

## 111 Online monitoring the effect of chemical inhibitor on the calcium carbonate precipitation and deposition

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### ABSTRACT

*The formation of mineral scale particularly calcium carbonate is a problem for industries ranging from oil and gas to desalination plants. Various techniques have been studied to prevent the formation of scale. The use of chemical inhibitors to prevent calcium carbonate scaling is widely studied. The present study attempts to show that the online monitoring technique is useful tool for laboratory experimental investigation of scaling phenomenon. This method is successful in providing the induction time of scaling. It has shown that presence of inhibitor delays the precipitation and affects the deposition of calcium carbonate. In addition the method is found useful in determining minimum inhibitor concentration and also to screen various types of inhibitors for the selection. The influence of an inhibitor is studied on scaling solution of various calcium ion concentrations.*

**Keywords:** Chemical Inhibitor, online, calcium carbonate, precipitation, deposit.

### 1 INTRODUCTION

Scale deposition has proved to be an expensive problem in industries using water as a means of cooling or to provide heat or as process water in oil industry. The potential for scale formation control has been extensively researched by numerous researchers who developed variety of inhibitors aiming at reducing or even possibly eliminating mineral scale formation. Of all methods used to combat scale deposition, the use of chemicals is the most effective (Katz et al 2002; MacAdams et al 2004), in the last decade, there has been considerable advances in the development of chemicals, effective in small concentrations for the control of scale deposits. The only challenge to be solved, being the choice of the most suitable inhibitor, the amount and concentration, the design of the system for application and injection into the oil well and other industrial applications. In addition the difficulty in choosing an inhibitor for a particular application is that the fundamentals of inhibition mechanisms are inadequately understood, particularly from their quantitative aspects and that the literature provides very little guidance on the expected performance (Vetter 1976). Thus application of Inhibitors relies heavily on experimentation.

The experimental techniques employed in studying calcium carbonate precipitation and deposition are based on offline and indirect methods. Similar experimental techniques are used in studying effect of inhibitor on calcium carbonate scaling. The data obtained from offline calcium ion concentration analysis was used to study the effect of inhibitor (Hasson 1968; Koutsoukow 1984; Koutsoukow 1994; David Hasson 1998). (Dong-Jin Choi, 2002) used weight loss technique to determine the inhibition effect by using carbon steel coupons. While (Okandan 1989) used stainless steel scaling rods.

One of the advantage of the present work is that the online technique is used to monitor the effect of inhibitor on the precipitation and scaling. The present online method for monitoring effect of inhibitors is relatively simpler as compared to other methods reported in literature such as radiotracer technology ((E. Stamatakis et al 2005)) and Quartz crystal microbalance ((Abdel- Aal and Sawada 2003))

The present method is based on the Focused beam reflectance measurement technique (Mettler Toledo) which measures the chord size distribution of crystals in solution. (Nasser et al 2008) showed the application of FBRM in determining the precipitation kinetics of calcium carbonate.

Nasser et al has also shown that calcium carbonate scaling or deposition rates can be obtained from the FBRM technique. The use of FBRM in monitoring the effect of inhibitor is novel and it is shown that it proves to be useful in determining the minimum inhibitor concentration required for a given type of inhibitor and hence its application in laboratory experimental investigation of effect of inhibitor on scaling phenomenon. The effect of Inhibitor on the scaling solutions of various calcium ion concentration is studied.

