

PREDICTING SCALE FORMATION IN WASTEWATER DISPOSAL WELLS OF CRUDE-OIL DESALTING PLANTS

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Abstract

Scale formation and well plugging due to the incompatibility of injected wastewaters is a critical field problem in wastewater disposal wells. When different wastewaters are mixed, it is necessary to evaluate their compatibility prior to the injection into disposal wells. The individual wastewaters may be quite stable at all system conditions and present no scale problems. However, once they are mixed, reaction between ions dissolved in the individual wastewaters may form insoluble products that cause permeability damage in the vicinity of the wellbore.

In this paper, the composition of different wastewaters, collecting from a few disposal wells of southwest Iranian crude oil desalting plants, were analyzed critically. Laboratory studies as well as field experience have shown that formation damage in wastewater disposal wells may occur mainly due to the conception of Iron Sulfide in the case of mixing a wastewater, which contains Iron ions with a wastewater containing H₂S. In this respect, a new correlation has been developed for estimating the critical concentration of Iron ions, Fe(2+) (ferrous ion), which will stay in solution at various pH values and a wide range of H₂S concentration in crude oil desalting plants' disposal wastewaters. This correlation eliminates the need for compatibility assessment, which is usually assessed either by solubility calculations or by experimental testing, for water mixtures that contains Iron ions and dissolved H₂S. Finally, a real case field problem was analyzed and based on the correlation's results, three different potential solutions were recommended for further field trial implementation.

Keywords: Crude Oil; desalting; wastewater; scale formation.

1. Introduction

Production of salty wet crude had affected the quality of Iranian crudes and a number of wells had to shut in for lack of treating facilities. The produced water with crude in Iranian oil fields contains salts in the concentration of 150,000 to 220,000 ppm. In almost all cases, the salt is found dissolved in the water that is dispersed in the crude oil. This salt water is present in the crude in the form of emulsion (water-in-oil) and its separation is not an easy task. Application of right technology and installation of proper desalting facilities were required to solve this problem. Therefore, it was decided to install electrostatic desalting plants progressively in Iranian oil fields. By end of 2007 more than 20 plants with a total capacity of 207 Mm³/Day (1.3 MMSTB/Day) of treated crude has been installed. It is expected that production of wet crude raise to 400 Mm³/Day (2.5 MMSTB/Day) in Iran by the year 2010. The performance of the majority of current desalting plants have been tested and found satisfactory. Figure 1 depicts the schematic of typical desalting plants in Iranian oil fields. In the desalting process considerable amount of salt will be removed by addition of comparatively fresh water to the crude; this addition of fresh water dilutes the original brine so that the salt content of the water that remains after treatment is within acceptable limits.

The desalting process is undoubtedly associated with generation of considerable amount of wastewater that needs to be disposed properly. Its volume is typically about 15% of the crude oil desalting plant capacity, consists of 10% associated formation water and 5% of added wash water. The wastewater processed through wastewater treating system before it

is injected into disposal wells. The wastewater treating system consists of a skimmer tank, API gravity separator, filter, and disposal tank.

Different crude oils bearing different formation waters are desalted in the Iranian desalting plants resulting in production of different wastewaters compositions. When different wastewaters are mixed it is necessary to evaluate their compatibility prior to the injection in the disposal wells. One of the primary causes of scale formation and injection well plugging is mixing two or more wastewaters which are incompatible. The individual wastewaters may be quite stable at all system conditions and present no scale problems. However, once they are mixed, reaction between ions dissolved in the individual wastewaters may form insoluble products that cause permeability damage in the vicinity of the wellbore. Depending on the amounts of each constituent present, the pH, temperature, and the ratio in which the two waters are mixed, you might expect any or all of the following precipitates to result: Calcium carbonate, calcium sulfate, barium sulfate or Iron Sulfide.

