INNOVATIVE CORROSION INHIBITOR FOR HYDROCARBON STREAMS IN REFINERY INDUSTRY AND OIL-FIELD APPLICATIONS

***Roman Kempiński*, Barbara Gaździk, Stefan Ptak, Kamil Pomykała, Michał Pajda.**
PACHEMTECH, Kobialka 7a,09-411 Płock, POLAND, office@pachemtech.eu,
Oil and Gas Institute- National Research Institute, Lubicz25A, 31-503 Krakow, POLAND, gazdzik@inig.pl

PACHEMTECH Company and Oil and Gas Institute-National Research Institute are conducting the Project "Innovative chemicals with the application of modified imidazoline for the refinery, oil, metallurgy and machinery industries", co-financed by The National Center for Research and Development, as part of the Applied Research Program. Innovative technology of corrosion inhibitor for use in oil-field industry (trade name Pachem-CWR-1011) and innovative corrosion inhibitor for refinery crude oil distillation units (trade name Pachem-CR-1012) have been developed as the result of the Project.

The phenomenon of corrosion is a serious problem, both in the oil production industry as well as during its processing in refineries. The produced crude oil is always accompanied by a stratal water. It contains inorganic salts, such as chlorides (of sodium, potassium, calcium, magnesium), sulphates (of sodium, potassium, magnesium) and carbonates. Electrochemical corrosion processes occur in solutions containing salts, caused by the action of galvanic cells, formed between a passivated metal surface and a surface that does not have such film [1].

Crude oil often contains even several percent of hydrogen sulphide, although crude oils containing more than a dozen percent of this compound are also known. Hydrogen sulphide when dissolved in water reduces its pH and causes very aggressive corrosion. Sulfide FeS and hydrogen H_2 are formed as a result of the hydrogen sulphide reaction with iron. Iron sulphide creates a coating on the metal surface which, in the first phase, inhibits "acidic" corrosion. However, even minor damage to the coating is the cause of intensive corrosion. “Acidic type” corrosion causes pitting and some hydrogen penetrates steel and becomes the cause of steel blisters and hydrogen embrittlement [2].

$$Fe^o + H_2S \rightarrow FeS + H_2$$

Large corrosive demage is caused by the presence of carbon dioxide during the production of crude oil. Corrosion caused by the presence of carbon dioxide is often called "neutral or sweet" corrosion. Carbon dioxide dissolved in water forms carbonic acid (H_2CO_3) that reacts with iron forming iron carbonate ($FeCO_3$) and hydrogen. A characteristic feature of corrosion caused by the presence of carbon dioxide are smoothed edges of the installation [3].

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 + Fe^o \rightarrow FeCO_3 + H_2$$

MIC (Microbiologically Induced Corrosion) is a process intensified by the action of bacteria, and the products of the bacterial metabolic transformations, such as hydrogen sulfide, organic and inorganic acids, cause corrosion and increase its rate. In oil mines, corrosion processes are caused mainly by the action of sulphate reducing bacteria (SRB) - the anoxic

Desulfovibrio Desulfuricans species, which multiply under anaerobic conditions in crude oil. These bacteria are the most active under the scale surface formed by sediment deposition. SRB bacteria cause the reduction of sulphate ions to hydrogen sulphide and/or sulphides according to the reaction [4]:

$$4Fe + SO_4^{2-} + 4H_2O = 3Fe(OH)_2 + FeS + 2OH^-$$

$$Fe^{2+} + H_2S = FeS + 2H^+$$

The corrosion rate in oil mines increases with the oxygen content in the system. It is also determined by the temperature and reaches a maximum at a temperature of about 70°C.

Corrosion rate can be from 1 to even several mm/year in oil/gas mines not protected by corrosion inhibitors. The reduction of the wall thickness of the installation apparatus and transfer pipes as well as deep pits (which can lead to leakage of the pipes and a strong decrease in their strength properties) are the effects of corrosive processes.

To prevent corrosion in oil mines, corrosion inhibitors are used. They are dosed continuously at typical rate of 10 - 50 ppm. It is assumed that proper corrosion protection should ensure a decrease in the corrosion rate of steel to the level below 100 micrometers/year.

Crude oil, after initial cleaning from deposits in the oil field, is delivered to the refinery. However, it still contains many impurities from the oil-field site, transportation pipes, reservoirs and other devices with which oil was in contact on its way to the refinery. These include mineral deposits, corrosion products, paraffins and asphaltenes.

The crude oil delivered to the refinery contains from 30 to 1500 mg/dm^3 of inorganic salts and 0.1-1.0% (v/v) of water. Salts derived from seawater contain 70-80% (m/m) NaCl, 10-20% (m/m) $MgCl_2$ and 10-20% (m/m) $CaCl_2$. Magnesium and calcium chlorides are responsible for the most intense corrosion during refinery oil processing.

