CORROSION PROBLEMS IN PETROLEUM INDUSTRY AND THEIR SOLUTION

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Corrosion costs the oil industry billions of dollars a year. Corrosion affects every aspect of exploration and production, from offshore rigs to casing, and reviews the role of corrosion agents such as drilling and production fluids. Methods of control and techniques to monitor corrosion, along with an explanation of the chemical causes of corrosion are discussed.

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INTRODUCTION

Corrosion costs of the oil industry are billions of dollars in a year. Corrosion affects every aspect of exploration and production, from offshore rigs to casing. Methods of control and techniques to monitor corrosion, along with an explanation of the chemical causes of corrosion are discussed.

DISCUSSION

Corrosion in petroleum industry[1-3]

The Petroleum industry contains a wide variety of corrosive environments. Some of these are unique to this industry. Thus it is convenient to group all these environments together. Corrosion problems occur in the petroleum industry in at least three general areas: (1) production, (2) transportation and storage, and (3) refinery operations.

Production

Oil and gas fields consume a tremendous amount of iron and steel pipe, tubing, pumps, valves, and sucker rods. Leaks cause loss of oil and gas and also permit infiltration of water and silt, thus increasing corrosion damage. Saline water and sulphides are often present in oil and gas wells. Corrosion in wells occurs inside and outside the casing. Surface equipment is subject to atmospheric corrosion. In secondary recovery operations, water is pumped into the well to force up the oil.

Condensate wells

Condensate wells handle fluids (gas containing dissolved hydrocarbons) at pressures up to1,751,300 Nm. Depths run up to 4572 m Carbon dioxide is the chief corrosive agent, with organic acids contributing to the attack. Approximately 90 % of the corrosive condensate wells encounter conditions as follows: (1) depth greater than 1524 m, (2) bottom hole temperature above 71º C and pressure above 262,695 Nm (3) a carbon dioxide partial pressure above 2,626.95 Nm, an (4) a wellhead pH of less than 5.4.

Corrosion characteristics of a well are determined by (1) inspection of surface equipment, (2) analysis for carbon dioxide, organic acid, and iron, (3) coupon exposure tests, and (4) tubing-caliper surveys. Determination of iron content and tubing-caliper surveys are used to measure the effectiveness of inhibitor treatment.

Earlier practices involved addition of neutralizers such as ammonia, sodium carbonate, sodium hydroxide, and sodium silicate, but these were replaced in many cases by organic inhibitors, available in oil-soluble, water-dispersible, or water-soluble forms. In some applications, alloy steels have replaced the medium-carbon manganese steels (J-55 and N-80) previously used. Straight chromium and nickel on corrosion of steel by condensate-well fluid. Straight chromium stainless steels, Stellite, Monel, and copper-base alloys are commonly used for valves and other wellhead parts. Galvanic corrosion is apparently not a factor because substantial amounts of high-conductivity water are not present.

Sweet oil wells

It appears that corrosion in high-pressure flowing wells that produce pipeline oil has become almost commonplace in many areas. Three methods are used to combat this corrosion – coated tubing, inhibitors, and alloys. Coated tubing has found most favor, and until recently, backed-on phenolics have been used for almost all coating installations. Air-dried and baked epoxy resins are now being used in increasing amounts.

Sour oil wells these wells handle oil with higher sulfur contents than sweet wells and represent a more corrosive environment. In high H2S wells there may be severe attack on the casing in the upper part of the well where the space is filled with gas. Water vapor condenses in this area and picks up H_2S and CO_2.

Corrosion is reduced by inhibitors which are injected continuously or periodically depending on the well corrosivity.Offshore drilling Offshore drilling presents many interesting corrosion problems. Platforms are built over the water and supported by beam piles driven into the ocean floor. Each beam is surrounded by a pipe casing or protection. Similar platforms are used far out at sea for radar towers.

A variety of corrosion prevention methods are used in such structures. These include: (1) Adding inhibitors to the stagnant seawater between beams and casings, (2) Cathodic protection, with sacrificial anodes or impressed currents, of underwater structures, (3) Paints and other organic coatings to protect exposed structures above the splash zone, (4) Monel sheathing at the casing splash zone. This portion of offshore structures is the most susceptible to rapid corrosion.