## 2 EXPERIMENT SETUP AND PROCEDURE

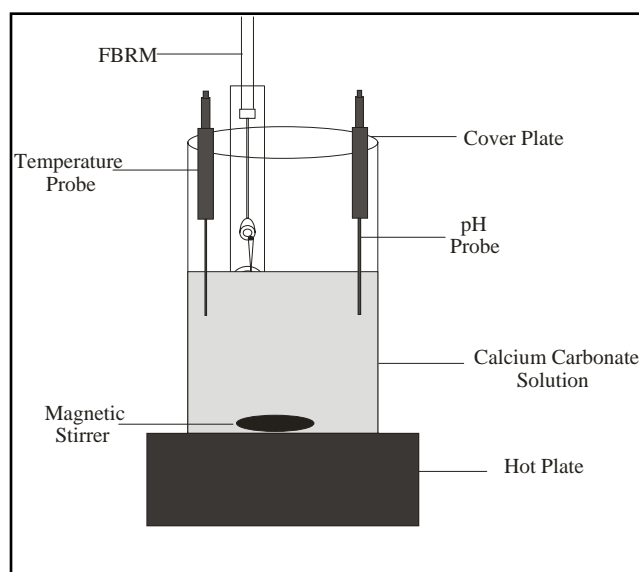


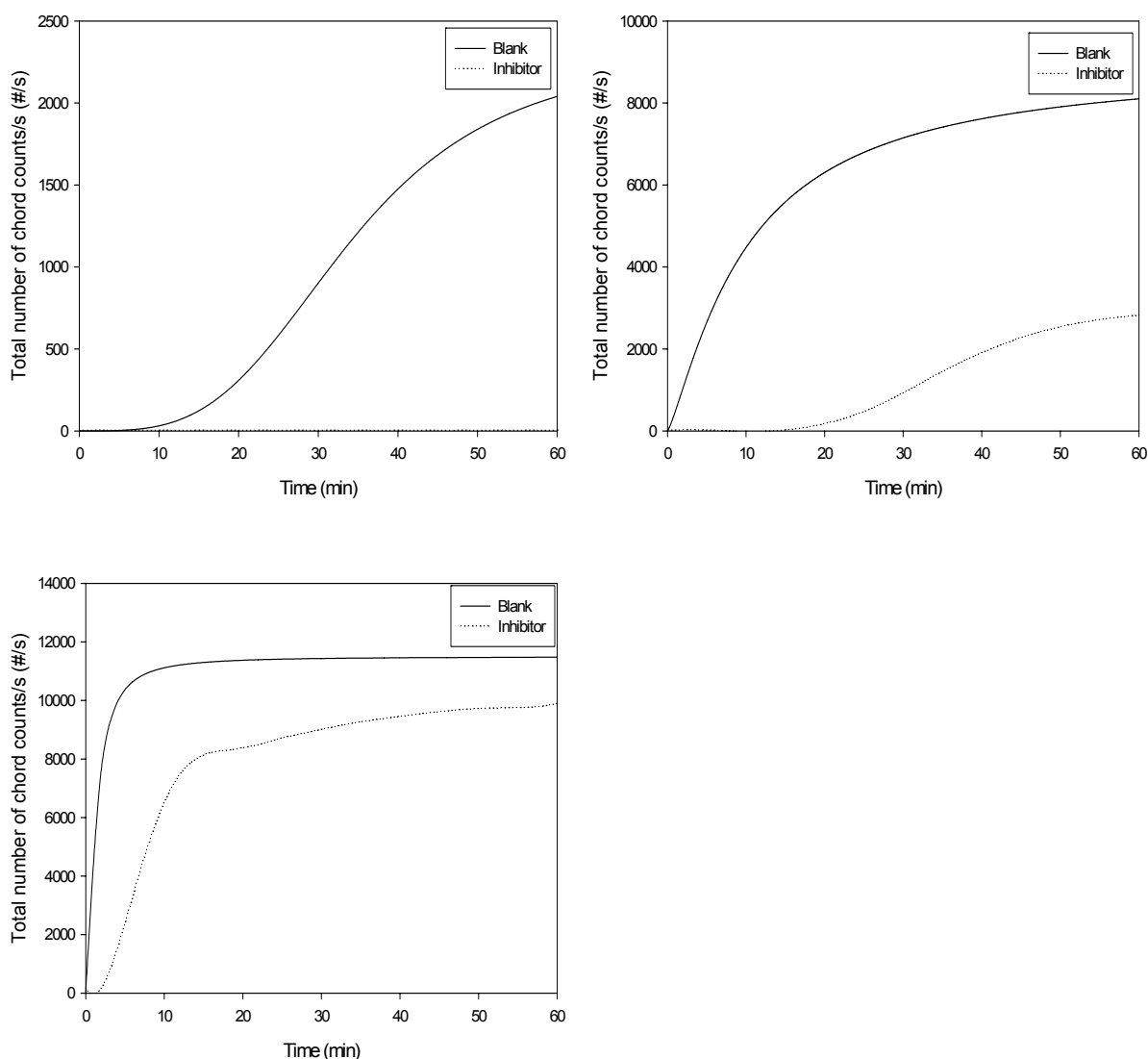
Figure 1: Experimental setup for online and offline measurement

The experimental procedure is as follows: Firstly, solutions required for precipitation of calcium carbonate were prepared. The sources of calcium ions and carbonate ions were  $(\text{CaCl}_2 \cdot 2\text{H}_2\text{O})$  and  $(\text{NaHCO}_3)$ . The chemicals were provided by Analar and the purity was  $>99\%$ . One Litre solution of each chemical was prepared using distilled water. The two solutions poured into the 3L beaker placed on a hot plate as shown in Fig. 1 and set at the required solution temperature, at this moment the FBRM and temperature measurements were started simultaneously. The numbers of particles within the solution were recorded after every two seconds by FBRM (Mettler Toledo). Mixing was brought about by a magnetic stirrer at a speed sufficient to give good mixing in order to keep all the crystals in suspension without settling. The experiments were conducted at various calcium ion concentrations from 0.01 - 0.05 mol/L at  $25^\circ\text{C}$  temperature.