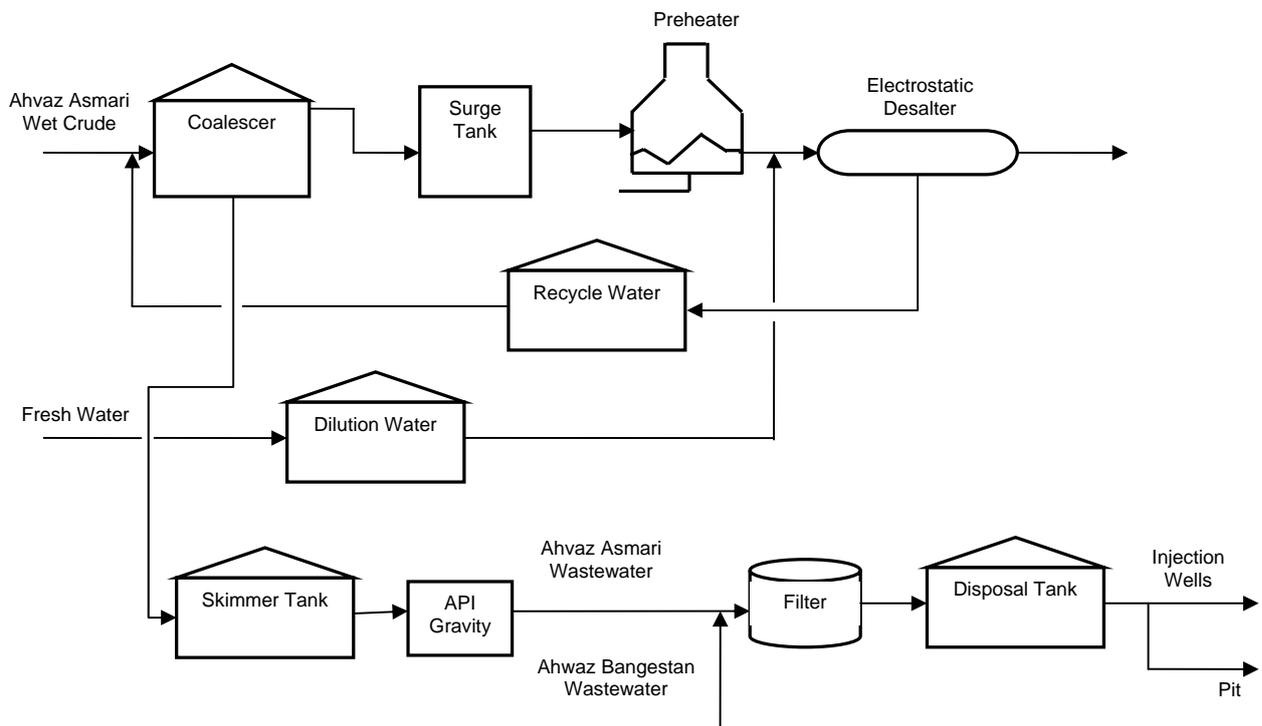


Figure 1 Schematic of Ahvaz Desalting Plant in Southwest of Iran

Mixing two or more incompatible waters on the surface for subsurface injections obviously is undesirable. The second area where problems may arise from incompatibility is when the injection water is not compatible with the natural formation water in the zone where injection is occurring. Surprisingly very few plugging problems due to incompatibility occur in the injection well because there is only a small area of contact between the injection and formation waters, and little mixing occurs. The severe problems occur after breakthrough of the injection water into the producing wells.

2. New Correlation Predicting Iron Sulfide Stability in Incompatible Wastewaters

Iron Sulfide scale is a major field problem that caused by the mixture of water contained Iron ions with a water contains H_2S . It often plugs flow paths in the reservoir, perforations, pump intakes, and tubulars, causing restricted flow path. Obviously, it would be a mistake to mix a wastewater which contained Iron ions with a wastewater containing H_2S . Because the precipitation of Iron Sulfide may occurs. Depending on the amounts of each constituent present, the pH and the ratio in which the two waters are mixed, you might expect Iron Sulfide.



The chemistry of Iron compounds is much more complex than other compounds. This is due primarily to the fact that Iron commonly exists in two oxidation states in water, Fe(2+) (ferrous) and Fe(3+) (ferric). These two ions form compounds with the same anions that possess very different solubilities and it is important to prevent their formation.

Iron ions present in water may be either naturally present in the water or the result of corrosion. Formation waters normally contain only a few mg/l of natural Iron and values as high as 100 mg/l are rare. Higher Iron contents are invariably the result of corrosion.

Corrosion is usually the result of CO₂, H₂S or oxygen dissolved in the water. Most of the scales containing Iron are corrosion products. However, Iron compounds can also form by reaction with natural formation Iron even if corrosion is relatively mild. Hydrogen Sulfide will form Iron Sulfide as a corrosion product which is quite insoluble and usually forms a thin, adherent scale. Suspended Iron Sulfide is the cause of "black water". The hydrogen Sulfide then reacts with metallic compounds such as Iron to form Iron Sulfide, apparent in many producing systems as a black scale soluble in hydrochloric acid.