Transportation and storage

Petroleum products are transported by tankers, pipelines, railway tank cars, and tank trucks. The outside submerged surfaces of tanks on the outside surface of underground pipeline s are protected with coatings and by using cathodic protection. Cathodic protection is also applied to the inside of tankers to prevent corrosion by seawater used for washing or ballast. Gasoline-carrying tankers present a more severe internal corrosion problem than oil tanks because the gasoline keeps the metal too clean. Oil leaves a film that affords some protection. Tank cars and tank trucks are coated on the outside for atmospheric corrosion.

The main reason for internal corrosion of storage tanks is the presence of water which settles and remains on the bottom. Coatings and cathodic protection are used. Alkaline sodium chromate (or sodium nitrate) has been found to be an effective inhibitor for corrosion of domestic fuel oil tanks.

Internal corrosion of product pipelines can be controlled with coatings and inhibitors (a few parts per million) such as amines and nitrites. Ingenious methods for coating pipelines in place underground have also been developed.

Refinery operations

Most of the corrosion difficulties in refineries are due to inorganics such as water, H_2S, CO_2, sulfuric acid, and sodium chloride, and not to the organics themselves. For this reason, the petroleum industry has much in common with the chemical industry.

Corrosive agents may be classified into two general categories: (1) those present in feedstock or crude oil, and (2) those associated with processes or control.

Water is usually present in crude oils, and complete removal is difficult. Water acts as an electrolyte and causes corrosion. It also tends to hydrolyze other materials, particularly chlorides, and thus forms an acidic environment.

Carbon dioxide has, in recent years, come to be recognized as one of the most important corrosive agents, especially in operations where gas is the feedstock, or raw material. Many gas wells produce large quantities of carbon dioxide.

Salt water is produced in most oil wells, and relatively large quantities of it get into the refinery, either in the water emulsified in the crude or in the crystalline form dispersed in the crude. The salts are calcium chloride, magnesium chloride, and sodium chloride. Desalting methods include washing and settling, addition of chemicals such as sulfonates to break the emulsion, centrifuging, and filtering. Salts and water are usually removed as quickly as possible, but the operations are frequently incomplete. If they are not removed, or only partially removed, hydrochloric acid often forms. Magnesium chloride is readily hydrolyzed. In this case, ammonia may be needed in amounts equivalent to three times the stoichiometric equivalent of sulphide and chloride ions.

Hydrogen sulphides, mercaptans, and other sulphur compounds are present in many of the crudes and gases processed by refineries. These are removed by reaction with sodium hydroxide, lime, iron oxide, or sodium carbonate, but for various reasons they are frequently not removed until the final operation is approached. Corrosion problems are associated with the refining process itself or with processes utilized to remove sulfur compounds.

Nitrogen is becoming an important consideration in some of the newer processes. Nitrogen is present in some crudes, but a more important source is the nitrogen in air. Large quantities of air are used in some of the burning operations associated with catalytic cracking processes. Ammonia and cyanides will form under certain conditions when nitrogen is present. The former can damage heat exchangers made of copper-bearing alloys. Cyanides are an important factor controlling the diffusion of hydrogen into steel.

Oxygen (or air) is drawn into tanks and other equipment as they are emptied, or enters during shutdown periods. It could also be drawn into the system by pumps. Oxygen can also be present as result of reactions of other compounds, such as water and carbon dioxide. The water used in the system often contains oxygen in solution.

Sulphuric acid is used in large quantities in many refinery operations such as alkylation and polymerization. The acid becomes contaminated and its corrosion characteristics may change. Utilization of this acid and its recovery or concentration presents corrosion problems that are extremely important to the refinery. For example, sludges often contain large quantities of carbon or carbonaceous material which make the acid strongly reducing in nature. These may attack stainless steels, and under the same conditions the copper-base alloys will give better performance.

Ammonia is used to control the pH of water and to reduce chloride acidity in the process streams. This procedure works well if the pH is 7, but is damaging to copper-bearing alloys if the pH is 8 or above. Ammonia is added to vapors in the process and also to condensers to neutralize acid condensate. It is desirable to add ammonia just before the aqueous phase forms.

Hydrochloric acid forms because of hydrolysis as described earlier. Sometimes it is an intentional addition to the process stream. This is fairly volatile acid so it is often present in distillation columns and also in the condensed petroleum fractions (hydrofluoric acid is used in one alkylation process).

