Acrolein Provides Benefits and Solutions to Offshore Oilfield-Production Problems


Summary

Offshore production systems can be impacted negatively by numerous problems attributed to bacterial activity, associated hydrogen sulfide (H$_2$S) and biogenic iron sulfides (Fe$_x$S$_y$), and mercaptan (R-SH) production. Examples of these problems include microbiologically influenced corrosion (MIC); underdeposit corrosion because of Fe$_x$S$_y$ deposition; equipment fouling because of biomass accumulation; impaired oil/water separation, leading to poor water quality and overboard oil-in-water problems; and not achieving pipeline specification because of excess H$_2$O and/or R-SH content.

Acrolein provides a distinctive all-in-one chemical solution to assist in resolving these problems. The key to this solution is four-fold: Acrolein scavenges H$_2$S, it scavenges R-SH, it is a potent microbiocide, and it dissolves Fe$_x$S$_y$.

This paper details the use of acrolein in the context of an offshore application with respect to the issues and problems unique to an offshore environment. Acrolein treatment programs can provide effective production-odor control and can achieve pipeline specifications from the perspective of H$_2$S and R-SH scavenging. The unique dual solubility of acrolein in oil and water enables it to penetrate and remove oil-coated Fe$_x$S$_y$ solids and sessile bacteria from production systems. Because of its low minimum-inhibitory concentration, acrolein provides cost-effective biocide treatment not only in batch applications but also in continuous-treatment programs. Well-established application protocols using a closed delivery system minimize potential chemical exposure, an important health, safety, and environment (HSE) consideration. The high order of reactivity and biodegradability of acrolein lends itself well to usage in a sensitive offshore environment.

A series of case histories highlighting the benefits of using acrolein in offshore systems to mitigate related production problems is presented in this paper. Multiple benefits can be realized with the application of one product.

Introduction

The efficient operation of oil-production systems can be impaired by numerous detrimental factors. These include excessive bacterial activity, sulfide generation, and R-SH production. Any of these contaminants either alone or in conjunction with one another can cause multiple problems, including production- and injection-pipeline corrosion and failure, separation-equipment fouling and impairment of operation, near-wellbore fouling and plugging, and serious risk to both the environment and operations personnel. In addition, production of excess sulfides (i.e., H$_2$S) and R-SH can force operators to shut in production, resulting in significant deferred production costs. Pipeline and/or equipment failures resulting from corrosion can have serious repercussions for the operator and for the public. It is in the best interests of offshore producers to treat these problems effectively to mitigate any potential loss of system integrity.

Problems Common to Oil-Production Systems

Bacterial Activity and Sulfide Generation. Sulfate-Reducing Bacteria (SRB). SRB are obligate anaerobes that use dissipatory sulfate reduction as a means of acquiring energy. In this process, sulfate ions, which are present in most water, brine, soil, and drilling muds, provide an energy source for SRB to use during their metabolism of organic compounds. Ultimately, the reduction of sulfate yields sulfide ions that are released into the external environment. Sulfide ions can combine with iron to produce Fe$_x$S$_y$ and/or react to form toxic H$_2$S. Both end products of sulfate reduction by SRB are potential problems in an oil field and in water-disposal systems. H$_2$S contributes to corrosion throughout oil-field systems. After H$_2$S is formed, it migrates from the site of active bacterial growth. Although this H$_2$S migration creates an alkaline local environment, it causes acidity (souring) elsewhere. This acidic environment leads to corrosive pitting of metals throughout the system. In addition, H$_2$S can result in the formation of iron sulfide or other metal sulfides. From a regulatory standpoint, operators in many cases must maintain total H$_2$S content within their production-gathering systems below strict limits to maintain pipeline registrations, or they might face pipeline reregistration issues and costs.

Fe$_x$S$_y$ as a result of biogenic sulfide generation is a common problem in water-disposal systems. The sulfide (S$^{2-}$), which is formed by means of sulfate reduction, reacts with soluble iron to produce Fe$_x$S$_y$. Fe$_x$S$_y$ is a concern because it can lead to increased corrosion, disposal-well plugging, and decreases in water quality. Fe$_x$S$_y$ deposits can accelerate underdeposit corrosion failures and, when coupled with potential associated H$_2$S releases, can lead to serious personnel and environmental exposures with potentially catastrophic results.

