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Review

# Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review

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ABSTRACT

This review summarizes the corrosion inhibition of steel materials in acidic media. Numerous corrosion inhibitors for steels in acidic solutions are presented. The emphasis is on HCl solutions, lower-grade steels, and elevated temperatures. This review is also devoted to corrosion inhibitor formulation design – mixtures of corrosion inhibitors with (mainly) surfactants, solvents, and intensifiers to improve the effectiveness of individual compounds at elevated temperatures. The information presented in this review is useful for diverse industrial fields, primarily for the well acidizing procedure, and secondly for other applications where corrosion inhibitors for steel materials are needed.



## 1. Introduction

Human demand for fossil fuels is still growing even though alternatives to such energy are currently being sought. Oil and natural gas account for 60% of all global energy demands [1]. It is thus not expected that the conventional method of extracting fossil fuels will disappear within the next few decades. The extraction of geothermal water for use as an energy source is also of paramount importance and its usage is increasing. The methods required to maximize production typically comprise formation stimulation and subsequent well cleaning, both of which can induce a corrosive environment for the steel involved, as it is the main construction material of wells.

Corrosion is worth investigating in oilfield applications, because corrosion problems represent a large portion of the total costs for oil and gas producing companies every year worldwide. Moreover, appropriate corrosion control can help avoid many potential disasters that can cause serious issues including loss of life, negative social impacts, and water resource and environmental pollution. Corrosion in oilfields occurs at all stages from downhole to surface equipment and processing facilities. It appears as leaks in tanks, casings, tubing, pipelines, and other equipment [2–4]. Corrosion problems are usually connected with operating problems and equipment maintenance, leading to recurrent partial and even total process shutdown, resulting in severe economic losses [5]. Moreover, Garcia-Arriaga et al. [5] reported that the economic costs linked to the corrosion of natural gas sweetening ($CO_2$ corrosion) and oil refining plants range between 10% and 30% of the maintenance budget.

In the petroleum industry, general and localized corrosion are the most common types of corrosion occurrences. The other large problem in operating pipe flow lines is internal corrosion [6], mainly due to stress corrosion cracking. Martinez et al. [7] claim that the combination of corrosion and erosion is the main problem in pipe deterioration. Also noted recently is an increase in the occurrence of galvanic corrosion problems associated with the use of different dissimilar materials, which has garnered much attention. Wilhelm [8] reported that the most common situation of coupling dissimilar materials in wells consists of a tubing string made of corrosion-resistant alloy in contact with lower-grade steel casing. Moreover, the metal contacts also cause crevice corrosion in the occluded area between tubing and casing.

The primary focus of this review is to summarize different research relating to corrosion and its inhibition regarding mild, carbon, and low-alloy steel – lower-grade steels – in different acidic solutions encountered in the crude oil and natural gas sector. These materials are used in well construction. In the petroleum industry, one facet of the development of new oil and gas production is the stimulation process. Overall, the stimulation process involves many different aspects, including the acidizing portion utilized to stimulate the carbonate reservoir or for dissolving fines.

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**Nomenclature**

*Abbreviations*

| | |
|---|---|
| API | American Petroleum Institute |
| CI | corrosion inhibitor |
| CIF | corrosion inhibitor formulation |
| CR | corrosion rate |
| CRS | cold rolled steel |
| CRMS | cold rolled mild steel |
| CS | carbon steel |
| EIS | electrochemical impedance spectroscopy |
| EFM | electrochemical frequency modulation |
| $\eta$ | inhibition effectiveness |
| LCS | low carbon steel |
| $j$ | current density |
| $J$ | current |
| LPR | linear polarization resistance |
| LSW | linear sweep voltammetry |
| MS | mild steel |
| $R_p$ | polarization resistance |
| T | temperature |
| WL | weight loss |
| SEM | scanning electron microscope |

Typically, highly concentrated acids, between 5 and 28 wt.%, are used which make the environment corrosive to mild, carbon, and low-alloy steels. Hydrochloric, hydrofluoric, acetic, or formic acids are injected into the well during the acidizing stimulation process and cause serious corrosion issues. In the absence of corrosion inhibitors (CIs), the general CR (corrosion rate) can be extremely high (>100 mm/y) and can increase exponentially with increasing temperatures and acid concentrations [9]. Due to the extreme corrosion conditions of this process, developed technology can then be translated to other industries. In particular, this can be relevant for acid pickling, industrial cleaning, and acid descaling, where corrosion conditions are usually milder. This may be a secondary source of information for readers of this review. It has to be pointed out that the petroleum industry is the largest consumer of CIs. This review only addresses individual CIs for application in HCl mediums with different steels because HCl is the most prevalent acid used in stimulation.

