



**STATISTICAL ANALYSIS OF SOUR AUTOCLAVE TESTING WITH AND WITHOUT
CORROSION INHIBITOR PRESENT**

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ABSTRACT

In qualification of corrosion inhibitors (CI) sour autoclave tests are often utilized to determine performance and the ability of the CI to minimize localized corrosion. In this paper a statistical analysis of > 500 sour autoclave tests are presented. The general corrosion rate and localized corrosion rates of these tests were analyzed with general statistics, ANOVA and partitioning analyses to determine major factors contributing to higher general and localized corrosion. The corrosion factors are analyzed with and without CI present.

KEYWORDS: sour static autoclave, H₂S corrosion, sour corrosion, statistics, ANOVA, partitioning platform, H₂S corrosion factors

INTRODUCTION

The control of sour corrosion is a major concern in the oil and gas production arena. In particular, corrosion due to H₂S is not fully understood and constitutes a large knowledge gap in the industry. The mechanism of CO₂ corrosion has been extensively studied in the last decade while the mechanism of H₂S corrosion remains a distant second. Limited information is available on which factors significantly impact general corrosion rates and pitting in sour dominant corrosion. Recently, two papers have tried to determine leading and secondary factors contributing to H₂S corrosion. Bonis *et al.*^{1,2} have attempted to determine these factors through analysis of a database containing multiple field examples. This database, with more than 500 sour autoclave tests, is analyzed in a similar method as Bonis *et al.* to determine if any factors leading to increased corrosion rates can be determined from a standard corrosion test method. This analysis is intended to serve as a guide in the evaluation of potential factors leading to higher general corrosion rates and maximum pits depths in sour corrosion autoclave testing. The results of the analyses are open to manipulation and interpretations and this author only hopes to help the reader to understand the complex issues of sour dominated corrosion mechanisms.

METHOD DEVELOPMENT

Experimental Test Method

Autoclave Test Apparatus. The autoclaves used are constructed of Hastelloy 276C and have a capacity of approximately 300 ml. The tests were carried out in 250 ml of synthetic brine in each cell. The tests were performed using 0.1 inch thick horizontal disk corrosion coupons having a diameter of 1.25 inches. The coupons are secured in a PEEK apparatus which sits inside the bottom of the test cells. The specimen's holders are raised to allow room for a Telfon® coated stir bar underneath. The surface area of 10.2 cm² has been used throughout corrosion rate calculation. A thermostatic probe monitors the autoclave fluid temperature. The autoclave is charged by means of a Hastelloy tube fitted with a pressure gauge. Performance evaluation was based on weight loss and maximum pit depth. Each autoclave test was run for seven days.

Statistical Analysis

General Distribution Statistics. The data for the autoclave tests were compiled into an Excel and JMP 8(Footnote) table containing 630 independent results. The results are reviewed using the capabilities of Excel and a statistical data interpretation program called SAS JMP8(reference?). General statistics are compiled on each set of data including mean, median, standard deviation, standard error mean, upper and lower 95% mean, count, maximum values, minimum values, 75% quartile, 25 % quartile and related histograms.

ANOVA. The Oneway ANOVA platform analyzes the distribution of a numerical continuous Y variable across groups defined by a categorical X variable. Group means can be calculated and tested, as well as other statistics and tests. This platform utilizes a scatter plot to show the distribution of values within each data set and can perform a one-way analysis of variance to fit means and to test their equality. The platform performs nonparametric tests, tests for the homogeneity of variance, does multiple comparison tests on means, constructs means comparison circles, presents outlier box plots

overlaid on each group and shows power details for the one-way layout. In this paper, a multiple comparison test on means with means comparison circles is utilized.³

Partition Platform. The partition platform recursively partitions data according to a relationship between the X and Y values creating a tree of partitions. It finds a set of cuts or groupings of X values that best predict a Y value. It does this by exhaustively searching all possible cuts or groupings. These partitions of the data are done recursively forming a tree of decision rules until the desired fit is obtained. The technique is often taught as a data mining technique because it is good for exploring relationships without having a good prior model; it easily handles large problems and the results are easy to interpret. The factor columns (X's) can be either continuous or categorical (nominal or ordinal). If X is continuous then the splits (partitions) are created by a cutting value. The sample is divided into values below and above this cutting value. If the X is categorical then the sample is divided into two groups of levels.

The response column (Y) can be either continuous or categorical. If Y is continuous then the platform fits means and creates splits that most significantly separate the means by examining the sums of squares due to the means differences. If Y is categorical then the response rates (the estimated probability for each response level) become the fitted value and the most significant split is determined by the largest likelihood-ratio chi-square statistic. In either case, the split is chosen to maximize the difference in the responses between the two branches of the split.³ This is a powerful platform, since it examines a very large number of possible splits and optimizes selections.

RESULTS AND DISCUSSION

Overview of Autoclave Results

Over the last 15 years sour autoclave testing has been conducted and documented. **Table 1** provides a high level summary of the entire database. The database has several conditions that were found to be important and thus documented. The table includes significant factors considered and the corresponding values in the database. These factors are used in the statistical analysis and are explained below.

**TABLE 1
SOUR AUTOCLAVE SUMMARY OF CORROSION CONDITIONS**

Number of Tests	630
Continuous Product	Inhibitor A, Inhibitor B
Dosage Rate for Continuous (ppm)	500, 700, 1000, 1100, 1200, 1250, 1300, 1400, 1500, 2000, 2500, 3000, 3500, 4000, 5000, 10,000 15,000, 25000 200000
Batch Product	Inhibitor C, Inhibitor D
Batch Dosage (%)	10, 50, 100
Contact Time (sec)	1, 5, 10, 15,
Pre corrosion	Yes, No
Temperature (°C)	25, 35, 41, 45, 50, 52, 54, 55, 60, 65, 66, 70, 110
H₂S (psi)	12, 13, 14, 21, 30, 48, 50, 60, 76, 80, 100, 103, 105, 112, 150, 155, 160, 190, 200, 203, 210, 220, 224, 225, 238,250,252, 254, 255, 258, 260, 381
CO₂ (psi)	9, 12, 13,14, 15, 16, 18, 19, 20, 28, 30, 35,38, 39, 43, 44, 45, 50, 55, 75, 80, 90, 100, 112, 130, 160, 165, 205
H₂S/CO₂ ratio	< 1.0, 1, 2, 3, 4, 5, 8, 10, 16

Chloride Concentration (ppm)	100, 1000, 3000, 4000, 5000, 10000, 19000, 20000, 23000, 25000, 29000, 30000, 45000, 50000, 70000, 75000, 90000, 100000, 120000, 130000, 140000, 168800, 180000, 254000
Sulfur (g)	0, 0.05, 0.1, 0.3, 1, 5
FeS (g)	0, 0.1, 0.5, 1, 5
Pre-partitioning	Yes, No

- Number of tests - Total independent entries.
- Continuous product - Inhibitor A is a sour corrosion inhibitor at 15% active, inhibitor B is a sour corrosion inhibitor at 60% active.
- Dosage rate - Continuous corrosion inhibitor dosed amount ranging from 500 -200,000 ppm.
- Batch product - Inhibitors C and D are used in batch applications and can be used either by itself or in conjunction with a continuous application.
- Batch dosage - If the test includes a batch product then the coupons are “dipped and dripped”. The dosage refers to the amount of inhibitor diluted in diesel for the dipped application.
- Contact time - “Dipped and dripped” refers to the amount of time the coupon immersed in a solution and typically ranges from 1-15 seconds. The dripped time remains constant over the course of the tests at 15 minutes.
- Pre-corrosion – Refers to coupons that were exposed to a corrosive environment before being inhibited
- Temperature – The test temperature ranges from 25-110 °C.
- H₂S partial pressure – The partial pressure of H₂S ranging from 12-381 psi.
- CO₂ partial pressure – The partial pressure of CO₂, ranging from 9-205 psi. Note: the total pressure is the sum of H₂S and CO₂ partial pressures.
- H₂S/CO₂ ratio – This ratio is obtained by dividing the H₂S partial pressure by the CO₂ partial pressure and ranges from <1 – 16.
- Chloride concentration – Refers to the amount of chloride found in brine. The brine is either only sodium chloride or field synthetic brine, and in our database only chloride concentration is recorded. The ranges from 100- 254,000 ppm.
- Sulfur – Refers to the amount of sulfur placed on the coupons, usually in the form of a chip.
- FeS – Refers to the amount of iron sulfide placed on the coupons and is in the form of a fine powder
- Pre-partitioning - Some test condition include an inhibitor partitioning step before placing the brine into the autoclave.

Uninhibited Autoclave Results

Within this database a portion of the recorded autoclave tests are uninhibited. The set of data is explored first to gain insight to any leading factors that contribute to an increase in the general corrosion rate or an increase in pitting. The uninhibited results are classified into 5 categories as described by Bonis *et al.* The categories are as follows:

- Very Low (VL) : < 4 mpy (0.1 mmpy)
- Low (L): 4- 12 mpy (0.1 – 0.3 mmpy)
- Medium (M): 12- 40 mpy (0.3 – 1 mmpy)
- High (H): 40- 120 mpy (1 – 3 mmpy)
- Very High (VH) > 120 mpy (3 mmpy)

Table 2 indicates the parameter ranges for the blank section of the database.

TABLE 2
SUMMARY OF CORROSION CONDITIONS FOR UNINHIBITED SOUR AUTOCLAVES

Number of Tests	53
Pre corrosion	Yes, No
Temperature (°C)	25, 35, 41, 45, 50, 52, 54, 55, 60, 65, 66, 70, 110
H₂S (psi)	12, 48, 50, 76, 80, 190, 200, 220, 250, 254, 255, 258
CO₂ (psi)	9, 12, 20, 30, 35, 50, 55, 58, 75, 112
HS/CO₂ ratio	0.7, 1, 2, 3, 4, 5, 8
Chloride	100, 3000, 5000, 10000, 20000, 25000, 45000, 50000, 70000, 75000, 90000,
Concentration (ppm)	100000, 120000, 180000,
Sulfur (g)	0
FeS (g)	0, 0.1, 0.5, 1, 5

The graph in **Figure 1** summarizes the corrosion categories for the 53 blank test results. Unlike the results from the Bonis *et al.* paper, most of the results fall into the low and medium corrosion categories. The conditions found in this database were not moderate enough to produce general corrosion rates less than 4 mpy, nor severe enough to produce corrosion rates >120 mpy. This is mostly likely due the fact that no elemental sulfur is present during the uninhibited tests. The presence of elemental sulfur would substantially increase the corrosion rate to reach values higher than 120 mpy.

