Horseshoe Arena - Midland Texas

Common Misconceptions about ClO_2 Generation

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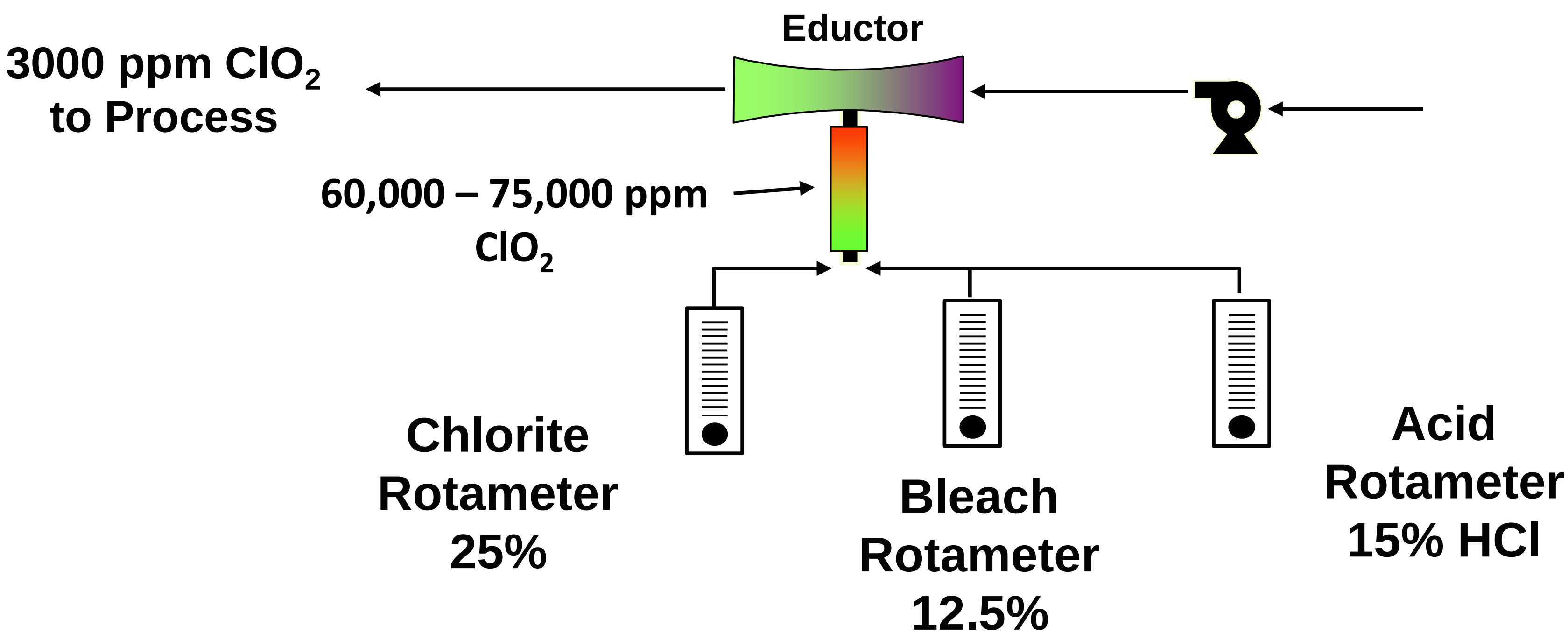
Overview

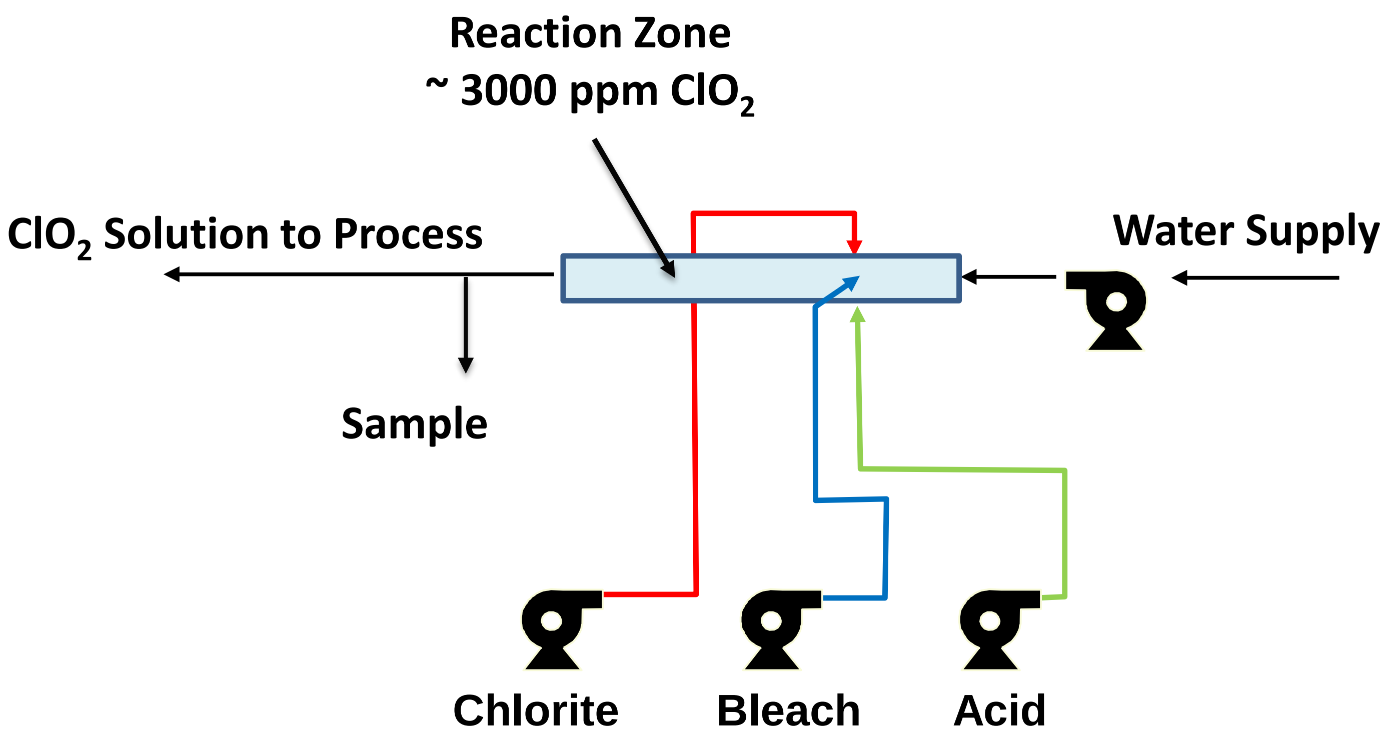
- Eductor & Pump-Based 3-Chemical Generator
- Common Pre-Conceptions
- Analytical
- Generator Testing
  - Step 1 – Screening Study and Results
  - Step 2 - Optimization Study and Results
- Conclusions