The chlorides content in the crude oil supplied to Distillation Unit should not exceed 10 mg/dm^3 of oil, because it causes intense corrosion of the Unit, especially corrosion of top sections of the distillation columns.

The main corrosion factors at crude oil distillation units are acidic gases: H_2S and CO_2, inorganic acids: HCl, H_2SO_3, H_2SO_4, H_2CO_3 and organic naphthenic acids. High temperature of the process is the corrosion intensifying factor. Hydrocarbons containing water vapor, hydrogen chloride and hydrogen sulfide, are the most corrosive and cause intensive corrosion processes when leaving the distillation column at temperature of 120-130 °C [1.4 - 10].

Large corrosion damage in refineries is caused by the action of hydrogen chloride. Hydrogen chloride (HCl) is formed by the hydrolysis of calcium and magnesium chlorides during the heating up process of the crude oil or decomposition of organic chlorine compounds in the distillation of crude oil [9].

The effects of corrosion processes in the refinery include the Unit walls thickness reduction, deep pitting, and so-called steel bladder, hydrogen embrittlement, intergranular corrosion reducing the strength of construction materials and formation of deposits clogging heat exchangers, bundles of pipes, filters, pipes, valves and technological pipelines. Indirect effects of corrosion are necessity for earlier repairs of the installations, quality of distillates deterioration as well as increased pollution of the environment [8].

Corrosion prevention at crude oil distillation units (CDU) includes injection of the corrosion inhibitor as well as demulsifiers and acidic vapors neutralizers. Corrosion inhibitors are injected continuously to hydrocarbon streams at 5 to 20 mg/kg rate. It is assumed that proper corrosion protection should ensure the corrosion rate of steel below 0,11-0,25 [mm/year], the level of steel hydriding <0.2 [ppm H_2/month], and the sediments volume <2.0 [g/m^2/day].

PACHEM-CWR-1011 is a corrosion inhibitor for protection of crude oil mining equipment and pipelines transporting crude oil in oil and gas mines. It is a film forming-type corrosion inhibitor. It contains components forming a durable protective film on the surface of the installation, which prevents pitting and uniform corrosion.

<table>
<tr><th>Parameter</th><th>PACHEM-CWR-1011</th></tr>
<tr><td>Appearance, 20°C</td><td>clear liquid, amber color</td></tr>
<tr><td>Density, 20 °C , according to PN-EN ISO 12185</td><td>0,900-0,940 g/cm^3</td></tr>
<tr><td>Flash Point, according to PN-EN ISO 2719</td><td>+ 56°C</td></tr>
<tr><td>Pour Point, according to PN-ISO 3016</td><td>- 78 °C</td></tr>
<tr><td>Solubility</td><td>it dissolves in crude oil, in aromatic and aliphatic solvents , disperses in water</td></tr>
<tr><td colspan="2">Investigation of the tendency to form emulsions, according to ASTM G170
Test conditions: 90 % (v/v) crude oil and 10 % (v/v) stratal water , test temperature 50 °C</td></tr>
<tr><td>Separation below 30 seconds at 50 ppm treat rate.</td><td>complete phase separation for crude oil and stratal water, no interphase</td></tr>
<tr><td colspan="2">Wheel Test Method Used for Evaluation of Film-Persistent Corrosion Inhibitors for Oilfield Applications. According to NACE 1D182.
Test conditions: 50 % (v/v) crude oil 50 % (v/v) stratal water, saturated with CO_2 i H_2S; test bottles rotation speed 30 RPM; Sand blasted mild steel Shimstock plates; temperature 65°C, test duration 72 hours.</td></tr>
<tr><td>protection level at 15 ppm dosing</td><td>97,5 %</td></tr>
<tr><td>Corrosion rate at 15 ppm dosing</td><td>0,029 mm/year</td></tr>
</table>

- dosage: 5 - 25 ppm , continuously, based on the volume of crude oil and water;
- creates extremely durable films protecting against corrosion, it perfectly protects the installations against uniform and pitting corrosion;
- perfectly prevents the formation of emulsions of oil-stratal water;
- no foaming tendency;
- cost effective;
- Industrial tests of PACHEM-CWR-1011 at oil-gas mine, proved that even at low dosage below 15 mg/l of crude oil and water, corrosion rate was below 0,1 mm/year.

PACHEM-CR-1012 is the corrosion inhibitor for protection of refinery installations, especially crude oil distillation units (CDU).

The corrosion inhibitor PACHEM-CR-1012 protects the distillation columns, condensation systems and pipelines from corrosion by injecting into the vapor pipes and reflux pipes of distillation columns. PACHEM-CR-1012 is a film-forming corrosion inhibitor. It contains components forming a durable protective film on the surface of the installation, which prevents pitting and uniform corrosion. It is a mixture of corrosion inhibitors, amines and surfactants in hydrocarbon solvents.