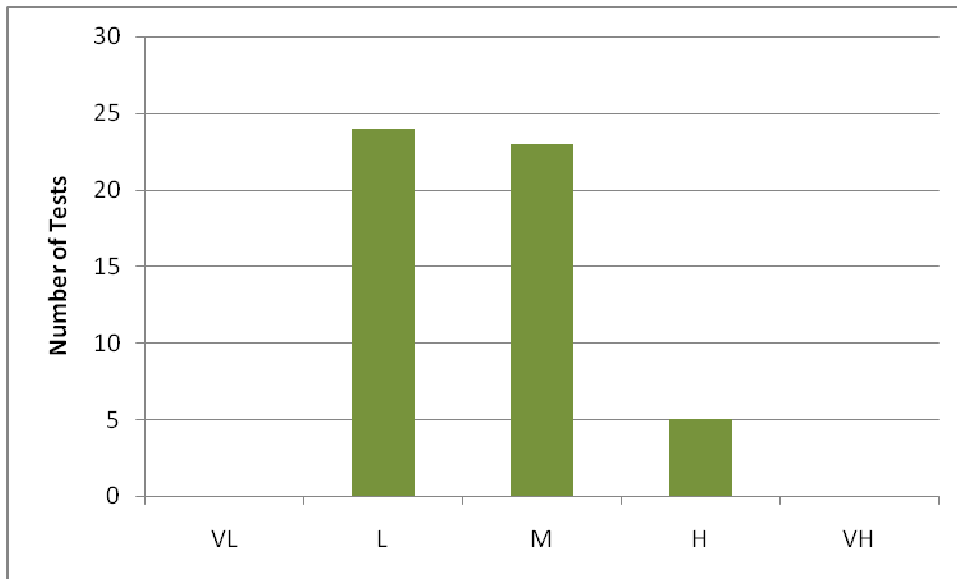
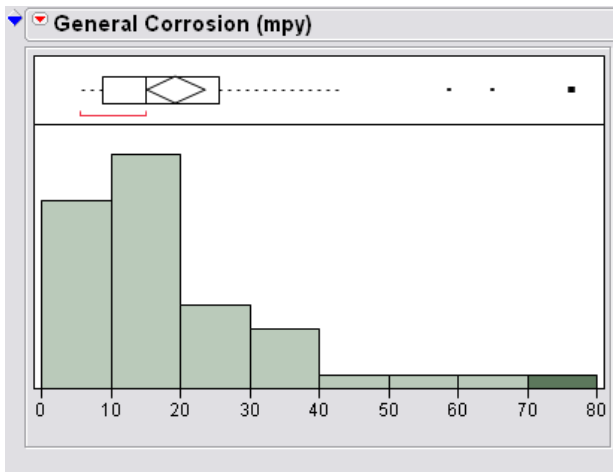


FIGURE 1- Corrosiveness Classification for Uninhibited Sour Autoclave Test

The general weight loss corrosion rates are displayed in the **Table 3** along with their associated statistics. The average blank corrosion rate is 15 mpy, the maximum corrosion rate observed was 76.40 mpy and the lowest corrosion rate observed is 5.56 mpy. As shown in the histogram in **Table 3**, the majority of the corrosion rate results fall in the range of 15-23 mpy.

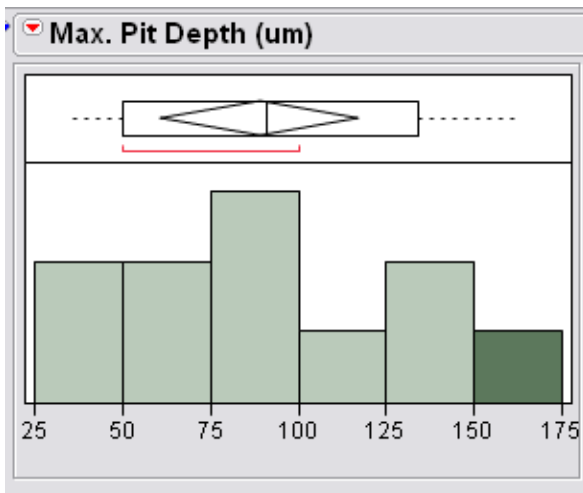
TABLE 3
HISTOGRAM AND STATISTICS FOR SOUR UNINHIBITED GENERAL CORROSION RATES



General corrosion rate (mpy)				
100.0%	maximum	76.40	Mean	19.40
99.5%		76.40	Std Dev	15.21
97.5%		72.66	Std Err Mean	2.11
90.0%		36.31	Upper 95% Mean	23.64
75.0%	quartile	25.64	Lower 95% Mean	15.17
50.0%	median	15.08	N	52
25.0%	quartile	8.86		
10.0%		6.72		
2.5%		5.56		
0.5%		5.56		
0.0%	minimum	5.56		

If the coupons exhibited pitting, the maximum pit was documented and their statistics are displayed in the **Table 4**. Note that if the coupon did not exhibit any pitting it is not included in this analysis. The average maximum pit depth is 89.1 um with a maximum pit depth recorded at 162 um and a smallest maximum pit depth of 36 um. The majority of pit depths fall in the range of 60-117 um.

**TABLE 4
HISTOGRAM AND STATISTICS FOR SOUR UNINHIBITED MAXIMUM PIT DEPTHS**



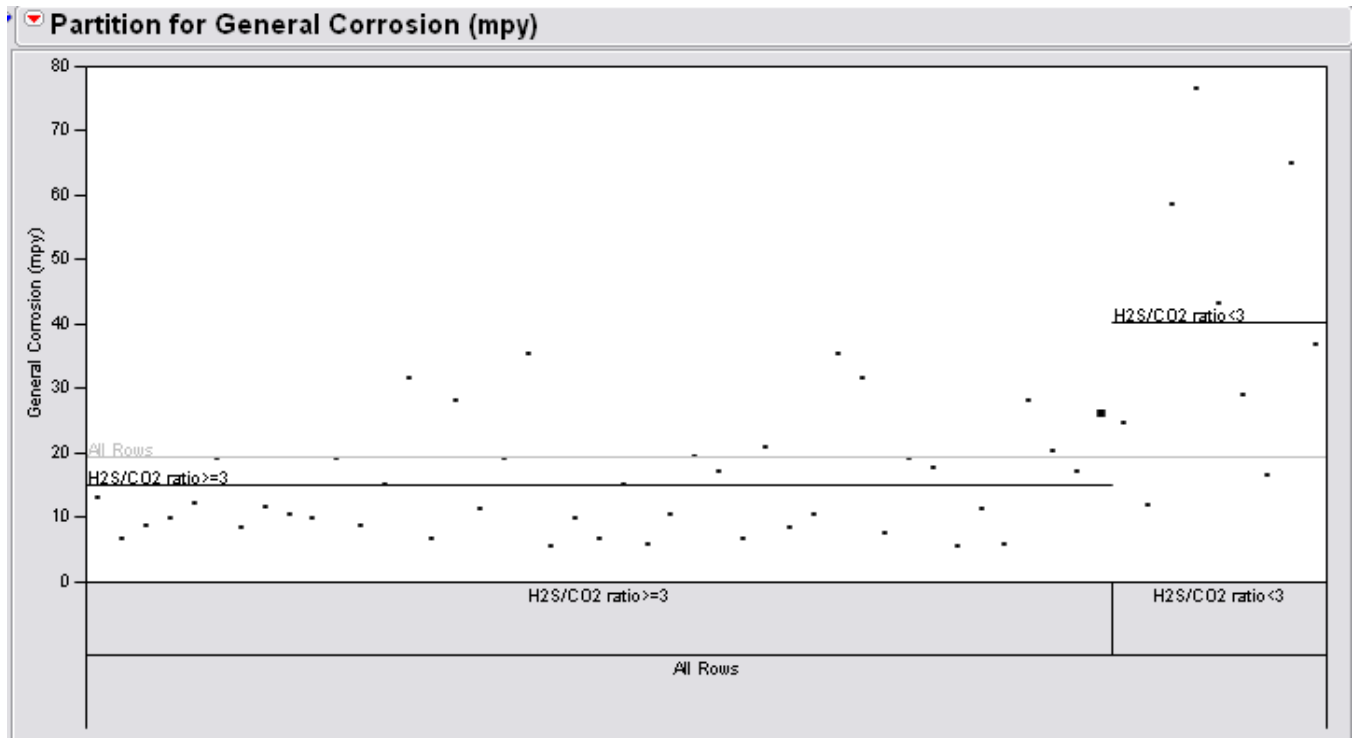
Max Pit Depth (um)				
100.0%	maximum	162	Mean	89.1
99.5%		162	Std Dev	41.8
97.5%		162	Std Err Mean	12.6
90.0%		156	Upper 95% Mean	117.2
75.0%	quartile	134	Lower 95% Mean	60.9
50.0%	median	91	N	11
25.0%	quartile	50		
10.0%		36		
2.5%		36		
0.5%		36		
0.0%	minimum	36		

A partition platform was utilized to determine the factors contributing to the largest general corrosion rates in the uninhibited corrosion testing. The partition platform recursively partitions data according to a relationship between the X and Y values, creating a tree of partitions. It finds a set of cuts or groupings of X values that best predict a Y value. Y value is either general corrosion rate or max pit depth. In this case, X represents our contributing factors as listed below:

- Pre-corrosion
- Temperature
- H₂S partial pressure
- CO₂ partial pressure
- H₂S/CO₂ ratio

- Chloride concentration
- FeS

Results for the partition study of 52 samples are shown in **Figure 2**.



