

Studying the use of tetrakis(hydroxymethyl)phosphonium sulfate (THPS) as zinc sulfide and lead sulfide scales dissolver and the factors influencing the dissolution

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Abstract

Tetrakis(hydroxymethyl)phosphonium sulfate (THPS), regarded as one of the most effective oilfield biocides in fighting SRB, is also found being able to dissolve iron sulfide scales which are known difficult to be solubilized. In this work the dissolution behavior of THPS on zinc sulfide and lead sulfide scales was studied. A combination of THPS up to 30 wt.% with ammonium chloride up to 12 wt.% is effective to zinc and lead sulfide scales. The THPS showed limited dissolution behaviour with all other additives which contain ammonium ion or chloride ion alone, which suggests that ammonium chloride is a critical ingredient of the dissolution process. The phosphonates additives also showed no dissolution behavior. The dissolution reaction is temperature and time dependent as the maximum dissolution was obtained at 85°C and after 24 hours. The corrosivity of the proposed mixture was generally less than that of the inhibited acid solutions.

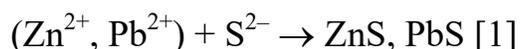
Key words: THPS, biocide, ammonium chloride, zinc sulfide, lead sulfide, scale dissolver.

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Introduction

Zinc and lead sulfide scales have recently become a concern in a number of oil and gas fields such as along the Gulf Coast of the USA and within the North Sea Basin [1, 2]. These deposits have occurred within the production tubing and within the topside process facilities [3]. They can cause serious operation problems if not controlled. The Ras Shukair Field in Egypt has experienced the zinc and lead sulfide scale problems in almost all production areas, which sometimes lead to loss of production, long term shut-ins and excessive costs for mitigation.

The likely mechanism of formation of zinc and lead sulfides can be expressed as below :



The potential sources of zinc and lead ions include formation minerals such as spherite ZnS and galena PbS, completion fluids (ZnBr_2) lost into the formation during drilling and workover operations (ZnBr_2), reaction of injected water with the formation rocks enriched with heavy metal ions. The potential sources of sulfide ion include hydrogen sulfide in reservoir fluids, decomposition of drilling compounds and corrosion inhibitors, and microbial activities [2].

The use of acid is the simplest way to dissolve such a deposit, but this type of dissolvers generates large volumes of highly toxic H_2S gas, which is an undesirable by-product. Also, the acid treatment has the potential to cause severe corrosion even formulated with corrosion inhibitors [4]. Moreover, the acid treatment in the downhole could cause formation damage. Using an oxidizing agent may avoid such toxicity hazards but produces oxidizing products including elemental sulfur which promotes localized corrosion. Acrolein, although showing effectiveness, is a difficult material to handle [4].

Tetrakis(hydroxymethyl)phosphonium sulfate (THPS) is an environmental friendly biocide commonly used in oil field for both downhole and topside. It is also widely applied in other variety of water treatment processes including industrial cooling and paper manufacture. It is primarily utilized to control sulfate reducing bacteria due to its enhanced performance, higher thermal stability and low foaming potential [5].

It was discovered that the THPS is also able to dissolve a range of iron sulfides formed in oil wells. This led, in some instances, to the use of THPS solely for this purpose although often the dual functionality (as biocide and iron sulfide dissolver) significantly increased the economic effectiveness of this form of treatment.

Talbot *et al.* [4] studied the dissolution of iron sulfides in THPS based solutions over a range of conditions and showed that its performance was comparable to or even better than the uninhibited hydrochloric (HCl) acid with actual field scale samples as well as pure authigenic minerals, particularly in combination with ammonium chloride or organic phosphonate scale inhibitor. In their study, the THPS also displayed an ability to dissolve pyrite, which is generally considered insoluble in hydrochloric acid. Wang *et al.* [5] performed further evaluations using iron sulfide scales formed in high temperature sour gas wells.