Compatibility of water mixtures is assessed either by solubility calculations or by experimental testing. Experimental determinations are far more dependable if sample of the waters to be mixed are obtained. However, compatibility test can not be relied upon to give an accurate indication of precipitation of Iron Sulfide because both are quite sensitive to pH changes. Therefore it is necessary to develop a new correlation to predict the stability of Iron Sulfide in incompatible wastewater. Two important parameters that affect the stability of Iron Sulfide are H₂S concentration (ppm) and wastewater pH. On the basis of field data and the previous works practical data ^[1] the following correlation is developed to predict the formation of Iron Sulfide in desalting plants wastewater.

$$C_{Fe^{2+}} = \text{Exp}[29.7315 - 4.6722(\text{pH}) - 2.2313 \log(C_{H_2S}) + 0.1392(\log(C_{H_2S}))^2] \quad (3)$$

where in the above equation, C_{Fe²⁺} is Fe²⁺ concentration (ppm), C_{H₂S} is H₂S concentration (ppm), and pH is the pH index.

Table 1 shows the performance of new correlation for Iron Sulfide stability in Crude Oil Desalting Plants Wastewaters.

Table.1 Performance of new correlation

H ₂ S Concentration (ppm)	pH	Calculated iron ion (ppm)	Practical iron ion (ppm) ^[1,3]
0.1	6	58.4867	55
0.1	6.5	5.6559	5
0.1	7	0.5469	0.5
0.1	7.5	0.0529	0.05
1	6	5.4646	6.3
1	6.5	0.5285	0.5
1	7	0.0511	0.05
10	5.5	6.9748	7.5
10	6	0.6745	0.75
10	6.5	0.0652	0.06
100	5	11.76	10.3
100	5.5	1.1372	0.95
800	4.5	30.0272	28
800	5	2.9038	2.6

3. Field Example

The rate of wastewater production in the southwestern Iranian oil fields has been increasing as a result of increase in the wet crude production. There are few gigantic oil fields located in this area that has been faced with such problem in particular Ahwaz and Maroun oil fields with a rate of 140 Mm³/Day (880 MSTB/Day) and 112 Mm³/Day (700 MSTB/Day) respectively.

There are many smaller oil fields exist in this area like Abteymoor, Mansouri and Kupal oil fields contributing significantly to the country's oil production; and it is believed that they will be watered out in near future.

Some of these oil fields consist of several smaller reservoirs adding up to the problem. The problem arises mainly due to the variation of H₂S concentration in each oil field stream. The produced wastewater from each stream may stay stable in all system conditions but it results in Iron Sulfide precipitation once it get mixed with another incompatible wastewater produced from another reservoir.

Ahwaz oil filed would be a good example of such field problem occurrence. This filed consists of two main reservoirs, Ahwaz Asmari and Ahwaz Bangestan, and both of them produce wet crude. Ahwaz Asmari considered being shallow compared with the Ahwaz Bangestan reservoir. Ahwaz Asmari current production rate is 112 Mm³/Day (700 MSTB/Day) and its pressure is around 25786 kpa (3740 psi). It consists of 6 zones and 10 layers and its cumulative production up to date is more than 1500 MMm³ (9300 MMSTB). The average production rate of each well is 588 m³/Day (3.7 MSTB/Day) and there are approximately 190 active wells present in this reservoir. Ahwaz Bangesatn current production rate is 29 Mm³/Day (180 MSTB/Day) and its pressure is around 32405 kpa (4700 psi). It consists of 3 zones and 2 layers and its cumulative production up to date is more than 127 MMm³ (800 MMSTB). The average production rate of each well is 270 m³/Day (1.7 MSTB/Day) and the number of active wells in this reservoir is 105 wells.

The bottom hole temperatures, that could explains the high difference in H₂S concentration of these two reservoirs, are 104°C (188°F) and 122°C (220°F) for Ahwaz Asmari and Ahwaz Bangestan respectively. Table 2 and 3 shows the reservoir fluid composition for these two reservoirs.

