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Green Corrosion Inhibitors in High Temperature and Saline Geothermal Fluids

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ABSTRACT

Geothermal energy is heat derived from deep inside of the earth's surface, this geothermal energy is carried via water or streams through pipes from deep sub-surface and bought to the earths ground where with the help of various post processing techniques we can use this geothermal energy for warming and refrigeration purpose or else this energy can be utilized to form clean electric energy. The major concern while carrying out geothermal fluid is of corrosion, due to fluid temperature and salinity, internal corrosion can be observed. Not only internal corrosion can be exploded we can even see corrosion of external piping and vessels at geothermal fields. To overcome this internal corrosion effect, plant extracts can be used as a green corrosion inhibitor. Plant extracts can become important as an environment friendly, nontoxic, readily available and can be easily renewed. Tannins which are a class of natural, innocuous and economical polyphenolic compound can be easily extracted from plant sources such as pine (Pinus sp.), Quebracho (Scinopsis balansae), Quercus robur, Pomegranate peels and certain amount of its concentration can be added in acidic medium and can be used as corrosion inhibitor for geothermal fluids. We can inhibit the effect of these plant extracts (by selecting the right concentration) on steel corrosion in geothermal fluid using Gravimetric method.

1. INTRODUCTION

Scale formation is one of the most sever factor which occur during transportation of geothermal fluid and accounts the lifetime effectiveness of system and productivity. The scale formation occurs due to dissolubility of calcium carbonate. Geothermal fluids medium plays an important role in corrosion effect. To prevent corrosion, inhibitors are one of the most suitable method which can be used. Recently those inhibitors which are innocuous or less harmful are given much preference. In the 21st century "green" or "environment-friendly" corrosion inhibitors has been highlighted towards the goal of using cheap effective compound at low or null environmental consequence. As being both economic and environmental benefits we can use plant extracts as green inhibitors in inhibiting corrosion of metal under various environments and especially in acid medium.

Tannins which are plant extracts and a class of polyphenolic composition can be used as corrosion resistance in dilute solutions. Tannins are classified as two polymeric classes. Hydrolyzed and other condensed. Hydrolyzed one are egallic acid which get hydrolyzed in acid medium and condensed one are polymeric flavonoids. Although there is a much research on tannin but there is little information of corrosion activity of Quercus robur, Oak, pomegranate peels pine and Quebracho which are rich in tannin. Pomegranate include tannin too; they include especially hydrolysable tannins.

In this study corrosion preventing character of tannin which is extracts from Quercus robur oak, pomegranate peels, pine and Quebracho extracts reexamined and is found that extracts have shown inhibition of geothermal fluid in corrosion.

2. EXTRACTION OF TANNIN FROM PLANTS

The nuts of the Quercus robur is peeled and meshed into 500 small grind, the same procedure is done with pomegranate peels, pine bark and Quebracho, the samples are then dried out in air for approximately 5-6 days under room temperature (25-30 degree Celsius), then this dried sample are kept in water bath with methanol under 40-45(degree Celsius) for 3-4 days, then peels are separated from their extracts with methanol by filtering process, then methanol is removed from the mixture by rotary evaporator under vacuum, we get viscous liquid with dark brown color.

The above procedure is done for getting tannin from PMNE extract, after getting viscous liquid from the above procedure that viscous liquid is dissolved under 1mol /L HCL at 25 degree Celsius in four different test tube with different composition of that viscous liquid (200 mg/L,400 mg/L,600 mg/L, 800 mg/L) to prepare a stock solution and then distilled water is added into it and after than ethyl alcohol in amount 25 %, is added into it in order to not cause degradation of the stock solution.

The same above procure is done for tannin extract from Quebrachos but instead of 1mol /L we have used 0.1M HCL with (500 mg/L, 1500 mg/L,6000 mg/L) querbrachos in four different test tube and the temperature under which the stock solution was prepared was at 70 degree Celsius.

For pomegranate peels we have prepared the stock solution with 5 M HCL and 40 g/L concentration of viscous tannin liquid, viscous liquid is prepared by following the same procedure which was done for Quebrachos and PMNE.

3. WEIGHT LOSS TEST (GRAVIMETRIC METHOD)

3.1 Procedure for Weight Loss Test (Gravimetric Method) for PMNE Extract

A small specimen of Q235 Steel was taken into account whose dimensions are (30mm× 15mm× 3mm) for gravimetric method experiment to determine rate of corrosion and inhibiting efficiency. The specimen was polished with different abrasive paper of

coarse and fine grade, then it was washed with tap water and degrased with acetone and dried under room temperature. Then specimen was weighted, after that specimen was added to the stock solution and after weighing we added the specimen to a 300 mL of a 1 mol/L HCl solution whose pH was 0.1 , with the addition of PMNE extract tannin at concentration of 0 g/L (bno tannin concentration), 200 mg/L, 400 mg/L, 600 mg/L, and 800 mg/L in 5 test tube .The temperature was set at 25 ℃ and the specimen were allowed to soak 4h, after that the specimens was taken out, rinsed with tap water, washed with acetone, dried and was weighted again, different readings were noted for different concentration of the stock solution in test tube.