No work has been done to investigate the use of THPS as a dissolver for lead and zinc sulfide scale deposits formed in oil producing wells. The objective of this work is to study the effect of THPS as a dissolver for this type of scales formed in downhole oil producing well. The effect of varying factors on the dissolution behavior will be investigated.

Experimental

Scale Sample

A field sulfides scale sample was used for this study. The scale sample was collected from downhole tubular of oil well at depth 3820' during intervention. This well produces from a sandstone reservoir with downhole temperature 282°F and pressure 2780 psi, and the water

production rate is 262 bbl/day. Table 1 summarizes the chemical composition of scale sample analyzed using the ICP–OES technique. It can be seen that the zinc and lead sulfides were the dominant species. This was confirmed by further X-ray diffraction (XRD) analysis (Figure 1). The XRD analysis was performed at 45 kV and 30 mA using Cu K α radiation with $\lambda = 1.5404 \text{ \AA}$.

Table 1. Scale sample composition by ICP–OES.

Source	Composition (%)
Paraffin wax	11
Halite	3
Iron sulfide	3
Zinc sulfide	47
Lead sulfide	26
Calcite	1
Barium & strontium sulfate	0.5
Sand residues	8.5

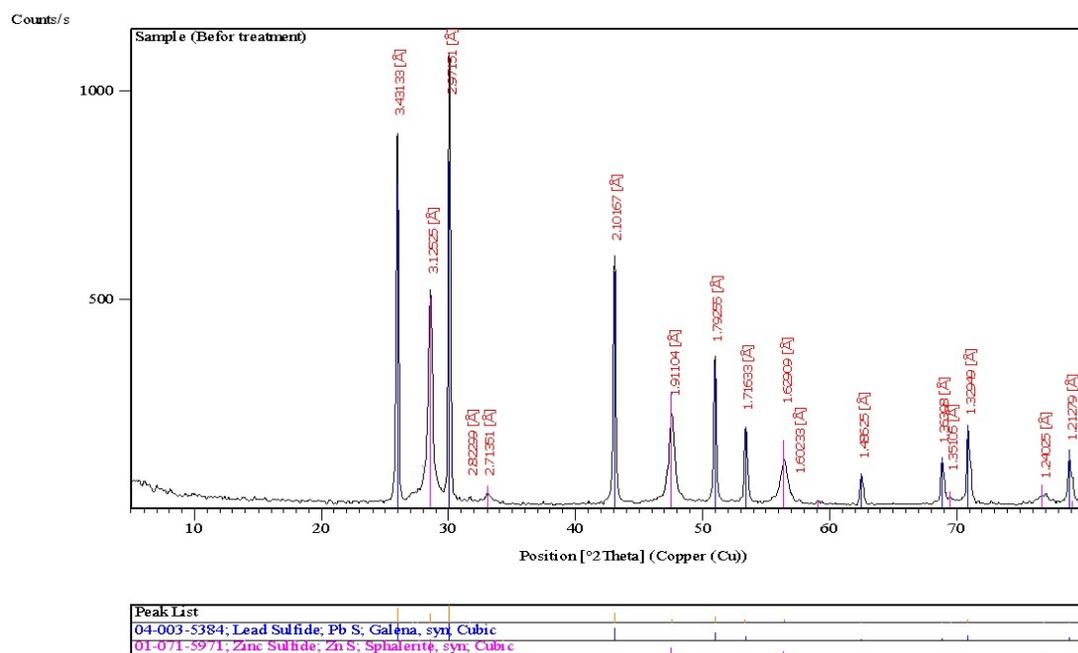


Figure 1. X-Ray diagram of the studied sulfide scale samples which showed main component of zinc sulfide and lead sulfide.

The raw deposit sample was in the form of flakes and chunks. The dissolution tests were conducted with the samples without grinding. The only pre-treatment was using chloroform to remove the hydrocarbon and fine particles. The sample was washed

repeatedly till the solvent became clear. Then the sample was dried in the oven at 105°C for one hour before use.

