

Deployment of Real-Time Scale Deposition Monitoring Equipment to Optimize Chemical Treatment for Scale Control During Stimulation Flowback

by D. H. Emmons, N. D. Feasey, S. A. Smith, T. Weathers and M. M. Jordan

ABSTRACT

A field offshore USA produces fluids from both carbonate and sandstone formations. It contains three fixed platforms and the different produced brines vary in composition such that some contain high amounts of bicarbonate while others have high calcium concentrations. Processing of the combined fluids takes place on a central facility onshore and hence treatment is needed to prevent calcium carbonate scale from forming. When wells are acid stimulated the initial flowback contain very high calcium concentrations with a much higher tendency for scale formation in the short term. Proper scale control during this period is important and to understand the exact risk a monitoring program using a novel in-line deposition monitoring probe was instigated.

After review the probe was located in-line at the onshore processing facility. Here it logged the brine stability both before and during the flowback from acid stimulation. Several different events were logged including a process shut-in, deposition of heavy oil residue that fouled the probe during a period of poor separation, and scale deposition upon reduced chemical treatment.

The real-time data obtained from two acid stimulations demonstrated the benefits of the in-line deposition monitoring probe compared to conventional monitoring

techniques such as ionic analysis. This included the ability to optimise scale inhibitor dosing in real time.

Introduction

Platforms P1, P2 and P3 are situated offshore USA. The associated brines (Table 1) are sent to a processing facility located onshore by means of a sub-sea pipeline. First these fluids combine at the P2 platform. These brines have a positive calcium carbonate scaling index and thus they are each dosed with a phosphonate scale inhibitor. Additionally an emulsion breaker is added at the processing facility onshore before the free water knock-out (FWKO) vessel and heater treaters. Solids and residual oil are then removed by means of a media filter. Scaling potential is reduced by adding hydrochloric acid. The heat from the processed fluid is transferred to incoming emulsion crude via a heat exchanger before finally treatment at a bio-processing station and offshore discharge.

To prevent calcium carbonate scale formation from platform to shore scale inhibitor is added. Once the crude emulsion is received onshore process changes may cause scale formation. Firstly at the heat exchanger the temperature of the stream is initially raised and it is well established that higher temperatures favour calcium carbonate formation. Through the rest of the process further heating in heater

Table 1. Produced brine chemistry from Platforms P1, P2 and P3 along with the combined brine chemistry and the composition of Well A1 during the acid flowback stage.

Ion	Unit	Platform P1	Platform P2	Platform P3	P1, P2, P3 Combined	Well A1
Sodium	mg/L	12000	13000	13000	13000	13000
Potassium	mg/L	150	110	110	120	120
Magnesium	mg/L	120	21	22	85	85
Calcium	mg/L	540	89	260	190	25000
Strontium	mg/L	35	19	25	21	21
Barium	mg/L	8.4	15	13	11	11
Iron	mg/L	0.53	0	0	0	0
Chloride	mg/L	18400	19500	19800	17200	17200
Sulfate	mg/L	138	35	8	155	155
Alkalinity	mg/L	1900	3000	3700	2600	200
TDS	mg/L	32000	36000	37000	34000	34000
CO ₂ (gas phase)	%	2.36	1.34	3.67	4.62	3.74
H ₂ S (gas phase)	%	0	0.0659	0	0	0
pH	--	7.63	8.03	7.71	7.47	6.8

treater units and the overall duration both promote such scale formation.

When acid stimulations are undertaken the risk of carbonate scale formation is much higher. Since the hydrochloric acid reacts with carbonate minerals within the reservoir the calcium level in the crude emulsion increases. Consequently the scaling index of the brines greatly increases (Table 2) once the pH increases. High calcium levels can also cause problems in terms of compatibility with the scale inhibitor which potentially could precipitate and hence stop providing protection.

Conventionally such methods as analysis scaling ion concentration and measuring scale inhibitor residuals have been used to monitor such treatments. Recently the introduction of real-time monitoring for scale deposition has provided a more effective tool for assessing treatment programs.