3.2 Procedure for Weight Loss Test (Gravimetric Method) For Quebrachos Extract

A specimen of SAE 1010 was taken into account whose dimensions are (10mm× 10mm× 19mm) for gravimetric method experiment to determine rate of corrosion and inhibiting efficiency. The specimen was polished with different abrasive paper of coarse and fine grade, then it was washed with tap water and degrased with acetone and cooled under room temperature. Then specimen sample was weighted after specimen was added to the stock solution and after weighing we added the specimen to a 300 mL of a 0.1 M HCl solution, with the presence of QUEBRACHOS extract tannin at concentration of 500 mg/L , 1500 mg/L and 6000 mg/L in 3 test tube .The temperature was set at 70 ℃ and the specimens were allowed to soak 168h(7 days), after that the specimen was taken out and rinsed with tap water, wash with acetone dried and weighted again, different readings were weighted for different concentration of the stock solution in test tube.

3.3 Procedure for Weight Loss Test (Gravimetric Method) for Pomegranate Peel

A specimen of Mild steel was taken into account whose dimensions are (25mm× 50mm× 2mm) for gravimetric method experiment to determine rate of corrosion and inhibiting efficiency. The specimen was polished with different abrasive paper of coarse and fine grade, then it was washed with tap water and degrased with acetone and cooled under room temperature. Then specimen was weight after specimen was added to the stock solution and after weighing we added the specimen to a 300 mL of a 5 M HCl solution, with the presence of POMEGRANATE extract tannin at concentration 40g/L in a test tube .The specimen was allowed to soak 168h(7 days), 336 h, 504h and 672 h, after that the specimen was taken out and rinsed with tap water, washed with acetone dried and weight again, different readings were weighted for different concentration of the stock solution in test tube.

4. RESULT AND DISCUSSION

Using Gravimetric method we can find the corrosion rate and inhibiting efficiency of different plant extracts in the specimen by weighing the weight of specimen before and after the submerge of specimen into the acidic medium of different concentration with specified amount of tannin extracts with different exposure /immersion time of specimen in the acidic medium so that we can get to know the corrosion reaction when the geothermal fluid is kept running inside the medium. By this method, we can find the corrosion rate of specimen using the below equation,

$$CR(MYP) = \frac{534W}{DAT}$$

Using the above stated equation we can find corrosion rate of specimen with tannin content(CRi) and corrosion rate of specimen without tannin content (CRo), After finding CRi &CRo we can use both of the value to find inhibition efficiency (IE%) using equation,

$$IE\% = \left(1 - \frac{CRi}{CRo}\right) \times 100$$

4.1 Inhibition Efficiency of Corrosion in Absence and Presence of PMNE Extract

Inhibition efficiency for Q235 steel in a 1 mole /Litre of HCl solution with and without the presence of PMNE extract at 25 °C.

Table 1: Inhibition Efficiency for Q235

CONCENTRATION (g/L)	INHIBITION EFFICIENCY (IE%)
200 mg/l	88
400 mg/l	90
600 mg/l	92
800 mg/l	93

From the above table we can see that rate of corrosion behavior of Q235 steel in a 1mole/Litre HCl solution, at 25 degree Celsius when inhibitor concentration was 800 mg/L the corrosion rate of specimen was 3.6 g/m^2 h, which states that excellent inhibition efficiency 95% as compared with corrosion rate of 79.9 g/m^2 h in the absence of inhibitor.

4.2 Inhibition Efficiency of Corrosion in Absence and Presence of Quebrachos Extract

Inhibition efficiency for SAE 1010 in a 0.1 M HCl solution in the absence and presence of Quebrachos extracts at 70 °C.

Table 2 Inhibition Efficiency for SAE

CONCENTRATION (g/L)	INHIBITION EFFICIENCY (IE%)
500 mg/l	29
1500 mg/l	79
6000 mg/l	38

From the above table we can see that corrosion behavior of SAE 1010 in a 0.1 M HCL solution, at 70 degree Celsius when inhibitor concentration was 1500 mg/L the Inhibition efficiency of corrosion was 79 % as compared to when the inhibitor concentration in the solution was 500s mg/L .With rise in the amount of the tannin the inhibitor efficiency increases at some peak that with too much of concentration there is fall in the inhibition capacity.

4.3 Inhibition Efficiency in Presence of Pomegranate Peel at Different Exposure Time.

Inhibition efficiency for Mild Steel in a 5 M HCl solution in the absence and presence of 40g/L Quebrachos extracts at different exposure time

Table 3: Inhibition efficiency for Mild Steel

EXPOSURE TIME (IN HOUR)	INHIBITING EFFICIENCY (IE%)
168	88.2
336	96
504	95.4
672	95.4

From the above table it can be inferred that as we keep the specimen in contact with the acidic medium of 5M HCL which contain Quebrachos extract of 40g/L, we can see that the corrosion inhibition efficiency increases as compared to when the specimen is not in the contaminant with Quebrachos extract or in less contaminant with Quebrachos extract.