An effort has been made herein to combine different works by the same authors in a single paragraph, even though not all authors of different articles or patents appear together all the time. In this review, when steel materials in general are written about, lower-grade steels are being referred to. All concentrations in % are always reported as a mass fraction if not stated otherwise. Moreover, when concentrations in various articles were reported in parts per million (ppm), herein they are converted to mg/L.

This work discusses the well acidizing procedure in general so that readers of this review can gain an impression of the severe corrosion conditions during that process. Moreover, the steel materials used for well construction and associated with corrosion problems are discussed. The corrosion of these steel materials and previously tested CIs for HCl solutions are reviewed. This review also explains aspects of a corrosion inhibitor formulation design in order to increase the success of these CIs at elevated temperatures or under other well environmental conditions. Furthermore, it also presents environmental concerns in corrosion inhibition processes, environmental friendly methanesulphonic acid, and some recommendations for correct test methods regarding acid CIs.

## 2. The well acidizing procedure

Limestone formations or carbonate-bearing sandstone carry many hydrocarbon reservoirs [10]. A very important step in the oil, gas, and geothermal water drilling industry is the well acidizing procedure, which is a rock reservoir (the origin of the natural resource or water – a geological subterranean formation) stimulation technique used to improve productivity. Acids are forced under high pressure through the borehole into the pore spaces of the rock formation, where they react chemically with rocks to dissolve them (usually calcite, limestone, and dolomite), which enlarges the existing flow channels and opens new ones to the wellbore [11–15]. Acidizing is used in conjunction with hydraulic fracturing techniques and matrix acidizing techniques [16]. In fracture acidizing treatments, one or more fractures are produced in the formation and acidic solution is introduced into the fracture to etch flow channels in the fracture face. The acid also enlarges the pore spaces in the fracture face and in the formation [12,13]. The fractures are then filled with sand or other material in order to prevent the fractures from closing and allow the penetration of natural resources or water. Acids are often also employed for scale removal treatments (pickling of the well tubing) and for the removal of drilling mud damage in newly drilled wells before being brought into production [17]. For example, the combination of fluorosilicate with metal ions such as $Na^+$ may cause the precipitation of gelatinous compounds, which need to be removed [10]. Scale removal treatments are usually done with 15% HCl at temperatures up to 60 °C in order to remove iron oxides and carbonated minerals [18]. Acidizing steps are frequently repeated. All these procedures involve the injection of acids into the well system made of steel tubes. In deep wells the downhole temperature may exceed 200 °C [19,20]. During the acidizing process metallic materials can also come into contact with acid solution and sometimes with $H_2S$ and $CO_2$ at elevated temperatures. Due to the above listed problems, the acidizing process requires a high degree of corrosion protection of tubular materials and other equipment employed.

### 2.1. The use of acids in the acidizing procedure

Different acids are employed depending on the underground reservoir characteristics. The treatment normally involves the injection of acid at 15% concentration (sometimes from 5% up to 28%) [11,21–23]. A standard 15% acid concentration had been chosen before 1960 due to the insolubility of arsenic inhibitor, the primary inhibitor of the industry at the time, because it was not soluble in HCl concentrations higher than 17% [24]. The most common conventional acids are HCl, HF, acetic, and formic acids. It has also been noted that mixtures of these conventional acids with sulphamic, sulphuric, phosphoric, methanesulphonic, nitric, citric, and chloroacetic acids are employed [9,12,13,15,25–28].

The majority of acidizing treatments carried out utilize HCl at concentrations of 5–28% [24]. HCl has an advantage over the other mineral acids in the acidizing operation because it forms metal chlorides, which are very soluble in the aqueous phase. Other acids have been employed historically, but they were not so successful compared with HCl. One of the reasons was that, for example, sulphate, nitrate, and phosphate salts have lower solubility compared with chloride salts in aqueous media [29]. HCl is widely used for stimulating carbonate-based reservoirs such as limestone and dolomite. Alternatively, sandstone formation can occur and for a successful stimulation process HF is needed. Sometimes a