

Proposed Corrosion Control Method for Fire Fighting Systems in Oil Fields

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THE FIRE fighting systems are found in all oil production and processing fields. The water used in these systems is mostly underground-, sea-, fresh- and could be formation - water. The corrosion control of these systems is achieved by injection of corrosion inhibitor, biocide and oxygen scavenger chemicals, either separately or mixed (multifunction). In the present paper, replacement of the currently used multifunction chemicals by $\text{Ca}(\text{OH})_2$ is proposed as more economic and effective corrosion control regime. Inhibition in this case depends on increasing the pH of the water to about 12 leading to deposition of the calcium ions of the water as carbonate and/or sulfate layer on the tank surface. This barrier layer in addition to the passivity of the steel surface in this basic water could achieve the required corrosion control. The result obtained, compared with the currently used multifunction chemicals indicate more higher corrosion inhibition of the proposed method for both general and local corrosion.

Fire fighting systems (F.F.S.) are found in all production and processing petroleum companies. These systems generally use sea water, underground water, fresh water and some may use oil-associated (formation water). They are treated with corrosion inhibitors, oxygen scavengers and biocides, either separate or in multifunction form to control corrosion and biofouling of the mild steel tanks and pipes, in addition to cathodic protection (sacrificial anodes).

The corrosion control of steel in saturated $\text{Ca}(\text{OH})_2$ solution has been severally reported⁽¹⁻³⁾. The inhibition by $\text{Ca}(\text{OH})_2$ depends on increasing the pH of the water to about 12 leading to deposition a barrier layer of calcium ions of the water as carbonate and /or sulfate layer on the tank surface⁽²⁾.

In this paper, more simple and economic method of control is proposed. This method depends on saturated calcium hydroxide and corrosion inhibitor instead of the three additives. The corrosion control of steel in saturated $\text{Ca}(\text{OH})_2$ solution has been severally reported⁽¹⁻³⁾.

Experimental

Carbon steel was tested in water sample used in fire fighting system of a

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petroleum production company, before injection. The analysis of this water is given in Table 1. The chemical composition of the used steel is given in Table 2.

TABLE 1. Analysis of the used water.

Item	Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Sr ⁺⁺	Ba	Fe ⁺⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻
Concentration (ppm)	1730	112	403	397	44.2	0.1	4.4	4120.7	126	560.6

TABLE 2. Analysis of the used carbon steel.

Element	C	Mn	Si	P	S	Cu	Cr	Ni	Ti	Al	Mo	Sn
Amount,%	0.047	0.289	0.037	0.017	0.013	0.054	0.049	0.057	0.02	0.003	0.002	0.02

The corrosion tests were conducted by weight loss and cyclic polarization methods to measure the general and pitting corrosion, respectively. The general corrosion was measured by immersing clean carbon steel coupons (2x10x0.2 cm) for five days in the test water at ambient temperature under static condition.

In the polarization tests, steel electrode with 1 cm² subjected area was used, with Pt counter and saturated calomel electrodes. The measurements were conducted by EG&G potentiostat (Galvanostat Model 273A). After reaching steady potential, E_{cor} (about 40 min.), the pitting susceptibility was characterized by means of cyclic anodic polarization curves. A potential scanning rate of 0.2 mV/Sc was used⁽⁴⁾. The current limit for reversing the potential scan was 10⁻³ A/cm². The pitting potential (E_p) was defined as the potential value at which the current density sharply rises. This polarization technique has been widely used to study the corrosion of carbon steel and other steels in alkaline solutions^(3, 5, 6).

Results and Discussion

General corrosion

The corrosion rate values of steel in the F.F.S. water alone (C.R.Bl) and in saturated Ca(OH)₂ in water (pH about 12) (C.R. Inh.) were measured. From these values, the corrosion inhibition was calculated as:

$$\text{Inh. Eff., \%} = \frac{(\text{C.R.Bl}) - (\text{C.R. Inh.})}{(\text{C.R.Bl})} \times 100$$

The results are given in Table 3.

TABLE 3. General corrosion of carbon steel in the F.F.S. water.

Corrosion rate, mpy		% Inhibition
Water alone	Ca(OH) ₂ sat. water	
3.1	0.53	83

The results show saturation with Ca(OH)₂ achieved high corrosion inhibition

for steel (83 %), which is expected. This is also seen from the surface of the steel coupon immersed 15 days in the test waters (Fig. 1).

