



SPE 141583

Modeling the Effect of Triazine Based Sulphide Scavengers on the *in situ* pH and Scaling Tendency

N. Goodwin (Scaled Solutions limited), J.M. Walsh (SPE, Shell, Amsterdam), R. Wright, S. Dyer & G.M. Graham (SPE, Scaled Solutions Limited)

Copyright 2011, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE International Symposium on Oilfield Chemistry held in The Woodlands, Texas, USA, 11–13 April 2011.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

Amine-based chemicals used for scavenging of hydrogen sulphide will cause precipitation of carbonate scales, under a wide range of conditions. They are effective as scavengers, and have health, safety and environmental advantages compared to other scavenger chemicals. Unfortunately, they significantly raise the pH of all process waters that they are mixed with, and thus exacerbate the scaling tendencies of dissolved carbonate minerals. Calcium carbonate, magnesium carbonate and iron carbonate scales can occur over a wide range of temperatures, pressures, and carbonate concentrations. In many process configurations there is no alternative but to allow the mixing of scavenger with produced water. In those cases, extensive laboratory work is typically required to select an appropriate scale inhibitor. It is usually necessary in such studies to understand in detail the chemistry of the solution and its pH and alkalinity characteristics.

We have developed a modelling methodology which can approximate the effect of triazine type H₂S scavengers using an analogue amine as an effective weak base. The effective weak base has a base dissociation constant of the right order compared to monoethanol amine. It therefore simulates the pH effects, and the titration curves of the amine / CO₂ / carbonate buffer system that were measured in the lab. Using this methodology we show how the production process has a significant impact on the *in situ* scaling potentials and how improved modelling and laboratory tests are able to better simulate the field conditions and aid understanding of the process chemistry issues and solutions.

Introduction:

One of the options for removing H₂S from produced hydrocarbon gas is to inject an amine-based chemical scavenger. While such scavengers can be effective at removing H₂S, scaling is a common problem. Both the unreacted scavenger and its reaction products contain alkaline amines. If either the scavenger or its reaction products are mixed with produced water containing carbonates, the increase in the pH will increase the probability of carbonate scale.³⁻⁵

One of the strategies used to prevent scaling is to inject the scavenger directly into the gas stream. This can be accomplished downstream of any one of several gas/liquid separation vessels in a facility. By adding the scavenger to the gas, the scavenger does not immediately contact the produced water. This strategy works well to prevent scaling in the injection system.

However, transporting the reacted scavenger through a production facility, and ultimately disposing of reaction products often poses a challenge. Many questions arise regarding the ultimate fate of the reacted scavenger. Fouling and corrosion of downstream equipment is a major concern among operators. When considering disposal into a subsurface reservoir, the possibility of scaling in the reservoir and injectivity impairment are issues that must be addressed. If the reservoir is a producing reservoir, then souring from a nitrogen food source must also be considered. When considering overboard disposal, the Environmental Impact must be assessed.

Often it is not possible to completely segregate the scavenger reaction products from the produced water in a facility. The process configuration may not provide two parallel water-based processing systems. At some point, there may not be any alternative than to mix the produced water and the scavenger reaction products together.

Process constraints may leave no alternative than to mix the scavenger reaction products with the produced water and to mitigate the consequences with scale inhibitor. Laboratory tests are usually required to select an appropriate scale inhibitor and to determine the required minimum dosage. Laboratory conditions must mimic the conditions in the field, at least with respect to the important variables such as temperature, and solution composition. It becomes critical to understand the pH and alkalinity effects of the fluids, before and after the scavenger has been added. The mitigation of scale formation becomes in this case a complex problem involving solution chemistry. The extent to which the chemical vendors are willing to help solve such problems, or are even aware of the issues varies significantly from one vendor to another.

Solution Chemistry:

Commonly used H₂S scavengers contain a triazine-type chemical as the active ingredient. Examples are tri(hydroxyethyl) triazine and trimethyltriazine (see Figure 1). The tri(hydroxyethyl)triazine is the more water soluble of the two, and is generally favored when it is likely that the scavenger will come in contact with produced water. The trimethyltriazine is the more oil soluble and is often used when the scavenger will contact predominantly oil-based produced fluids. This latter compound however, does have finite partitioning into both oil and brine. Both of these triazine examples contain a similar amine structure and therefore undergo similar hydrolysis and scavenging reactions.^{1, 2} The product of these reactions include primary amines. The scavenging reactions for tri(hydroxyethyl)triazine are shown in Figure 2. As shown, electrophilic attack on the nitrogen groups by hydrogen sulfide results in sulfur substitution into the cyclic structure. Also, a primary amine (ethanolamine in the example) is produced in each step of the sequential reaction.

As indicated in Figure 2, both the unreacted triazine and the reaction products are amine-type compounds. Thus, the pH of the solution will be alkaline along the entire reaction path. In a typical application, only a fraction of the scavenger will react. Therefore the product of the scavenging treatment will contain both reacted and unreacted scavenger. In fact, complete reaction of the scavenger (Figure 2, part D) results in a cyclic sulfur compound that is insoluble in either hydrocarbon or brine. If that compound is allowed to form, it will precipitate on pipe walls and vessel internals. Scavenger is therefore normally applied in excess of the stoichiometric ratio, and the contact time between scavenger and H₂S-containing gas is controlled within certain limits. Both of these actions help prevent the formation of the insoluble reaction product, while still achieving the desired scavenging target. However, a consequence is the presence of unreacted scavenger in the product. Thus, the product of typical scavenger applications in the oil and gas industry is a complex mixture of unreacted triazine, partially reacted triazine, and primary amines.

