

Utilization of Industrial Waste for Developing the Corrosion Inhibitors for Acidizing Wells

Submitted as a part of the requirement for the partial fulfillment of the course work of CSIR-Harnessing Appropriate Rural Interventions and Technologies (CSIR-HARIT) for the award of Degree of PhD



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Declaration – I, Ramesh Nath Goswami, hereby certify that the work presented in this Report entitled “**Utilization of Industrial Waste for Developing the Corrosion Inhibitors for Acidizing Wells,**” in partial fulfillment of the course requirement for award of the Degree of PhD, being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of Project Research work carried out by me at CSIR-IIP Dehradun during the period January 2019 to August 2020 and under the supervision of **Dr Anjan Ray**.

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1) Introduction

Corrosion is a naturally occurring phenomenon, commonly defined as the deterioration of a substance/material (usually metal) through its reaction with the surrounding environment. The corrosion progressively leads to materials and, eventually, financial losses to civil infrastructure to marine vessels, pipeline distribution systems to refineries and chemical industries, automotive to domestic installations [1]. The economic loss due to the direct and indirect involvement of corrosion is estimated to be 3-4% of the annual GDP [2]. The oil and gas industries incurred massive losses due to corrosion, including maintenance, repairing, and new installation besides the indirect cost such as environmental, toxicological, and health hazards associated with leakages from corroded bodies. The \$170 billion annual cost due to corrosion is bear by various industries in the United States, with a significant contribution from the oil and gas industries [3].

Corrosion can be classified into two types; Uniform and Localized corrosions. The uniform corrosion, also known as general corrosion, is the most common form of corrosion that uniformly corrodes the metal substrate [4]. The cathodic protection, coatings, paints, and inhibitors are used to control such corrosion. Localized corrosion takes at a particular place of the substrate/vessel in such a way that a specific part of the metal corrodes at a faster rate than the remaining parts due to the accelerated attack of metal in a corrosive environment [5].

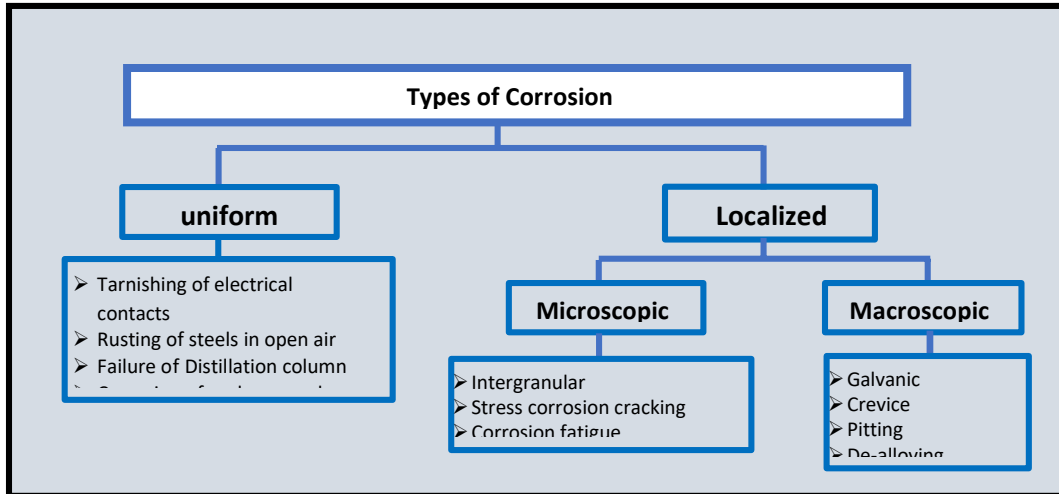


Figure 1: Flow chart showing the types of corrosion [6]

Corrosion is a common phenomenon in the petroleum industry, leading to several direct and indirect damages. The two most crucial types of corrosion that affect the oil and gas pipelines are sweet, i.e., CO₂ corrosion, and sour corrosion, i.e., caused by H₂S. Both of them cause severe damages to the internal surfaces of oil and gas pipelines [7].