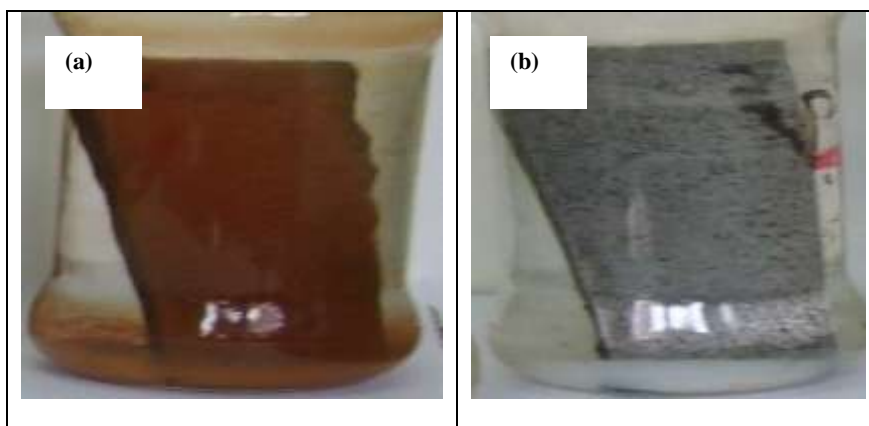


Fig. 1. Photos of the surface of steel coupons immersed for two weeks in the test water in absence (a) and presence of $\text{Ca}(\text{OH})_2$ (b).

From these results, it could be suggested that in presence of $\text{Ca}(\text{OH})_2$, there is no need for O_2 -scavenger. The corrosion inhibition in this system depends on the formation of a passive layer contaminated or covered with adsorbed layer of Ca and Mg sulfate and carbonate. The presence of O_2 in this case could have beneficial action for the passivation process.

Concerning biocide addition, it is not sure that sulfate reducing bacteria (SRP) could live in this alkaline environment ($\text{pH} = 12$), this should be confirmed.

It appears useful to refer here to the results of evaluation of multifunction chemicals previously conducted (in our Lab.) for the fire fighting system mentioned above. Examples from these results are given in following Table:

Multifunction Chemical	% Inhibition of General Corrosion	% Inhibition of Pitting Corrosion
1	42	28
2	64	61
3	69	63
4	49	33

Comparing these results with that obtained in the present study indicate clearly more higher inhibition for the general corrosion in saturated $\text{Ca}(\text{OH})_2$ water.

Pitting corrosion

At the beginning, the detrimental action of the chloride content of the water was expected. On the other hand the other (cations and anions) contaminants with high concentration of chloride could have another action on the formed passivity and the layer

built on the steel surface⁽⁷⁻¹¹⁾. This means that the known effect of chloride ion on the passivity of steel in alkaline distilled water might not be the same in the present test water.

This expectation is supported by the reported mechanisms of breakdown of the passive film by chloride ions^(6, 12, 13). According to this mechanism, the breakdown occurs via adsorption of chloride ion on the passive film, then migration or penetration of this film to the metal surface. These two steps might be more difficult in the present formed film on the metal surface.

It thus appeared important at the beginning to conduct cyclic polarization curves for the carbon steel in distilled water saturated with $\text{Ca}(\text{OH})_2$ in presence of increasing concentrations of NaCl. The results are given in Fig. 2. The polarization curve in the F.F.S. water is shown in Fig. 3. This figure includes also the polarization curves in the same water (F.F.S) in presence of corrosion inhibitor.

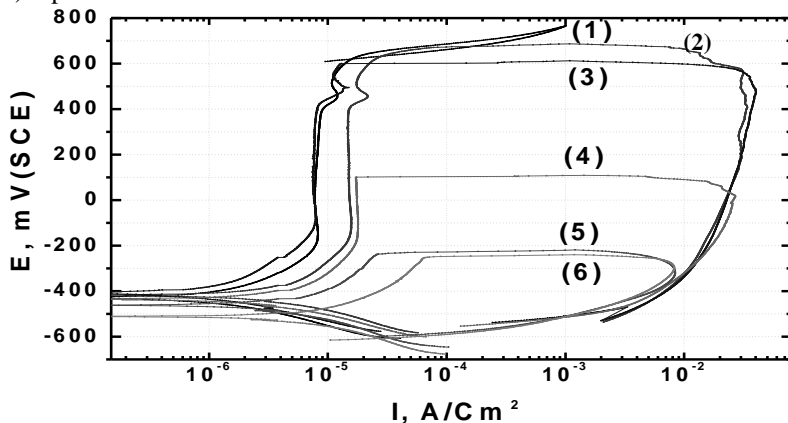


Fig. 2. Cyclic polarization curves for the steel in distilled water saturated with $\text{Ca}(\text{OH})_2$ in presence of increasing concentrations of NaCl. NaCl, %wt, 1(0.0), 2(0.2), 3(0.4), 4(1.0), 5(5.0), 6(10.0).