Cathodic depolarization, a mechanism for MIC, is another method by which SRB are able to reduce sulfate to sulfide. In the process of cathodic depolarization, SRB remove gaseous hydrogen that forms on the surfaces of pipelines, topside equipment, and injection wells. If not removed, the gaseous hydrogen forms a cathodic layer (polarization) that actually slows corrosion rates. The removal of hydrogen (depolarization) by SRB increases corrosion rates greatly, which can lead to corrosive pitting, causing equipment failure and increased HSE risks.

Acid-Producing Bacteria (APB). Included within the group of general aerobic bacteria (GAB) and facultative anaerobic bacteria are APB. These microorganisms are primarily facultative anaerobes, meaning that they can use oxygen as a terminal oxidizing agent but also obtain energy in its absence by shifting to fermentative reactions. The APB can release aggressive metabolites during metabolism such as organic (e.g., acetic, propionic, succinic, iso-
butyric) or inorganic (sulfuric) acids. Acid production by these organisms can lead to underdeposit corrosion by promoting electron removal from the cathode by hydrogen or by dissolution of protective nonmetallic films on stainless-steel surfaces. The aerobes and APB grow rapidly and can be detected and enumerated using media that are suitable for GAB (e.g., phenol red dextrose) (NACE Standard TM0194-2004).

**Sessile vs. Planktonic Bacteria.** Planktonic microorganisms are relatively easy to sample in bulk waters and can be enumerated accurately and quickly using a variety of commercially available techniques. Sessile bacteria are those microorganisms that are attached to any surface. Sessile bacteria are usually more difficult to kill because of the protection afforded by the biomass in which they live. Therefore, microbiocide treatments intended for control of planktonic populations of bacteria may not be effective against sessile populations. If an effective sessile kill has been achieved, these sessile bacteria usually require a significant amount of time for the population to return to unacceptable levels. For this reason, periodic slug treatments at concentrations higher than those required for control of planktonic bacteria can be effective in controlling sessile bacteria as well as MIC.

**Mercaptans.** R-SH, or thiols, are a class of organosulfur compounds. They are the sulfur analogous of alcohols and contain a carbon/sulfur (-S-H) group. R-SH variants have strong and often disagreeable odors. They can be a potential cause of corrosion within oil-production systems. Mercaptans such as t-butyl mercaptan are added to natural gas, which is odorless, to give it its distinctive odor for leak detection.

**R-SH can occur naturally in various hydrocarbon-production streams, including crude oil, condensates, and liquefied petroleum gas.** When these products contain high levels of the lower molecular-weight, more-volatile R-SH (i.e., C2-SH and C3-SH), the odor is a nuisance that can impact terminals processing the products as well as the surrounding communities. Regulatory authorities often require control of R-SH odors, and set ceiling limits of R-SH allowed within hydrocarbon sales pipelines that are monitored strictly.

**Utility of Acrolein in Oilfield Applications**

Acrolein has a long history of successful oilfield applications to treat problems associated with bacterial activity, H2S, and biogenic FeS. More recently, work has confirmed that acrolein is also an effective R-SH scavenger.

**Biocidal Performance.** Acrolein is a chemistry that has been used extensively for control of sessile bacteria in waterflood systems. This nonsurfactant, noncorrosive, water-soluble biocide demonstrates excellent oil solubility, allowing for penetration of oil-coated surfaces and biofilms to target sessile bacteria effectively. The mechanism of microbial attack by acrolein is the denaturing of protein and enzyme systems in bacterial cells by reacting with protein-SH and amine groups. Numerous reports of successful bacterial control are found in the literature.

A study documenting the maintenance of injection-water quality and protection of injection flowlines from MIC is reported by Law et al. (2001). An acrolein batch-treatment program successfully replaced a previous program that used continuous injection of a di-amine quaternary amine and could not adequately control SRB populations resultant from high-sulfate makeup water mixed with the injection water. Palacios and Hernandez (2003) report a 3-year evaluation of acrolein, glutaraldehyde, tetrazis hydroxymethyl phosphonium sulfate, and a quaternary amine to reduce MIC and control SRB growth in a produced-water facility. Acrolein batch treatments were able to reduce MIC to < 0.01 mils/yr whereas the other biocides could not meet the facility’s corrosion specifications. An account of sessile-bacteria control is reported by Penkala et al. (2005) in a 92,000-m³/d waterflood facility in Rincon de los Sauces, Argentina. Acrolein maintained control of sessile SRB and GAB in a system exhibiting up to 12 hours of transit to outlying wells in an economic fashion for the 3-year period of the study. Oates et al. (2006) report that transition to an acrolein batch-treatment program after conducting trials of numerous alternatives in an offshore Canadian seawater flood achieved the customer-specified key performance indicator for both SRB and GAB levels of ≤10 bacteria per mL and provided the customer with the most cost-effective treatment option.