Eductor-Based Generator



Eductor-Based Generator

Pump-Based Generator



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Pump-Based Generator

Common Pre-Conceptions

- A common belief is that the high concentration of precursors in the reaction column of an eductor-based generator (~ 75,000 ppm as ClO_2) leads to a more complete reaction than a more dilute concentration (~ 3000 ppm) of a pump-based generator.
- This work was initiated to determine, scientifically, whether or not this pre conception is accurate.

Analytical

- The four parts to the 4 step titration

Sample 1

  - Step A (mL) measures 1/5 ClO_2 and Cl_2
  - Step B (mL) measures the rest of the ClO_2 from step A (4/5) and unconverted ClO_2^- remaining from the generation process

Sample 2

  - Step C (mL) At pH 7, ClO_2 sparged out of solution leaving just hypochlorite and unconverted chlorite from the generation process. Titration measures only chlorine.
  - Step D (mL) The pH of Solution 2 is depressed to 2, allowing measurement of the unconverted chlorite from the generation process remaining from step C.

Calculations

- Chlorite
  - ClO_2^- (mg/L) = $$\frac{D(mL) \times Normality \times 16863}{Sample\ size\ (ml)}$$
- Chlorine Dioxide
  - ClO_2 (mg/L) = $$\frac{(B - D) \times Normality \times 16863}{Sample\ size\ (ml)}$$
- Chlorine

  Cl_2 (mg/L) = $$\frac{A - \left[\frac{(B - D)}{4}\right] X\ Normality\ X\ 35450}{Sample\ size\ (mL)}$$

Calculations

- % Efficiency =

$$\left[\frac{ClO_2}{ClO_2 + ClO_2^-} \right] \times 100$$

$$2NaClO_2 + NaOCl + HCl > 2ClO_2 + 2NaCl + NaOH$$

Calculations

- % Yield =

$$\left[\frac{ClO_2}{ClO_2 + Cl_2 + ClO_2^-}\right] X\ 100$$

$$2NaClO_2 + NaOCl + HCl > 2ClO_2 + 2NaCl + NaOH$$

ClO_2 Screening Approach – Design Sheet

Run	Acid	Bleach	Chlorite
1	-1	-1	-1
2	-1	-1	+1
3	-1	+1	-1
4	-1	+1	+1
5	+1	-1	-1
6	+1	-1	+1
7	+1	+1	-1
8	+1	+1	+1
9	0	0	0

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ClO_2 Screening Approach – Upper, Lower Limits

	Acid Flow mL/min	Bleach Flow mL/min	Chlorite Flow mL/min
-1	127	143	154
0	174	157	161
+1	221	174	170

ClO_2 Screening Results

Run	Acid Flow mL/min	Bleach Flow mL/min	Chlorite Flow mL/min	ClO_2 ppm
1	127	143	154	3120
2	127	143	170	3069
3	127	174	154	2597
4	127	174	170	3069
5	221	143	154	2934
6	221	143	170	3103
7	221	174	154	3221
8	221	174	170	3305
9	174	157	161	3373

ClO_2 Screening – Regression Analysis

Y-hat Model		ClO2			
Factor	Name	Coeff	P(2 Tail)	Tol	Active
Const		3386.25	0.0002		
A	A	88.500	0.2086	1	X
B	B	-4.250	0.9437	0.9990	X
C	C	84.250	0.2258	0.9983	X
AB		126.50	0.1067	1	X
BB		-334.00	0.1411	0.9972	X
	R^2	0.8214			
	Adj R^2	0.5238			
	Std Error	156.7551			
	F	2.7597			
	Sig F	0.2164			
	F_{LOF}	NA			
	Sig F_{LOF}	NA			
	Source	SS	df	MS	
	Regression	339054.4	5	67810.9	
	Error	73716.5	3	24572.2	
	$Error_{Pure}$	NA	0	NA	
	$Error_{LOF}$	NA	0	NA	
	Total	412770.9	8		

Regression analysis shows only a fair correlation for the model. R2 = 0.82

This was only a screening study to get a better handle on upper and lower acid and bleach feeds for optimization study.

