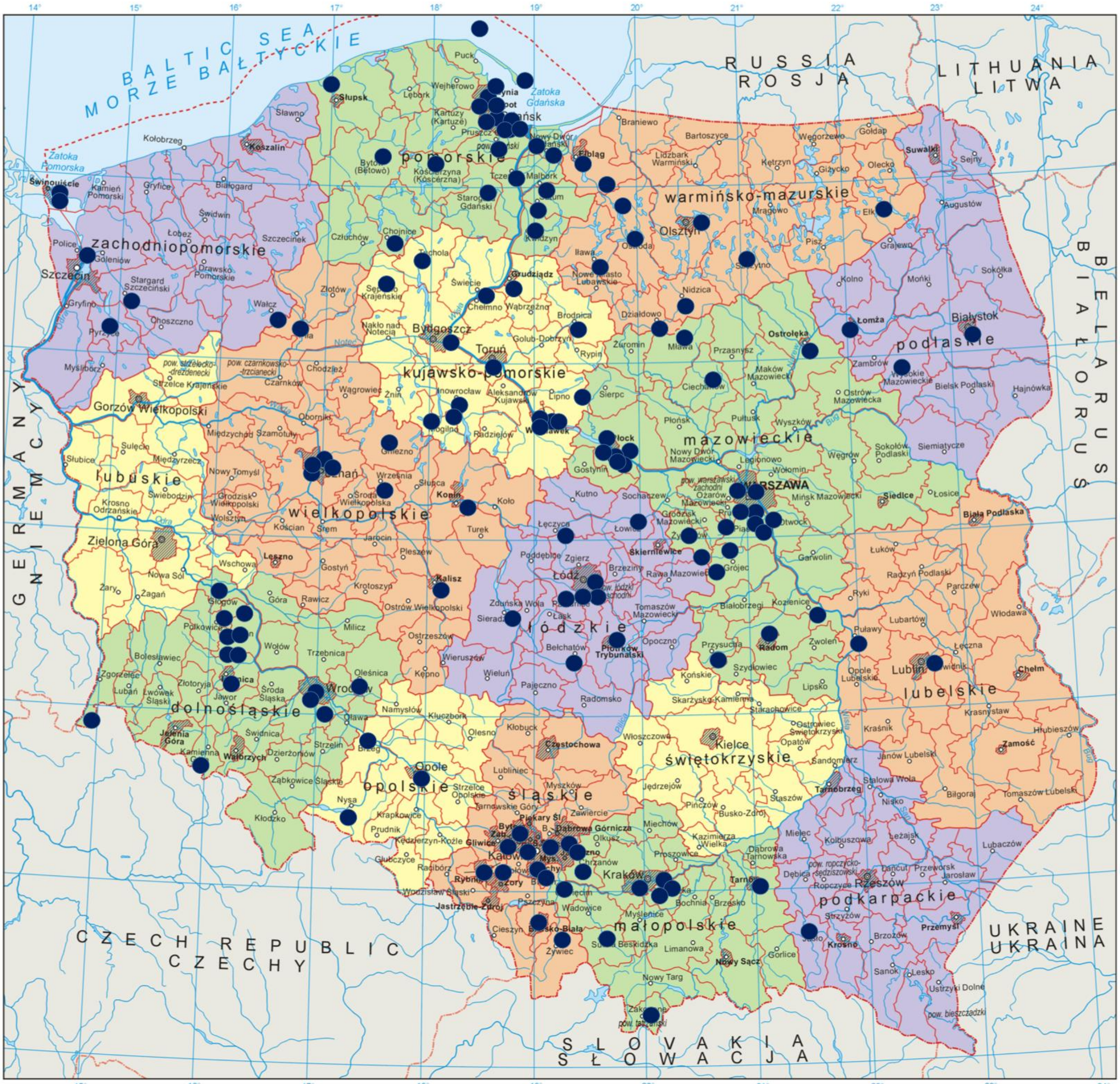
ELTEL Networks Energetyka S.A. ordered a research project involving calculations, analysis, and implementation of a protection regarding the impact of the designed WN 110 kV line on the DN500, DN450, and DN125 gas pipelines. The research included the analysis of continuous and short-circuit inductive interactions and galvanic interactions in terms of corrosion hazard and anti-shock safety. The calculations were made following the guidelines presented by the Gas Transmission Pipelines Operator GAZ-SYSTEM S.A.