Caustic (sodium hydroxide) and lime are sometimes added for hydrogen sulphide removal and for neutralization. Lime and caustic additions to the crude reduces the amount of HCl present in the overhead vapors. These chemical are dispersed in oil before adding to the stream for better mixing. Less than the theoretical additions are made to avoid an excess of alkali. Caustic sometimes causes deposits (and clogging) that are difficult to remove. It also causes stress corrosion.

Naphthenic acid, when present in oils, can be quite corrosive at 221 to 399 º C, and type 316 stainless is sometimes required as a constructional material. Substantial amounts of this acid are present in some oils. For less severe conditions 5 % Cr steel is satisfactory. Monel is used when temperatures are below 260 º C.

Polythionic acid causes rapid intergranular SCC of sensitized austenitic stainless steels in some refinery operations. Type 304 is susceptible. This attack is minimized if properly heat-treated (not sensitized) 304 or the low-carbon or stabilized types are used.

Refinery corrosion is sometimes separated into two classifications: (1) low-temperature corrosion and (2) high-temperature corrosion. The dividing point is usually 260 º C. Presumably, water can exist below 260 º C, and the mechanism of aqueous corrosion apply. The high-temperature mechanism takes over above260 º C. Perhaps another reason for the division at 260 º C is that ordinary carbon steel is economical for handling most crudes and naphthas up to this temperature, but alloy steels and other materials must be used at higher temperature. This is a general classification and should not be regarded as a strict division.

Such a classification is not entirely satisfactory, even if it applies directly for actual operating conditions at temperature. For example, high-temperature equipment is generally affected by water and other condensates that form when the equipment is shut down, when it is purged with steam or water, or when it is started up again. Many fail to recognize the effect of the conditions that exist when the equipment is not in operation – not only in refineries but in many other process industries as well.

Alloy used in refinery operations Ordinary carbon steel is by far the most important alloy, since it accounts for over 98 % of the construction materials used in the industry. As a general rule, every attempt should be made to use steel. This can be done by modifying the process in some manner such as lowering the temperature or adding inhibitors. Steel is the least expensive engineering metal aside from cast iron. In some cases, alloy steels are more economical because they have a longer service life, and they should be judiciously selected, where applicable.

Carbon steel is often unsuitable for heat-exchanger tubes because of corrosion by the cooling water. Brass, arsenical Admiralty Metal, red brass, and cupronickels are widely used. Austenic stainless steels are expensive and may crack in chloride-containing waters. These steels, however, are used for tubing in stills and gas-cracking tubes. In some cases, a single tower is lined with two or three different materials to take care of the changing corrosiveness from the top to the bottom of the tower.

Corrosion by sour crudes increases with temperature (increases rapidly around 800 F) and with increasing sulfur content. Chromium is the most beneficial alloying element in steel for resistance to sulfur compounds. Accordingly, the chromium content of steel is increased with increasing sulfur and temperature starting as low as 1% Cr. Experience indicates that 2.25% Cr, 1% Mo steel is generally adequate for less than 0.2% H2S in the gas stream. High sulphide contents require 5% Cr or higher. The Cr-Mo steel mentioned above and 4 to 6% Cr, 0.5% Mo steel are widely used in refineries.

In addition to the “naturally occurring” carbon dioxide, some severe problems have been encountered because of CO_2 injection or flooding to enhance recovery of oil. Two basic component s of the mechanism are consistent with actual experiment: (1) The main cathodic reaction is the reduction of undissociated carbonic acid or hydrogen ion, and (2) the expected high corrosion rates from the latter reaction are not achieved many systems because of the inhibiting effect of ferrous carbonate scale. The severe corrosion in amine-gas-treating systems occurs because the cathodic reaction involves carbonic acid, which comes from thermal decomposition of bicarbonate ion on heating surfaces.

Various inhibitors are used in petroleum industries in various stages. They are discussed in the following section.