We have developed a methodology to model this system using OLI ScaleChem[™] based on our laboratory data and comparison with data from production facilities.

As discussed above, the chemistry of the H₂S reaction with the amine scavenger is such that both unreacted scavenger and reacted scavenger both have high pH. Thus, the pH is expected to remain elevated over the entire course of the reaction. This conclusion does not take into account the presence of CO₂. In addition to the amine chemistry discussed above, it is necessary to consider the CO₂ / bicarbonate equilibrium, which tends to drive the pH to acidic values. That equilibrium also has a direct impact on scaling tendency since it determines the concentration of carbonate anions.



Routine monitoring in a gas processing facility where scavenger was being used provided some interesting results. In this facility, the scavenger was injected into a gas stream, just upstream of a set of gas coolers. The gas coolers caused water to condense from the gas. This condensed water was, of course, in equilibrium with the CO₂ in the gas. The partial pressure of CO₂ was 3 bar, and the temperature was roughly 60°C. The sample point for this water stream, containing reacted (and of course unreacted) scavenger, was downstream of the coolers. The measured pH of this stream was roughly 6.5 to 7.0.

Further downstream in the process, a second stream of condensed water mixed with the stream described above. This second stream of condensed water had a pH in the range of 4. The flow rate of this stream was 50% higher than the one above. Nevertheless, the product of mixing these two streams was a combined stream with a pH roughly 6.5 to 7.0. Obviously, the buffering capacity of the smaller stream containing the reacted scavenger was high.

This was an important set of observations so it was simulated in the lab. We have conducted an extensive laboratory and modeling study in order to fully assess the impact of the scavengers on the scaling potential and also the ability of conventional scale inhibitors to control scaling in this production system. This involved a range of tests conducted with and

without the presence of CO₂ at partial pressures similar to that observed in the field. Alkalinity titrations were then also conducted in order to allow comparative modeling of the impact of different bases on the resultant pH and alkalinity.

Factors affecting the pH in the laboratory

The laboratory work examined a wide range of factors:

- Brine composition: condensed water and high calcium export water ([Ca] ~ 5,000mg/l)
- Formulation: Two generic triazines namely; tri(hydroxyethyl)triazine or trimethyltriazine
- Concentration: 3,500, 6,000 ppmv
- Sparge gas: Nitrogen and Carbon Dioxide
- Pressure: 1 bar and 3 bar absolute.

In addition to recording the pH at 60°C, the test solutions were allowed to cool before recording the alkalinity and bicarbonate levels by titration.

The clear conclusion for the systems examined was that the sparge gas was the dominant factor in determining the pH, and use of CO₂ allowed the laboratory pH's to match those observed in the field. This is because in this field example an excess of CO₂ (partial pressure of 3 bar) was available to buffer the triazine without being consumed, even given the relatively large triazine concentrations. This was primarily due to the large gas to water ratio (GWR) as well as the CO₂ partial pressure in the produced gas stream. In effect, the field situation represents an open system with an almost infinite source of CO₂.

- Solutions containing triazine that were sparged with nitrogen had a pH between 8.6 and 10.0.
- Solutions sparged with carbon dioxide at 1 bar had a pH between 6.4 and 7.0
- Solutions sparged with carbon dioxide at 3 bar absolute had a pH between 5.9 and 6.4.

This is further illustrated in Figure 3 which shows the pH as a function of scavenger concentration for both sparged (1 bar CO₂) and non CO₂ sparged solutions. The results show that the concentration of the scavenger has a significant effect on the pH at low doses only. At low dose, the scavenger / water equilibrium produces a hydroxyl anion for almost every nitrogen added to the solution. As the concentration increases, the effect of weak basicity begins to be observed and there is little change in the pH, as expected.

Alkalinity Titrations:

Following sparging with and without CO₂, solutions were titrated to measure total alkalinity. The titrations showed, as expected, that the alkalinity varies with the selection of scavenger and its concentration

Figure 4 shows the alkalinity titrations recorded at different scavenger concentrations for both the trimethyltriazine and the tri(hydroxyethyl)triazine. The alkalinities for similar tests are summarized in Table 1. *[Note the higher alkalinity for the 6,000 ppm solution of trimethyltriazine relates partly to its lower molecular weight and also to the significantly higher active content of the sample examined]*

Table 1: Recorded alkalinity for generic triazines.

Triazine	activity	Dose (ppmv)	Alkalinity	
			mmol/l	mg/l bicarb
Tri(hydroxyethyl)	~45%	3,500	21.5	1,300
		6,000	36.3	2,200
trimethyl	~95%	6,000	118.7	7,200

The titrations also show, not unexpectedly, the impact of the CO₂ sparge gas. When the solution is sparged with CO₂ prior to titration the initial pH is relatively low. The forward titration drives the CO₂ out of the solution and the reverse titration then follows the same pH curve as the solution that is sparged only with N₂ and without CO₂. This is as expected. In general, it is well known that CO₂ does not contribute to alkalinity.

The pH results reported above, and the titration results reported in this section are as expected. While there is nothing new in these results, they do provide the data necessary to construct a scaling tendency model for the system. Mechanistically what is happening is the following. Solutions with excess CO₂ present have significant buffering capacity. Addition of a base removes protons from the system. This causes more carbonic acid to dissociate which is replaced by carbon dioxide coming into solution.