Monitoring

Scale inhibitor programs have conventionally been monitored by such techniques as monthly coupon analysis, inhibitor residuals, water analysis and more recently water filtration along with Environmental Scanning Electron Microscopy (ESEM)/Energy Dispersive X-ray (EDX) analysis (1-3). Fluid pressure differentials across the treatment facility may also be used. Laboratory experiments using standard methods are frequently used to establish if a field treatment provides protection (4). This is only relevant if there is

confidence in the correlation between such laboratory tests and the actual field conditions. If the amount of scale inhibitor present is above the laboratory established Minimum Inhibitor Concentration (MIC) then the system is considered protected. Such conventional performance monitoring provides, at best, an indirect measurement of program performance.

Even though well established the use of the analysis of scale inhibitor residuals combined with MIC can be problematic. Frequently as fields with water flood injection water mature produced brine composition changes. Hence MIC experiments need repeating to ensure they are relevant to the field conditions. This is time consuming and indeed it may not be possible to accurately generate the field brine in the laboratory. Consequently there may be a discrepancy between a laboratory recommended rate and the actual field treatment rate required to control scale. Additionally the analysis of scale inhibitor residuals in field brine is not always straightforward. Sometimes samples need to be shipped to authorized laboratories when analytical facilities in the field are unavailable. This results in a slow turnaround time and where scaling severity and risk is high this can prove unacceptable.

Monitoring is further complicated in acid stimulation treatments where the spent acid solution co-mingles with normal produced fluids. This results in changes in brine chemistry that are both large and rapid. Within a few hours the concentration of scaling ions can change by orders of

Table 2. Scale index and mass of calcium carbonate (Calcite) scale that is predicted to form at different ratios of the combined platform brine and Well A1 brine during the acid flowback stage. Assessed at platform and onshore arrival conditions.

% Platform Brine	Calcite Scale Index		Calcite Mass (mg/L)	
	Platform	Onshore	Platform	Onshore
100	1.39	1.16	386	424
90	1.71	1.5	780	938
80	1.9	1.72	1098	1423
70	2.04	1.9	1307	1680
60	2.16	2.04	1432	1767
50	2.25	2.18	1500	1786
40	2.33	2.31	1523	1763
30	2.39	2.44	1498	1695
20	2.42	2.55	1398	1552
10	2.36	2.62	1121	1227
0	0.9	1.4	101	132

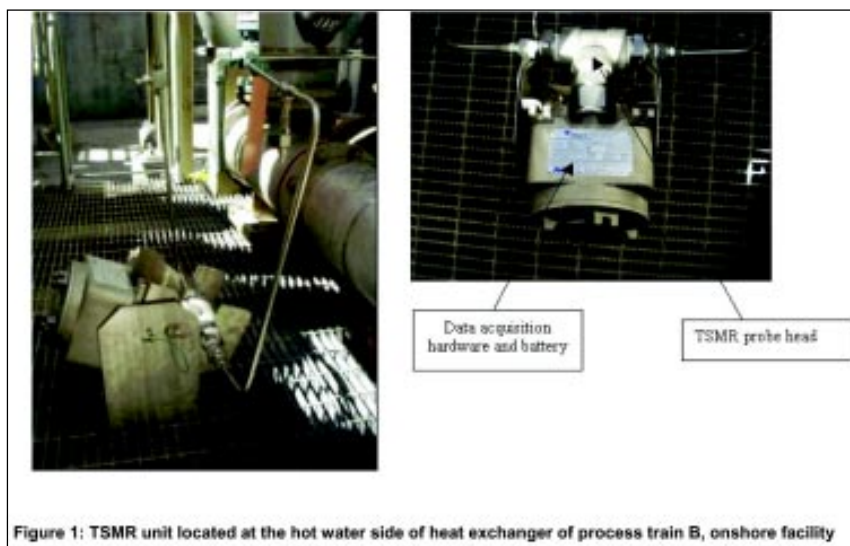


Figure 1: TSMR unit located at the hot water side of heat exchanger of process train B, onshore facility

wafer, with metal electrodes on either side. When a potential is applied across the wafer shear deformation results at a characteristic frequency (5). If a deposit form on the wafer surface the resonant frequency changes, and this change can be converted to units of mass per area. Quartz crystal microbalances are based on this principle (6). Refinement of the circuitry, to include measurement of resonator damping, has allowed extension of this principle to measurements in the liquid phase (7, 8). The technique is very sensitive with deposits of the order of microgrammes per square

magnitude. The conventional methods of monitoring, as mentioned above, are better suited to a steady state. They are not sensitive enough to respond in a situation such as acid flowback where rapid changes occur. Thus they are inappropriate for timely adjustment of scale inhibitor treat rate in a dynamic scaling regime.