A) Green Inhibitors

Green inhibitors in acid medium[4]

During acidizing stimulation or cleanup operations, metal tubulars, down hole tools/valves, surface lines, etc. are exposed to acidic fluids and are prone to corrosion. Because corrosion rates drastically increase in high-temperature wells, controlling corrosion is critical and must be dealt with carefully. In addition, corrosion protection is important for maintaining the integrity and long life of down hole tools installed in a well. Several corrosion inhibitors, such as quaternary ammonium compounds, propargyl alcohol-based compounds, etc., have been effectively used in the industry. However, because of stringent environmental regulations, attention has focused on the development of new corrosion inhibitors that are environmentally benign. Food-grade products that are considered "green" chemicals have significant potential as corrosion inhibitors in the oil and gas industry. Chicory has been used as a corrosion inhibitor for high-temperature and strong-acidic conditions. Chicory is a perennial bush plant available in many parts of the world. The root of the chicory plant can be roasted and ground for use as a coffee substitute or additive. Chicory is environmentally acceptable and, being of plant origin, is widely recognized as biodegradable in nature. It has been found that chicory can provide corrosion protection for alloys, such as N-80, 13Cr-L80, and 1010 steel, in the presence of either inorganic or organic acids at temperatures up to 121 °C. Considering its good performance, low price, and no toxicity issues, chicory has significant potential for acid corrosion-inhibition applications. The mixing procedure for preparing the blend, experimental setup and test procedure, and laboratory results of high-pressure/high-temperature (HP/HT) corrosion tests are well established.

Medicinal plants as green corrosion inhibitors[5]

Pipelines are the safest and most economical means of transporting oil and gas in offshore and onshore production facilities. Corrosion inhibitors continue to play a significant role in protecting the pipelines from internal corrosion. A number of corrosion inhibitors have been developed with low environmental impact without compromising on their inhibitor efficiency. Recently geographical location specific-regulations for several regions have been implemented. The most prominent of these are the environmental regulations far the North Sea (UK, Norway, Denmark, The Netherlands), US Gulf Coast, Eastern Canada etc. Taj et al., describe the investigations using aqueous extracts of leaves of medicinal plants A, B and C; and root of plant D as environmentally friendly corrosion inhibitors of mild steel in synthetic ocean water by weight loss method. These natural products were designed for application in Indian oil and gas industry and other environmentally sensitive platforms; exploiting their low toxicity-as medicinal plants and ease of biodegradation-as water soluble extracts. Aqueous extracts of plant materials A, B, C and D were investigated for Bioaccumulation. All the extracts exhibited low bioaccumulation and good corrosion protection. These preliminary investigations conducted to select green inhibitors revealed that aqueous extracts of C and D exhibited better corrosion performance than A and B. Weight loss studies results at 50ppm and l00 ppm in the absence and presence of Hydrogen sulphidede further support this fact. Taj et al., also give a brief overview of the principal criteria the inhibitor developers must follow to determine whether a given corrosion inhibitor is environmentally acceptable in a given region.

Polyglucosides as green corrosion inhibitors[6]

The chemical application of corrosion inhibitors is a widely adopted practice in production and processing operations in the oil and gas industry. Particularly challenging is the development of new chemistries, which maintain good protection of materials under a variety of conditions while being environmentally acceptable. Craddock et al., illustrate patented work in the chemistry of alkyl polyglucosides (APGs) and their synergistic effect with polyaspartates .They outline the development of this inhibitor class, which demonstrates good general inhibitor performance in a number of oilfield brines, shows good filming characteristics under conditions of shear, and also has an excellent environmental profile. The base chemistry of alkyl polyglucosides is explained. The effect of inhibitors in a number of sweet and sour conditions as well as under various temperature conditions in a variety of oilfield waters has been illustrated. The results of laboratory tests under these conditions, such as linear polarization resistivity (LPR) the so-called "bubble test," and the rotating cylinder electrode (RCE), are presented and discussed.

B) Biocidal Inhibitors

Microbial control strategies and treatments[7]