Dissolver and Additives

The dissolver solutions were prepared from a THPS (50%) commercial product with different additives formulated. The additives included ammonium chloride, phosphonates (diethylenetriamine pentamethylene phosphonate (DETPMP) and bis(hexamethylene)-triamine pentamethylene phosphonate (BHTPMP), ammonium hydroxide (Sigma Aldrich 99%), potassium chloride (Fisher Scientific 99%), sodium azide (Sigma Aldrich 99.5%), and ammonium oxalate (Sigma Aldrich 99.5%). The best THPS-additive mixture was then selected to study the effects of variable parameters on the dissolution efficiency, such as THPS concentration, additive concentration, pH, temperature, and soaking time. Effects of pH, temperature and soaking time were studied by using solutions with 15% THPS. The pH adjustment was achieved by adding concentrated HCl or NaOH solution, and the amounts of additives were kept at the maximum miscibility with the THPS.

Test Procedure

All experiments except for temperature effect were performed at 85°C. Each test used 1.00 gram of the scale chunks, and 50 ml of dissolver mixture. A Sani glass bottle was filled with the dissolver solution and then the scale sample was added and the test bottle was placed in a water bath at test temperature for the specified period of time. The remaining scale in the Sani glass bottle at the end of test was difficult to recover because of the formation of greasy phase (Figure 2). Thus the dissolution behavior of the dissolver solution was evaluated by measuring the concentrations of the dissolved zinc and lead ions in the spent dissolver solution. The aliquot of the supernatant was diluted with distilled water and preserved with 1% HNO₃, and the analysis was done by inductively coupled plasma method (ICP-OES).

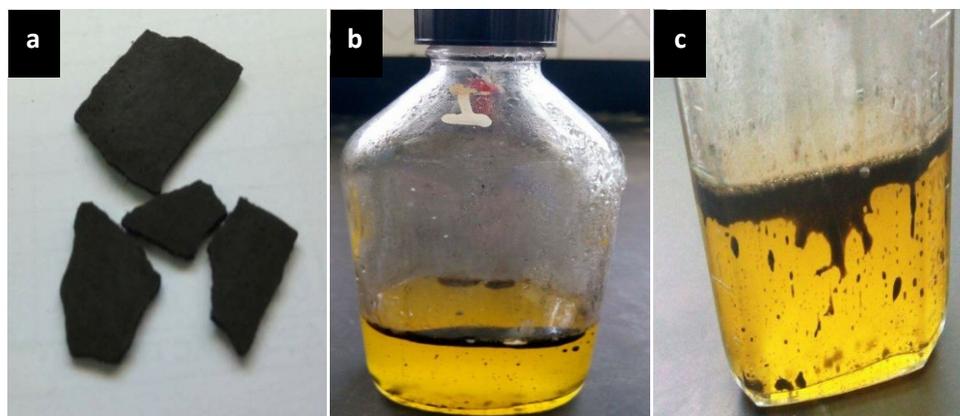


Figure 2. Sulfide scales used in the study (a) before dissolution (b&c) after dissolution.

Corrosion test

Corrosion test was performed according to NACE standard RP0775-2005 [6] to compare the corrosivity of the THPS mixture with uninhibited and inhibited 15% HCl acid. The acid corrosion inhibitor was 2% in the inhibited 15% HCl acid. Tests were performed both in the presence and absence of scale samples.

Results and Discussion

The dissolution performance of THPS with different additive's mixtures was studied at different parameters on the scale sample and the results indicated in graph for easy comparison.

Effect of additives

The first experimental trial conducted with THPS (15%) showed poor dissolution efficiency on zinc and lead sulfide scales, with 27 ppm Zn and 48 ppm Pb in the final solution. Then different additives were used with THPS to study their behavior.