Real Time Monitoring

The limitations of conventional methods led to the introduction of real-time monitoring for scale deposition. This technique directly measures the stability of oilfield brines with respect to scale deposition. A Thickness Shear Mode Resonator (TSMR) allows direct measurement of solids deposition from a brine. It utilizes a piezoelectric

centimeter being determined.

The TSMR has been deployed within an in-line been device for monitoring deposition. This allows continuous monitoring of deposition form the liquid phase in real time. The technique offers the advantage of on-site measurement with rapid generation of results. A key point is that the response of the probe depends on the brine stability and is independent of the scale inhibitor present. Many field applications have been run with this technique (9-11) that demonstrate its value. The continuous monitoring capability and sensitivity of the TSMR unit provide a realistic way to monitor the water portion of the onshore facility during acid stimulation flowback and rapidly account for changes in the system.

Acid Stimulation

An acid stimulation job was performed on one of the offshore wells A1, from platform P1. This aimed to stimulate the Monterey formation, which has high calcium carbonate content within the formation. It used the following fluids and volumes:

24 bbl	40/60 methanol/ 2% ammonium chloride
476 bbl	xylene
476 bbl	DAD (20/80 xylene/HCl with surfactant)
143 bbl	15% HCl
1000 bbl	12/3 Mud Acid (HCl/HF)
1997 bbl	2% ammonium chloride

Verification of Treatment Program Prior to Acid Stimulation

Treatment dosage was optimized at the onshore facility. This was accomplished by lowering chemical dosage rate in the B-train line and monitoring with the TSMR unit on the hot water side of the B-train fluids. The equipment was placed inline as shown in Figure 1. The established treatment rate of 30 gallons per day (gpd) was monitored for 20 to 24 hours. It was then reduced by 25% to 22 gpd for 20 to 24 hours, and then similar reductions to 15 gpd and 7 gpd for 20 to 24 hour periods. As shown in Figure 2, the readings for 30, 22, and 15 gpd treatment rates vary to some degree, but show no deposit buildup. All readings are within plus or minus 2 $\mu\text{g}/\text{cm}^2$. However, the data from the time span in which the treat rate was 7 gpd shows a continuous deposition event for the first 10 hours followed by a period of erratic readings. The first 10 hours of testing shows deposit (scale) build-up on the probe crystal surface. The decrease in frequency did not continue for the duration of the test, but rather erratic readings are not unusual for a system that is slightly undertreated. To confirm that the observed behaviour was indeed a result of carbonate scale deposition, the probe head was removed and the sensor cleaned. The

first cleaning was with xylene to remove any organic deposit. No significant loss of mass from the sensor was noted after cleaning. This indicated that no organic fouling was on the sensor. The sensor was then cleaned with dilute hydrochloric acid to remove any carbonate scales. Acid treatment showed visual effervescence and the loss of mass from the sensor that would be consistent with carbonate scale removal.

It was concluded that the treatment rate of this system could be lowered based on the treatment optimization study. The recommendation was made to lower the treatment rate and run an extended test (two weeks to a month) to ensure system protection.

Acid Stimulation Flowback Monitoring

Completion of the acid stimulation of well A1 was scheduled for Sunday, March 4th with flowback to begin late evening of the 4th. Fluids from the well had a transport time of four hours from the P1 platform to P2 platform and then an additional transport time of eight hours to the onshore facility. As full management of the chemical treatment would require emulsion treatment, scale treatment and asphaltene treatment at both the P1 platform and at the onshore facility personnel were in place at both units to monitor water hardness, pH, emulsion, solids, and other fluid properties as well as the fluid levels in separator units, etc. The in-line TSMR probe was used to provide monitoring during flowback at the onshore facility to support the adjustment of scale inhibitor dosage and to determine if scaling was occurring during the rapid change in brine composition during flowback.