Worldwide, the production of natural gas and now oil from shale basins (source rock) has been embraced as a commercially viable way of producing unconventional energy resources leading to a revolution in gas production in the US. Developments to invest in and tap into this alternative way of gas production are taking off in Europe and Asia. Hydraulic fracturing is a proven technology, used for many years to develop hydrocarbon resources. Successful strategies with hydraulic fracturing include the safe and effective use of chemical additives, proper well casing and robust water management programs. During the exploitation of hydrocarbons from shales, chemical additives such as corrosion inhibitors, gelling agents, biocides etc, have to be used in the fracturing of wells. Sustainable chemistries and effective product stewardship programs are required to minimize environmental and human exposure hazards. The addition of water with organic molecules to the actual fractured wells makes these environments subject to unwanted growth of microorganisms and biofilm development, which has detrimental effects on hydrocarbon flow and leads to pipeline/equipment corrosion. Often the presence of sulfate reducing microorganisms leads to unwanted H_2S production and subsequently souring. Due to this, water cycle management and properly designed microbial control programs for all water sources including injected water or produced water, are required. Because the microbial challenges and environmental parameters of these water sources vary, different microbial control strategies and treatments are required for each source. New formulations of biocides and control programs aimed at the needs of the gas and oil industry have been developed, e.g. improved heat stability and the reduction in biocide levels to achieve the same level of microbial control.

Bactericidal inhibitor in oil wells of Azerbaijan[8]

At present, Caspian Sea water is injected for reservoir pressure maintenance for oil production in Azerbaijan. There are different groups of bacteria, sulfate ions and organic matter in this water. This leads to corrosion and the destruction of oil-gas field equipment. The injection of bactericidal inhibitor in wells is used for protecting oil-gas field equipment from corrosion and microbiological wear in offshore conditions. Results of sulfonated and neutralized products of catalytic cracking of gasoil fraction are known. These were investigated under both laboratory and field conditions. SNQF reagent is a mixture with properties of bactericidal inhibitor which efficiently resists anode and cathode reaction of steel. Also the SNGF reagent efficiency persists over 7 day later. Results of field testing and the availability of raw bactericidal inhibitor ensure recommending of the SNQF reagent for a wide range of application. Structures of the active species have been confirmed by analytical data. The synergistic corrosion inhibition by these species has been proved.

Estimation of onshore plant effluent concentrations[9]

When assessing environmental risks from industrial discharges it is a prerequisite to properly estimate concentrations of many chemicals in the discharge effluent. For many chemicals (e.g. hydrocarbons, metals) analytical methods are available and effluent concentrations can directly be measured. However, for many man-added, process chemicals (e.g. biocides, corrosion inhibitors) no analytical methods are available and concentrations need to be estimated based on the amounts used and physical chemical behavior of the components. For this purpose a designated model has been developed to be applied to oil refineries and terminals. The Onshore Plant Effluent Model (OPEM) estimates the annual average effluent volume and concentrations of chemical components in the discharged water from upstream oil plants. OPEM can be tailored to a specific facility by using a generic process diagram in which all relevant parts of the process can be included; creating a system that represents the facility that the model will be run for. To be able to run and provide accurate output, the model needs information including composition of each process chemical, physico-chemical properties, effect thresholds (i.e. PNECs) and basic toxicity data. This data is stored in databases that form an integrated part of OPEM. Another input for the model is the characterization of the inflows. Here a selection can be made from flows of oil with traces of water and chemicals from a specific field, flows of chemicals that are applied directly to the system and additional water flows like rain and drainage water. Finally, mass balance data must be entered, which represents a quantification of the inflows or chemicals used. OPEM uses dilution and mass balance equations to calculate the effluent concentration of each component in any part of the facility including the discharged effluent. For every chemical component OPEM produces a pie-chart presenting the origin of the component (where is it used and in which process chemicals). Even though developed for upstream oil industry, OPEM is a generic model that can be used for complex effluent concentration calculations for any process facility. Estimated effluent concentrations of chemical components together with the information on the origin of the components are an important input for environmental risk management.

Potential of Bacillus strain B21 as a biocontrol agent to fight corrosion in the oil industry[10]