Between 1996 and 1998, we cooperated with the Polskie Sieci Elektroenergetyczne S.A. We were commissioned with research work involving the assessment of the corrosion risk caused by the designed underwater high-voltage cable line (HVDC) between Sweden and Poland. The issue was complex due to existing urban layouts, local gas networks, as well as water and sewage networks. More information about the cable line and our research is available at the following homepage:

https://forumakademickie.pl/media/archiwum/98/1/artykuly/15-nauka.htm

The analysis concerned three potential locations of a power cable serving as a cathode in a single-lead system. Based on, among others, field measurements of changes in soil resistivity, calculations simulating the condition of the cable, analyses of impacts and potential threats, the Słupsk location was selected. The SwePol Link high-voltage direct current underwater cable line connects the Stärnö peninsula near Karlshamn in Sweden and the town of Wierzbięcin near Słupsk in Poland. Its length is 254.05 km, of which 238 km are under the seabed. It can conduct 600 MW of electricity at 450 kV.

5. MAP OF MAJOR IMPLEMENTATIONS AND EXPERTISE



Applied research and expert opinions were also conducted outside Poland, in countries such as: Germany, Estonia, Ireland, Canada and Lithuania

6. SUMMARY OF APPLIED RESEARCH

The most effective form of combating the destructive influence of corrosion processes is prevention. This activity must be supported by the development of awareness and knowledge about corrosion processes. In order to implement this remedial policy, I established the Department of Electrochemistry, Corrosion and Materials Engineering - a modern, one of the most important corrosion centres in Europe. There, I organized corrosion directions of study, postgraduate studies, and certified corrosion courses.

Based on specialized research staff, I undertook increasingly significant and complex applied research challenges. This activity, focused on cooperation with industry, was a continuation of the policy outlined by my predecessor as head of the department, Professor Romuald Juchniewicz. The corrosion problems we solved were, in many cases, of great importance in maintaining the production regime and reducing renovation shutdown periods. These issues were and are extremely important in the petroleum and petrochemical sector based on the ORLEN and LOTOS concerns. Corrosion monitoring in this sector also reduces failures and accidents that are extremely dangerous from the point of view of safety and environmental protection and, of course, involve financial losses. Anticorrosion protection of fuel terminals and stations is of similar importance. Efficient, reliable transmission of gas and oil is crucial for the development of companies and households.

We solved corrosion problems in the mining industry. Cathodic protection of production towers and water injection installations was of strategic importance for the crude oil extraction process. The corrosion risk assessment at the KGHM Ore Enrichment Plants resulted in anticorrosion protection of classifiers, hydrocyclones, ball mills, crushers, settlers, and other feed processing facilities. Corrosion monitoring of the discharge pipelines leading to the Żelazny Most reservoir was crucial. The created corrosion hazard atlas is currently a guideline in the selection of construction materials used in KGHM. Also in the energy sector, maintenance and anticorrosion protection of environmental installations is of fundamental importance. The efficient, continuous operation of flue gas desulfurization installations, electrostatic precipitators, and sewage treatment plants is of great pro-ecological importance. Just like maintenance and anticorrosion protection of discharge pipelines and stacks. The principles of coating protection of transmission power lines that we developed became the basis of the TAURON Company Standard.

We have always operated in the area of maritime economy. In the maritime industry, we dealt with anticorrosion protection of port installations, facilities, and quays, research and selection of coating systems for the protection of vessels. A separate issue was the modernization of cathodic protection systems and the minimization of the electromagnetic field of warships.

Municipal water systems are of great importance for the development of cities. We also made a significant contribution in this field by designing and implementing corrosion monitoring systems for municipal water installations in the Gdańsk and Kraków agglomerations. We solved the corrosion problems of the water ozonation station in Warsaw. We have designed effective anticorrosion protection of the Czerniaków water intake. Our corrosion tests of geothermal water installations were of significant importance.

We have documented anticorrosion achievements in the vegetable and fruit processing industry, in the brewing and dairy industries, diagnosing corrosion damage, and elaborating remedial measures.

The applied research and the implementations we made have defined our scientific position in various fields of the economy. In recognition of these achievements, the Board of the 'Pomeranian Employers' organization awarded me the 'Primum Cooperatio' ('Cooperation above all else') award for outstanding scientific activity combined with its documented implementation in the economy. The Main Board of the Polish Chemical Society awarded me the Ignacy Mościcki Medal for outstanding technological achievements of a global dimension. For all my implementation achievements, I was awarded the Knight's Cross of the Order of Polonia Restituta.

End of part three