Figure 3 shows that the THPS–ammonium chloride mixture gave the best dissolution performance on both zinc and lead sulfide scales. Other additives of ammonium salts had poor performance. The ammonium citrate formulation had 285 ppm Zn and 47 ppm Pb; the ammonium oxalate mixture had 102 ppm Zn and 97 ppm Pb. Ammonium sulfite, which was used as oxygen scavenger, showed improved zinc sulfide dissolution with 691 ppm Zn. They were much less effective than ammonium chloride (5723 ppm Zn, 2603 ppm Pb). The dissolution was limited to 23 ppm Zn and 26 ppm Pb with sodium azide. When KCl was added to increase chloride concentration, dissolution was not improved (111 ppm Zn, 26 ppm Pb). These results indicate that the dissolution reaction is selective to ammonium chloride.

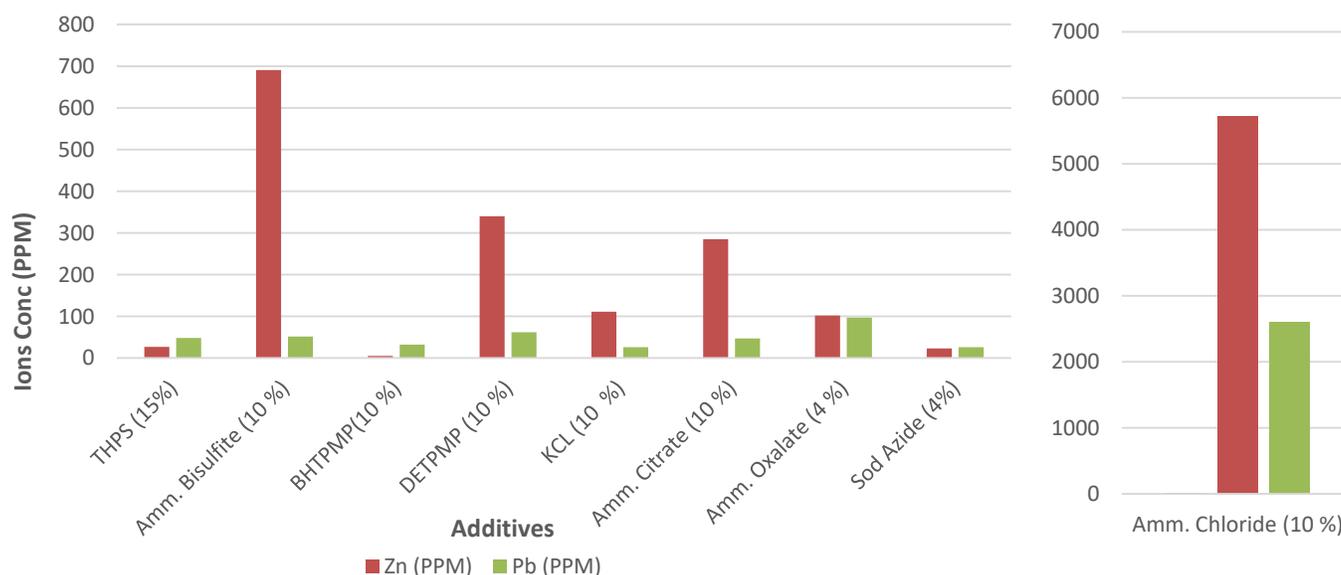


Figure 3. The dissolution behaviour of different additives mixed with THPS.

Phosphonates were also evaluated as additive. Gilbert *et al.* [4] showed that phosphonate was a promising additive with THPS to dissolve iron sulfide. DETPMP and BHTPMP were used from commercial scale inhibitor. The results obtained in this study indicated that they were not beneficial. The final concentrations in the spent dissolvers were 340 ppm Zn and 62 ppm Pb with DETPMP, and BHTPMP showed 5 ppm Zn and 32 ppm Pb with BHTPMP.