Parameter	PACHEM-CR-1012
Appearance at 20°C	clear liquid, amber color
Density at 20°C, according to PN-EN ISO 12185	0,860 – 0,930
Flash Point, according to PN-EN ISO 2719	above + 25
Pour Point, according to PN-ISO 3016	below - 25
Solubility in crude gasoline from CDU, according to ASTM G170	clear solution, no sedimentation
Investigation of the tendency to form emulsions, according to ASTM G170 **Test conditions: 90 % (v/v) crude oil and 10 % (v/v) stratal water , test temperature 40 °C**	
Separation below 30 seconds at 50 ppm treat rate.	complete phase separation for crude gasoline and water, no interphase
Wheel Test Method Used for Evaluation of Film-Persistent Corrosion Inhibitors for Refinery Applications. According to NACE 1D182. Test conditions: 50 % (v/v) gasoline 50 % (v/v) water, saturated with CO_2 i H_2S; test bottles rotation speed 30 RPM; Sand blasted mild steel Shimstock plates; temperature 65°C, test duration 72 hours.	
protection level at 15 ppm dosing	96,2 %
Corrosion rate at 15 ppm dosing	0,03 mm/year

- dosage: 5-15 ppm, continuously, based on the volume of gasoline from (CDU);
- it is perfectly soluble in light hydrocarbon fractions, i.e. in raw gasoline from CDU; the solution is completely clear, suitable for long-term storage;
- it shows high anti-corrosive properties in relation to carbon and alloy steels, even at low dosing of the inhibitor from 5 -20 mg/liter,
- it creates extremely long-lasting films protecting the surfaces of distillation columns, condensation systems and pipelines against corrosion, perfectly protects CDU against uniform and pitting corrosion;
- perfectly protects against the formation of hydrocarbon emulsions with steam/water;
- no foaming tendency;
- raw gasoline, obtained at CDU column, is a clear liquid, with no water or impurities;
- the water condensate from the settler is a transparent liquid, without suspensions or sediments, with low Chemical Oxygen Demand (what is beneficial for environment);
- cost effective.
- The Distillation Unit industrial tests of PACHEM-CR-1012 proved that, even at low dosage below 15 mg/liter, corrosion rate below 0,1 mm/year and iron ions content in condensate below 0,01 mg/liter were obtained.

References:

[1] Baszkiewicz J., Kamiński M.: Korozja materiałów, OWPW, Warszawa, 2006.

[2] Stachowicz A.: Korozja rur wydobywczych odwiertów gazowych z zawartościa CO_2. Nafta-Gaz, 06, 2011, str.395-400.

[3] Reiss Ł., Toporowski R.: Korozyjne niszczenie metali w górnictwie naftowym wywołane siarkowodorem. Konferencja Naukowo-Techniczna, AGH, Kraków, 2-3 VII,1998 r.

[4] Arora Anshul, Pandey Siddharth Kumar: Przeglad materiałow zabezpieczajacych przed wystepowaniem korozji w przemysle naftowym. Rajiv Gandhi Institute of Petroleum Technology, Rae Bareli, Indie, 2012; na potrzeby prezentacji podczas Międzynarodowej Konferencji nt Korozji w Przemyśle Naftowym w Aberdeen, Wielka Brytania, 28-29 maj 2012.

[5] Chen Huey J., Hong T., Jepson W. P.: High temperature corrosion inhibition performance of imidazoline and amide, International Conferences CORROSION 2000, Houston, USA, 2000.

[6] Groysman A.: Zabezpieczenia antykorozyjne, zarzadzanie jakością i środowiskiem. Oil Refineries Ltd., P.O.Box 4, 31000 Hajfa, Izrael.

[7] Kuznetsov Yu. I., Vagapov R.K.: On Steel Protection with Volatile Corrosion Inhibitors in H_2S-Containing Media. Protection of Metals, 2000, vol.36, no.5, , pp 474-478.

[8] Papavinasam S.: Ocena i dobór inhibitorów korozji. CANMET Materials Technology Laboratory, Uhlig's Corrosion Handbook, Second Edition, Edited by R. Winston Revie, John Wiley & Sons, Inc., 2000, (67), pp. 1169-1178.

[9] Pawłowska B, Olszewska J.: Problemy korozji w rafinerii. [W:] Surygała J.: *Ropa naftowa: właściwości, przetwarzanie, produkty*", Vademecum rafinera. WNT, 2006; s. 540-560.

[10] Tishkevich L.F., Vartapetov A.S., Kamlyk A.S., Filippov N.G., Frolov K.I., Miklyasheva I.V.: Tests od Dodigen 481 Inhibitor in Corrosive Media at the Perm' Petroleum Refinery. Chemistry and Technology od Fuels and Oils, 1996, vol.32, no.1, pp 27-28.