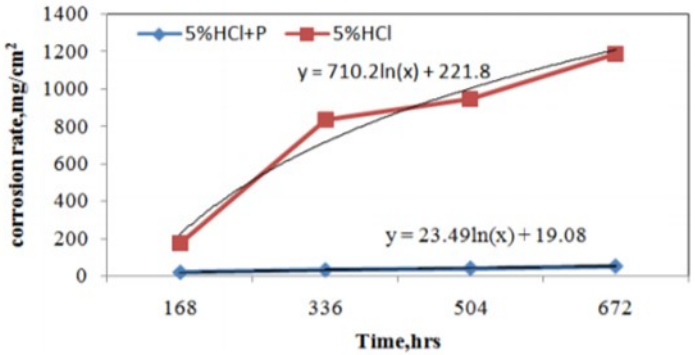

Figure 1 the connection between corrosion rate and exposure time with and without the presence of tannin extracts

4.4 CHEMICAL REACTION OF TANNIN WITH THE METTALIC SURFACE.

To depict the chemical reaction between metallic surface and tannin, we have exemplified it by taking metallic surface as iron. OH-groups in the ortho position on the aromatic rings, tannins able to form chelates with iron and other metallic cations and formation of ferric tannate with condensed tannin. Fe2+ ions can easily form ferrous-tannates which is easily oxidized into ferric-tannates, a blue-black deposit which when in contact with oxygen, inhibit the oxidation of Fe2+ ions into ferric oxides oxyhydroxides (Fe3O4, FeOOH) and resist the rust formation. The given below are the equation which shows the reaction,

n FE3+ + ne- nFe2+ (1)

tannins tannate + ne- (2)

n Fe3+ + tannins (Fe2+)n tannate (3)

Consequently, (Fe2+)n tannate (Fe3+)n tannate + ½ H2O (4)

(½ O2)n tannate + ¼ n O2 + nH+ (Fe3+)n tannate + ½ nH2O (5)

The tannate transformed from the inhibition of Fe3+ -oxyhydroxides formation on clean steel surface and Fe3+ - oxyhydroxides.

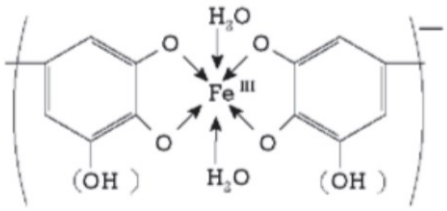

Figure 2 Ferric tannate complex

5. CHALLENGES AND FUTURE SCOPE

One of the major challenges which can be seen in "green corrosion inhibitor" in geothermal energy is that when the right concentration of the tannin is used for inhibiting corrosion then only, we can resist the specimen form corrosion otherwise when the right concentration is not used, in some cases we might see the inward graph in the corrosion resistance of specimen. Therefore, the right concentration is must important factor for maintaining the specimen from corrosion, other challenges is that tannin exhibit the corrosion resistance only in certain medium, so Ph level of the geothermal fluid is also an important factor in maintaining the pipes form corrosion. The future scope of green corrosion inhibitor is simple straight forward, due to being innocuous, environment friendly and readily available corrosion inhibitor it can be easily researched and used for corrosion inhibitor in geothermal plants, where the efficiency of the plant can be increased by protecting the pipes and other equipment's from corrosion. Due to its innocuous behavior, we can see a rapid growth in inhibitor factor since last few years and many ongoing research have proved the best utility of plant extracts as corrosion inhibitor.

6. CONCLUSION

Geothermal fluid act as a corrosive in nature, to overcome that plant extracts have been used, as its been proved that tannins can be extracted from plants, so by extracting tannin from plants and then by applying some procedures we can get thick viscous solution which can be added to the acidic medium in some proportion and then with the help of geothermal fluid we can utilize our prepared stock solution to protect the surface from corrosion. As we can see that corrosion harms the total productivity of geothermal plant by degrading the quality of the pipes and reducing the efficiency to carry geothermal fluid, so to overcome from huge maintenance which is required while preventing corrosion, tannins a natural biodegradable class which is not toxic can be used as an corrosion inhibitor . From the weight loss method we have proved that tannins which are extracted from plants like pmine, Quebrachos, Quercus robur oak and pomegranate peels which when used under proper tannin concentration can inhibit corrosion effect, the proper concentration of tannin and the exposer time of fluid is must because as we can see during the experiment, that in some tannin extracts when the concentration of the tannin were excess in acidic medium then required then the inhibiting of the corrosion decrease and hence generally when the concentration is properly used it proves to be the best inhibitor and while in the case of exposer time when the exposer time is increased in acidic medium the corrosion inhibiting proportion increases and makes it excellence Green corrosion inhibitor which is biodegradable, cheap and less environment harmful.

7. REFERENCE

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