Flowback from the well was continuously monitored on the cold water side of B-train with frequency sampling set to one minute increments scaled back to three minute increments on March 7th. Acquired data was downloaded every hour and appended to existing data and then reviewed

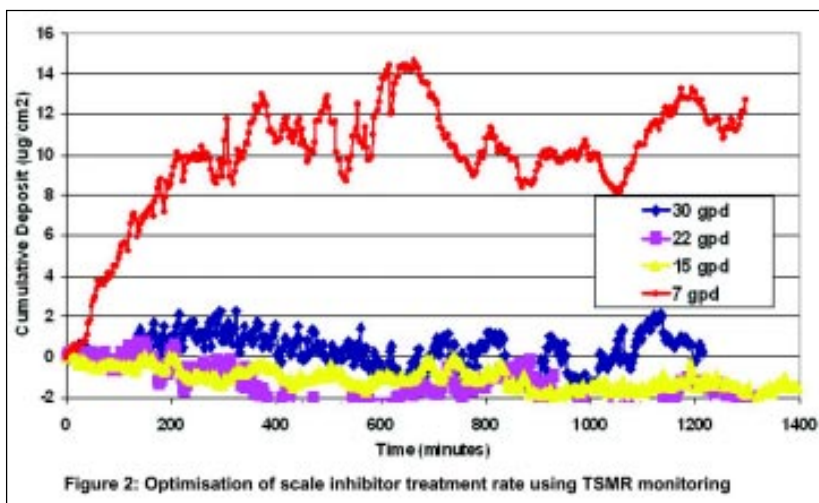
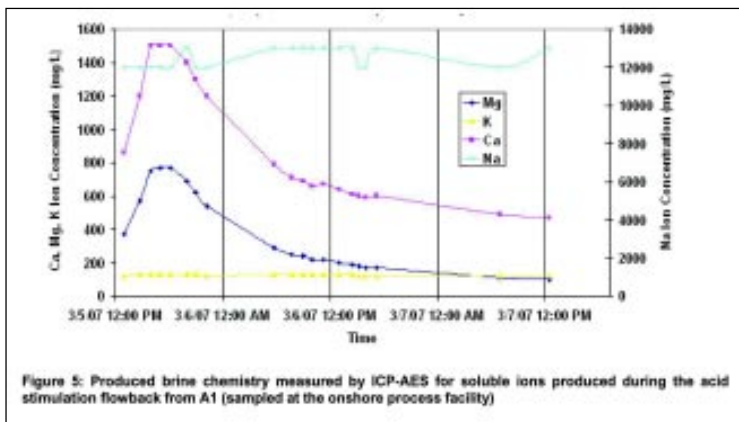
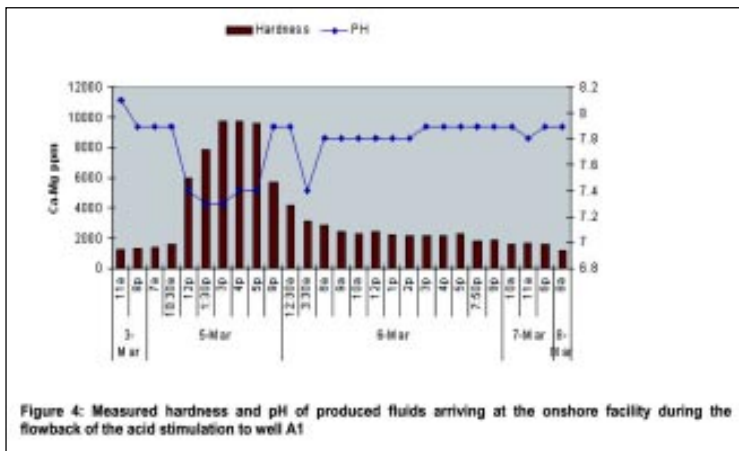
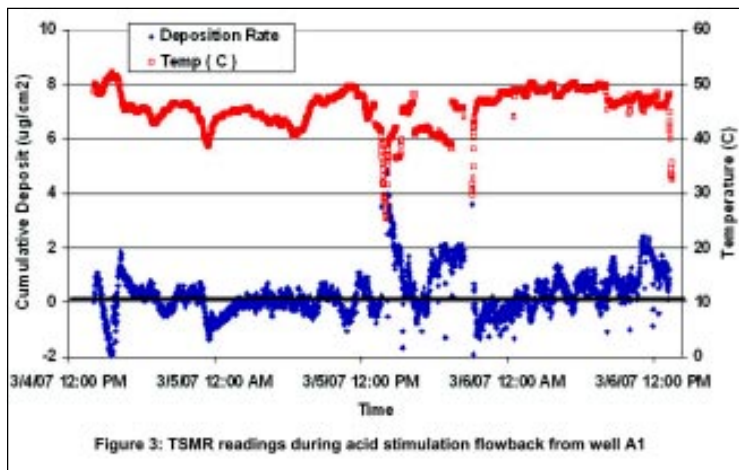