Table 3 Ahwaz Asmari and Ahwaz Bangestan heavier fractions properties

Reservoir	Component	Mole %	Molecular Weight	Liquid Density (Kg/m ³)	Total GOR (SCF/STB)
Ahwaz Asmari	C ₇₊	30.1	252	886	765
Ahwaz Bangestan	C ₇₊	44.24	301	926.3	422

Desalting and dehydration of Ahwaz wet crude results in a production of two types of wastewaters. Ahwaz Asmari's wastewater rate is 9.2 Mm³/Day (58 MSTB/Day) and contains Iron ions whereas Ahwaz Bangestan's wastewater contains considerable amount of dissolved H₂S and its rate is 4 Mm³/Day (25 MSTB/Day). Table 4 and 5 shows the compositional analysis of these two wastewaters. These two wastewaters are mixed and injected in to 6 disposal wells in the depth of 2995 meters (9828 ft). The mixture of these two incompatible wastewaters has created enormous problems in the filed. The scale formation due to the precipitation of Iron Sulfide at the reservoir sand face has been resulting in a continuous decrease in the injection rate and eventually well plugging.

Table 4 Ahwaz Asmari typical disposal wastewater composition

Component	Unit	Quantity
Na+K	ppm	27099
Ca	ppm	5520
Mg	ppm	778
Fe	ppm	43
Cl	ppm	53401
SO ₄	ppm	550
HCO ₃	ppm	156
Total Hardness	ppm	17000
Temporary Hardness	ppm	
Suspended Solid	ppm	4744
Total Dissolved Solid	ppm	87547
Sp.Gr @15.6 C	-	1.0895
pH	-	5.7

Table 5 Ahwaz Bangestan typical disposal wastewater composition

Component	Unit	Quantity
Na + K	ppm	4852
Ca	ppm	640
Mg	ppm	97
Fe	ppm	-
Cl	ppm	8496
SO ₄	ppm	450
HCO ₃	ppm	137
Total Hardness	ppm	2000
Temporary Hardness	ppm	-
Suspended Solid	ppm	4744
Total Dissolved Solid	ppm	14672
Dissolved H ₂ S	ppm	340
Sp.Gr @15.6 C	-	1.0115
pH	-	6.1

Applying the new developed correlation can predict the conditions for different scenarios in which the mixture of these two wastewater streams would not produce any Iron Sulfide precipitation. Figure 2 shows the region where the iron ions would stay in solution for different system conditions, the pH and dissolved H₂S concentration in solution. This figure indicates that for pH solution greater than 5.3 the Iron ions would precipitate immediately almost regardless of H₂S concentration. For the pH range of 4.5 to 5 the amount of Iron ions that can stay in solution increases exponentially as the H₂S concentration decreases. However, the maximum allowable Iron ion concentrations in solution would be limited to less than 50 ppm if the H₂S concentration is in the range of few hundreds ppm for the pH of less than 4.7. Given the fact that the H₂S concentration is about 340 ppm in Ahwaz Bangestan wastewater and the Iron ions is about 43 ppm in Ahwaz Asmari, the mixture of these two wastewater streams would yield in a water that contains 102 ppm H₂S and 30 ppm Iron ions and a pH in the range of 5.7 to 6.1. Having these figures in mind and comparing them with the correlation results, the following three options are available in order to overcome the current Ahwaz filed Iron Sulfide scaling problem. Solutions are limited to adjusting the three key parameters of Iron ions concentration, solution pH, and H₂S concentration:

- Removing the Iron ions from the flow stream would not be an easy task. Besides, its 30 ppm estimated value is only its measured concentration at the desalting plants discharge. Adding up the pipeline networks from the desalting plant to the well head plus the casing and tubing which all are made of Iron alloy and they are in direct contact with the dissolved H₂S will definitely increase the Iron ions in solution concentration.
- Lowering the solution pH from 5.8 to slightly above the 4.5 would be a possible solution but it dose not guarantee the removal of scaling problem. Also, operating the system in such low acidic range may accelerate the corrosion problem resulting in the failure of surface facilities.
- Perhaps the best solution would be a scenario(s) in which the H₂S concentration lowered as much as possible. One way to do this is to dilute Ahwaz wastewater with the adjacent fields free H₂S wastewaters prior to the injection and if it is necessary utilizing relatively low acidic solutions in lowering the solution pH slightly. Another scenario is an installation of H₂S scavenger that lowers the H₂S concentration to few ppms and being free minded of the Iron Sulfide problem for the current field conditions. However, the first scenario demands a filed feasibility study and the second scenario is relatively costly and an economical evaluation needs to be considered.