More-recent work reported by Penkala et al. (2008) indicates very effective APB control was achieved in an Oklahoma waterflood using acrolein. A regular batch-treatment program applied in the surface-separation equipment provided a reduction of 99.99% in APB levels throughout the water-injection system, with an associated 50% reduction in injection-well failures. Horaska et al. (2009) detail the effective treatment of a waterflooding system in Oman, with results indicating a 90% reduction in planktonic SRB and 72% reduction in planktonic GAB over the course of the trial. Additionally, dissolved H2S levels were lowered by 50%, with a consequent downward trend in oil-free suspended solids. The impact on injection-water quality was significant, reflected by a ninefold improvement in water-filterability slope-test results (Barkman and Davidson 1972).

**Treatment of Sulfides.** Acrolein is a three-carbon vinyl aldehyde that is a highly reactive chemical because of the conjugation of the carbon/carbon double bond with the carbonyl bond of the aldehyde group (Fig. 1). These conjugated double bonds leave the acrolein molecule in an elevated energy state, thus making the acrolein molecule highly reactive. Critical to the successful performance of acrolein in oilfield systems is its ability to remove sulfides (i.e., H2S and FeSx). The reaction results in the formation of water-soluble irreversible reaction products (Kissel et al. 1985; Howell and Ward 1991; Salma 2000; Ramachandran et al. 2008). Acrolein reacts with H2S in a 2:1 molar ratio; normally, 1.0 ppm of H2S consumes approximately 4 ppm acrolein (Fig. 2). This is an added benefit such that not only may SRB responsible for biogenic H2S be targeted by means of the biocidal pathways endemic to acrolein, but the toxic and corrosive product of their metabolism (H2S) can be removed as well. Similarly, with FeSx, acrolein can dissolve these solids, thereby resolving issues such as black water, FeSx scale and plugging, FeSx-stabilized emulsions, and formation damage. Acrolein reacts with H2S that is in equilibrium with soluble iron and sulfide and follows the same reaction process as described previously for H2S (Fig. 3) (BHI 2009).

Dickinson et al. (2005) showed that optimizing acrolein-treatment strategies and injection points in a California waterflood re-
A three-phase program designed to remediate completely plugged water-injection wells, remove SRB-generated Fe$_x$S$_y$ solids and biomass, and provide ongoing maintenance to effectively manage an Alabama water-disposal facility serving a 200-Mscf/D gas plant receiving offshore production.

**Removal of Mercaptans**. Acrolein reacts with R-SH to form thioether aldehydes, thereby scavenging R-SH from hydrocarbon product streams (Fig. 4). It reacts at faster rates with the lower-order, more-volatile, and strongest-smelling R-SH species. This preferential reaction makes the treatment efficient for odor reduction. Acrolein will also react with the higher-order, less-volatile R-SH, making it a broad-spectrum scavenger. The reaction becomes increasingly slow as the carbon-chain length of the R-SH present increases. It is important to note that although the inherent R-SH value within the treated hydrocarbon will decrease, the total sulfur will not; the R-SH is converted to the thioether aldehyde reaction product.

When designing a mercaptan-scavenger treatment, the background H$_2$S, bacteria, and any potential Fe$_x$S$_y$ loading levels within the target system must be accounted for when determining initial treatment rates. Recent work indicates that following treatment with acrolein, R-SH levels in the subject hydrocarbon stream can be lowered successfully to acceptable specification levels and, subsequently, the hydrocarbon can be transported safely following treatment (Arensdorf and Horaska 2011).