The overall effect is that the basic amine forms a primary amine bicarbonate salt. This results in the solution having a lower pH. The alkalinity is unchanged, but the total level of bicarbonate / carbonate / carbon dioxide in solution is increased (also described as the superficial bicarbonate level). Since this effect is not seen in the alkalinity measurements, a scaling tendency model is usually used. Input to the model is pH, alkalinity, and CO₂ partial pressure. Together these variables provide a more complete understanding of the solution chemistry.

Modeling the Laboratory Titration Curves:

All of the modeling for this paper used OLI ScaleChem™ (Version 3.2.58). That software package does not allow the addition of triazine based H₂S scavengers to a brine solution. Although triazines *per se* could be incorporated into ScaleChem™, the authors feel that modeling the detailed effect of the scavenging and hydrolysis reactions could be challenging, and given that detailed chemical information and activities would not normally be available for commercial formulations it was thought appropriate that an approach considering an “effective” base to simulate the triazines would provide a suitable solution.

Therefore the modeling was carried out using an “effective base”. Selecting the effective base analog was based on the following criteria. The analog must allow adjustment of pH into the alkaline region. Also, it must mimic the pH titration curves measured in the laboratory and reported in the previous section. In other words, the selected analog must be a weak base in the sense that it must only partially dissociate according to chemical equilibrium. It is not necessary for our purposes to model specific triazine reactions.

The quantity of effective base required to mimic the effect of triazine is determined in the modeling itself. The optimal concentration of effective base is that which gives the best match of laboratory equilibrium pH, alkalinity and the overall shape of the titration curve. The procedure for generating the model titration curves is given below.

Initial modeling used sodium hydroxide. It was obvious from the start that sodium hydroxide would not satisfy the above criteria of a weak base since sodium hydroxide completely dissociates in water. Nevertheless, it is instructive to see what effect this would have. Matching the initial pH of the laboratory titration curves was straight forward. However the modeled titration curves did not replicate the experimental titration curves. Example results are shown in Figures 6 and 7. In Figure 6, the laboratory solution is not equilibrated with CO₂, and CO₂ is not used in the model. In Figure 7, the laboratory solution is equilibrated with CO₂, and CO₂ is used in the model. Neither set of modeling results shows the result obtained in the laboratory, *i.e.* the initial slow drop in pH, followed by a sudden drop and inflection point. In comparing the two sets of modeling results, a tenfold increase in sodium hydroxide is required to match the initial pH in the presence of CO₂. But in both cases it is apparent that the laboratory titration curve is strongly affected by the weak base equilibrium of the amine.

Further investigation showed that ammonia is a much better effective base analog for triazine. This is in part due to the fact that the pK_b values for ammonia and monoethanolamine (the key hydrolysis and scavenging by-product as illustrated in Figure 2) are similar:

Monoethanolamine; $K_b = 3.0 \times 10^{-5}$ at 25°C
Ammonia; $K_b = 1.8 \times 10^{-5}$ at 25°C.

The quantity of ammonia required in the model to give the best overall representation of the laboratory data was determined by trial and error. In theory it would be possible to calculate the quantity of ammonia based on the relative pK_b values and molecular weights, the scavenger dose, the activity of the scavenger formulation and the presence of other acids and bases within the scavenger. However, as some of these factors are unknown, especially for commercial scavengers, it is preferable to derive the effective ammonia concentration from the experimental data.

The procedure used for curve matching was as follows:

1. Brine compositions added to ScaleChem™.
2. Initial ammonia concentration estimated.
3. Reconciled with 70 mole % CO₂ in gas fraction.
4. pH recorded.
5. Small quantity of acid added.
6. pH recorded.
7. Steps 5 and 6 repeated to produce a curve.
8. Comparison between lab and modelled curve.
9. Steps 2 – 8 repeated with different ammonia concentrations.
10. Use derived effective ammonia concentration for further lab (model verification) and field modelling

For tests using carbon dioxide, saturation at 70% gas fraction was used in ScaleChemtm: this allows water to equilibrate in the gas phase.

Based on this procedure we achieved a good match between the model titration curves and the laboratory titration curves. An example of this match is shown in Figure 8. This procedure resulted in with the experimental data for each of the scavengers under one set of conditions (Figure 8) and calculated the relationship between the scavenger dose and the ammonia concentration required to replicate the pH curve for a number of different scavengers, examples of which are shown in Table 2.

Table 2: Ratio of effective ammonia to triazine dose based on curve matching.

Triazine	Field	1,000ppm in condensed water	6,000ppm in Low Calcium Export Water
Trihydroxyethyl (45%)	1	--	÷ 10.2
Trihydroxyethyl (~60%)	1	--	÷ 8.0
Trihydroxyethyl (77%)	2	÷5	--
Trimethyl	2	÷ 2.8	--

Note that the brine composition can have an effect on the quantity of ammonia required and this would lead to further complications if trying to model the system without comparison to field specific experimental data.

Scaling Tendencies:

Three factors affect the scaling tendency of carbonate minerals. All three factors relate to the concentration of carbonate anion. The higher the carbonate anion concentration, the higher is the scaling tendency.

The first is the CO₂ partial pressure. In the field, there is an almost infinite supply of CO₂ as gas continuously sweeps over the produced water. As scavenger is injected, the pH has a tendency to increase. But this increase in pH is counteracted by additional CO₂ from the gas.