Effect of THPS concentration

Figure 4 shows the effect of THPS concentrations (5, 10, 15, 20, 25, and 30%). Results indicate that the dissolution performance was proportional to THPS concentration for lead sulfide scale. The dissolved lead ion concentration increased with increasing the THPS concentration, whilst a maximum dissolved lead concentration was achieved at 30% THPS. While the maximum dissolved zinc concentration was achieved at 15% THPS and any further increase in THPS did not increase the dissolved zinc ion concentration. This could be caused by the increased dissolver viscosity at higher THPS concentration. It is possible that the mass transfer rates of reactants and reaction products surrounding scale surface were decreased in high THPS solutions.

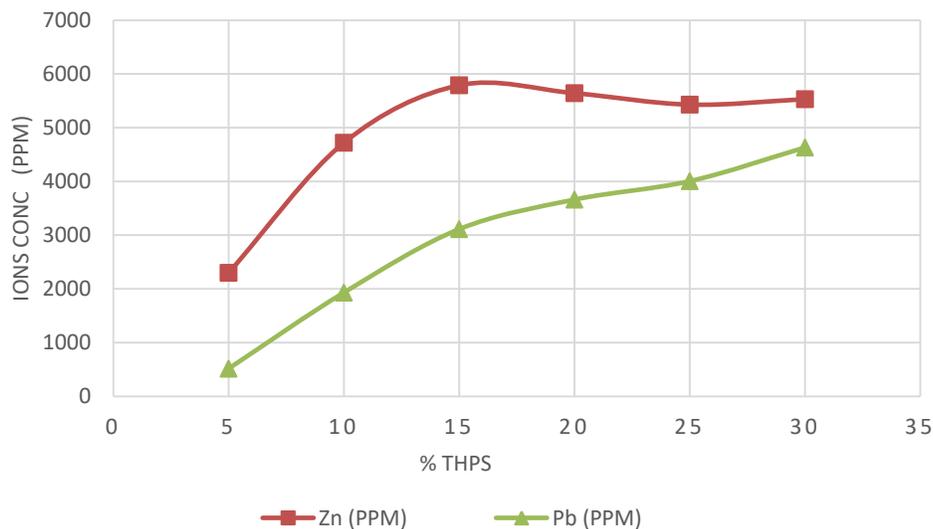


Figure 4. The effect of THPS concentration.

Effect of NH₄Cl concentration

Above results demonstrated that the solutions with THPS or NH₄Cl alone has very poor dissolution performance on zinc and lead sulfide scale deposits. But the dissolution efficiency of THPS was significantly enhanced by NH₄Cl. Further tests showed that with increasing the concentration of NH₄Cl in the mixture, the dissolution amount could be increased, Figure 5 shows the effect of NH₄Cl concentration with 15 % THPS solutions. Increasing NH₄Cl concentration from 2% to 4% elevated the dissolved zinc from 671 to 1501 mg/L and lead from 85 mg/L to 471 mg/L. With 8% NH₄Cl, dissolved zinc was

4669 mg/L and the dissolved lead was 1086 mg/L. Further increasing NH_4Cl to 12% yielded the dissolved zinc to 6261 mg/L and dissolved lead to 4070 mg/L.