The role of the antagonistic potential of nonpathogenic strain B21 against sulfate-reducing bacteria (SRB) consortium has been enlightened. The inhibitor effects of strain B21 were compared with those of the chemical biocide tetrakishydroxymethylphosphonium sulfate (THPS), generally used in the petroleum industry. The biological inhibitor exhibited much better and effective performance. Growth of SRB in coculture with bacteria strain B21 antagonist exhibited decline in SRB growth, reduction in production of sulphides, with consumption of sulfate. The observed effect seems more important in comparison with the effect caused by the tested biocide (THPS). Strain B21, a dominant facultative aerobic species, has salt growth requirement always above 5% (w/v) salts with optimal concentration of 10-15%. Phylogenetic analysis based on partial 16S rRNA gene sequences showed that strain B21 is a member of the genus Bacillus, being most closely related to Bacillus qingdaonensis DQ115802 (94.0% sequence similarity), Bacillus aidingensis DQ504377 (94.0%), and Bacillus salarius AY667494 (92.2%). Comparative analysis of partial 16S rRNA gene sequence data plus physiological, biochemical, and phenotypic features of the novel isolate and related species of Bacillus indicated that strain B21 may represent a novel species within the genus Bacillus, named Bacillus sp. (EMBL, FR671419). The application potential of Bacillus strain B21 as a biocontrol agent to fight corrosion in the oil industry has been established.

Sulphite-reducing bacteria corrosion risk in oil fields[11]

Sulphite-reducing bacteria are generally considered to have a profound impact on the petroleum industry as their sulphide production activity contributes to reservoir souring and pipeline corrosion. SRB can be controlled by injecting biocides into pipelines and above-ground facilities. A recent "green" alternative for controlling reservoir souring is to inject nitrate, as nitrate is relatively harmless and is ultimately reduced to nitrogen gas. Resident nitrate-reducing bacteria (NRB) reduce nitrate to nitrite, which is a strong inhibitor of SRB, thereby inhibiting sulphide production. However, NRB-mediated oxidation of sulphide with nitrate and/or chemical reaction between nitrite and sulphide can generate sulphur-polysulphide (S-PS), which can expedite corrosion. S-PS is also rapidly formed by chemical reactions, when sour produced waters, containing substantial sulphide concentrations, are exposed to air. Once formed, S-PS can be removed by either of two alternative routes, which may thus reduce corrosion risk. In the presence of (i) excess electron acceptor (e.g. nitrate), NRB may further oxidize the S-PS to sulphite, whereas in the presence of (ii) excess electron donor (oil organics, e.g. acetate) the S-PS may be reduced back to sulphide. A specialized group of sulphur-reducing bacteria catalyzes this reaction. A representative of this group, *Desulfuromonas acetoxidans*, derives energy for growth from the reaction: 4 sulphur + acetate = 4 sulphide + 2CO_2. Because oil field waters tend to be electron donor rich and electron acceptor poor, one would expect S-PS to be removed by the second route. A survey of the microbial community in produced waters from an oil field with low bottom hole temperatures indicated *Desulfuromonas* species to be common. Hence, once S-PS is formed by reaction of excess sulphide with a limiting concentration of nitrate or oxygen, it may subsequently be effectively removed through the activity of sulfur-reducing bacteria such as *Desulfuromonas*.

Fouling of pipelines[12]

Naphthenic acids (NAs) are partially uncharacterised complex mixtures of carboxylic acids, resulting from the microbial oxidation of petroleum hydrocarbons. They are associated with the fouling of pipelines and process equipment in oil production and with corrosion in oil refineries. As byproducts of the rapidly expanding oil (tar) sands industries, NAs are also pollutants and have proved to be toxic to a range of organisms. They also have important beneficial uses as fungicides, tyre additives and, paradoxically, also in the manufacture of corrosion inhibitors. These features make the characterization of NAs an important goal for analytical chemists. Here we describe the synthesis of amide derivatives of NAs for characterization by liquid chromatography/ electrospray ionization multistage mass spectrometry (LC/ESI-MS-n). The method was applied to commercially available carboxylic acids, novel synthetic NAs, commercial NAs refined from crude oils, crude oil NAs and Athabasca oil sands NAs. In addition to confirming the number of alicyclic rings and length of alkyl side chain substituents (confirming information from existing methods), the MS n results provided further structural information. Most important of these was the finding that bi- to polycyclic acids containing ethanoate side chains, in addition to alkyl substituents, were widespread amongst the oil and oil sands NAs. The latter NAs are known end members of the ?-oxidation of NAs with even carbon number alkanoate chains. Since such NA mixtures are toxic, they should be targets for bioremediation. Bioremediation of NAs can also be monitored better by application of the methods described herein.