The second is the pH. As pH increases, there is a shift in the CO₂ / bicarbonate / carbonate equilibrium. At acidic values of pH the dominant species is the bicarbonate anion. At higher pH, in the range of 8.5 and above, the dominant species is the carbonate anion. As mentioned, the concentration of carbonate anion contributes directly to the scaling tendency.

The third factor that affects the scaling tendency of carbonate minerals is the alkalinity. In the systems considered here, alkalinity is provided by the scavenger. The presence of CO₂ does not contribute to alkalinity. However, the alkalinity contributes to the concentration of bicarbonate, and hence carbonate anions in solution.

To assess the overall impact of these variables on the scaling tendency requires modeling together with lab tests of scaling tendency. While these variables can be studied experimentally, modeling provides detailed insight.

Modeling is used to evaluate the effect of pH, alkalinity and CO₂ partial pressure on the scaling tendency. Using the effective ammonia concentrations described above, scaling tendencies are predicted across a range of production scenarios.

Table 3 provides a comparison between the laboratory-measured and modeled pH's (at 21°C), together with the predicted scaling tendencies (at 60°C). This also shows that the model can be used to predict the *in situ* pH and scaling tendency and that these show good correlation with the experimental data. Comparison with data from the production facility also shows good correlation between the field observations and the scale predictions.

Table 3: Comparison of laboratory and modeled pH with and without CO₂ sparging for tri(hydroxyethyl) triazine in field 2.

Temperature	[Scavenger] (ppmv)	Laboratory pH	Modeled		Scaling of CaCO ₃	
		21°C 1bar	21°C 1bar	<i>In situ pH (dynamic test @ 60°C)</i>	ST	Time to Scale dynamic test @ 60°C (mins)
60°C	0	4.02	3.97	4.04	0.003	> 180
	6,000	6.02	5.56	5.22	19	20

Table 4 shows the results obtained for simulations conducted on a different field brine with lower scavenger doses to examine the impact of the triazine (modeled as effective amine) in the absence of CO₂ and in the presence of CO₂. These show a good

correlation between the modeled and recorded pH for each dose of scavenger, and show the link between the pH and the time taken to form scale in a dynamic flow rig. In short, these concur with laboratory findings and field observations, with significantly reduced *in situ* pH's and consequently increased scaling times when tests are conducted in the presence of CO₂. Clearly, in the absence of CO₂, increased pH's and more rapid scaling is observed and therefore further illustrates the importance of the buffering effect of CO₂ on the triazine and the need to include such weak base / weak acid equilibria, and CO₂ partitioning effects, when simulating these conditions either in the laboratory or when determining the expected scaling potential and *in situ* pH's in a field application.

Table 4: Comparison of laboratory and modeled pH with and without CO₂ sparging for field 2.

Scavenger dose ppmv	Effective ammonia mg/l	Nitrogen sparged			CO ₂ sparged		
		Modeled pH	Laboratory pH	Scale time (mins)	Modeled pH	Laboratory pH	Scale time (mins)
0	0	6.45	6.41	>180	5.49	5.50	>180
125	25	--	7.05	29	5.53	5.57	>180
250	--	--	--	18	--	--	--
500	100	--	7.95	6	5.62	5.54	>180
750	--	--	8.10	4	--	--	--
1000	200	--	8.10	--	5.71	5.63	>180

Summary and Conclusion

This work was initially conducted in order to understand the effect of triazine-based scavengers on the *in situ* pH's and scaling tendencies in gas production streams. The work initially identified a considerable impact of the *in situ* pH and scaling conditions due to the buffering capacity of the excess CO₂ present in this system partitioning into the water phase and neutralizing the triazine, the net result being to considerably reduce the impact of the triazine on both the *in situ* pH and carbonate scaling tendency. While performing this work, it was evident that modified modeling methodologies had to be developed to simulate these effects more appropriately, since the use of strong bases such as NaOH was not effective. Ammonia was therefore selected and shown to be appropriate as an effective base, allowing any conventional commercial triazine to be simulated following some preliminary titration measurements. The modeling methodology has now been validated in a large number of conditions and scavengers and shown to model effectively the laboratory conditions and more importantly to provide results which closely mimic field observations

Although the use of ammonia *per se* may be limited due to its volatility, additional work (not covered in this paper) has shown that this can readily be overcome within the model calculations. It is noted finally however that the considerable reduction in the *in situ* pH and scaling tendencies recorded for the systems described here reflects the high GWR ratios and relatively high partial pressure of CO₂ providing an almost inexhaustible supply of CO₂ to buffer the triazine. This however would not be expected in other systems producing at lower GWR and lower CO₂ contents where the CO₂ the effect would be limited.

In summary, a laboratory and modeling methodology is described which allows effective representation of the effects of triazine based scavengers on calcium carbonate scaling.

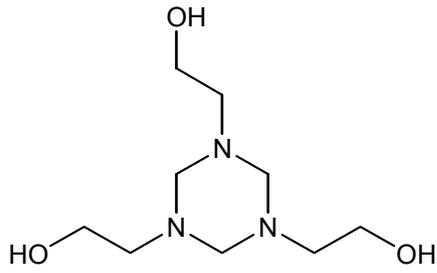
We have developed a modelling methodology which can approximate the effect of triazine type scavengers using an analogue amine as an effective weak base. This has a base dissociation constant of the right order required in order to simulate the pH effects, and the carbon dioxide – carbonate buffer system. Also, it is essential to include the carbon dioxide effects in order to estimate the pH values at which laboratory testing of scale inhibitors should be conducted, differences between calculated pH with and without carbon dioxide are frequently over 2 pH units. Here we show how the production process has a significant impact on the *in situ* scaling potentials and how improved modelling and laboratory tests are able to better simulate the field conditions and aid understanding of the process chemistry issues and solutions.