All Rows			
Count	52	LogWorth	Difference
Mean	19.404615	8.2579934	25.1372
Std Dev	15.21402		

H2S/CO2 ratio >=3		H2S/CO2 ratio <3	
Count	43	Count	9
Mean	15.053953	Mean	40.191111
Std Dev	8.5697047	Std Dev	22.410076

FIGURE 2 - Partitioning Analysis for Uninhibited Sour Autoclave Test (52 Results Used)

As seen in **Figure 2**, the results of the partitioning analysis reveal that after the first split a grey horizontal line appears for each group involved in the split. Below the graph are boxes containing numeral information regarding the split. The information includes count, mean, standard deviation and log worth. These lines and information are labeled with the variable and the level of the split. In this case, the split is on the H₂S/CO₂ ratio variable at 15.05 mpy for H₂S/CO₂ ratio of ≥3 and 40.19 mpy for H₂S/CO₂ ratios of <3. Essentially, the largest impact on general corrosion in this data set of data is the

ratio of H₂S/CO₂ with smaller H₂S/CO₂ (<3) ratio having larger corrosion values than higher H₂S/CO₂ (≥3) ratios.

Continuous Inhibited Autoclave Results

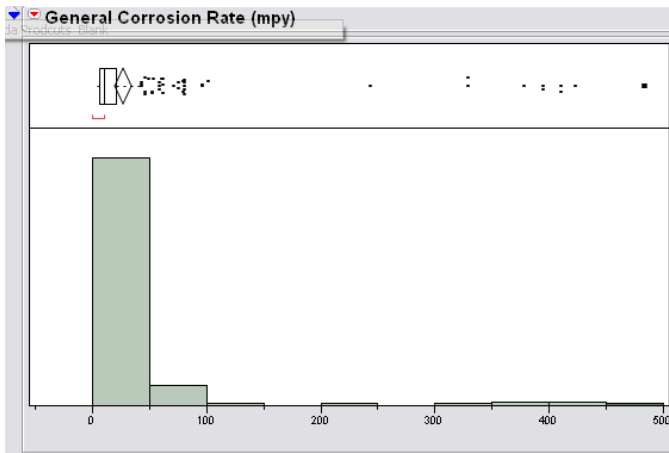
The database contains a large portion of autoclave testing comprising only continuous inhibition. This data is also explored to see if any factors contribute to a higher general corrosion rate and if the any of these factors contributed to a decrease in overall corrosion inhibitor performance. This section introduces the use of elemental sulfur which is reported as the leading corrosion factor in a sour system. **Table 5** indicates the parameters of the continuous inhibited section of the database.

**TABLE 5
SUMMARY OF CORROSION CONDITIONS FOR CONTINUOUS INHIBITED SOUR AUTOCLAVES**

Number of Test	336
Product	Inhibitor A and Inhibitor B
Dosage (ppm)	500, 700, 1000, 1100, 1200, 1250, 1300, 1400, 1500, 2000, 2500, 3000, 3500, 4000, 5000, 10000, 15000, 25000
Pre corrosion	Yes, No
Temperature (°C)	25, 35, 41, 50, 54, 55, 60, 65, 70
H₂S (psi)	12, 14, 30, 48, 50, 60, 76, 80, 103, 105, 112, 150, 155, 160, 190, 200, 203, 210, 220, 225, 238, 250, 252, 254, 255, 258, 260
CO₂ (psi)	9, 12, 13,14, 15, 16, 19, 20, 28, 30, 35, 38, 39, 43, 45, 50, 55, 58, 75, 80, 90, 100, 112, 130, 160, 165, 205
H₂S/CO₂ ratio	< 1, 1, 2, 3, 4, 5, 6, 8, 9, 10
Chloride	0, 60, 100, 1000, 3000, 5000, 10000, 20000, 25000, 29000, 30000, 45000, 50000, 70000, 75000, 90000, 100000, 120000, 130000, 140000, 168800, 180000, 254000
Concentration (ppm)	
Sulfur (g)	0, 0.05, 0.1, 0.3, 1
FeS (g)	0, 0.1, 1
Pre-Partitioning	Yes, No

The general weight loss corrosion rates are displayed in **Table 6** along with their associated statistics. The average blank corrosion rate is 23.3 mpy, the maximum corrosion rate observed is 483.2 mpy, and the lowest observed corrosion rate is 0.1 mpy. As shown in the histogram in **Table 6**, the majority of corrosion rate results fall in the range of 10-30 mpy. The 10 highest corrosion rates observed are isolated and analyzed to determine why these are higher than the blank corrosion rates.

**TABLE 6
HISTOGRAM AND STATISTICS FOR SOUR CONTINUOUS INHIBITED GENERAL CORROSION RATES**



General corrosion rate (mpy)		mpy
100.0%	maximum	483.2
99.5%		442.4
97.5%		329.2
90.0%		51.8
75.0%	quartile	20.6
50.0%	median	10.3
25.0%	quartile	6.0
10.0%		1.7
2.5%		0.3
0.5%		0.1
0.0%	minimum	0.1
	Mean	27.29
	Std Dev	65.47
	Std Err Mean	3.57
	Upper 95% Mean	34.33
	Lower 95% Mean	20.26
	N	335

Table 7 lists the ten largest corrosion rates. Several of the factors in the individual test conditions vary slightly such as the levels of chloride, H₂S, CO₂, the H₂S/CO₂ ratio and test temperature. The only consistent factor throughout the ten tests is the amount of elemental sulfur. Sulfur, in combination with the chloride and H₂S, provide an aggressive environment that drastically increases both general corrosion rates and maximum pit depths. It is interesting to note that increasing the dosage rate of either Inhibitor A or B does not significantly decrease corrosion rates and pit depths. In this case, the tested corrosion inhibitors were not able to decrease corrosion that was due to elemental sulfur. A partition study confirmed that sulfur in that range of ≥1 gram gave statistically higher corrosion rates than test containing 0, 0.05, 0.1, 0.3 grams of sulfur.

**TABLE 7
SUMMARY OF THE 10 LARGEST CORROSION RATES FOR CONTINUOUS INHIBITED RESULTS**

Inhibitor	Dosage (ppm)	General Corrosion Rate (mpy)	Max. Pit Depth (um)	Pre-corrosion	Temp (°C)	H ₂ S Pressure (psi)	CO ₂ Pressure (psi)	H ₂ S/CO ₂ ratio	Chloride Concentration (ppm)	Sulfur (g)	FeS (g)
B	500	242.8	450	Yes	60	155	15	10.3	168800	1	0
A	500	329.2	710	No	60	155	15	10.3	168800	1	0
A	500	329.2	710	Yes	60	155	15	10.3	168800	1	0
A	2500	377.4	275	Yes	50	80	112	0.7	45000	1	1
A	1000	394.8	470	No	60	155	15	10.3	168800	1	0
A	1000	394.8	470	No	60	155	15	10.3	168800	1	0
A	2000	410.0	460	No	60	155	15	10.3	168800	1	0
A	1000	410.1	460	No	60	155	15	10.3	168800	1	0
B	1000	423.2	400	No	60	155	15	10.3	168800	1	0
B	2000	483.2	900	No	60	155	15	10.3	168800	1	0

A partition analysis is used to determine which factors contribute to the largest general corrosion rate without elemental sulfur. These studies are performed in the absence of elemental sulfur, and where X represents the remaining contributing factors:

- Pre-corrosion
- Temperature
- H₂S partial pressure
- CO₂ partial pressure
- H₂S/CO₂ ratio

- Chloride concentration
- FeS
- Pre-partitioning
- Dosage

The results for the partition statistics of 225 samples are displayed in **Figure 3**.

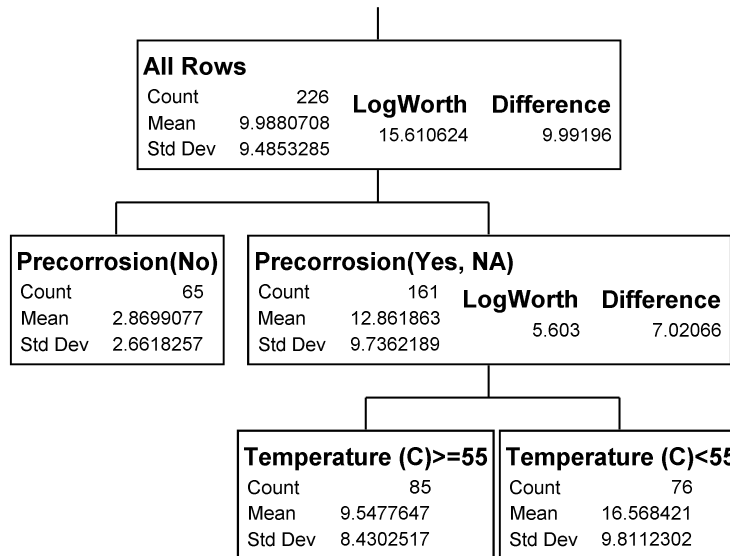
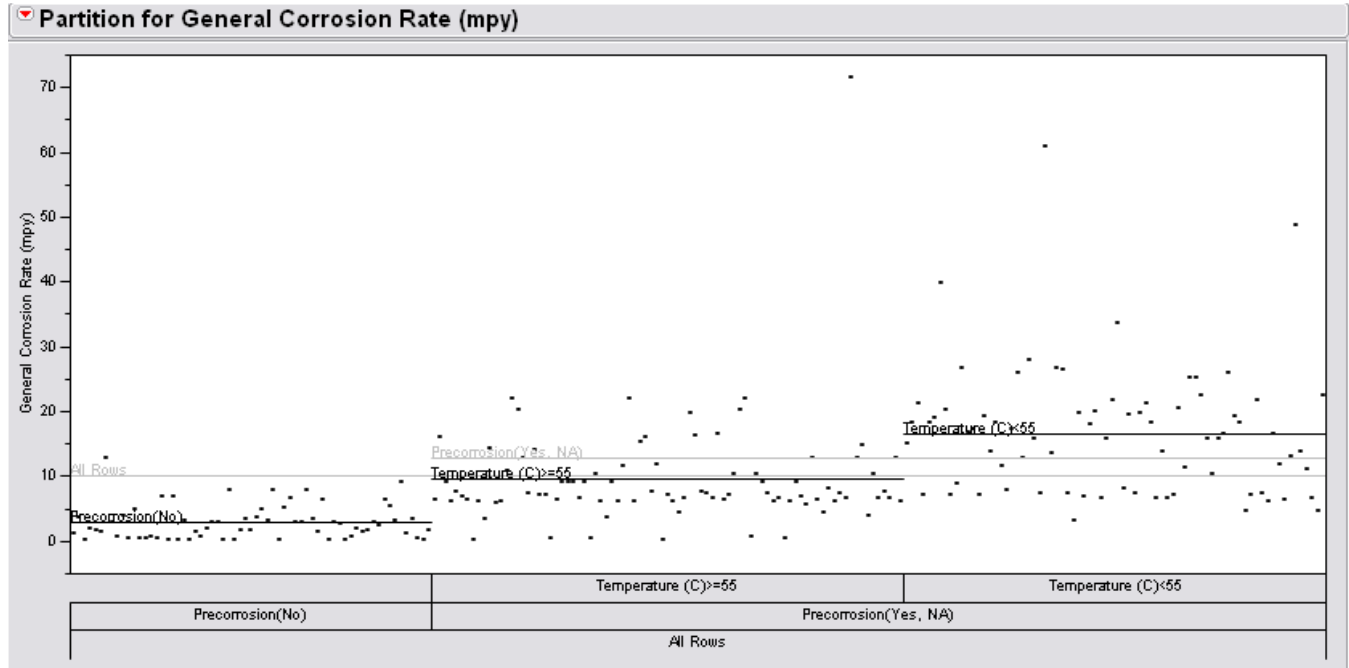