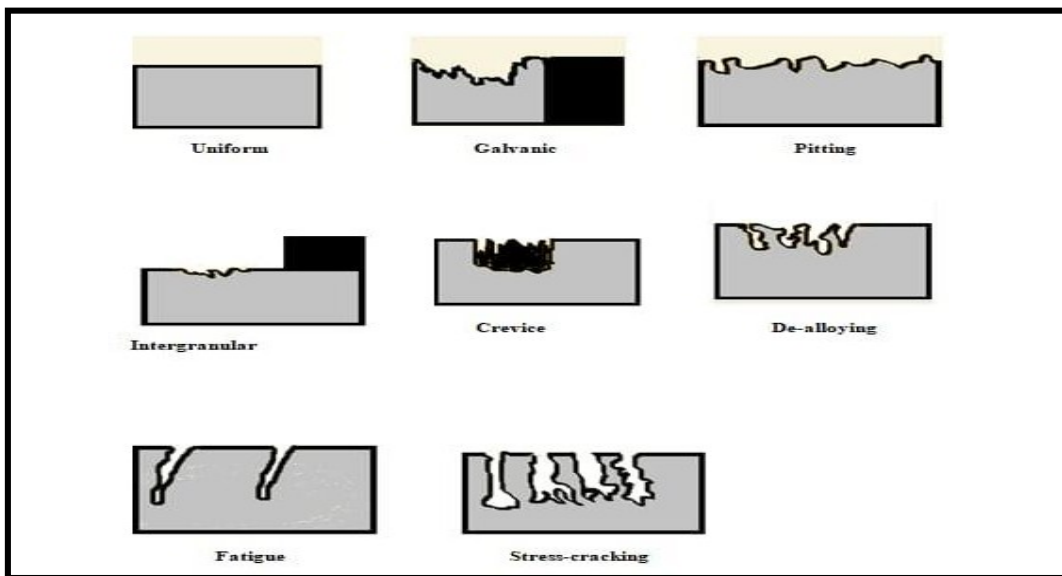


Figure 2: Schematic illustration of different types of corrosion [8]

The economic loss in the oil and gas industries due to corrosion is exceptionally high; therefore, combating corrosion is necessary for these industries [9]. It is not feasible to eliminate the corrosion, but the rate of corrosion can be controlled to subsidize the corrosion to a significant extent. The degradation of metal when it comes in contact with H₂S and CO₂ is called sour and sweet corrosion, respectively [10]. In the oil and gas processing system, dry CO₂ gas is not corrosive at room temperature. Still, it becomes severely corrosive when it is dissolved in water by forming carbonic acid, leading to low pH, as demonstrated in Figure 3 [11].

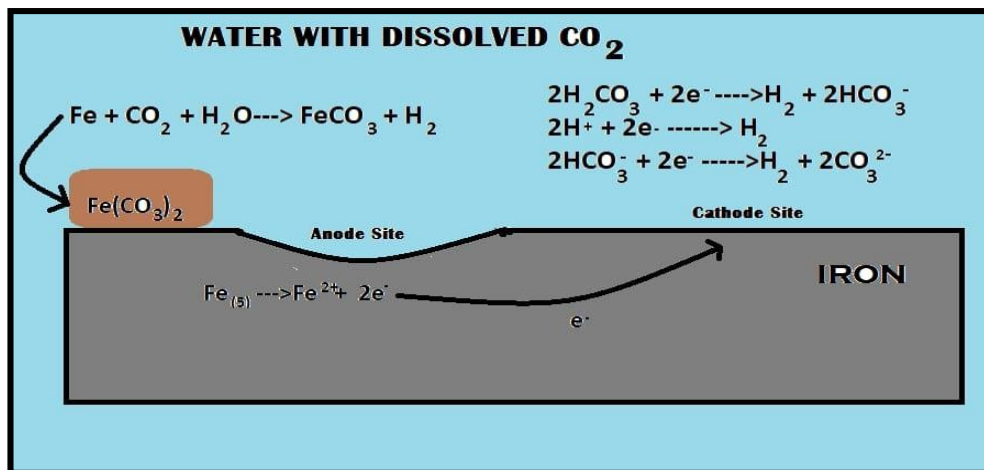
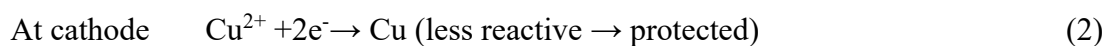
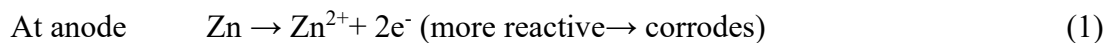


Figure 3: A schematic view of sweet corrosion caused by CO₂ [12]

The electrochemical corrosion occurs when two different metals are joined in the presence of electrolyte [13].



The presence of narrow spaces or openings between metal-to-metal or non-metal-to-metal components can increase localized attacks [14]. Erosion corrosion is caused by the movement of corrosive fluid with high speed to the metal surface resulting in mechanical wear of material [15]. The combined effect of tensile stress and a corrosive environment result in the growth and formation of a crack in the material, which is called stress corrosion cracking [16].