References

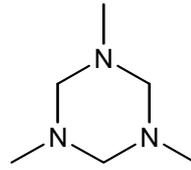
- 1) J. M. Bakke, J. Buhaug, J. Riha, "Hydrolysis of 1,3,5-Trishydroxyethyl)hexahydro-s-triazine and its Reaction with H₂S" *Ind. Eng. Chem. Res.* **2001**, 40, 6051-6054
- 2) J. M. Bakke, J. B. Buhaug, "Hydrogen Sulphide Scavenging by 1,3,5-Triazines. Comparison of the Rates of Reaction" *Ind. Eng. Chem. Res.* **2004**, 43, 1962-1965.
- 3) C.D. Sitz, D.J. Barbin, and B.J. Hampton, "Scale Control in a Hydrogen Sulphide Treatment Program". Paper SPE 80235, Presented at the 2003 International Symposium on Oilfield chemistry, Houston, Texas, USA 5-7 February 2003

-
- 4) M.M. Jordon, K. Mackin, C.J. Johnson, and N.D. Feasey, "Control of Hydrogen Sulphide Induced Scale and the Associated Challenge of Sulphide Scale Formation within a North Sea High Temperature / High Salinity Fields Production Wells. Laboratory Evaluation to field Application. Paper SPE 87433
 - 5) H. Williams, S. Dyer, M.C.M. Bezerra, G.M. Graham, . and R. Wright, "The Effect of Sulphide Scavengers on Scaling Tendency and Scale Inhibitor Performance" Paper SPE 131115 presented at 2010 International Conference Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May **2010**.

Figure 1: Structures of Triazine based scavengers



1,3,5-Tris(2-hydroxyethyl)hexahydrotriazine



1,3,5-trimethylhexahydrotriazine.

Figure 2: 1,3,5-Tris(2-hydroxyethyl)hexahydrotriazine and its reaction with hydrogen sulphide.

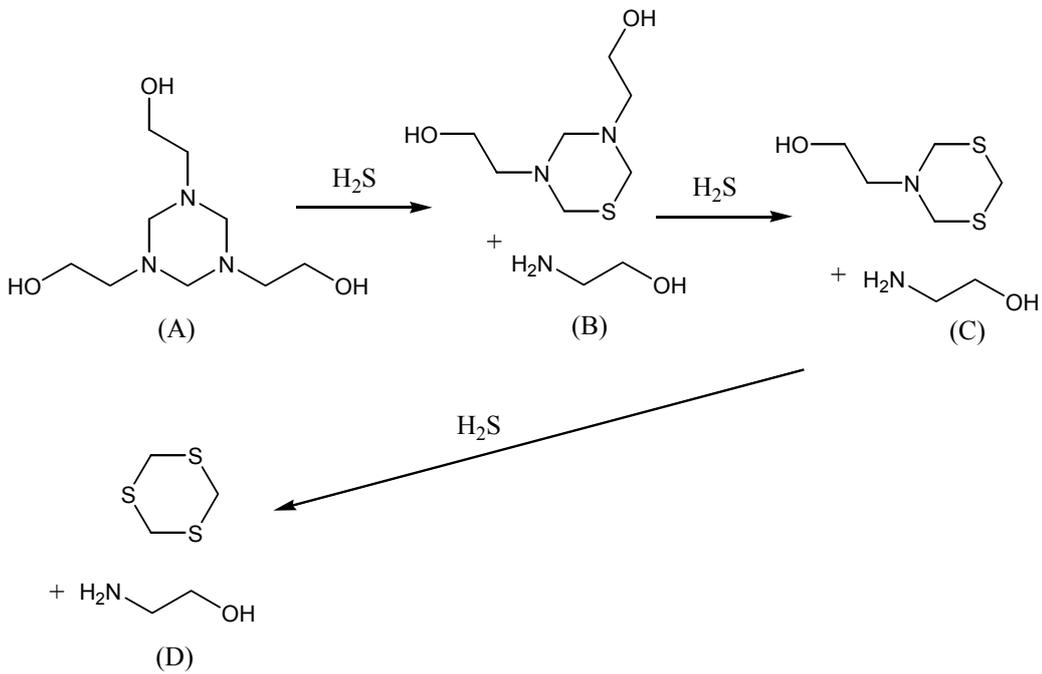


Figure 3: Effect of saturation gas and scavenger concentration – 45% active trir(hydroxyethyl) triazine