FIGURE 3 - Partitioning Analysis for Continuous Inhibited Sour Autoclave Test

In this set of data, the partition analysis reveals the first split, represented as the grey line, is whether the sample was treated under pre-corrosion conditions or not. The absence of pre-corrosion results in an average corrosion rate of 2.86 mpy however, with the coupon exposed to pre-corrosion the

corrosion rate increases dramatically to 12.85 mpy. Therefore, in this data set the largest impact on inhibited general corrosion rates is whether or not the coupon sample is pre-corroded before exposure to a corrosion inhibitor.

The next split performed on the larger data set of pre-corroded samples indicated that temperature was a significant factor. A lower corrosion rate was found when the temperature is ≥ 55 °C, exhibiting a corrosion rate of 9.5 mpy, whereas with temperatures <55 °C a higher corrosion rate is observed. This can be attributed to the less dense iron sulfide layer forming at lower temperatures. Surprisingly, the product and dosage rate of corrosion inhibitor does not seem to impact the overall corrosion rate.

Batch Inhibited Autoclave Results

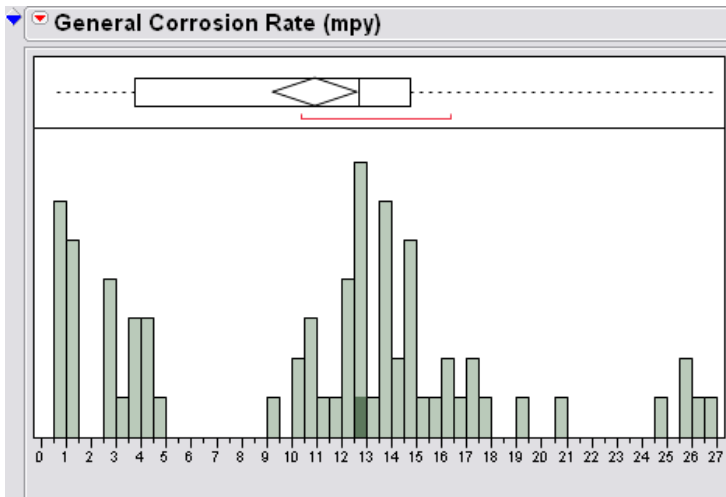
The database contains a small portion of autoclave tests that were treated with batch inhibition only. This data is also explored to see if any factors contribute to higher general corrosion rates or to a decrease in overall corrosion inhibitor performance. **Table 8** indicates the ranges of the parameters for the batch inhibited section of the database.

**TABLE 8
SUMMARY OF CORROSION CONDITIONS FOR BATCH INHIBITED SOUR AUTOCLAVES**

Number of Test	71
Product	Inhibitor C and Inhibitor D
Dosage (%)	10, 50, 100
Contact Time (s)	5, 10, 15, 30
Pre corrosion	Yes, No
Temperature (°C)	45, 50, 52, 60, 66, 110
H₂S (psi)	13, 21, 50, 80, 105, 150, 155, 224, 255
CO₂ (psi)	14, 15, 16, 18, 20, 39, 50, 55, 90, 205
H₂S/CO₂ ratio	< 1, 1, 2, 5, 10, 16
Chloride Concentration (ppm)	100, 1000, 10000, 19000, 20000, 23000, 50000, 70000, 75000, 100000, 168800,
Sulfur (g)	0, 0.1, 0.3, 1, 5
FeS (g)	0, 0.1, 1, 5

The batch only corrosion rates are displayed in **Table 9**. The average corrosion rate is 10.95 mpy, a value lower than the overall corrosion rate for the continuous application. The largest corrosion rate is 28.8 mpy. Visual inspection of the histogram in **Table 9** reveals three discrete corrosion levels at > 25 mpy, 9-21 mpy and < 5 mpy. Upon manual review of these three sets of data, no obvious patterns emerge to distinguish the three levels. Therefore, a partition analysis is conducted to gain additional insight.

**TABLE 9
HISTOGRAM AND STATISTICS FOR SOUR BATCH INHIBITED GENERAL CORROSION RATES**



General corrosion rate		mpy
	(mpy)	Mean
100.0%	maximum	26.8
		Std Dev
99.5%		26.8
		Std Err Mean
97.5%		26.5
		Upper 95% Mean
90.0%		19.1
		Lower 95% Mean
75.0%	quartile	14.7
		N
50.0%	median	12.7
25.0%	quartile	3.7
10.0%		1.0
2.5%		0.5
0.5%		0.5
0.0%	minimum	0.5

In this partitioning analysis the X represents the following factors:

- Batch Product
- Batch Dosage
- Contact Time
- Pre-corrosion
- Temperature
- H₂S partial pressure
- CO₂ partial pressure
- H₂S/CO₂ ratio
- Chloride concentration
- Sulfur
- FeS
- Pre-partitioning
- Dosage

Results for the partition statistics of 71 results are displayed in **Figure 4**.

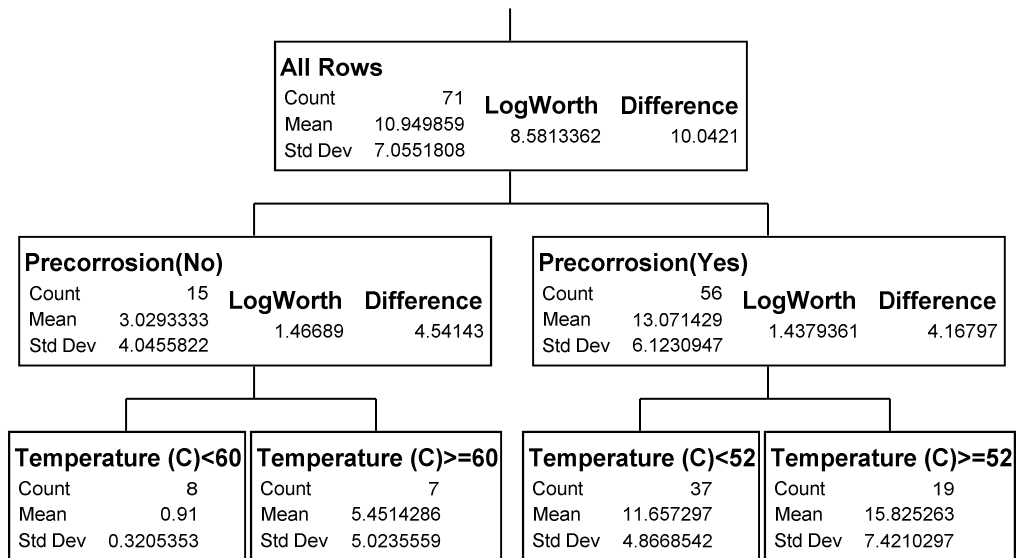
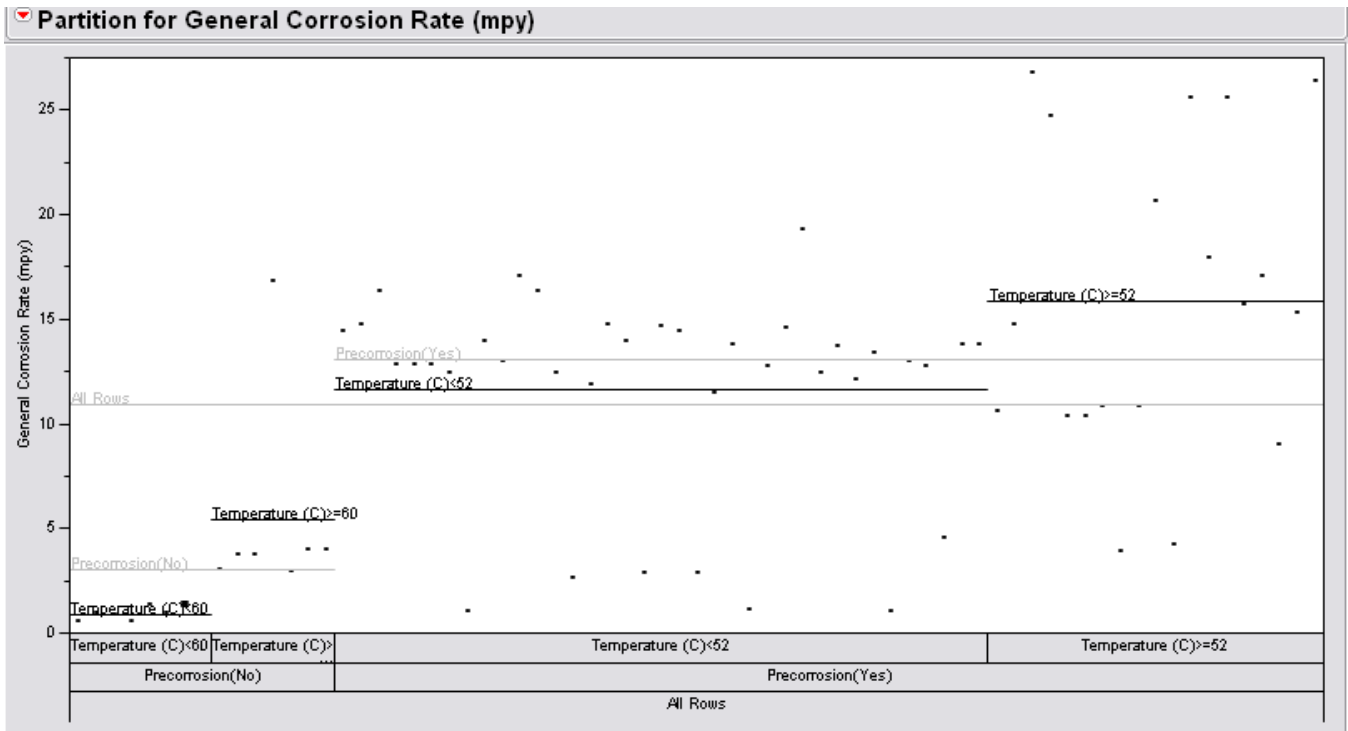