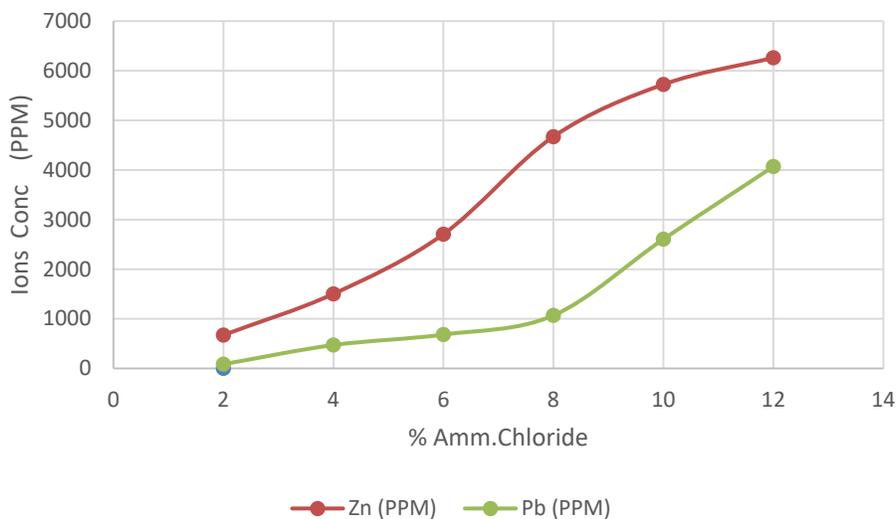


Figure 5. The effect of NH_4Cl concentration.

Effect of dissolution duration

Figure 6 shows the effect of reaction (soaking) time on the dissolution performance of THPS– NH_4Cl mixture. The results indicated that the dissolution by THPS– NH_4Cl mixture increases with increasing soaking time up to 24 hours. Then the amounts of dissolved sulfide scales remained unchanged for the next 24 hours, suggesting that the dissolution reaction was completed within the first 24 hours.

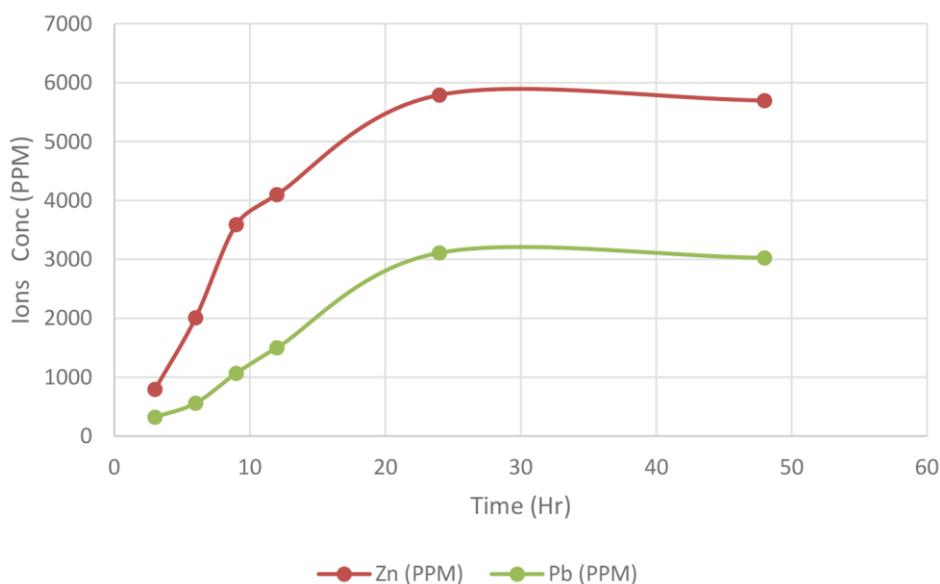


Figure 6. The effect of dissolution duration.

Effect of temperature

Wang *et al.* [5] found that the performance of THPS–NH₄Cl mixture was temperature sensitive and proposed that the dissolution reaction includes thermal decomposition of ammonium chloride to ammonia and HCl acid., Results from our study supported this proposal. At ambient temperature and 35°C the mixture showed poor or almost no dissolution of the scale solids. The dissolver mixture started to work at 45°C. The dissolution performance at 75°C was about half (2836 ppm Zn) of the dissolved zinc at 85°C (5723 ppm Zn) and one fourth (659 ppm Pb) of the dissolved lead at 85°C (2605 ppm Pb) (Figure 7).