**Acrolein Suitability for Offshore Application**

Acrolein products are uniquely suited to offshore application and usage. Among the benefits provided by proper design and implementation of an offshore acrolein-treatment program are the high degree of reactivity of acrolein with oilfield contaminants; the dual solubility of acrolein in both oil and water, enabling penetration of oil-wet solids and biofilms; the cost-effective bacterial treatment afforded to the producer; and the transportation- and application-equipment design, processes, and procedures used by certain acrolein service providers in the safe delivery of these products to offshore operators.

**Acrolein Reactivity and Biodegradability**. As already detailed, acrolein is a highly reactive chemistry that provides effective bacteria control, rapid scavenging of H$_2$S, dissolution of Fe$_x$S$_y$, and treatment of R-SH in hydrocarbon production. Another factor supporting acrolein usage in offshore applications is its environmental profile. Acrolein hydrolyzes in water to form β-hydroxypropanal, a highly biodegradable water-soluble degradation product. With contributing factors such as elevated temperature, salinity, and presence of organic matter, acrolein has been shown to have a half-life of 8 to 24 hours in typical water systems that lack the presence of H$_2$S. This relatively short half-life compared with other, more environmentally persistent biocides offers a favorable environmental profile for acrolein with respect to treatment of offshore production installations. The presence of H$_2$S and other reactants within normal oilfield-produced fluids will only hasten the degradation of any acrolein present.

Smith et al. (1995) showed that under both aerobic and anaerobic conditions, analysis of acrolein-degradation products proved that the ultimate metabolic fate of acrolein breakdown in water is carbon dioxide (CO$_2$) and water. This work was completed in support of the registration of acrolein as an aquatic herbicide for use...
in agricultural irrigation water-delivery systems (BHI 2009). Note that the amount of CO₂ formed as a result of this degradation reaction is minimal, with no negative impact on the offshore facility; the acrolein is applied originally in the ppm concentration range, and CO₂ results only from this breakdown of acrolein in water—acrolein that reacts with bacteria, H₂S, Fe₃S₄, and R-SH does not form CO₂ as a reaction byproduct.

**Dual Solubility of Acrolein.** Acrolein is a hydrocarbon, but exhibits the unique property of also being soluble in water (Smith 1962). This dual solubility in oil and water and its high degree of reactivity with both bacteria and sulfides enable acrolein to maintain high water quality for water-injection systems as well as overhead water discharge for offshore installations. Because biogenic Fe₃S₄ deposits in production systems often promote the formation of sessile-bacteria colonies in water tanks, injection lines, and injection wells by providing locations for these bacteria to proliferate, acrolein provides a comprehensive approach to treating a system by addressing bacterial control as well as sulfide management and water-quality improvement. These sessile-biomass and biogenic-Fe₃S₄ deposits are preferentially oil-wet. Unlike other conventional nonsurface-active biocides currently available, acrolein is able to penetrate the oil layer and treat these accumulations effectively.

**Cost-Effective Treatment of Offshore Oilfield Problems.** Acrolein is delivered to the field in essentially neat form (i.e., minimum of 95% activity) (MSDS CASH 107-02-08 2009). This activity differs dramatically in comparison with other conventional biocides, sulfide-treatment, or R-SH-scavenging chemicals available commercially. Consequently, significantly less chemical is required to provide the same, or in many cases superior, results with respect to bacteria treatment, sulfide abatement, and R-SH treatment within oilfield systems. Work reported by Penkala et al. (2004) determined that in 25 out of 28 planktonic time/kill studies, acrolein was the most cost-effective biocide for control of GAB and SRB when compared with conventional biocide chemicals.

A fundamental advantage of using acrolein in an offshore treatment strategy is that the treatment will provide more than one benefit with the injection of a single chemical, as detailed previously. In addition to the multifaceted benefit afforded to the operator, the use of a single chemical also minimizes the number of injection points required within the production system. The use of a single chemical also minimizes the deck space requirements of a multiple chemical-injection program, yielding better offshore-installation operational efficiency.