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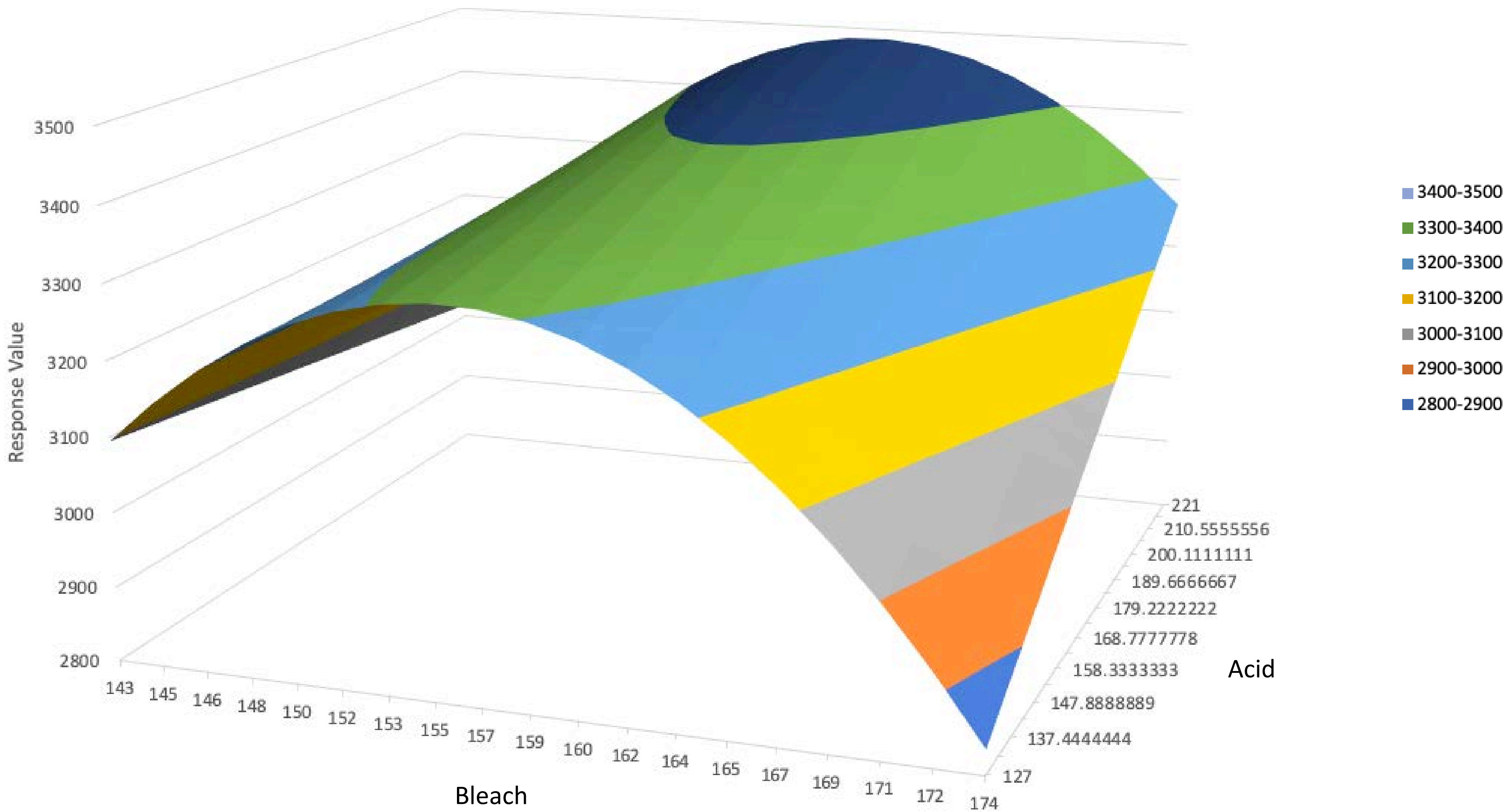
ClO_2 Screening – Contour Surface

Chlorite – 162 mL/min



Modelling – Change in Limits

Screening Limits

	Acid Feed mL/min	Bleach Feed mL/min	Chlorite Feed mL/min
-1	127	143	154
0	174	157	161
+1	221	174	170

Optimization Limits

	Acid Feed mL/min	Bleach Feed mL/min	Chlorite Feed mL/min
-1	168	106	226
0	233	162	226
+1	299	217	226

The acid and bleach numbers were not quite wide enough to see the ClO_2 maximum. In this optimization experiment, we made the following changes.

1. We increased chlorite a little and held it constant.
2. We increased the bleach range a bit.
3. We increased the acid concentration a bit to account for the increase in chlorite.
4. To provide for greater statistical significance testing was done in triplicate.

ClO_2 Results – Composite Surface

Factor	A	B		ClO2		
Row #	HCl	Bleach		Y1	Y2	Y3
1	168	106		2293	3002	2698
2	168	217		2782	3541	3845
3	299	106		1754	1855	1956
4	299	217		3423	3575	4064
5	233.5	161.5		3524	3575	3912
6	168	161.5		3136	3862	4114
7	299	161.5		3558	3862	3035
8	233.5	106		2057	2361	2378
9	233.5	217		3389	3457	4654

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ClO_2 as Dependent Variable – Regression Analysis

Y-hat Model

Factor	Name	Coeff (ClO2)	P(2 Tail)	Tol	Active
Const		3703.44	0.0000		
A	HCl	-121.72	0.2016	1	X
B	Bleach	687.56	0.0000	1	X
AB		276.83	0.0232	1	X
AA		-125.50	0.4413	1	X
BB		-670.67	0.0004	1	X

R^2	0.7949
Adj R^2	0.7461
Std Error	391.7063
F	16.2791
Sig F	0.0000
F_{LOF}	0.1773
Sig F_{LOF}	0.9104

Source	SS	df	MS
Regression	12488785.4	5	2497757.1
Error	3222110.6	21	153433.8
$Error_{Pure}$	3129652.0	18	173869.6
$Error_{LOF}$	92458.6	3	30819.5
Total	15710896.0	26	

The regression analysis of these data shows an R2 value which is lower than the screening experiment, due to the scatter in testing data.