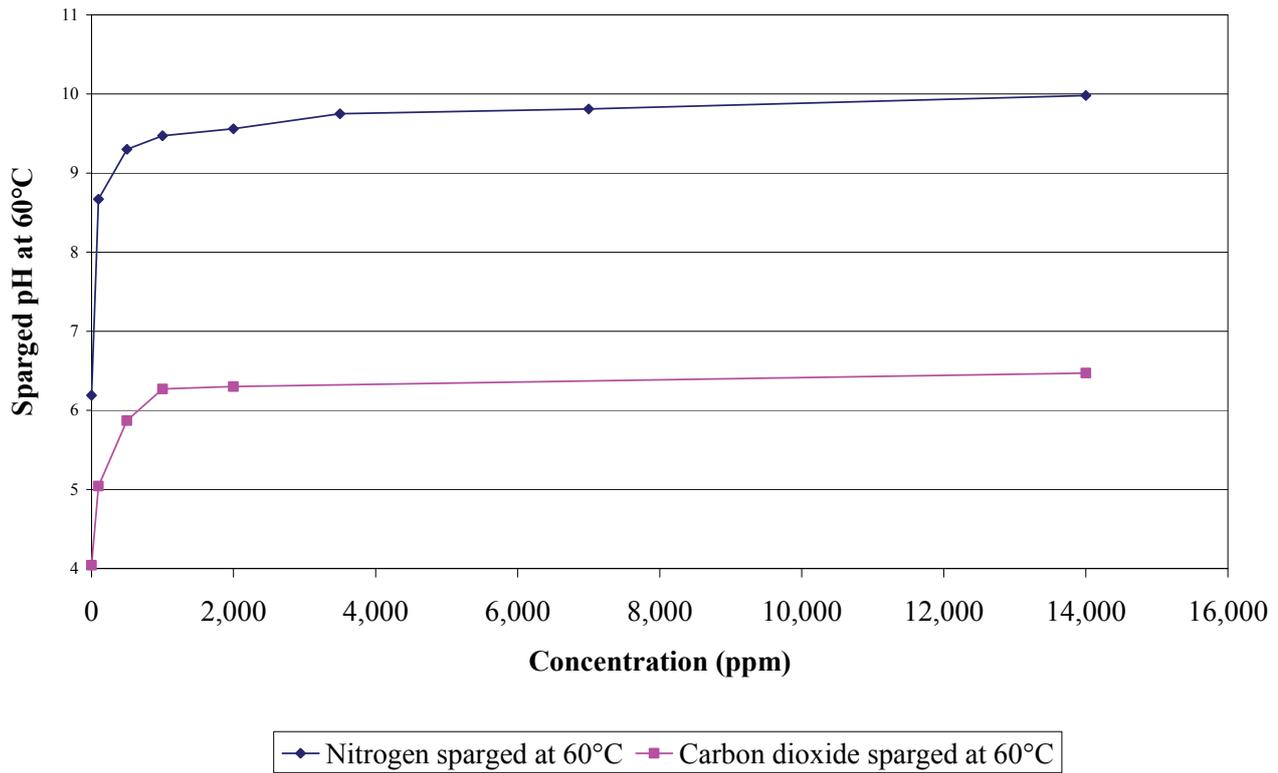


Figure 4: Effect of scavenger dose and activity on the titration curve:

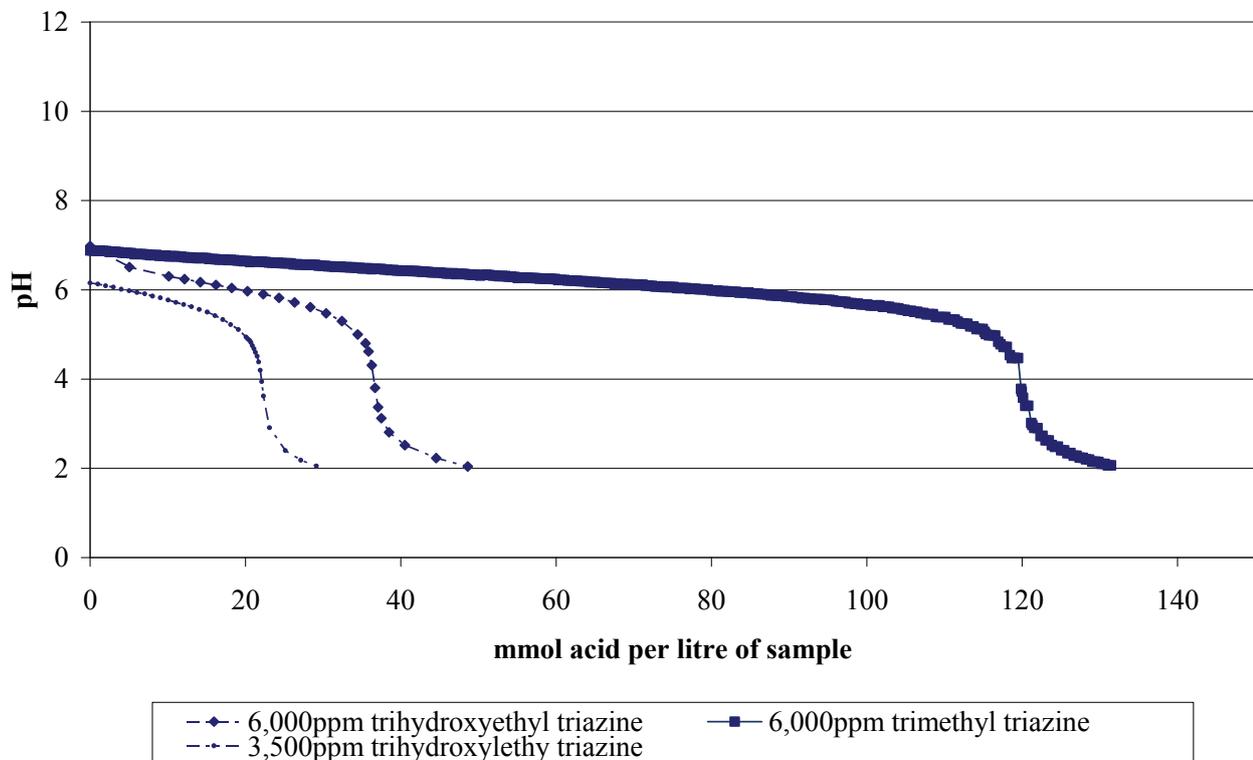


Figure 5: Forward and back titrations for 6,000ppm of tri(hydroxyethyl)triazine sparged with CO₂ or N₂