C) Inhibitors for biological corrosion[13]

The sulfate-reducing bacteria growth kinetics and the biotransformation of sulfate into hydrogen sulphide were studied under laboratory conditions, using batch and continuous assays to determine the effect of molybdate and nitrate as metabolic inhibitors. The microorganisms were isolated from water coming from a natural gas dehydration plant, where they were associated with Microbiologically Influenced Corrosion (MIC) processes, and later cultured in plank tonic and sessile states. The addition of 5 mM molybdate showed a growth reduction to levels of non - detectable floating cells and a six order of magnitude reduction in biofilms, concomitant with a sulphide decrease of around 100% in all cultures inhibited by this compound. The addition of 75 mM nitrate showed a four order of magnitude reduction in free bacterial cells and a two order of magnitude reduction in adhered bacterial cells, respectively, as well as a sulphide decrease of around 80%. The decreased corrosion rate detected suggests that these inorganic salts could be nonconventional biocides for an effective and environmentally non contaminant way of controlling and mitigating internal biocorrosion processes in storage tanks and pipelines in natural gas and petroleum industrial systems.

D) Others

Inhibition of corrosion of carbon steel in H_2S containing medium[14]

Understanding and controlling hydrogen sulphide (H_2S) corrosion becomes increasingly important in the petroleum industry. Iron sulphide is formed on the internal pipeline surface as a corrosion product of carbon steel in an environment containing H_2S. Some of the iron sulphide particles are suspended in the liquid phase or deposited at the bottom of a pipeline. Iron sulphide decreases the corrosion inhibition efficiency due to the adsorption of corrosion inhibitor on the surface of iron sulphide particles. The effect of iron sulphide on the efficiency of a corrosion inhibitor in a highly sour environment and to explore effective technical methodologies to study H_2S corrosion and inhibition has been investigated. Experiments have been performed in a series of autoclaves with a total pressure of 896 kPa (538 kPa CO_2 290 kPa H_2S, and 69 kPa water vapor). Iron sulphide effects were studied separately in two different cases: directly deposited on the steel surface or suspended in the test solution. In the experiments, weight loss was applied to study the corrosion inhibition efficiency. Corrosion product films/scales formed on the surface of the steel were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX).

Carbon steel wet gas pipeline in Thailand[15]

As a primary energy source, natural gas continues to play a major role in meeting Thailand's energy requirements and is preferred for generating the country's electricity. As energy demand increases, a fully integrated pipeline integrity program for wet gas pipelines becomes necessary to ensure safe production from Thailand's gas fields. Corrosion mitigation and monitoring strategies implemented on a 63.5 km (40 mile) long, 385 mm (15.2 in) maximum internal diameter, carbon steel wet gas pipeline. The pipeline is in Khon Kaen Province, located northeast of central Thailand. Extensive pre-startup analysis was conducted, such as pipeline dynamic flow modeling and corrosion prediction modeling, from which the final corrosion management strategy was derived. Advanced corrosion measurement tools have been developed for continuous data collection, such as high-resolution metal loss probes and high-sensitivity ultrasonic wall thickness transducers. Performance data have been collected. Key performance indicators for corrosion control, including hydrogen sulphide measurements, iron counts, corrosion inhibitor residuals, and sulfate reducing bacteria, along with pipe wall corrosion measurements and cathodic protection potentials, are also considered. Recent in-line inspection data has been used to correlate the continuous monitoring data collected over the last several years with the recorded pipeline condition to evaluate the effectiveness of the corrosion management program.

Polyacrylamide based polymers as efficient corrosion inhibitors for carbon steel[16]

Owing to superior properties such as temperature resistance and salt tolerance etc., modified polyacrylamide (PAM) as one of the main injected polymers has been widely investigated to enhance oil production in reservoirs. A novel poly(AM-co-A-β-CD-co-AE) polymer was synthesized by utilizing β-CD and AE to copolymerize with AM and characterized by FT-IR and SEM. Furthermore, the temperature resistance and salt tolerance of poly(AM-co-A-β-CD-co-AE) polymer were explored. It is observed that the presence of the poly(AM-co-A-β-CD-co-AE) polymer better achieved temperature resistance and salt tolerance properties than is the case with PAM, which has potential application for enhancing oil recovery in the high-temperature and high-mineralization oilfield. On the other hand, the inhibition performance of poly(AM-co-A-β-CD-co-AE) polymer as corrosion inhibitor was evaluated by SEM and electrochemical techniques. SEM observations of the carbon steel surface confirmed the protective role of the corrosion inhibitor. The results of potentiodynamic polarization and EIS measurements on the corrosion inhibition of carbon steel samples in 0.5 M sulfuric acid solutions revealed that the highest inhibition efficiency of it over 90 % was obtained, indicating poly(AM-co-A-β-CD-co-AE) polymer acts as a more efficient corrosion inhibitor for carbon steel.