FIGURE 4- Partitioning Analysis for Batch Inhibited Sour Autoclave Test

After the first split, a horizontal line appears for each group involved. In this split, pre-corrosion is determined to have the largest impact on overall general corrosion rates. In this case, as in the continuous corrosion inhibitor application, the split is on the pre-corrosion variable giving a lower corrosion rate of 3.02 mpy for samples not exposed to a pre-corrosion. In comparison, the samples that were pre-corroded have a higher corrosion rate of 13.07 mpy. Unexpectedly, this pre-corrosion factor seems to be the largest impact the corrosion rate for both continuous and batch application.

The next factor that impacts the general corrosion rate on the larger pre-corrosion data set is temperature. This is a similar result to the continuous inhibited data set. However, in this pre-corroded data set the lower corrosion rate occurs when the temperature is <52 °C with a corrosion rate of 11.6 mpy whereas a temperature ≥52 °C yields higher corrosion rates with a mean of 15.8 mpy. Similar results are found when the no pre-corrosion data is split however; this data set is much smaller and therefore, may not have as much significance. The temperature split at <60 °C has a much lower corrosion rate than at temperatures ≥ 60 °C. Surprisingly, the product and dosage rates for corrosion inhibitors do not seem to impact the overall corrosion rate in this partitioning study.

Continuous and Batch Inhibited Autoclave Results

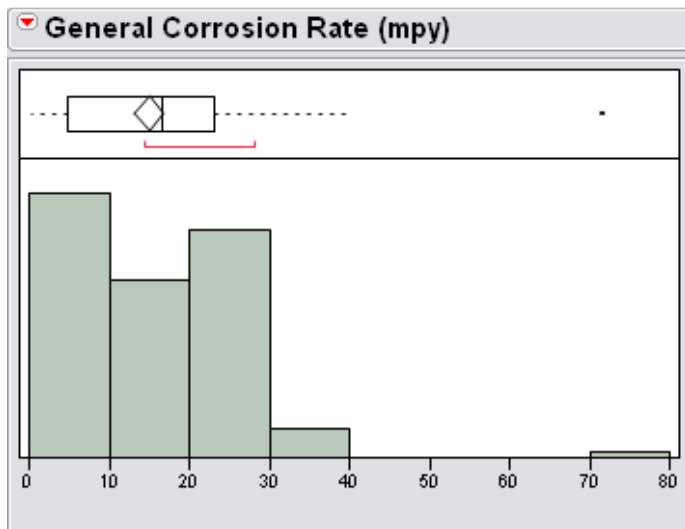
Finally, the last subset of data contains test conditions that utilize both continuous and batch application of the corrosion inhibitor. **Table 11** indicates the ranges of the parameters of the continuous plus batch inhibited section of the database.

TABLE 11
SUMMARY OF CORROSION CONDITIONS FOR CONTINUOUS PLUS BATCH INHIBITED SOUR AUTOCLAVES

Number of Test	151
Product	Inhibitor A, Inhibitor B, Inhibitor C and Inhibitor D
Dosage (ppm)	1000, 1200, 1500, 2500, 3000, 5000, 10000, 25000, 200000
Dosage (%)	10, 50, 100
Contact Time (s)	1, 5, 10, 15, 30
Pre corrosion	Yes, No
Temperature (°C)	25, 45, 50, 52, 55, 60, 70
H₂S (psi)	12, 14, 50, 80, 100, 105, 150, 155, 220, 224, 381
CO₂ (psi)	12, 13, 15, 20, 39, 44, 55, 75, 90, 100, 112, 205
H₂S/CO₂ ratio	< 1, 1, 2, 3, 6, 8, 9, 10
Chloride Concentration (ppm)	1000, 4000, 19000, 20000, 25000, 45000, 50000, 70000, 75000, 90000, 100000, 140000, 168800,
Sulfur (g)	0, 0.1, 0.3, 1
FeS (g)	0, 0.1, 0.5, 1
Pre-partitioning	No

The continuous and batch inhibited corrosion rates are displayed in **Table 12**. The average corrosion rate for the inhibited coupons is 15.1 mpy, lower than the overall corrosion rate for the continuous application but higher than the batched only coupon samples. The largest corrosion rate is 71.5 mpy for this set of results. Visual inspection of the histogram in **Table 12** reveals almost of the results fall in the range of 0.2-30 mpy.

**TABLE 12
HISTOGRAM AND STATISTICS FOR SOUR CONTINUOUS PLUS BATCH INHIBITED GENERAL CORROSION RATES**



General corrosion rate (mpy)		mpy
100.0%	maximum	71.5
99.5%		71.5
97.5%		39.8
90.0%		26.5
75.0%	quartile	23.2
50.0%	median	16.6
25.0%	quartile	4.8
10.0%		0.76
2.5%		0.26
0.5%		0.20
0.0%	minimum	0.20
	Mean	15.1
	Std Dev	11.2
	Std Err Mean	0.91
	Upper 95% Mean	16.9
	Lower 95% Mean	13.3
	N	151

The sample that gave the highest data point is highlighted in **Table 13**. After reviewing all the environmental factors within this one test it was decided that no one particular factor stands out as being an extreme value. This data point could be the result of the combination of elemental sulfur and too low of batch inhibitor dosage. The sulfur initiates a large pit, thus causing a high weight-loss at a particular point on the coupon.

**TABLE 13
SUMMARY OF THE LARGEST CORROSION RATE FOR CONTINUOUS + BATCH INHIBITED RESULTS**

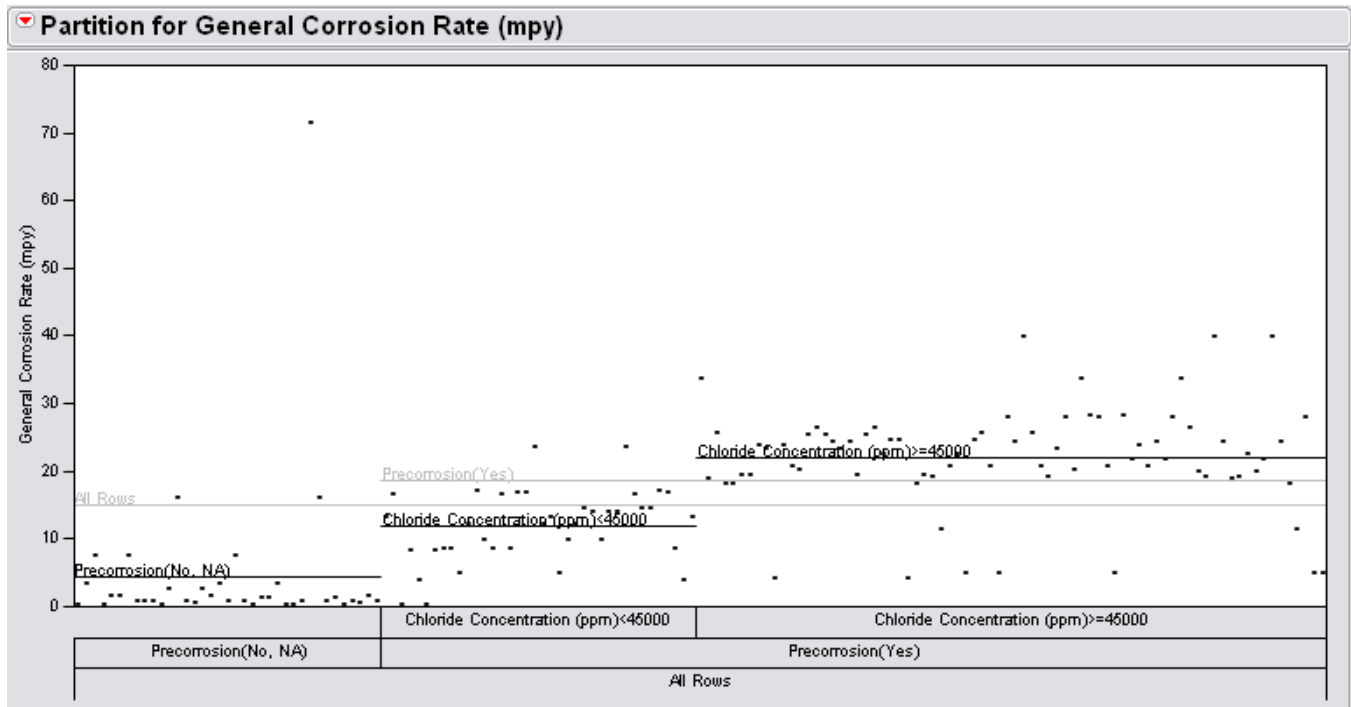
Inhibitor	B
Dosage (ppm)	2500
Batch Inhibitor	C
Batch Dosage	10%
Time Contact (Sec)	15
Corrosion Rate (mpy)	71.52
Max Pit Depth (um)	1166
Temp ((°C)	70
H ₂ S Pressure (psi)	14
CO ₂ Pressure (psi)	13
H ₂ S/CO ₂ ratio	1.1
Chloride Concentration (ppm)	90000
Sulfur (g)	0.1
FeS (g)	0.1

To determine the factors contributing to the largest general corrosion rate a partition platform was completed for this set of data. In this case, X represents our contributing factors and are listed below:

- Continuous Product
- Continuous Dosage

- Batch Product
- Batch Dosage
- Contact Time
- Pre-corrosion
- Temperature
- H₂S partial pressure
- CO₂ partial pressure
- H₂S/CO₂ ratio
- Chloride concentration
- FeS
- Sulfur
- Pre-partitioning

Results for the partition statistics on 151 samples are displayed in **Figure 5**.