Figure 2: Optimisation of scale inhibitor treatment rate using TSMR monitoring

for potential scale formation. Two times during monitoring on 5th March the probe was pulled from the system and cleaned to ensure that oil deposits were not building up as the water quality became poor due to surfactant from the acid stimulation passed through the facility. Throughout the flowback monitoring period there were no indications that scale was depositing at a detectable level nor were any oily deposits observed in spite of some water quality excursions. Many of the sudden changes in crystal frequency (blue data points in Figure 3) can be attributed to changes in system operations as indicated by similar modulations in the probe head temperature (red data points in Figure 3) during these rapid changes.



Throughout the period of time when the acid stimulation fluids were passing through the system additional monitoring methods such as pH measurement and hardness readings were used as supplemental data to correlate the observed frequency and temperature data from the TSMR probe. The data points collected during field monitoring are graphically depicted in Figure 4. As would be expected from addition of a large volume of acid to the production fluids the pH of the fluids during the flowback reduced significantly from

approximately pH 7.9 to as low as pH 7.3 for a short period of time and then returned to initial levels. Hardness measurements that include the combined level of calcium, magnesium, and other multivalent cations such as iron, zinc, and barium were also taken by EDTA titration of field samples during the active flowback period. Just as expected the hardness levels followed a progressive change similar to that observed in the fluid pH. Initial hardness was under 2000 ppm and rose quickly to nearly 10,000 ppm and then subsided back to initial levels. One difference between the hardness level and the pH value was that the regression from the high point back to normal levels was very rapid in pH change but substantially slower in hardness reduction, taking over twelve hours.

As a secondary measurement additional water samples were also taken during the flowback of the acid stimulation fluids and processed for ion levels using a more analytically precise method of detection with an Inductively Coupled Plasma (ICP) instrument. ICP analysis allowed analysis of the concentration of each individual ion so that the flowback fluids could be analyzed for changes in brine composition during the flowback period that would influence the scaling tendency of the fluids. The concentration of cations (Figure 5) such as sodium and potassium remained relatively constant throughout the process while the ions derived from acid soluble materials such as calcium and magnesium had a rapid increase that maximized at between four and five in the evening of 5th March 2009 and then gradually declined to normal levels over the next twenty-four to thirty-six hours. Both Figures 4 and 5 show the same information measured by two separate methods and having the same general results. The ion concentration and pH data combined confirm that the fluids from the acid stimulation flowback had an increased scaling potential over normal operational conditions on the onshore facility.

To inhibit scale formation throughout the acid stimulation flowback process scale inhibitor was injected into the flowlines at increased dosage throughout the system. The increase in scale inhibitor treatment rate followed the fluids as they made their way to the onshore facility from the P1 platform, Figure 6. The increase in treatment began on the P1 platform on March 4th with an increase to 120 gpd and was followed with an increase at P2 and at the onshore facility. After both hardness and pH levels had returned to