Nontoxic corrosion inhibitors for N80 steel in hydrochloric acid[17]

The protective ability of 1-(2-aminoethyl)-2-oleylimidazoline (AEOI) and 1-(2-oleylamidoethyl)-2-oleylimidazoline (OAEOI) as corrosion inhibitors for N80 steel in 15% hydrochloric acid has been evaluated. This may find application as eco-friendly corrosion inhibitors in acidizing processes in petroleum industry. Different concentrations of synthesized inhibitors AEOI and OAEOI were added to the test solution (15 % HCl) and the corrosion inhibition of N80 steel in hydrochloric acid medium containing inhibitors was tested by weight loss, potentiodynamic polarization and AC impedance measurements. Influence of temperature (298-323 K) on the inhibition behavior was studied. Surface studies were performed by using FTIR spectra and SEM. Both the inhibitors, AEOI and OAEOI at 150 ppm concentration show maximum efficiency 90.26% and 96.23 %, respectively at 298 K in 15 % HCl solution. Both the inhibitors act as mixed corrosion inhibitors. The adsorption of the corrosion inhibitors at the surface of N80 steel is the root cause of corrosion inhibition.

Environmentally friendly calcium carbonate scale inhibitor for high temperature and high pressure (HTHP) wells[18]

The formation of calcium carbonate mineral scale is a persistent and expensive problem in oil and gas production, especially in the high temperature and high pressure (HTHP) wells. Scaling of metallic or insulating walls in contact with hard water may cause unscheduled equipment shutdown and loss of production. Environmentally friendly calcium carbonate scale inhibitors have been developed for HTHP squeeze application in the oil and gas field water treatment. Typical commercial scale inhibitors, including several phosphonate based squeeze scale inhibitors and patented environmentally friendly polyacrylic copolymers have been tested based on thermally stability test, formation water compatibility test, dynamic scale loop test and core flood test. In this paper, an environmentally friendly calcium carbonate scale inhibitor has been developed to inhibit calcium carbonate scale deposition effectively under HTHP conditions. The characteristics of this product are as following:

•Thermally stable at high temperature.

•Excellent calcium tolerance at high temperature.

•Good inhibition performance on $CaCO_3$ deposition at high temperature.

•Long squeeze life and no formation damage based on core flood test.

•Environmentally friendly.

•Easy residual analysis by ICP, HPLC and hyamine methods.

This paper will gives a comprehensive study of developing environmentally friendly calcium carbonate scale inhibitors for squeeze application for HTHP wells in the oil and gas fields, which includes thermally stability, dynamic scale loop performance, adsorption and desorption performance, compatibility, residual analysis and environmental regulation.

Corrosion inhibitor and kinetic hydrate inhibitor for the pearl GTL project[19]

PEARL GTL (Gas to Liquids) project is a fully integrated project that will take 1.6 billion cubic feet per day of unprocessed gas from Qatar's North field into onshore gas processing plants, producing 140,000 barrels per day of GTL products and 120,000 barrels per day of natural gas liquids. There will be no processing facilities on the two offshore platforms - all produced fluids will be transported to shore via the main pipelines for treatment. The gas contains H_2S and CO_2 and is consequently corrosive so continuous injection of corrosion inhibitor into the pipelines is necessary. Sea bottom temperatures can be below hydrate formation temperature so it is necessary for part of the year to also inject kinetic hydrate inhibitor into the inlet of the pipeline to avoid hydrate formation. The challenging combination of highly corrosive conditions, minimal offshore intervention and very high plant uptime requirements means that corrosion control and flow assurance of the highest effectiveness is required.

CONCLUSION

Corrosion cost of the soil industry is very high. Oil industry faces corrosion problems at various stages, including oil wells, transportation, storage and refinery operations. Various inhibitors- organic and inorganic have been used to prevent corrosion in petroleum industry. Recently, green inhibitors and biocidal inhibitors have gained momentum in this area.

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