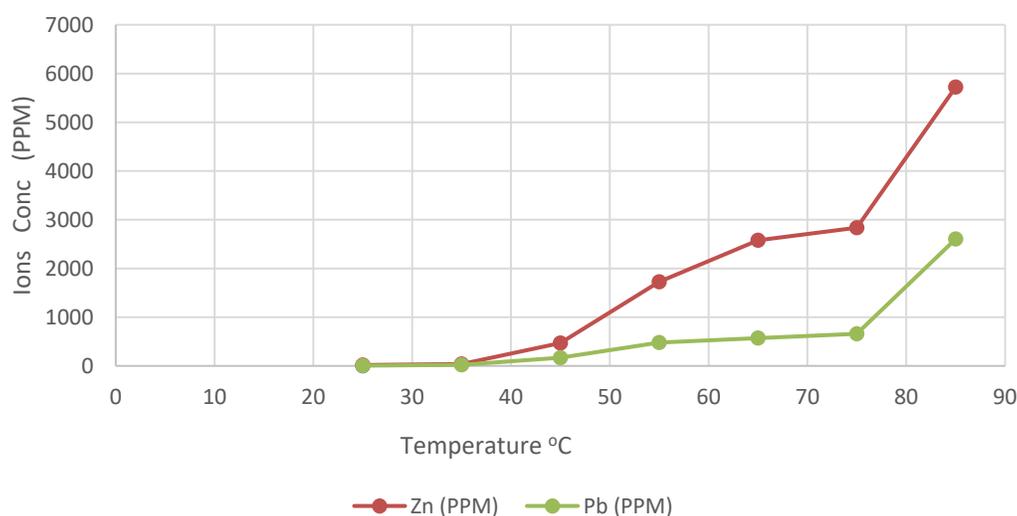


Figure 7. The effect of temperature.

Effect of pH

The initial pH of the THPS–NH₄Cl mixture is acidic (~ pH 3.1). The effect of solution pH on the dissolution efficiency of the THPS–NH₄Cl mixture is shown in Figure 8. The dissolution duration for this part of test was 8 hours. It was found that by decreasing the pH from 3.1 to 2.2, there was no obvious change on the dissolution efficiency of THPS–NH₄Cl mixture. With decreasing the pH from 2.2 to 1.2, significant increase in the dissolution efficiency of the mixture was observed. Further decrease in pH had little effect as shown in Figure 8. The pH of the spent dissolver was much lower than the fresh solution. This was in good agreement with the previous studies by Wang *et al.* [5].

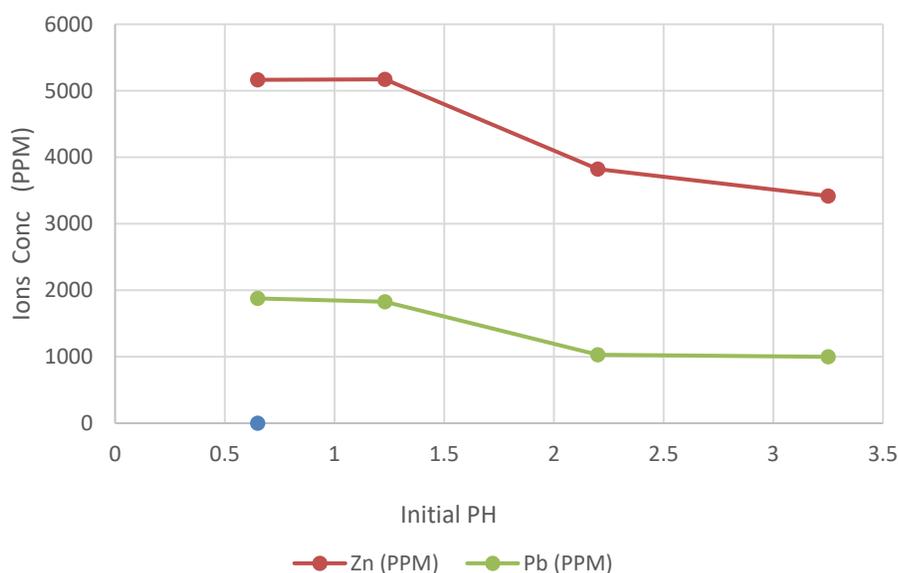


Figure 8. The effect of pH.