Figure 4: Stress Corrosion Cracking (from NACE)

Acidizing is the frequently used stimulation practice in the oil and drilling system for improving and enhancing the productivity of petroleum oil well [17]. Acids under high pressure are forced to pass into the pores of the rock formation, where they chemically react and dissolve with the portion of the channel, thereby opening up new media in the rock for the oil and gas to flow to the wellbore [18]. It is commonly done on new wells to increase their initial productivity and on old wells for the removal of scale deposits which cause low porosity of oil or gas, and decreasing the production of the wells [19]. Some critical parameters that affect the corrosiveness are; the type of oil well reservoir rocks, the acids used for stimulation, the oil well equipment such as tubing and casings, and the working conditions [20]. Different acids are used in the acidizing process, based on the underground oil well reservoir characteristics [21]. The most common acids that are generally used for acidizing treatments are hydrochloric acid, hydrofluoric acid,

formic acid, and acetic acid [22, 23]. The HCl is widely used for the stimulation of carbonate-based reservoirs, i.e., limestone and dolomite.

The use of corrosion inhibitors is one of the most practical methods for corrosion protection. The commercially available acidizing inhibitors are acetylenic alcohols, alkenylphenones, nitrogen-containing heterocycles (imidazoline-based, nitriles, imminum salts, quinoline derivatives, thiourea derivatives, thiosemicarbazide, pyridine, and its derivatives, etc.), aromatic aldehyde, and the condensation products of carbonyls and amines [17, 24]. Most of these compounds are harmful to the environment and living-beings [25]. Inorganic inhibitors cause severe damage to the ground and are less useful for protecting N80 steel in acidic medium. Organic compounds containing heteroatoms such as nitrogen, sulfur, or oxygen inhibit the corrosion in the acidic medium. They can be adsorbed on the metal surface and form a protective film, thereby reducing corrosion [26, 27].

2) Experimental Section

Materials: Alkylpyridines (industrial waste), 1- iododecane (98% Sigma Aldrich), ethanol (L.R. grade 96%). Carbon steel coupons of commercial-grade (size 2 cm × 2 cm × 0.2 cm). Different silicon carbide waterproof paper (220 – 1200 grit size) were used for polishing the specimen. Isopropyl, alcohol, and acetone were used to clean the coupons. The hydrochloric acid solution was used to create a corrosive environment.

Synthesis of inhibitor using solvent: In a typical experiment, 5g feed containing mixed alkyl pyridines was taken in a 100 ml round bottom flask and dissolved in ethanol (20 ml) as a solvent. In another beaker, 8.0454 g of 1-iododecane was dissolved in 15 ml of ethanol and added dropwise to the feed with continuous stirring. The reaction mixture was refluxed for 8 hrs with

constant stirring. After completing the reaction, the mixture was concentrated under vacuum, and the obtained crude product was thoroughly washed with diethyl ether to remove the non-reacted substrates. The obtained solid product was dried under vacuum at 50 °C for 10 hours.

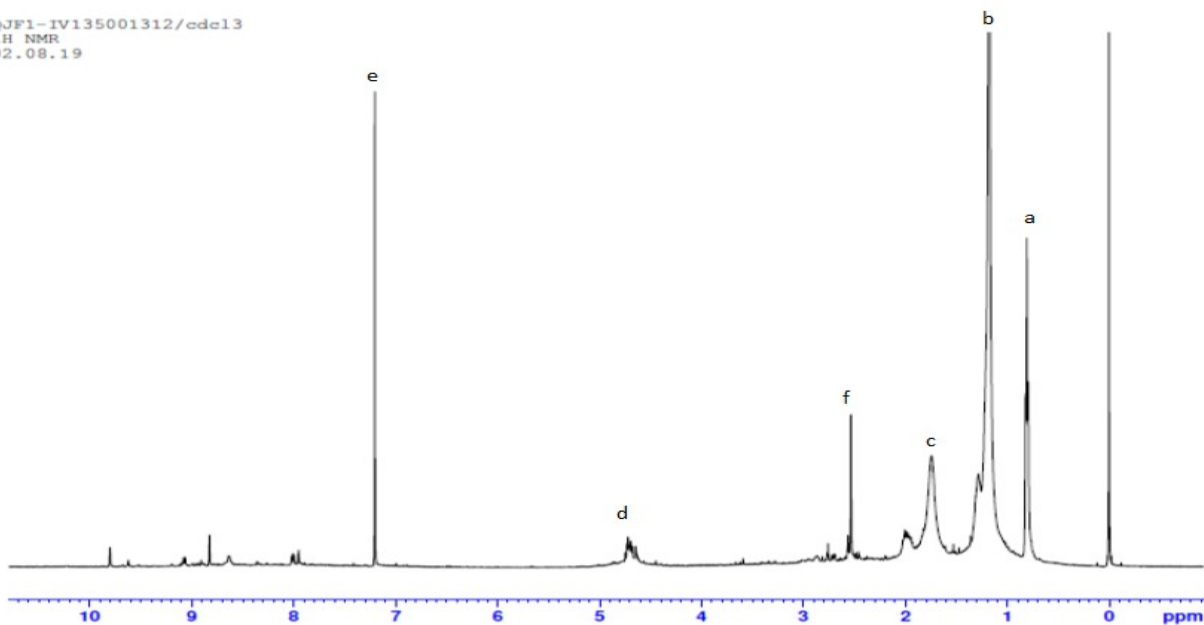
Synthesis of inhibitor without solvent: In a typical synthesis, 3 g feed containing mixed alkyl pyridine derivatives and 5.1 g 1- iododecane was taken in a round bottom flask. The resulting mixture was heated at 180 °C for 3 hours. Then after, the reaction mixture was diluted with dichloromethane, followed by the addition of diethyl ether and dried under vacuum at 50 °C for 10 hours. The product was isolated by decanting the solvent layer and was subjected to dry under vacuum at 50 °C for 10 hours.