Note that the P(2 Tail) values in red show the factors that have been identified as being significant by the software.

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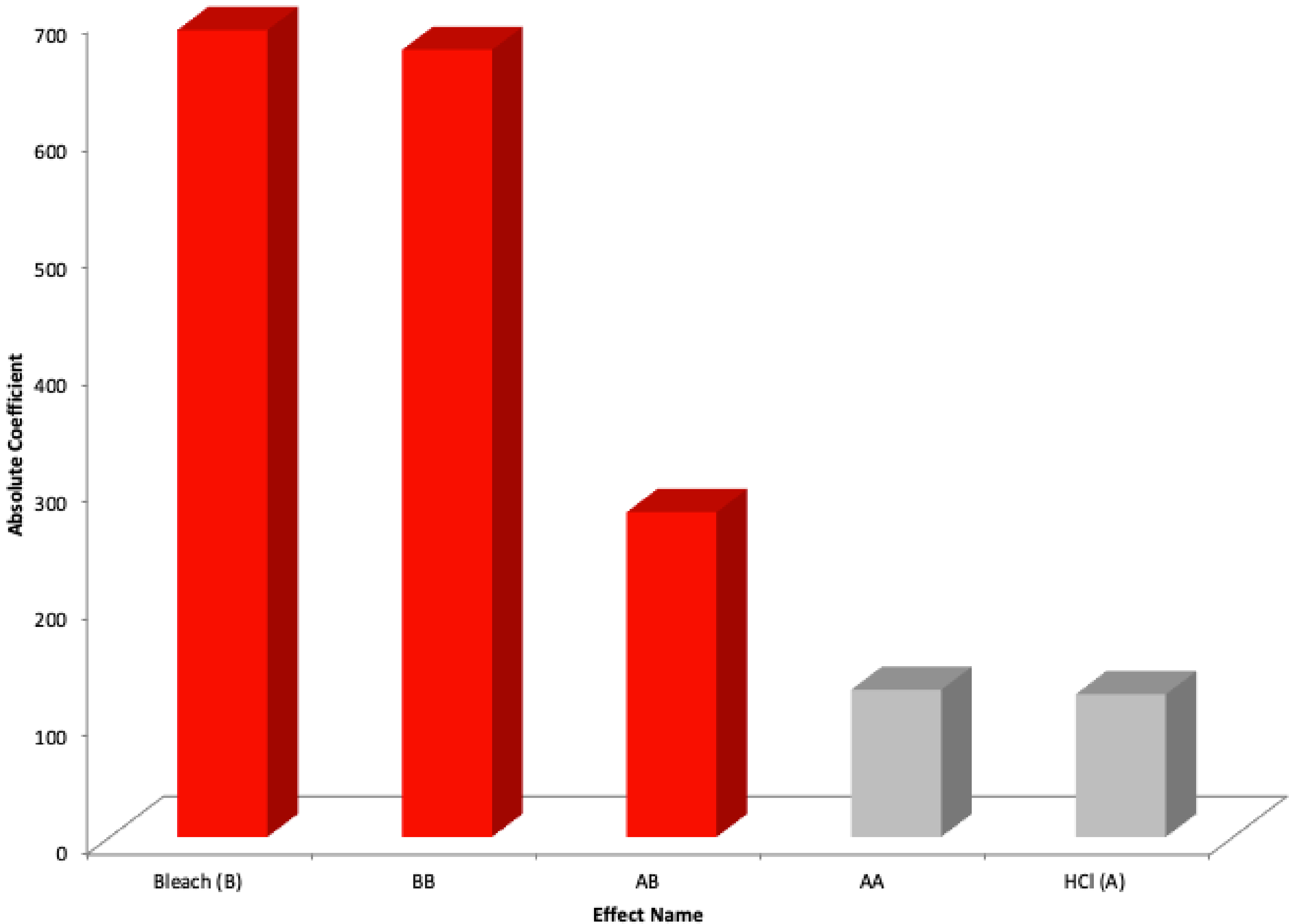
ClO_2 as Dependent Variable – Pareto Diagram