**Acrolein Containers, Application Equipment, and HSE Considerations.** Acrolein (2-propenal) is a highly effective micro-biocide and sulfide scavenger that has been available commercially since 1960 and has been widely used in the oil- and gas-production industry. Acrolein is a liquid product classified as a toxic inhalation hazard (MSDS CASH 107-02-08 2009). Consequently, it is supplied in and applied from specialized containers, eliminating potential releases from transfers between tanks. Acrolein is delivered in the dedicated containers under a blanket of inert nitrogen to exclude potential oxygen ingress and to enhance product shelf life. Using low nitrogen pressure, the chemical is delivered from the container through an internal dip tube into a closed-system chemical manifold. From the manifold, the product can be either applied directly into a low-pressure production system or directed to the suction of a diaphragm chemical pump for application to pressures exceeding those allowed in the chemical container. Significant resources and expertise have been invested by certain acrolein service providers in the design of safe application systems to enable chemical application on offshore production assets. Acrolein containers are designed to comply with all regulations for both domestic (US DOT 49 CFR 178 2008) and international (IMO IMDG Code 2008) transport. The development of a safety-management program and standardization of application equipment allow the usage of acrolein for applications with a risk comparable with, or in some cases lower than, conventional chemical products.

**Case Histories**

To help illustrate the utility of acrolein products with respect to offshore treatment of production problems, a series of case histories provides examples of recent successful applications. The case studies presented are:

- **Case History I—Offshore California Operator is able to continue producing sour field using acrolein treatment.**
- **Case History II—Floating production, storage, and offloading (FPSO) producer controls bacterial activity by use of acrolein.**
- **Case History III—Australian producer mitigates bacteria by use of batch acrolein treatment.**

A summary of each case study highlighting the benefits afforded the customer by the usage of acrolein is included in the following subsections.

**Case History I—Offshore California Operator Able To Continue Producing Sour Field Using Acrolein Treatment.** The operator of an offshore production platform in California was considering shutting down the facility because of high levels of H₂S in the gross production. At facility startup, the oil and gas production was sweet, averaging 1,000 BOPD, 9,000 BWPD and 2 MScf/D of gas. The lease operating permit and the metallurgy of the pipeline required <100 ppm H₂S in the pipeline, going to the onshore separation facility. After operating a seawater flood for several years, the production was increasingly sour. The facility was modified to separate some of the sour gas on the platform and sweeten it in an iron sponge process. However, the emulsion, with its entrained sour gas, would still violate the lease operating permit and had the potential for sulfide-cracking corrosion in the pipeline.

**Solution.** The acrolein service provider recommended continuous treatment using acrolein to sweeten the production. The only accessible injection point was just downstream of the gas separator, with approximately 50 ft of piping before the emulsion entered the pipeline. This injection point would allow for a few seconds of reaction time only to reduce H₂S levels from approximately 1,500 ppm to <100 ppm.
Results. Because of its rapid reaction with the $\text{H}_2\text{S}$ present, the acrolein-treatment program successfully met the criteria needed to keep the platform producing (Fig. 5). With a proven method to treat sour production, the operator drilled into an underlying sour reservoir and extended the life of the field by several more years. This treatment program was started in 1989 and continues today.

Case History II—FPSO Producer Controls Bacterial Activity by Use of Acrolein. Problem. An offshore Canadian producer was experiencing significant bacterial activity in the seawater-injection system. The seawater flood was initiated during FPSO startup to provide pressure maintenance to the producing formation. Previous chemical trials had failed to provide sufficient bacteria control [Figs. 6 and 7; note that because of the quantity of data, the average colony forming units per milliliter (CFU/mL) over monthly periods have been plotted]. Bacteria monitoring was routinely completed immediately before biocide batch treatment (“before biocide”) and after biocide treatment (“after biocide”) to gauge relative biocide efficacy. As a result of inadequate chemical treatment, the customer was experiencing a reduction in injection-water quality and volume as well as increased risk of formation souring because of SRB proliferation.

Solution. In an attempt to provide a solution to the problem, the FPSO operator was approached by the acrolein service supplier about a potential acrolein trial, using a regular batch-treatment protocol. A series of meetings was held involving local customer technical personnel and similar staff from the acrolein service supplier to discuss the technical merits of the proposed acrolein program. The chemical-treatment time line from FPSO startup to present is summarized as follows, and is identified on Figs. 6 and 7:

1. February 2002
   a. Start batch biocide treatment of seawater-injection system
   b. Biocide chemical: glutaraldehyde
   c. Chemical dosage and frequency: 200 ppm for an approximate 4-hour period once every 7 days
2. June 2004
   a. Change dosage and frequency to 200 ppm for an approximate 3-hour period once every 5 days
3. September 2007
   a. Change biocide-injection point from second stage of deaerator (DA) to DA inlet
4. June 2009
   a. Change biocide chemical from glutaraldehyde to acrolein
   b. Change dosage and frequency to 130 ppm for a 2- to 3-hour period once every 7 days