3) Corrosion testing and monitoring techniques: The ASTM G31 standard protocol was followed to carry out the corrosion test, known as the weight-loss corrosion monitoring technique. It helps analyze the relationship between the corrosion rate of metal and the time of exposure of metal in corrosive media [28]. The corrosion test can be run over a wide range of temperatures and different parameters like pH and the flow rate of corrodent, by following the ASTM G31 protocol. It can be customized to meet a specific requirement.

Characterization

The successful formation of the quaternized product was confirmed by ¹H NMR, as shown in the figure:

QJF1-IV135001312/cdc13
1H NMR
02.08.19



f/

Figure 5: Structure determination by ¹H NMR

4) Results and Discussion

The peak a and b attributed to a high shielded region (0.90 to 1.3 ppm) of the alkyl chain. And the deshielded methylene unit d exhibits at (4.7 ppm). The proton, which concerns with aromaticity is showed a chemical shift in the range of 7.2 ppm. Two methyl protons associated with aromatic (f) lie at (2.1 to 2.7 ppm).

Table 1: Corrosion inhibitor efficiency at 30 °C in 7N HCl

Additive	Details	Dosage, %					
		2%		2.5%		3%	
		Weight	Efficiency	Weight	Efficiency	Weight	Efficiency
		Loss (g)	(%)	Loss (g)	(%)	Loss (g)	(%)
1.None		0.32528	-	-	-	-	-
2.Old feed		0.00277	99.15	0.00135	99.58	0.00589	98.19
3.Old feed		-	-	0.00938	99.12	0.00613	98.16
	additive						
4.Additive	PRS-1	0.00335	98.88	0.00192	99.41	-	-
	New Feed -1						
5.Additive	PRS-2	0.00365	98.89	-	-	-	-
	new feed -2						
6.New feed -1		0.00158	99.51	0.00065	99.80	0.00063	99.81
7.New feed -2		0.00063	99.80	0.00080	99.75	0.00050	99.85

Table 1: shows the corrosion inhibitor efficiency at 30 °C in the 7N HCl solution. The table represents the inhibiting effect of various additives that were synthesized in the laboratory. At a 2% dosage level, new feed -2 showed the best inhibiting efficiency, whereas additive prepared for new feed -1, i.e., PRS-1, is the less effective. The best results at 2.5% dosage of new feed -2 maintain its performance and steady inhibition. The poor performance was shown by the additive prepared from the old feed. Due to the non-availability of a sufficient quantity of additives, tests

were not performed using additives PRS-1 and PRS-2 at this dosage level. At a 3% dosage level, new feed -2 shows the best inhibiting results, whereas both old feed and additive prepared from old feed show poor results.

Table 2: Corrosion inhibitor efficiency at 60 °C in 7N HCl

Additive	Details	Dosage, %					
		2%		2.5%		3%	
		Weight Loss (g)	Efficiency (%)	Weight Loss (g)	Efficiency (%)	Weight Loss (g)	Efficiency (%)
1.None		1.12425					
2.Old Feed	-	0.02816	97.50	0.05320	95.27	0.02247	98
3.Old Feed Additive	-	-	-	-	-	-	-
4.Additive New Feed -1	NQR-1	0.01057	99.06	0.00986	99.12	-	-
5.Additive New Feed -2	NQR-2	0.01416	98.74	0.00838	99.25	0.00758	99.33
6..	- NNQ-2	0.01760	98.43	-	-	-	-
7.	- BCL-2	0.03903	96.52	-	-	-	-
8.	- BRB-1	0.20698	81.59	-	-	-	-
10.	- BRB-2	0.22683	79.82	-	-	-	-

Table 2: shows the corrosion inhibitor efficiency at 60 °C under 7N HCl acid. A 2% dosage of NQR-1 additive exhibited best inhibiting performance, whereas the BRB-2 additive showed minimum corrosion inhibition efficiency among all samples. The marginally higher corrosion inhibition efficiency was furnished by NQR-1 and NQR-2 additives when their doses are increased.