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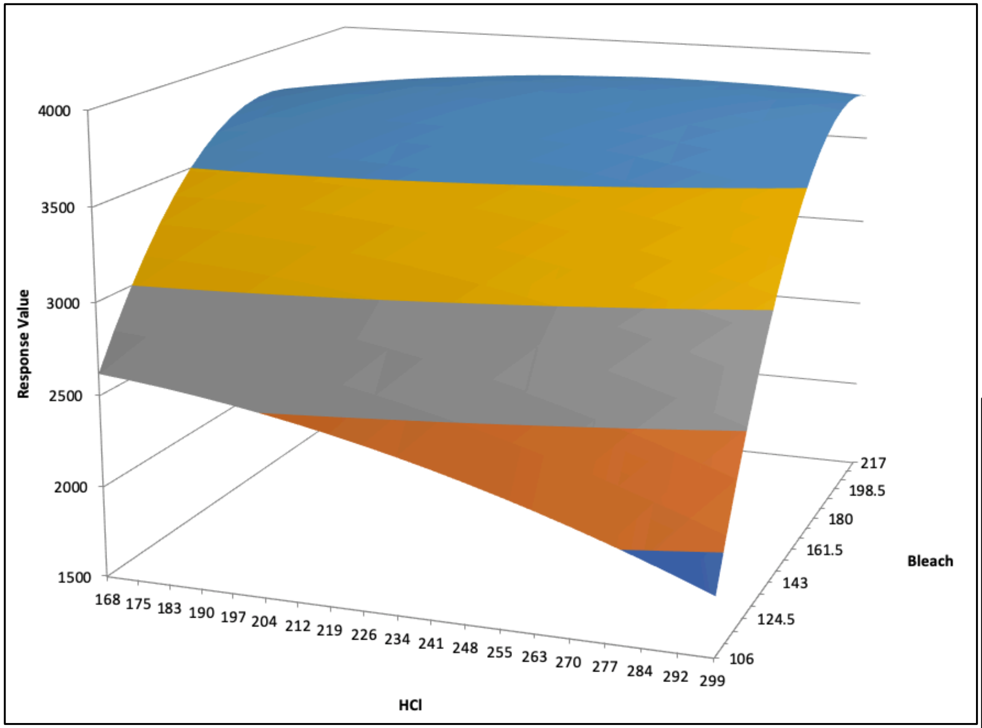
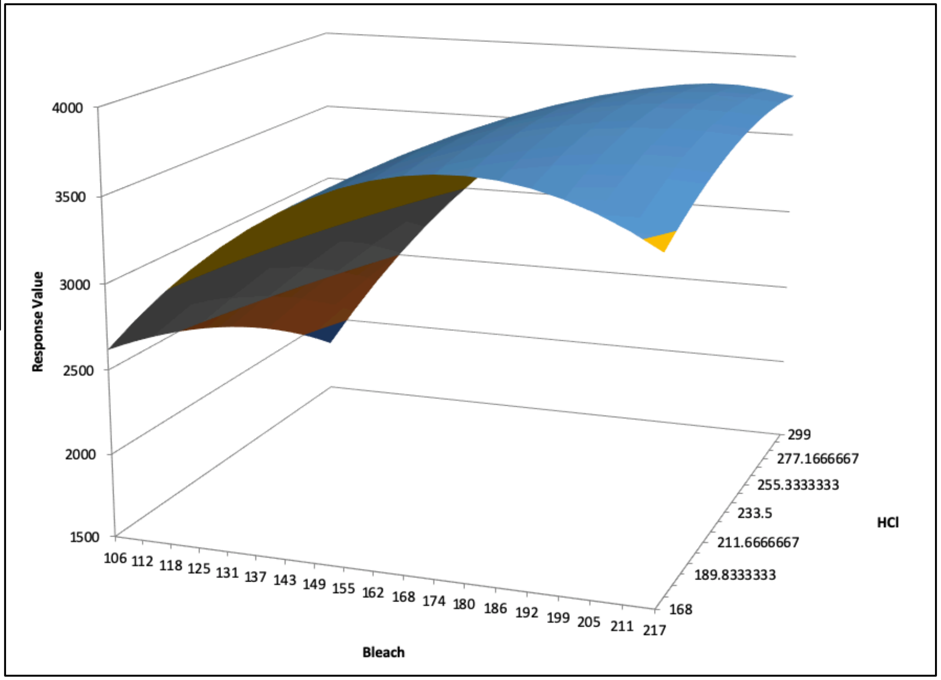
ClO_2 Production – Contour Surface



3500-4000
3000-3500
2500-3000
2000-2500
1500-2000



Optimization – Dependent Variables

- In the optimization study, we considered not only ClO_2 generation as a dependent variable but also analyzed generation efficiency and yield as dependent variables.
- Then generation efficiency was modelled.
- Finally, yield was modelled.

Efficiency Modelling – Regression Analysis

Y-hat Model — Efficiency

Factor	Name	Coeff	P(2 Tail)	Tol	Active
Const		92.837	0.0000		
A	HCl	-0.94444	0.3937	1	X
B	Bleach	19.928	0.0000	1	X
AB		2.600	0.0637	1	X
AA		-0.78889	0.6787	1	X
BB		-12.972	0.0000	1	X

R^2	0.9489
Adj R^2	0.9368
Std Error	4.6009
F	78.0298
Sig F	0.0000
F_{LOF}	0.7499
Sig F_{LOF}	0.5365

Source	SS	df	MS
Regression	8258.7	5	1651.7
Error	444.5	21	21.2
$Error_{Pure}$	395.1	18	22.0
$Error_{LOF}$	49.4	3	16.5
Total	8703.2	26	

This model is quite good, as shown by the regression coefficient, R2.

The significant factors identified by the software are the chlorite feed, bleach feed, and the bleach-bleach interaction.

Note that in this model, HCl feed is not considered significant although HCl-Bleach (AB) is approaching significance [P(2 Tail) = 0.06)].