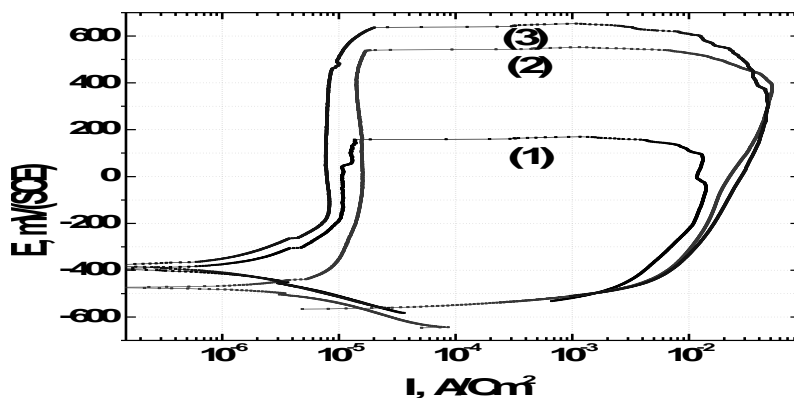
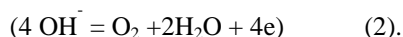


Fig. 3. Cyclic polarization curves for the carbon steel in F.F.S. water saturated with $\text{Ca}(\text{OH})_2$ in absence (1) and presence of 60 ppm (2) and 80 ppm molybdate inhibitor (3).

The cyclic polarization curves in saturated Ca(OH)_2 distilled water show that in absence of chloride, no sign of attack is seen. The sudden rise in current occurred at about 660 mV vs. SCE is caused by oxidation of $(\text{OH})^-$ ions.



Addition of 0.2 % NaCl caused no significant shift of the potential at which the jump of the current occurs, but the curve shows hysteresis, indicating initiation of pitting. The variation of the corrosion potential (E_{corr}), pitting potential (E_p) and the difference between the two values ($E_{\text{corr}}-E_p$) with increasing NaCl in saturated Ca(OH)_2 distilled water are given in Table 4 and graphically in Fig. 4.

TABLE 4. Variation of E_{corr} , E_p and ($E_{\text{corr}} - E_p$) in Ca(OH)_2 Saturated distilled water with NaCl concentrations.

% NaCl	E_{corr}	E_p , mV	$E_{\text{corr}} - E_p$, mV
0	-400	660 (O_2 evolution)	1060
0.2	-400	650	1050
0.4	-410	600	1010
1	-420	80	500
5	-450	-240	210
10	-500	-260	240

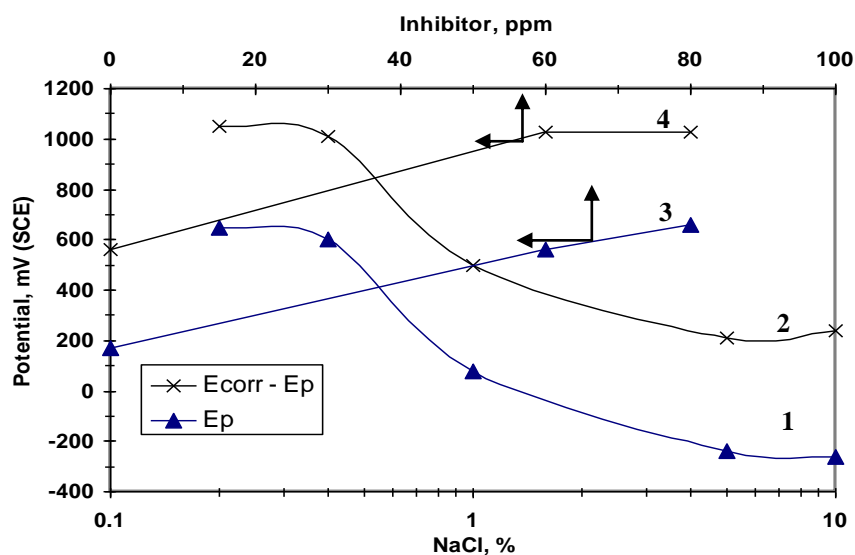


Fig. 4. The variation of E_p and ($E_{\text{corr}} - E_p$):
 Curves (1, 2) with NaCl in saturated Ca(OH)_2 distilled water
 Curves (3, 4) with molybdate base inhibitor in saturated Ca(OH)_2 F.F.S.

The results of Table 4 and Fig. 4 show clearly sudden drop in both E_p and $E_{\text{corr}}-E_p$ in presence of 1% NaCl, followed by slow variation till 5%, then no significant change till 10% NaCl. These results indicate also that the threshold concentration of NaCl for initiation of pitting of carbon steel in saturated $\text{Ca}(\text{OH})_2$ is about 0.4%, which is in agreement with previous data^(11, 14).