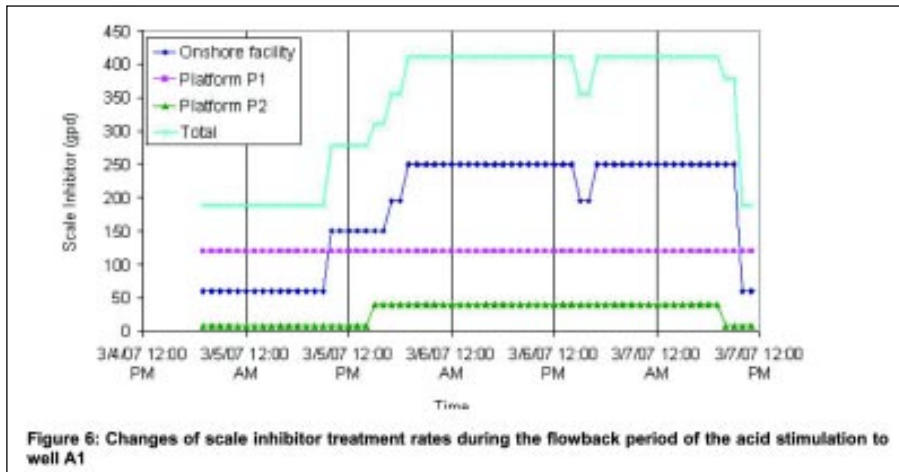


Figure 6: Changes of scale inhibitor treatment rates during the flowback period of the acid stimulation to well A1

normal and production levels were stable the chemical treatment rates were returned to former levels. It should be noted that the increase in chemical treatment rate on the P2 platform was made after discussion that determined that the waters were a substantial risk and no additional chemical could be added via the pumps at the P1 platform as they were at maximum capacity.

Discussion

The entire process of monitoring and maintaining system control during a very substantial acid stimulation job was successful. The combined team effort to plan prior to flowback and account for many of the possible hurdles that could be faced allowed for valid collection with a substantial number of data points. Many of the issues around monitoring the system during these times of rapid change in fluid composition once an upset occurs are reactive in nature and not proactive. In this exercise the action was nearly all proactive and minimized the difficulties seen during previous acid flowback.

TSMR monitoring provided a very rapid method of evaluating whether or not scale or other solids deposition was occurring during flowback. Observation made from data downloaded from the TSMR probe every hour and compared to other data such as water quality throughout the system and grind-out evaluation of the crude emulsion provided a complete picture of how well scale formation was inhibited. Based on these results water quality could also be monitored to some degree, as increased oil content in the fluids tends to increase the noise in the baseline readings of the TSMR probe. While it was not possible to obtain data from the crude emulsion with the limited amount of time at the site it is also possible that the incoming fluids could be monitored for deposition as well.

The use of TSMR data analysis along with ion analysis and pH monitoring built a comprehensive set of data providing a more complete picture of what occurred

during the flowback of the acid stimulation fluids from well A1. pH changes and total hardness provided a field method for determining when the fluids began to arrive at the onshore facility and showed the conditions that the TSMR probe surface would experience. The acid was mostly spent and acid exposure to the probe surface was not a risk. Total hardness and the individual ion concentrations provided a means to evaluate the degree of severity of the scaling regime. Increasing hardness from approximately 800

ppm to nearly 10,000 ppm showed the scaling risk was drastically increased. However, as demonstrated in the individual ion evaluation the relative ratio of calcium to magnesium did not change and thus the preferred morphology of scale expected to form did not change. The combination of TSMR along with the other techniques of pH, hardness and ion counts provided evidence that without treatment modification during the flowback of the acid stimulation fluids scale deposition would have occurred and would have deposited a large amount of solids.

Conclusions

The successful use of TSMR in monitoring of the flowback of the acid stimulation of well A1 from 04/03/07 to 08/03/07 was shown; no data indicated scale deposition. The treatment program adopted involved the use of additional chemical from platform P2 not involved in the acid stimulation job to boost the overall amount of chemical present in the fluids on flowback. This was successful and should be integrated into normal operating procedures for future stimulation work. Under normal operating conditions TSMR monitoring determined that there was not a significant deposition rate at the current treatment rate of 30 gpd on the B-train. Reduction in treatment rate to 22, 15, and 7 gpd on the B-train showed that by 15 gpd the deposition rate is significantly reduced to the point of no observed deposition over 24 hours of monitoring. To confirm that this is a sufficient treatment rate with operational changes and fluctuation in brine compositions over time this treatment rate should be monitored for an extended period of time (i.e. two weeks).

PP

PetroMin PipeLiner would like to show appreciation to D. H. Emmons, N. D. Feasey, S. A. Smith, T. Weathers and M. M. Jordan for this article which was presented at PETROTECH 2009, New Delhi, India.