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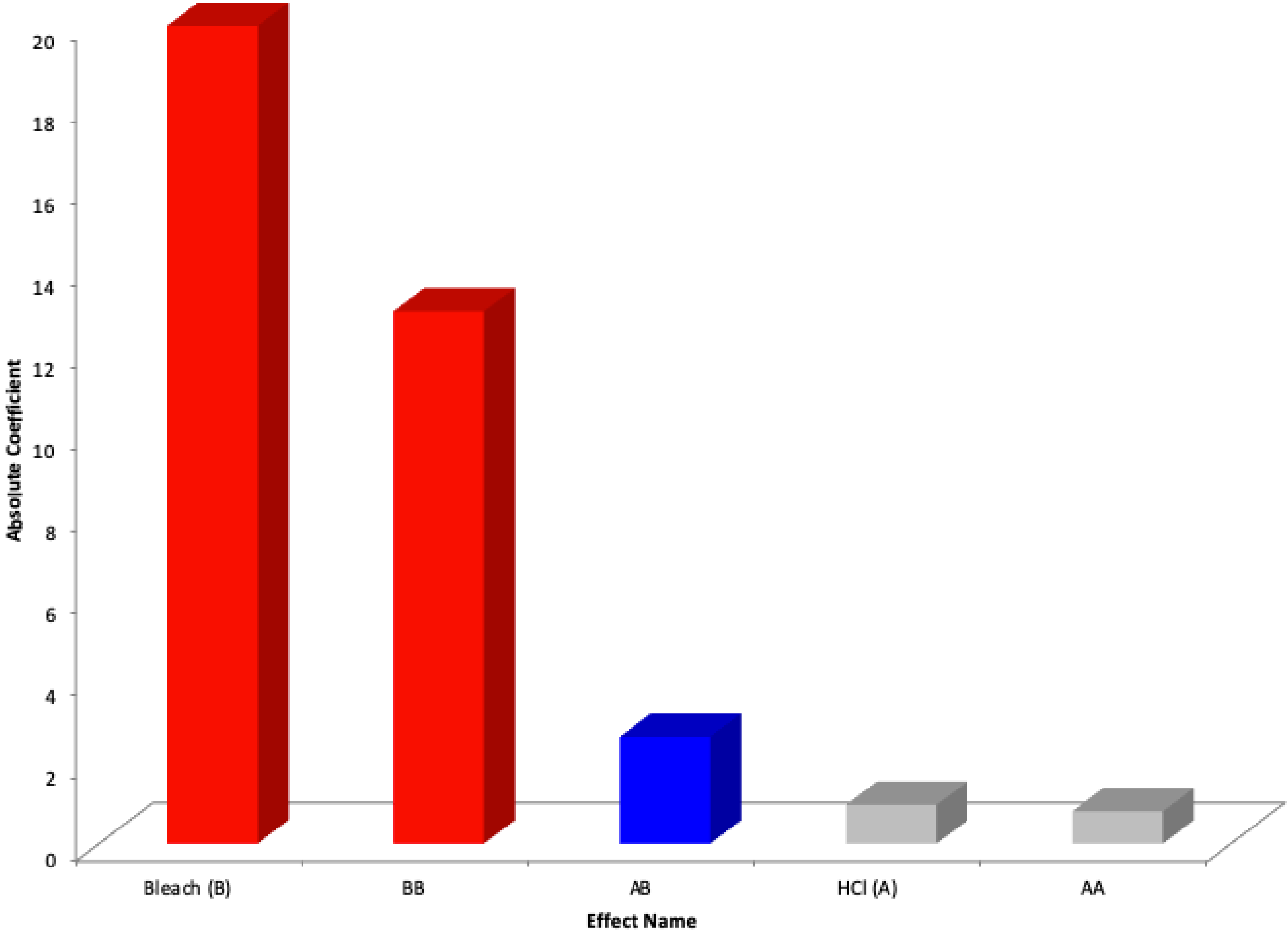
Modelling of Efficiency – Pareto Diagram



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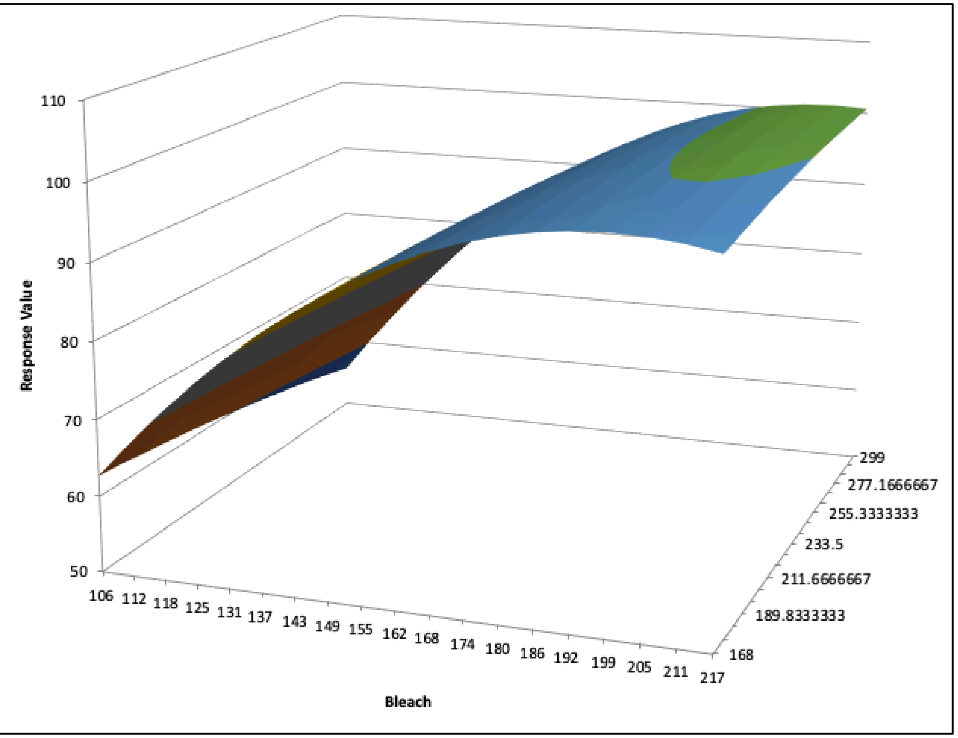
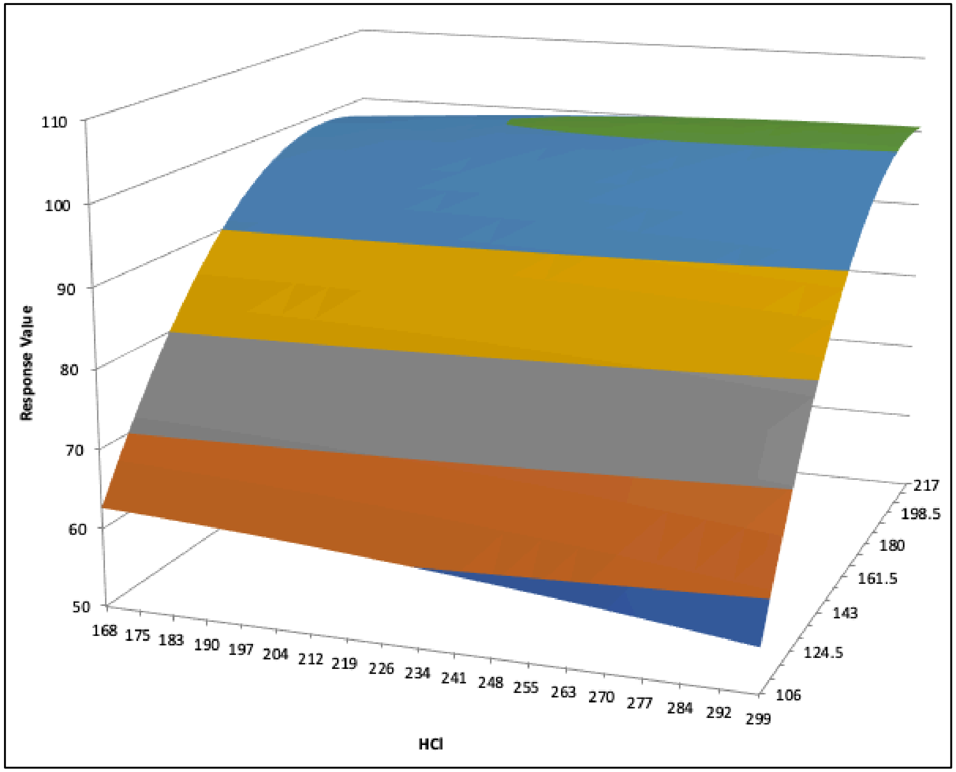
Efficiency – Contour Surface Model