Corrosivity test

The corrosivity of THPS–NH₄Cl mixture was compared to 15% HCl. Test results are presented in Figure 9. Based on the weight loss corrosion test the corrosivity of the dissolver mixture was 0.007 lb/ft² which is much lower than the corrosivity of HCl 15% (0.095 lb/ft²) and equals to the corrosivity of inhibited 15% HCl in presence of scale solids. When scale solids added to the mixture the corrosivity decreased to 0.006 lb/ft² compared to 0.054 lb/ft² of 15% HCl in presence of scale solids. When using inhibited solution of the dissolver by adding 2% of corrosion inhibitor the corrosivity further decreased to 0.005 lb/ft², which means using the dissolver mixture is quiet safer than HCl treatments and the action of the dissolver on the scale make the solution more passive toward the metallic parts of the tubing or downhole facilities.

Conclusion

This study evaluated THPS as scale dissolver for zinc and lead sulfide scales formed in the oil wells. It is found that the dissolution power of THPS alone on zinc and lead sulfide scales is poor, but its dissolution power can be significantly increased by adding NH₄Cl. The dissolution efficiency of THPS–NH₄Cl mixture increases with THPS concentration with maximum dissolution achieved at 15% THPS with for zinc sulfide and at 30% THPS for lead sulfide. The efficiency of the THPS–NH₄Cl mixture also increases with NH₄Cl concentration with maximum dissolution efficiency at 12% NH₄Cl. In addition, the dissolution behavior is time and temperature dependent. The optimal dissolution results are obtained at 24 hours and 85°C.

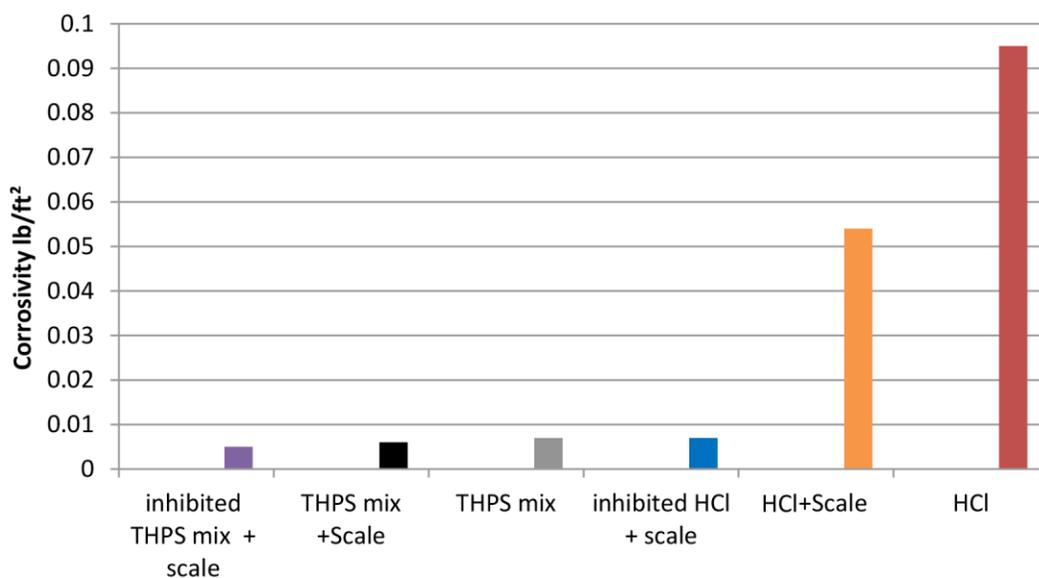


Figure 9. The corrosivity of THPS–NH₄Cl mixture vs. HCl based on 4 hours test.

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