The chemical inhibitor used was a trade named S. The inhibitor was added to 1L beaker containing calcium ion solution prior to mixing with carbonate ion solution. Micropipettes ranging from 1-50 $\mu\text{l}$  were used. The concentrations of the chemical inhibitor used were 50, 25, 10, and 5 ppm. Inhibition experiments were run for a period of one hour. Additional chemicals with trade names K, EDTA, PVC, and SC were used to study the influence of each inhibitor.

### 3. RESULTS

The raw data obtain from FBRM measurements require further treatment like data cleaning and smoothing. The methodology to obtain the smoothed data is reported earlier in (W.N Nasser et al 2008). The results reported henceforth are the smoothed data. Figure 2a shows typical plot for the total number of chord counts vs time measured by FBRM probe as a result of calcium carbonate precipitation. The number of chord counts increase with time for Blank experiment (without inhibitor) at 0.01 mol/L calcium ion concentration. But in presence of inhibitor no chord counts were detected. Similarly in Figure 2b the chord count is found to increase with time at 0.03 mol/L calcium ion concentration and the total number measured at the end of 60 minutes are higher than at 0.01mol/L but the same experiment performed in presence of inhibitor show less number of chord counts.



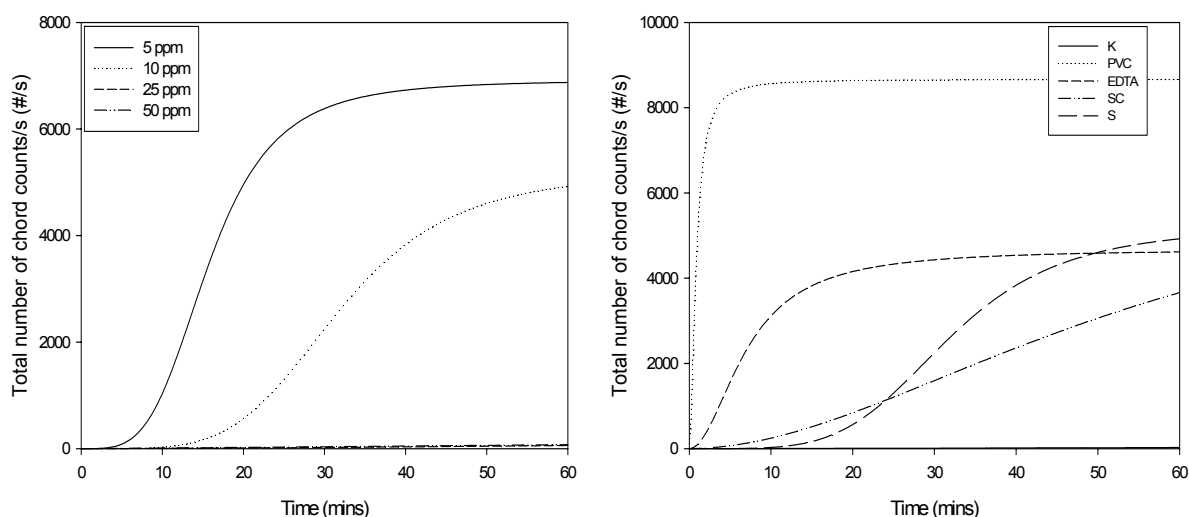
**Figure 2a, b and c: Effect of inhibitor for 0.01, 0.03 and 0.05 mol/L calcium ion concentrations.**

The number of chord counts in presence of inhibitor at 0.05 mol/L is found to increase but the number of chord counts is still less than the corresponding blank experiment.

In addition it can be seen that number of chord counts start to appear at later times in presence of inhibitor as compared to blank experiment. The delay in precipitation of calcium carbonate is indication of the induction period. It can be said that the induction period in presence of inhibitor decrease with increase in calcium ion concentration. For example, the induction period at 0.01 appears to be more than 60 minutes, while at higher calcium ion concentration experiments such as 0.03 it is 17 minutes which is further reduced to 3 minutes for 0.05 mol/L calcium ion solutions. Such presence of induction period is only observed at 0.01 mol/L calcium ion concentration for Blank experiment.