Results. Once all customer questions were answered, an acrolein field trial was awarded and yielded immediate positive impact on the bacteria levels within the seawater-injection system. The SRB control exhibited following implementation of the acrolein program was significant: Relative to the peak levels of SRB infestation noted before starting the acrolein program (March 2008–June 2009), the SRB levels were reduced from pretreatment levels to post-treatment levels by 99.8% using acrolein, vs. only 67.7% reduction afforded by the previous chemical-treatment program (Fig. 6). Similar analysis of the APB data (Fig. 7) yields comparable results: APB levels were reduced from pretreatment levels to post-treatment levels by 99.6% using acrolein, vs. only 89.4% reduction provided by previous treatments. The results of the field trial led to a permanent acrolein-application program.

Case History III—Australian Offshore Producer Mitigates Bacteria by Use of Batch Acrolein Treatment. Problem. An offshore Australian producer was dealing with significant SRB activity within the gross production subsea pipeline through to the

Fig. 5—Offshore California producer $\text{H}_2\text{S}$-treatment results using acrolein.
onshore processing facilities and water-injection system, with associated increases in $\text{H}_2\text{S}$ levels and decreases in injection-water quality and filter run times. Analysis indicated that prior chemical solutions were not providing the level of bacterial control required by the operator.

**Solution.** The producer collaborated with the acrolein service provider to design a field-trial strategy to compare results of an acrolein-treatment program with those of previously used chemistries. The field trial was conducted successfully (Shield et al. 2005) and led to the implementation of a permanent acrolein-treatment program for this offshore installation.

**Results.** The complete bacteria-monitoring data set from permanent program startup to present day is summarized in Fig. 8 [note that because of the quantity of data, the average SRB (log_{10} CFU/mL) over monthly periods has been plotted]. The downward trend of the cumulative data shows significant improvement with respect to SRB infestation within the system. In particular, a minimum five-order-of-magnitude (i.e., $10^5$) decrease in SRB populations is noted from the start of the program to the present day in that bacteria populations have dropped from background levels of $\geq 10^6$ CFU/mL to current levels of $10^1$ CFU/mL. Also of interest is the immediate impact of any interruption of the acrolein-treatment program on the SRB populations present in the system. Specifically, the data from early 2005 and 2009 indicate that any interruption of the regular batch-treatment protocol led to an immediate response of increased SRB activity in the system. The acrolein program continues to provide effective bacterial control within this system.

**Summary and Conclusions**

- Oilfield production systems can be plagued with various problems associated with bacterial activity, $\text{H}_2\text{S}$ production and generation, $\text{Fe}_x\text{S}_y$ precipitation and deposition, and R-SH production.
- Acrolein treatment can provide a solution to these problems with the use of a single chemical; multiple problems can be treated with one chemical application.
- Acrolein scavenges $\text{H}_2\text{S}$ from produced fluids quickly and efficiently.
- Acrolein can react with $\text{Fe}_x\text{S}_y$ to form irreversible water-soluble reaction products, thereby minimizing the potential for system plugging and potential sites for underdeposit corrosion initiation.
Acrolein can scavenge excess R-SH from hydrocarbon-production streams, enabling the operator to achieve pipeline specification and mitigating potential odor/environmental-release issues.

Acrolein is particularly suited to offshore applications to solve these oil-production problems.

Acrolein is a highly reactive chemical; it performs quickly and breaks down rapidly, thereby minimizing the potential for a long-term environmental impact.

Acrolein exhibits solubility in both oil and water, thus enabling it to penetrate oil-wet biofilms and solids to effectively treat sessile bacteria and solids deposits that are a prime cause of underdeposit corrosion and MIC.

Acrolein is a highly cost-effective microbiocide that yields superior bacterial control relative to other common oilfield biocides.

Engineered acrolein-handling and -application equipment and application protocols have been developed and refined by certain acrolein service providers to minimize the potential for personnel exposure during product application.

The case histories presented confirm the efficacy of acrolein use in an offshore setting to treat problems that are endemic to these oilfield production systems.

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