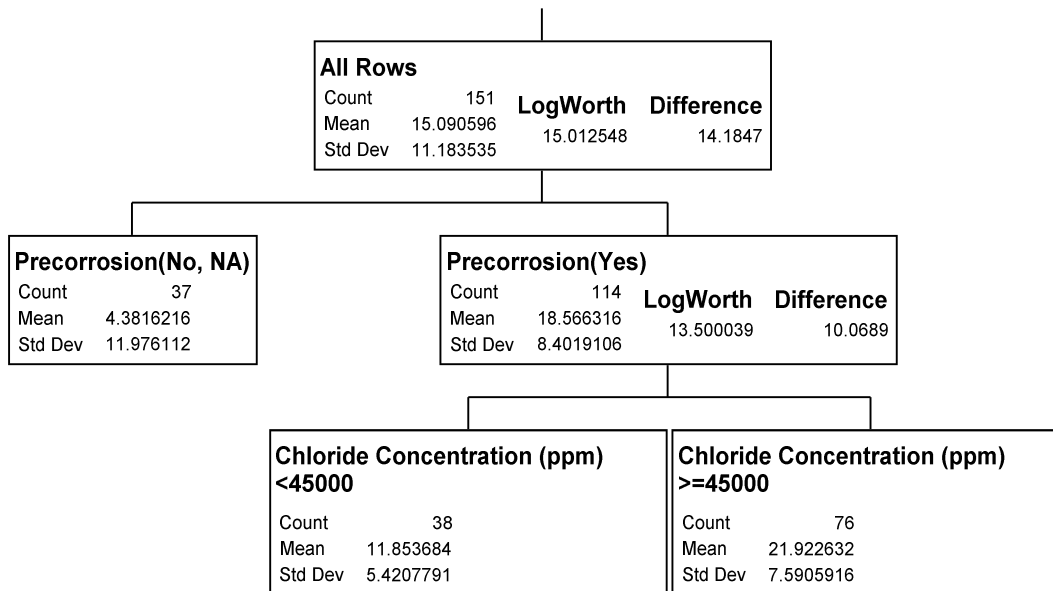


FIGURE 5 - Partitioning Analysis for Continuous plus Batch Inhibited Sour Autoclave Test General Corrosion Rates

The results of the partitioning analysis reveal that after the first split, a horizontal line appears for each group involved in the split. In this case, like in the cases of the continuous corrosion inhibitor and batch only applications, the split is on the pre-corrosion variable at 4.38 mpy for no pre-corrosion and 18.5 mpy for pre-corrosion. Surprisingly, this pre-corrosion seems to have the largest impact the corrosion rate for both continuous and batch applications. The split that impacts the general corrosion rate on the larger set of data of pre-corrosion is chloride concentration. Chloride concentration <45,000 ppm have lower general corrosion rates than samples containing $\geq 45,000$ ppm chlorides. Based on industry knowledge, water salinity (ie. chloride) levels have been indicated as leading indicators for increasing corrosion rates due to the increased conductivity and/or damage to film formation.

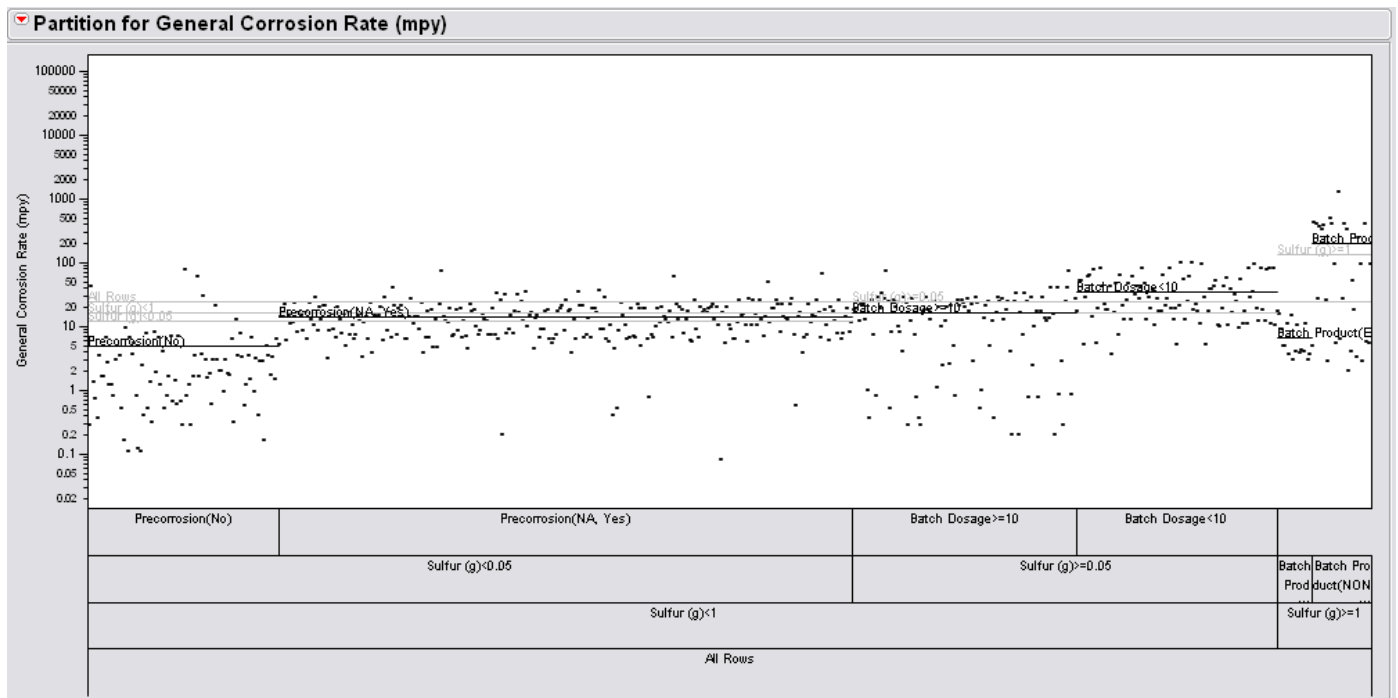
Results by Total Application

The last set of data reviewed was the entire database including uninhibited, continuous inhibited, batch inhibited and continuous plus batch inhibited results. Three separate analyses were performed on the entire set of data with the first being an overall partition analysis. In this case X represents our contributing factors as listed below:

- Continuous Product
- Continuous Dosage
- Batch Product
- Batch Dosage
- Contact Time
- Pre-corrosion
- Temperature
- H₂S partial pressure
- CO₂ partial pressure
- H₂S/CO₂ ratio
- Chloride concentration

- FeS
- Sulfur
- Pre-partitioning

Results for the partition analysis on 630 samples are displayed in **Figure 6**.



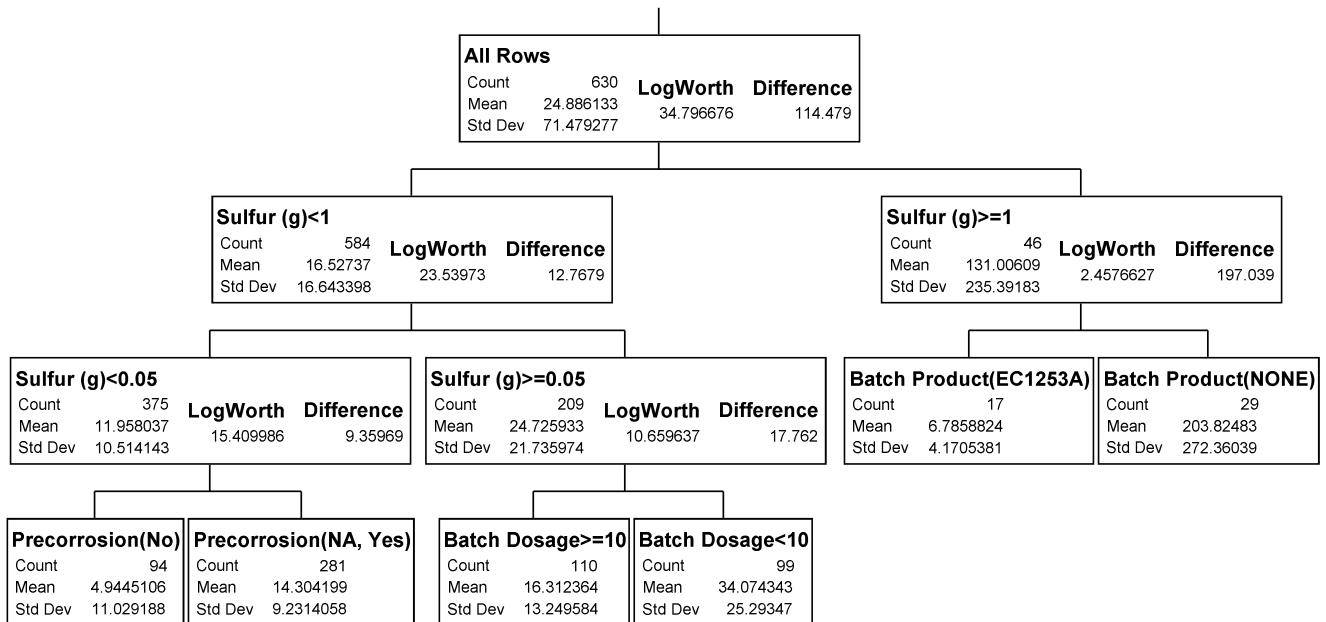


FIGURE 6 - Partitioning Analysis for All Autoclave Results General Corrosion Rates

The results of the partitioning analysis reveal after the first split that the data is separated into two sections having elemental sulfur contents of <1 g and ≥ 1 g. As predicted, the section comprising levels of elemental sulfur ≥ 1 g has a much higher corrosion rate with an average rate of 131.1 mpy. For the section comprising levels of elemental sulfur at <1 g, the average corrosion rate drops to 16.5 mpy.