The presence of induction period in presence of inhibitor indicates the delay in precipitation of calcium carbonate. However with increase in calcium ion concentration the supersaturation is increased which results in decrease in induction period. This is in agreement with the classical nucleation theory (Mullin 1992).

### 3.1 Determining minimum inhibitor concentration and effective inhibitor



**Figure 3a-b: Effect of inhibitor concentration and type of inhibitor on calcium carbonate precipitation.**

Figure 3a shows the influence of inhibitor concentration on the number of chord counts measured during precipitation of calcium carbonate at 0.04 mol/L calcium ion concentration and 25°C solution temperature. Each experiment was conducted at various concentration of S inhibitor. It is evident that increase in inhibitor concentration increases the induction period and delays the precipitation process. The present online technique thus can be utilised to determine the minimum inhibitor concentration required to delay the precipitation of calcium carbonate. These result in minimum wastes of chemical inhibitors.

Figure 3b shows total number of chord counts measured vs time at 0.04 mol/L calcium ion concentration and 25°C solution temperature for various types of chemical inhibitors. The influence of chemical inhibitors of trade names K, PVC, EDTA, SC and S were tested on the precipitation of calcium carbonate. The inhibitor concentration of 10 ppm was used for each type of inhibitor.

In presence of K very low number of chord counts was detected for the period of 60 minutes of measurement, which shows that the precipitation is completely inhibited during this time. In presence of PVC, the total number of chord counts measured is approximately 8200 which is similar to the measurement under blank conditions. This shows that under present conditions PVC has no influence on the precipitation of calcium carbonate. In presence of EDTA the number of chords measured was 4000 and the increase in number of chord counts with time is slower than in presence of PVC. In presence of S the precipitation was delayed by 10 minutes and in presence of SC the induction period is found to be 3 minutes and the increase in number of chord counts is slow.

This measurement method shows that among the inhibitors tested the K has the highest influence on the precipitation of calcium carbonate at 0.04 mol/liter calcium ion concentration and at 25°C solution temperature.

### 3.2 Scaling rate

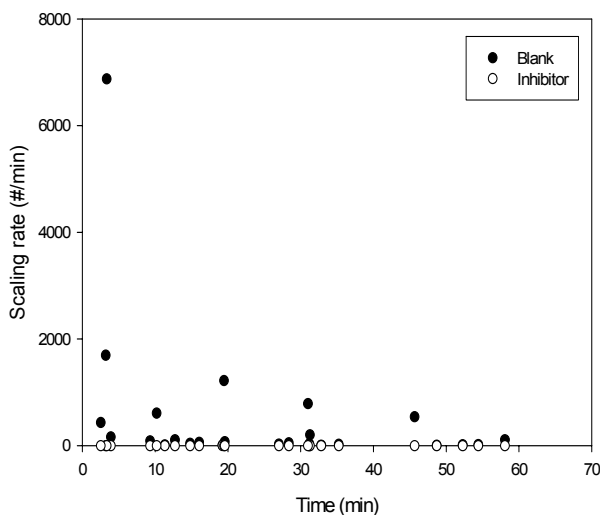


Figure 4: Effect of inhibitor on the scaling rate of calcium carbonate.

Figure 4 shows the scaling rate or deposition rate of calcium carbonate crystals obtained for blank and in presence of inhibitor. The detail description of the online scale measurement technique is explained in (W.N. Nasser et al).

Under blank conditions the scaling rate is found to decrease with time exponentially. The scaling rate values are high for first 10 minutes of the process, due to high deposition of calcium carbonate crystals on the surface probe. In presence of Inhibitor the deposition on the surface probe is negligible hence the scaling rate values close to zero. It is shown in Nasser et al that the mechanism for the deposition of calcium carbonate is through the heterogeneous precipitation rather physisorption process.

The results shown in previous section shows that presence of inhibitor directly affects the precipitation process of calcium carbonate. The precipitation of calcium carbonate is drastically reduced in presence of inhibitors and in some cases no precipitation is seen for finite time duration.

## 4. CONCLUSION

The present results obtain from the FBRM technique are in agreement with the literature. Increase in calcium ion concentration has reduced the induction period which is result of increase in degree of supersaturation. Increase in inhibitor concentration increase the induction period of calcium carbonate precipitation. It is found that only 25 ppm of S is required to completely inhibit the precipitation of calcium carbonate, FBRM technique prove to be useful in online assesment of various type of inhibitors and it is relatively simple technique to monitor the effect of inhibitor compared to others mentioned in literature.

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