Based on the above discussed possible solutions it is strongly believed that lowering the H₂S concentration would be the most feasible solution for this field problem.

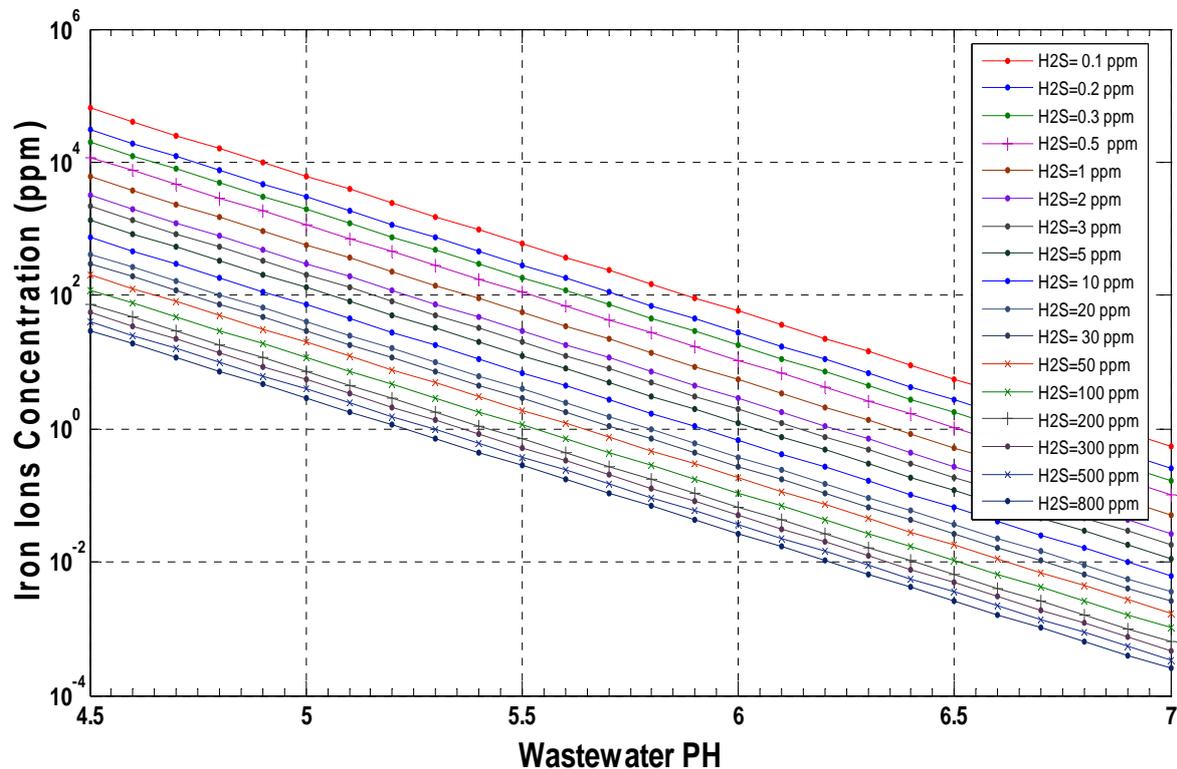


Figure 2-Effect of pH and iron ions concentrations on the formation of iron sulfide for different H₂S concentrations

4. Conclusion

A new correlation was developed to calculate the concentration of iron ions (Fe(2+) - ferrous Ion), which will stay in solution at various pH values (between 4.5 and 7.5) and a wide range of H₂S concentrations (0.1 ppm - 800 ppm) in crude oil desalting plants' disposal wastewaters. It has been demonstrated that there is a good agreement between the correlation results and the practical data at different hydrogen sulfide concentrations. By using this new correlation, it was shown that at pH values less than 4, virtually all of the present sulfides exist as H₂S. At low pH, the concentration of Fe²⁺, which reacts to form iron sulfide, is also high and therefore, the formation of iron sulfide rarely occurs. As the pH rises, more and more of the H₂S is ionized into HS⁻ and S²⁻. Thus, if the entire sulfide is to be removed, the pH must be lowered sufficiently into the acid range to convert it to H₂S and preventing the formation of Iron Sulfide. It was also illustrated that at higher pH, the wastewater is more sensitive and the formation of iron sulfide occurs in lower concentration of ferrous Ions.

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