The ≥ 1 g sulfur split was further split to determine the factor contributing to lower corrosion rates. In this case the presence of a batch inhibitor drastically reduces the overall general corrosion rate from 203.8 mpy without a batch inhibitor to an average corrosion rate of only 6.7 mpy in the presence of the batch inhibitor. This supports industry knowledge that the use of batch inhibition in sour systems with elemental sulfur can be one way to manage sour corrosion.

The larger data set comprising elemental sulfur <1 g was partitioned into the next two sections. Again elemental sulfur impacted overall corrosion rates. This time an overall corrosion rate of 11.9 mpy was observed with sulfur <0.05 g. An expected higher corrosion rate of 24.4 mpy was observed with results containing elemental sulfur ≥ 0.05 g. The larger data set allows for an additional partitioning of elemental sulfur <0.05 g and elemental sulfur ≥ 0.05 g. Pre-corrosion is the factor that contributes the most in the split when concerning the data set comprising elemental sulfur <0.05 g. As seen before in the data set of separate continuous, separate batch and the combination of continuous batch inhibition, partition analysis reveals that the coupon samples subjected to pre-corrosion yield higher corrosion rates. The partitioned sample of sulfur ≥ 0.5 g is split between samples that have batch dosage ≥ 10 . This means that a sample that is batched at 10, 50 and 100 % is able to drop the overall corrosion rate to 16.3 mpy as compared to sample containing batch dosage of <10 . Since the <10 batch dosage categories contains all samples that are only continuously applied, this would indicate that batch inhibition is an instrumental part of managing corrosion in sour environments.

The second analysis performed on the database is a One-way analysis (ANOVA) in order to determine whether the average uninhibited corrosion rates are statistically higher than the inhibited corrosion rates. In this statistic method, it is assumed that there is a normal distribution around the individual means, equal variance of each mean and that the measurements between subjects are independent. The results are outlined in **Figure 7** and **Table 14** where the green diamonds represent

the analysis by variance on each individual mean. The sample size for this statistical method is 630 samples.

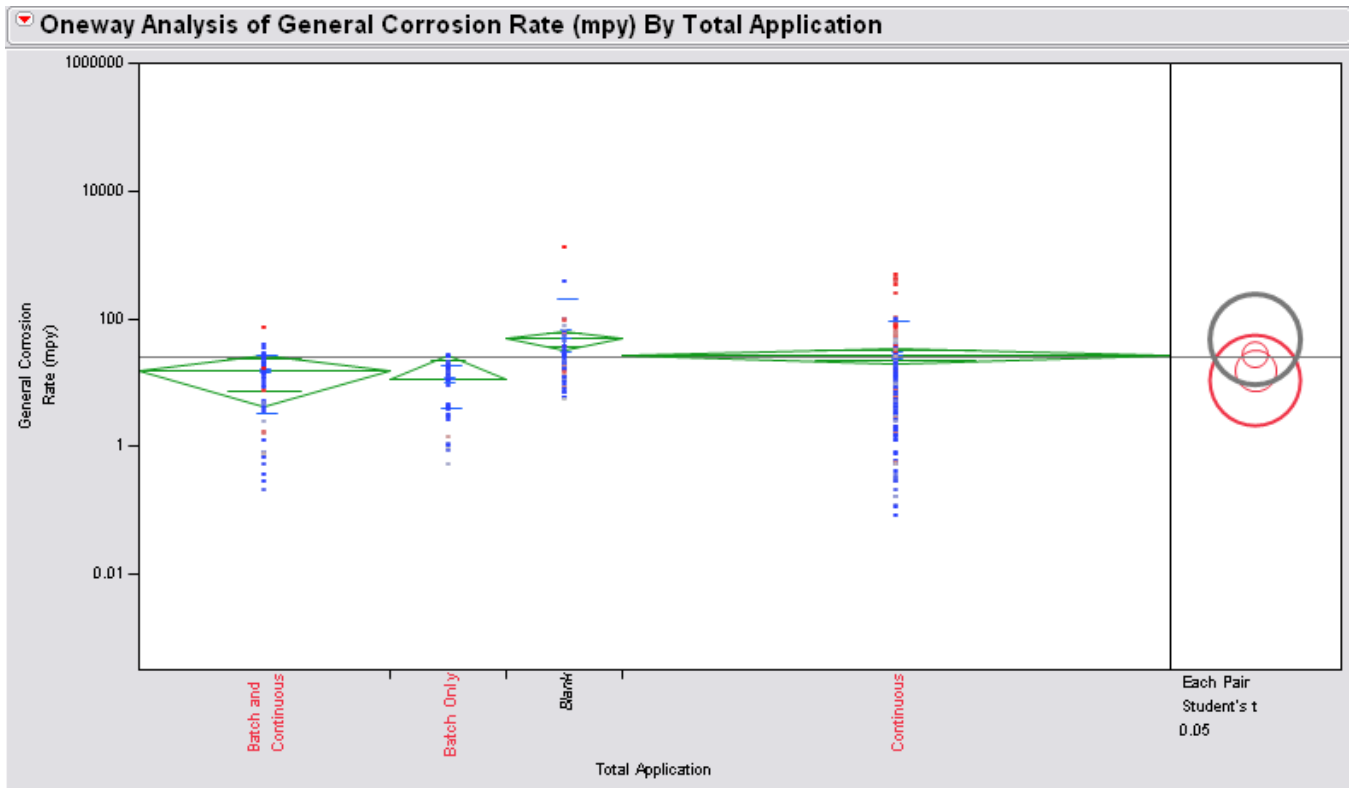


FIGURE 7 - ANOVA Analysis for All Autoclave Results General Corrosion Rates Comparison of Application

**TABLE 14
ANOVA STATISTICS FOR ALL AUTOCLAVE RESULTS BASED ON COMPARISON OF APPLICATION**

Oneway Anova Summary of Fit

Rsquare	0.021
Adj Rsquare	0.016
Root Mean Square Error	70.89
Mean of Response	24.88
Observations (or Sum Wgts)	630

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Total Application	3	67491.9	22497.3	4.4762	0.0040*
Error	626	3146249.7	5026.0		
C. Total	629	3213741.5			

Means for Oneway Anova

Level	Number	Mean	Std Error*	Lower 95%	Upper 95%
Batch and Continuous	153	15.36	5.73	4.11	26.61
Batch Only	71	10.95	8.41	-5.57	27.47
Blank	71	47.98	8.41	31.46	64.50
Continuous	335	27.29	3.87	19.69	34.90

* Std Error assumes a pooled estimate of error variance

Means Comparisons and Comparisons for each pair using Student's t

	t	Alpha
	1.96376	0.05

Abs(Dif)-LSD	Blank	Continuous	Batch and Continuous	Batch Only
Blank	-23.36	2.49	12.63	13.67
Continuous	2.499	-10.75	-1.65	-1.843
Batch and Continuous	12.63	-1.65	-15.91	-15.58
Batch Only	13.66	-1.84	-15.58	-23.37

* Positive values show pairs of means that are significantly different. Indicate this in Table with star?

Level		Mean
Blank	A	47.98
Continuous	B	27.29
Batch and Continuous	B	15.36
Batch Only	B	10.95

* Levels are not connected by same letter are significantly different.

The horizontal lines in the center of the diamond **Figure 7** denote the means with the top and bottom lines representing a 95% confidence level. This statistical tool allows determination of the difference between groups with a comparison error rate of 0.05. Means are considered statically different if the mean diamonds do not overlap. Graphically, this could be represented by drawing a horizontal line from one diamond to another, if the two diamonds intersect between the 95% confidence intervals it would indicate the means are statically not different. In **Figure 7**, the red circles on the right hand side illustrate results from this analysis where overlapping circles suggest that the means are not statistically different. The average blank corrosion rate is indicated by a circle with a thick grey line. The labels for continuous, batch and batch in conjunction with continuous inhibition are labeled in red and indicate a corrosion rate that is statistically different from the uninhibited corrosion rate. In addition, the texts labeled in grey and red reflect the color coordination of the circles. ANOVA analysis of the sour autoclave test reveals that the corrosion rates of the inhibited coupons are statistically lower than the uninhibited corrosion rate.

Partition for Pitting Level

The third and final analysis performed is a partitioning analysis of pitting. In order to complete a pitting analysis, the maximum pit data was categorized into five sections.

- None: no observable pits
- Low (L): 0-99 um
- Medium (M): 99-500 um
- High (H): 500-1000 um
- Very High (VH): >1000 um

Results for the partition analysis are displayed in **Figure 8**. The data is color coordinated to help with the analysis. Dark blue dots indicate that no pits are observed, light blue indicates the presence of low pits depths, grey indicates the presence of medium pit depths, pink indicates the presence of high pit depths and red indicates the presence of very high pit depths.