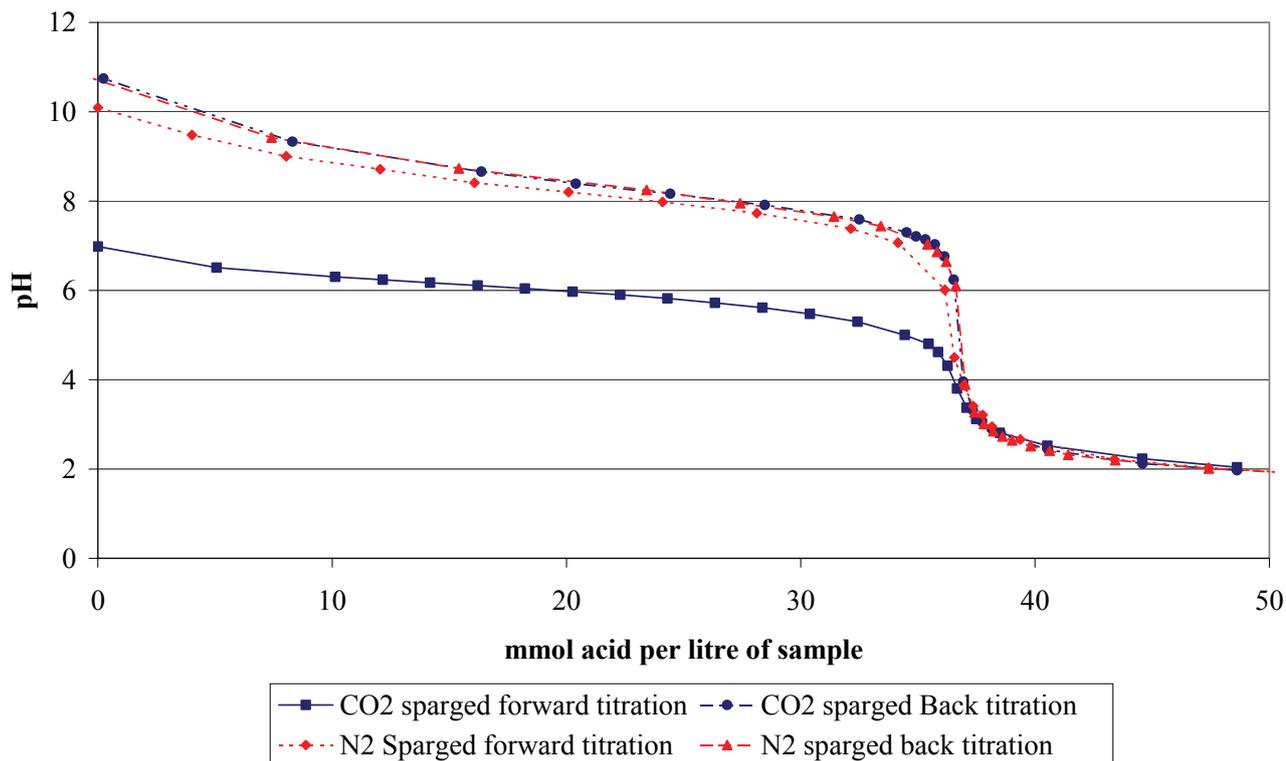


Figure 6: Titration of 3,500ppm triazine and simulation using 18.5mg/l hydroxide without carbon dioxide.