- 100-110
- 90-100
- 80-90
- 70-80
- 60-70
- 50-60



Yield Modelling – Regression Analysis

Y-hat Model

Factor	Name	Yield Coeff	P(2 Tail)	Tol	Active
Const		87.678	0.0000		
A	HCl	-8.133	0.0000	1	X
B	Bleach	21.622	0.0000	1	X
AB		3.908	0.0225	1	X
AA		-4.100	0.0819	1	X
BB		-12.533	0.0000	1	X

R^2	0.9447
Adj R^2	0.9315
Std Error	5.4954
F	71.7412
Sig F	0.0000
F_{LOF}	0.6039
Sig F_{LOF}	0.6209

Source	SS	df	MS
Regression	10832.8	5	2166.6
Error	634.2	21	30.2
$Error_{Pure}$	576.2	18	32.0
$Error_{LOF}$	58.0	3	19.3
Total	11466.9	26	

This model is quite good, as shown by the regression coefficient, R2.

The significant factors identified by the software are the chlorite feed, acid feed, bleach feed, acid-bleach interaction, and bleach-bleach interaction.

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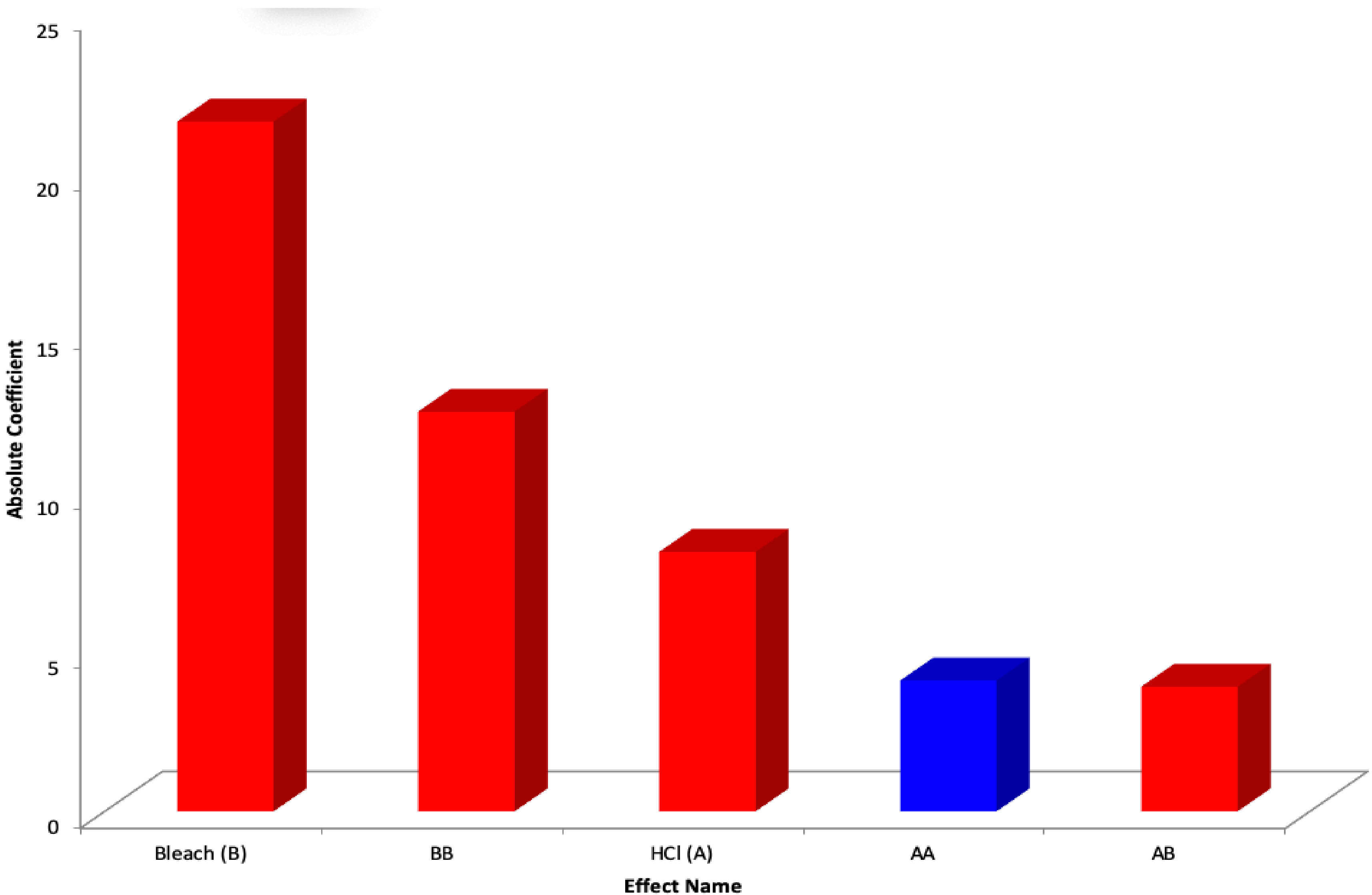
Modelling of Yield – Pareto Diagram