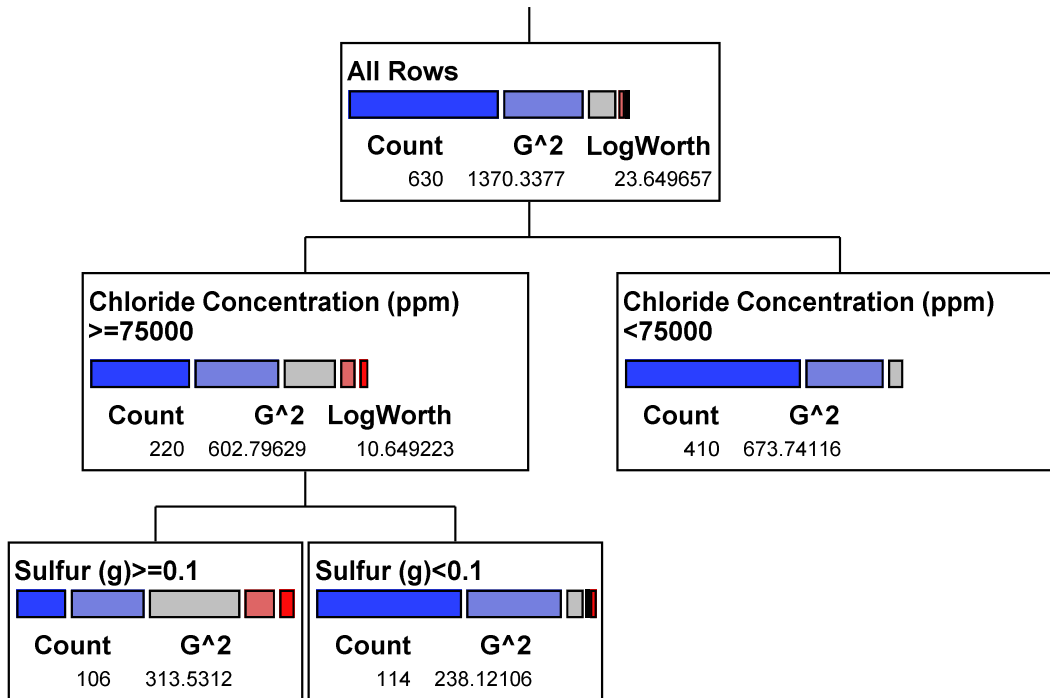
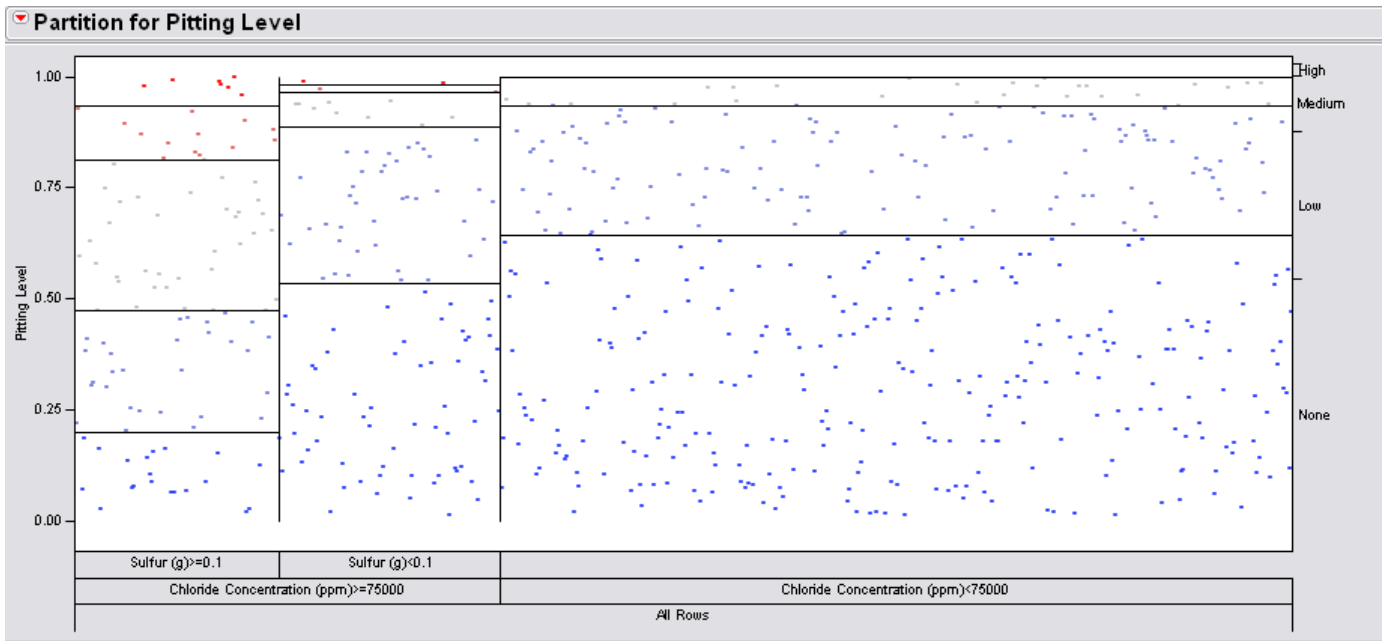


FIGURE 8 - Partitioning Analysis for All Autoclave Results Maximum Pit Depths (630 Results)

The results of the partitioning analysis reveal that after the first split the maximum pits depths are grouped into two sections. The first section that contains the majority of none and low maximum pits depths are grouped under the section with chloride concentrations of <75,000 ppm. The counter split contains chloride concentrations $\geq 75,000$ ppm and also have a larger portion of medium, high and very high maximum pit depths. As mentioned previously, the chloride concentration is thought to impact film formation and thus creates inequalities in the iron sulfide film. The different types of iron sulfide films formed could potentially form galvanic concentration cells leading to an increase in pitting and pit depths.

A further split was performed with the data correlating to a chloride concentration $\geq 75,000$ ppm to obtain more information about the high and very high max pits depths. The data was further split into two sections sulfur at ≥ 0.1 g and sulfur <0.1 g. Not surprisingly, the presence of elemental sulfur plays an instrumental role in maximum pit depths. As illustrated in **Figure 8** the higher amount of elemental sulfur (ie. ≥ 0.1 g) appears to increase the opportunity for the formation of high and very high maximum pit depths.

CONCLUSIONS

In this paper the impact of several factors were investigated to determine their overall impact on sour general corrosion and maximum pit depths. Key findings from this analysis are summarized below.

A large database of sour autoclave tests has been generated over the last decade. The large amount of information has allowed us to use statistics to assess factors that help to better understand sour corrosion mechanisms and the impact corrosion inhibitors have on them. As compared to previous papers utilizing field experience to gain insight to predict sour corrosion mechanism, this data in the paper utilizes conventional sour static autoclave testing to gain similar insight.

The first set of data extracted for statistical analysis comprises only uninhibited weight-loss coupons data. The uninhibited corrosion rates are categorized into five sections as described in the Bonis *et al.* paper. In our experience, the corrosion rates fell into only three of the five sections; the upper and lower categories were not used. This is most likely due to a couple of reasons. For the upper limit, the lack of elemental sulfur excluded corrosion rates exceeding 120 mpy. The lower limit was not observed because in general, corrosion testing is conducted under more severe conditions than the in the field, allowing for accelerated corrosion to occur in a short duration. A partition study revealed that under this set of data the uninhibited general corrosion rate was influenced by the ratio of H₂S/CO₂ with a smaller H₂S/CO₂ (<3) ratio having larger corrosion values than higher H₂S/CO₂ (≥ 3) ratios. With higher amounts of H₂S, the corrosion rate drops drastically as compared to those tests containing higher amount of CO₂.

The continuous inhibited autoclave results are analyzed and the through visual observation the ten largest general corrosion rates are isolated and determined to all have elemental sulfur present. The presence of elemental sulfur is necessary to increase the general corrosion rate and maximum pits depths. The partitioning analysis without the results containing elemental sulfur revealed pre-corrosion as major contributor of higher corrosion rates. This is really not surprising because the samples that were pre-corroded were not re-weighted after exposure to a corrosive environment. In the present analysis, the sample would have lost several mg of metal during the 12 hours pre-corrode period and if this is not taken into account during a final weight-loss measurement the general corrosion rate would be skewed to a higher value. Temperature also impacts the continuous inhibited corrosion rates with higher temperatures giving lower corrosion rates.

For batch inhibited autoclave results, the partition analysis results indicate that pre-corrosion also plays an instrumental role in increasing general corrosion rates. Additionally, like the continuous inhibited results, temperature seems to impact overall general corrosion rates. However, unlike in the continuous application, the batch result has lower temperatures giving lower corrosion rates. Why do the two sets of data give conflicting results in terms of temperature? Could this be due to an application issue? One theory could be that batch inhibitors are not as robust under higher temperatures whereas continuous inhibitors are not as sensitive to changes in temperature. Could the application of batch inhibitor damage iron sulfide films at higher temperatures?

The application of both continuous and batch corrosion inhibitors show similar results in the partition analysis. As in the continuous only inhibited and batch only inhibited data, the partition analysis of the combination of continuous and batch inhibitors reveals that the largest split occurs between samples of pre-corrosion or lack of pre-corrosion. However, in this case the next largest split occurs with chloride concentration and not temperature. Could the application of both continuous plus batch mitigate effects increase corrosion due to temperature influences? Another factor that seems to impact higher corrosion rates is higher chloride concentrations. These have been suggested as leading indicators for increasing corrosion rates due to the increased conductivity and/or damage to film formation.

Finally, the all the data is analyzed with the partitioning platform both for general corrosion rates and maximum pit depths. For general corrosion rates, the largest impact was from the presence of elemental sulfur. As predicted, the section with sulfur $\geq 1\text{g}$ has a much higher average corrosion rate average. Several splits were possible with the data set due to the large size. The next split comprising $\geq 1\text{g}$ elemental sulfur considered if batch product was utilized in the test. The presence a batch inhibitor drastically reduces the overall general corrosion rates. The larger data set of elemental sulfur $< 1\text{g}$ was partitioned into the next two sections. Again, elemental sulfur impacted overall corrosion rates. Finally, the last two splits highlight pre-corrosion and batch dosage as major factors contributing to general corrosion rates.

All uninhibited and inhibited results are analyzed using ANOVA. These results indicate that the corrosion rates of the inhibited coupons are statistically lower than the uninhibited coupon corrosion rate. The maximum pit depths are categorized into five sections for a categorical partition analysis. The first section, containing the majority of none and low maximum pits depths are group under the section with chloride concentrations of $< 75,000$ ppm. Alternatively the higher chloride levels lead to a higher propensity for formation of maximum pit depths. The data was also split into two sections comprising elemental sulfur ≥ 0.1 g and elemental sulfur at < 0.1 g. Not surprising, the elemental sulfur plays an instrumental role in maximum pit depths.

REFERENCES

1. Bonis, M., Girgis, M., Goerz, K., MacDonald, R. **NACE 2006**, Paper 06122.
2. Bonis, M., **NACE 2009**, Paper 09564.
3. JMP8, Statistics and Graphics Guide, **2002**, pg, 91-131, 561-577