The cyclic polarization curve in F.F.S. water saturated with $\text{Ca}(\text{OH})_2$, (Fig. 3), shows the sudden rise of current (pitting) occurs at $E_p = 170$ mV SCE, and $E_{\text{corr}}-E_p = 560$ mV. This water contains chloride equivalent to 0.89% NaCl, in addition to about 0.15% Na_2SO_4 . The total corrosive ions in this water is about 1% NaCl. At this concentration in saturated $\text{Ca}(\text{OH})_2$ distilled water $E_p = 80$ and $E_{\text{corr}}-E_p = 520$ mV.

The above results indicate that both E_p and $E_{\text{corr}}-E_p$ in the test water are more positive than the corresponding values for the distilled water, by about 80 and 40 mV, respectively. These results support the previously expected beneficial action of the other constituents of the water used in fire fighting system (underground, sea and formation water).

The polarization curve of carbon steel in the F.F.S water, (Fig. 3), shows the characteristics of pitting. However, no pits could be seen visually on the electrode surface. This suggests that it is crevice corrosion. To inhibit this local attack, molybdate base inhibitor was used. Curves 2, 3 in (Fig. 3) were recorded in presence of 60 and 80 ppm from this inhibitor.

These curves show clear shifts of both E_p and $E_{\text{corr}}-E_p$ to more positive potentials. In presence of 60 ppm molybdate inhibitor, E_p is shifted to 560 mV (SCE) and $E_{\text{corr}}-E_p$ to 1030 mV. Increasing the molybdate inhibitor to 80 ppm, the two parameters are shifted to 660 and 1030 mV, which are very close to the values of saturated $\text{Ca}(\text{OH})_2$ distilled water free from chloride, (Fig. 4). These results indicate a good inhibition efficiency of the used inhibitor. The high efficiency of molybdate in retarding both the general and localized corrosion of ferrous and non ferrous metals has been severally reported⁽¹⁵⁻¹⁸⁾. The formulation used in the present study has been previously prepared in our laboratory and tested in chemical plants⁽¹⁶⁾.

It appeared important to retest the inhibition of carbon steel in the F.F.S. water in presence of the recommended molybdate formulation (80 ppm).

The results of this test showed that the inhibition efficiency increased to 94% compared to 83% in absence of the inhibitor.

Conclusion

It could be concluded that the proposed method of corrosion control of fire fighting systems in oil production and processing is promising method. It basically depends on the use of saturation of the water with $\text{Ca}(\text{OH})_2$ and addition of limited concentration of molybdate base inhibitor.

The benefits of the proposed method are:

- More lower cost
- More higher inhibition for both the general and localized corrosion
- No need for both O₂- scavenger. The presence of O₂ in this case could beneficially affect the stability of the passive film.
- No need for biocide because the present alkalinity (pH 12), is not optimum for sulfate reducing Bacteria (SRP) surviving.

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طريقة مقترحة لتثبيط التآكل في أنظمة مكافحة الحرائق في مجال انتاج النفط

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تنتشر أنظمة مكافحة الحرائق في مواقع انتاج النفط والغاز والعمليات المترتبة عليها. فالمياه المستخدمة في هذه الأنظمة قد تكون جوفية او مياه بحار او مياه عذبة او المياه المصاحبة للزيت الخام. هذه المياه تضاف اليها كيماويات متعددة الوظائف عالية الثمن وملوثة بيئيا وذلك بغرض تثبيط التآكل، طرد الاكسجين أو قتل البكتريا كل على حدة او مجتمعين.

في هذا البحث تم اقتراح استبدال هذه الاضافات بهيدروكسيد الكالسيوم بتركيز معين كمادة رخيصة وامنة وذات فاعلية عالية في تثبيط التآكل. وجد ان إضافة هيدروكسيد الكالسيوم الي المياه المستخدمة أدت الى زيادة الاس الهيدروجيني الى حوالى 12 مما نتج عنه ترسيب طبقة عازلة من كربونات وكبريتات الكالسيوم والتي ادت بدورها الي الحد من تآكل الخزانات الفلزية .
بمقارنة النتائج التي تم الحصول عليها مع نتائج الاضافات الكيماوية المستخدمة لهذا الغرض، اظهرت النتائج ان هيدروكسيد الكالسيوم اكثر فاعلية واقل تكلفة وأمن بيئيا كامانع للتآكل خاصة في وجود نسبة ضئيلة من مثبط الموليبيدات مقارنة بالاضافات الكيماوية التجارية المستخدمة في هذا المجال.