Table 3: Corrosion inhibitor efficiency at 90 °C in 7N HCl

Additive	Dosage, %					
	2%		2.5%		3%	
	Weight Loss (g)	Efficiency (%)	Weight Loss (g)	Efficiency (%)	Weight Loss (g)	Efficiency (%)
1.None	5.26155	-	-	-	-	-
2.Old Feed	0.58493	88.88	0.34296	93.48	0.13827	97.37
3.New Feed -1	0.38997	92.59	0.28695	94.55	0.17549	92.59
4.New Feed -2	0.44216	91.16	0.32049	93.90	0.15956	96.97

Table 3: displays corrosion inhibitor efficiency at 90 °C in 7N HCl acid. The 2% dose of -1 additive showed the best corrosion inhibition efficiency, whereas Old feed exhibited minimum inhibition efficiency under identical conditions. The corrosion inhibition efficiency for all additives is noted to be increased by increasing their doses.

Digital image of Sample

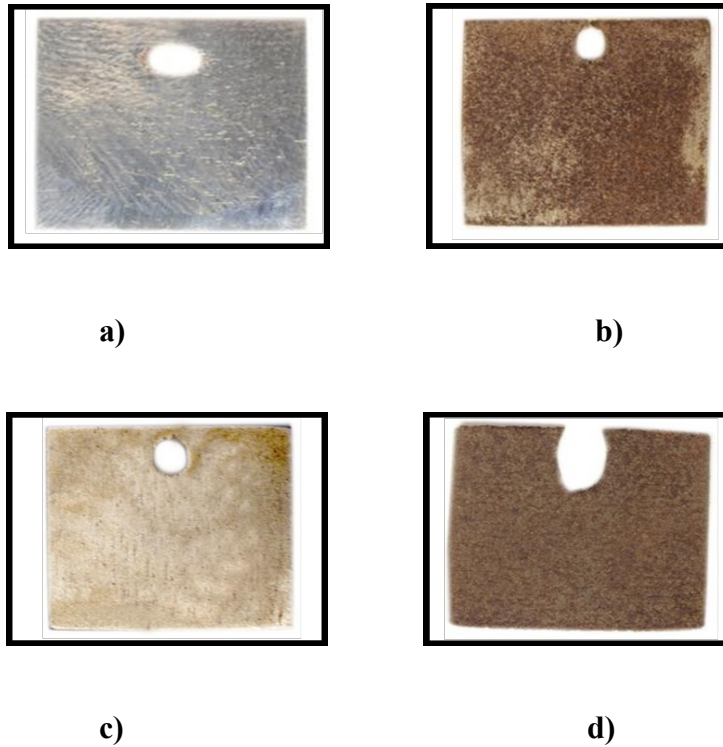


Figure 5: (a) Carbon steel coupon before the test, (b) carbon steel coupon after the blank test at 60 °C in 7N HCl, (c) carbon steel coupon after 2% NQR-2 test at 60 °C in 7N HCl, and (d) carbon steel coupon after the blank test at 90 °C in 7N HCl

5) Conclusions

Corrosion causes the oil and gas industry heavy damages infrastructure-wise and, in turn, financial losses. Thus, corrosion monitoring and detection is an essential step in hydrocarbon

industries to reduce economic loss. The corrosion owing to the acidization of oil wells is one of the very critical issues, and it requires corrosion inhibitors of excellent efficiency. The heteroatom-constituted compounds having the electron-donating ability exhibit good interaction with the metal surface and furnish the corrosion inhibition efficiency [29]. Herein, the corrosion inhibitors developed from the industrial waste of alkyl pyridines are demonstrated as inhibitors to suppress the corrosion of carbon steel under the simulated acidic condition. The NQR-1 and NQR-2 additives showed excellent corrosion inhibition efficiencies (>99%). Another advantage of these inhibitors is that they have been developed using industrial waste products and hence, allows us to follow the 3Rs policy of reducing, reuse, and recycle and helps in eliminating industrial waste.

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