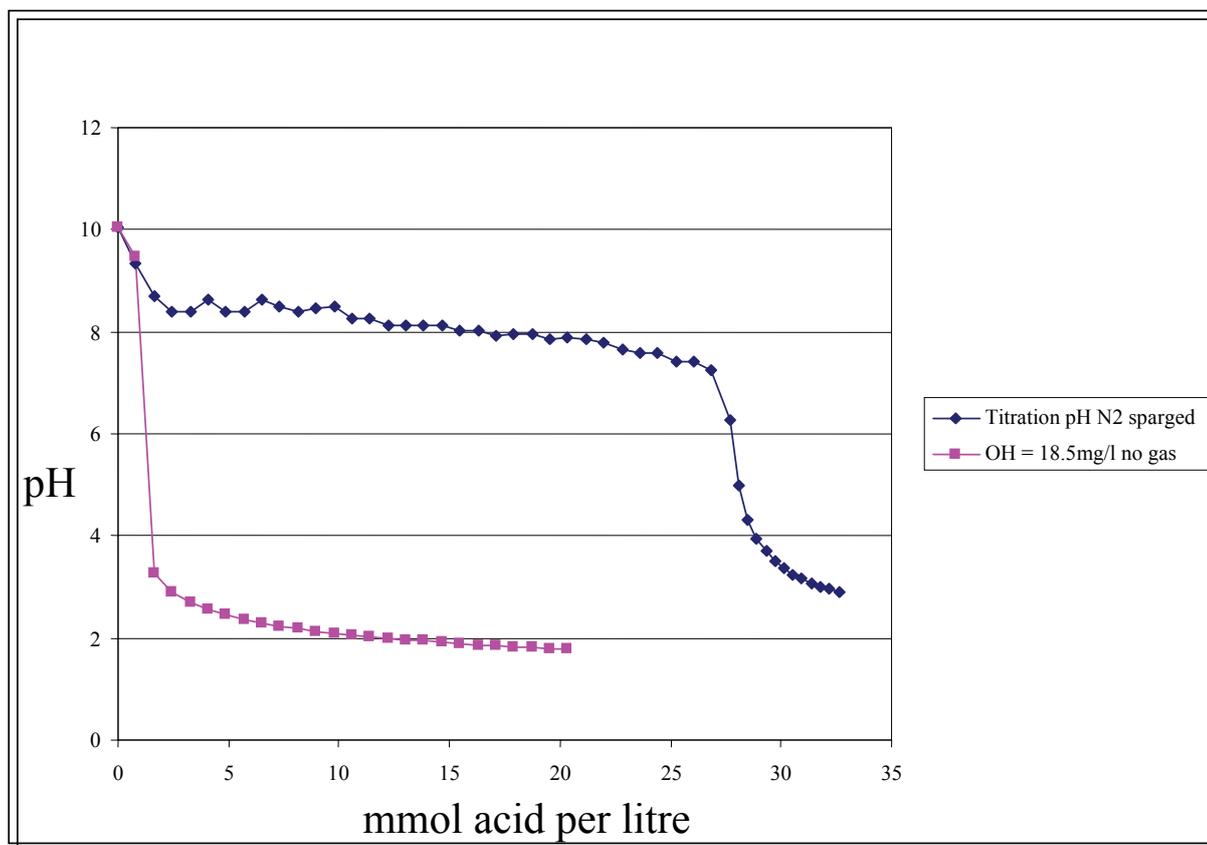


Figure 7: Titration of 3,500ppm triazine and simulation using 210mg/l hydroxide with carbon dioxide.

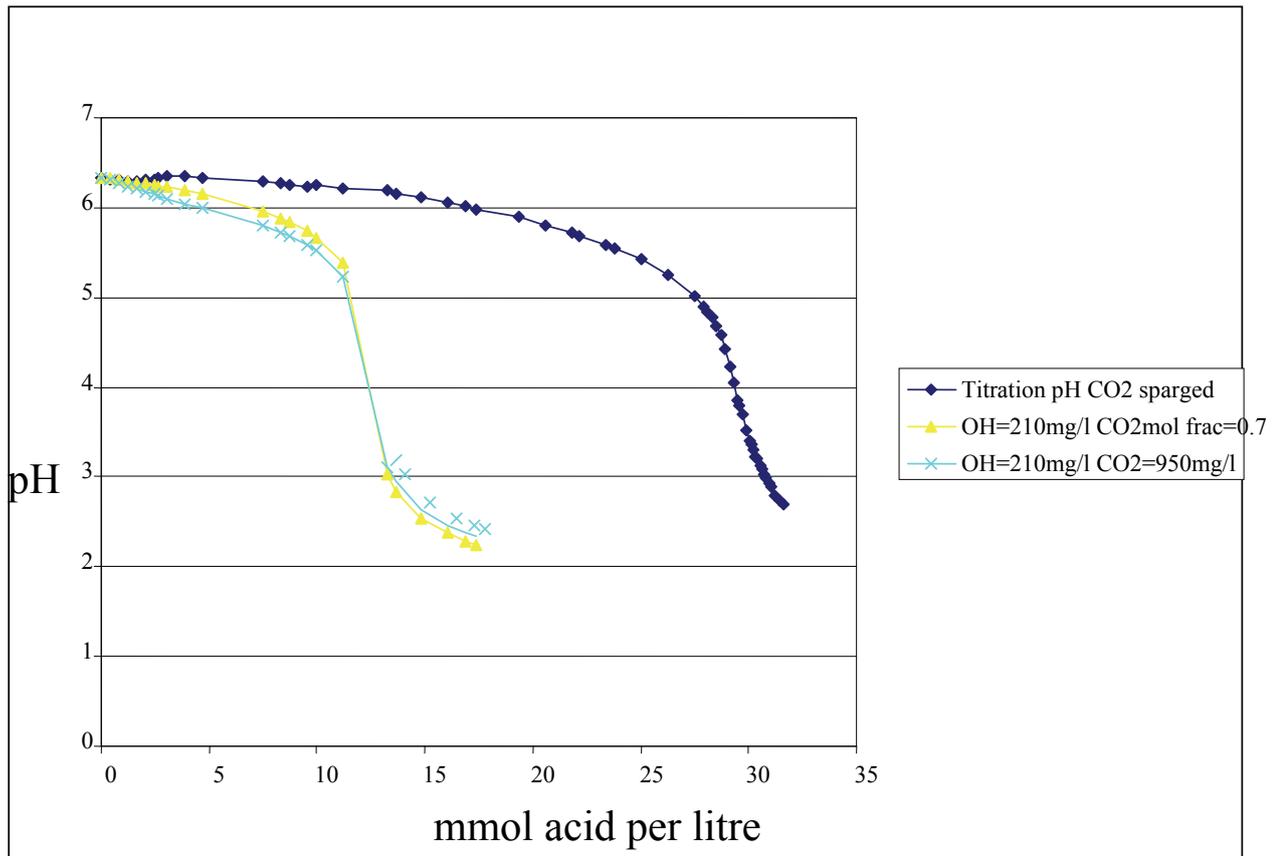


Figure 8 – Experimental titration curve and modeled curve with varying ammonia doses.