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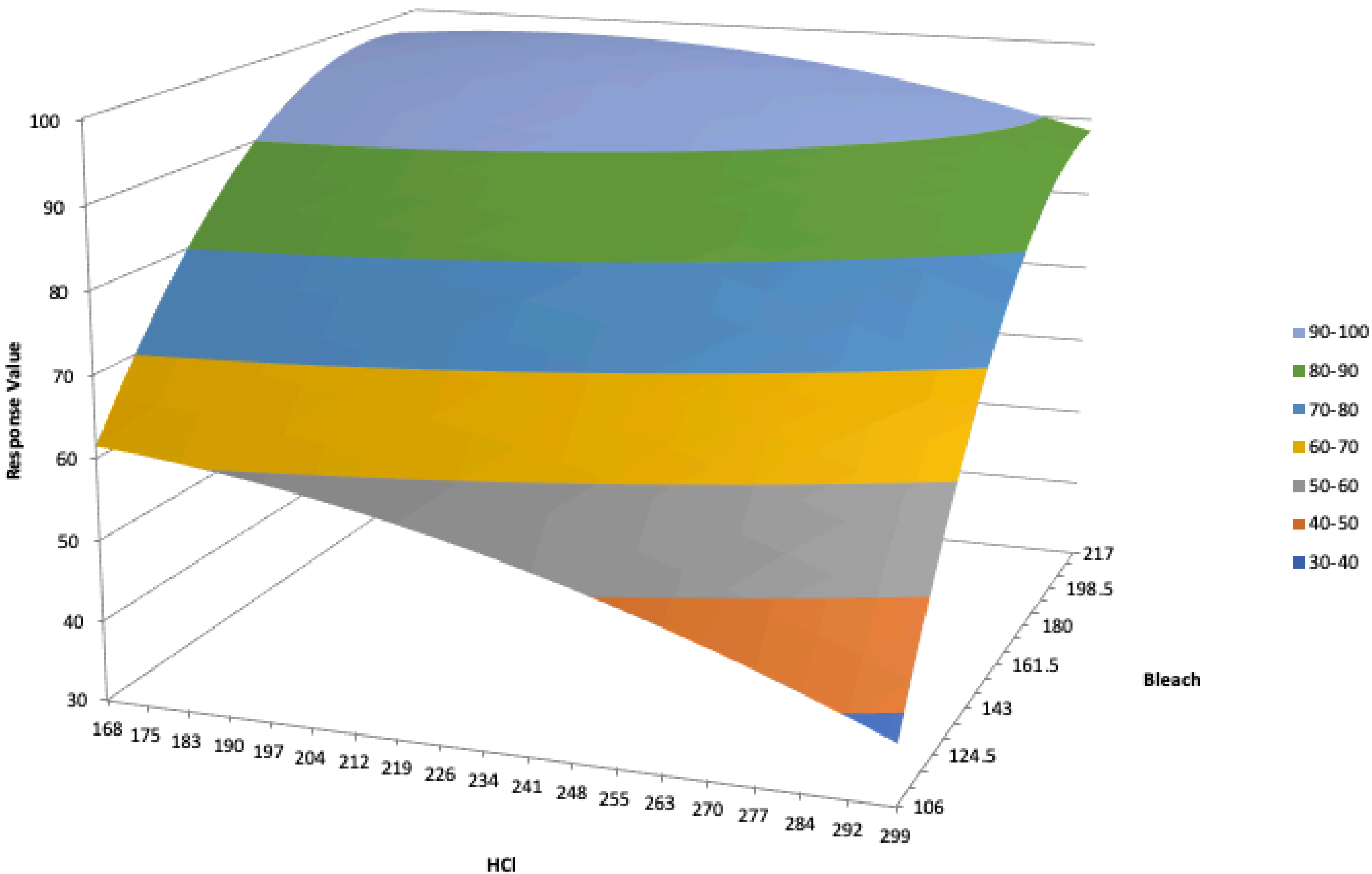
Yield – Contour Surface Model



Conclusions

- My pre-conceived belief that reacting precursors, in a high concentration, would provide greater reaction efficiency and yield than a reaction in a more dilute concentration, was found to be a False pre-conception.
- One explanation is that for chlorite, which is made from chlorine dioxide, there is a fairly strong driving force to return to ClO_2 under the right conditions. Thus there appears to be little difference between how the precursors are mixed from a practical standpoint.

Thank you

Questions?
Comments?
Suggestions?