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SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI AND SULPHUR SPECIES FOR COMBUSTION

Quarterly Report No. 8

for period June - August 1992

DOE Grant Number DE-FG22-90PC90285

Prepared by

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Submitted to

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**SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI AND SULPHUR
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DATA ANALYSIS

Regression analysis on experimental results of in Table A.1 to Table A.7 (Appendix) is presented in this report. The purpose is to generate continuous functional relationships between water insoluble alkali capture, sorbent injection temperature and alkali to sorbent loading ratio. The results in this section are then presented in the form of global response surfaces, from which models can be proposed to mathematically explain the alkali capture phenomena.

Results so far, show that alkali capture is dominated by the formation of water insoluble alkali aluminosilicates. In most cases, 99% of the alkali oxides sampled were found in the particle size range greater than $0.65\ \mu\text{m}$ (considered captured by sorbents). 80-90% of this captured fraction, depending on the flow alkali-sorbent loading ratio, is water insoluble. Energy Dispersive X-ray (EDX) area scans and Atomic Absorption (AA) bulk chemical analysis were shown to be in close agreement on the water insoluble alkali content of the particulate samples. EDX scans on $1\ \mu\text{m}$ size reacted particles, showed that 50% sorbent utilization (based on nephelinite formation) was possible. No higher utilization than this was recorded. Typical utilization, however, was in the range of 30-40%. The extent of sorbent utilization depended strongly on the sorbent injection temperature, flue gas environment and alkali to sorbent loading ratio. The effect of chlorine and that of sulfur, derived from this chapter, has been presented earlier. results.

WATER INSOLUBLE CAPTURE RESPONSE SURFACE

The water insoluble sodium content is proposed to be formed by the gas-solid reaction of equation (1) with the product as nephelinite. Capture is presented as fraction

mass of Na₂O per unit mass of sorbent (predominantly Al₂O₃ and SiO₂). The theoretical capture limit corresponds to a mass gain of 0.27gm Na₂O/gm sorbent.

An alkali-Sorbent equivalence ratio based on capture reaction above is defined as: If

$$\varphi = \frac{gm[Na_2O]}{(gm[Al_2O_3] + gm[SiO_2]) \times 0.27} \quad 2$$

impactor samples are obtained isokinetically, then φ can be calculated from total impactor sample mass of Na₂O, Al₂O₃ and SiO₂. It has been shown that if variable sorbent injection point experiments are carried in which the initial alkali concentration is kept constant, then the set of independent variables that determine alkali capture are: (1) sorbent injection temperature (T), (2) particle residence time in the alkali gas phase regime (τ), (3) alkali to sorbent equivalence ratio(φ), (4) sorbent sample point/temperature (T_{ex}), (5) particle size(d_p) and (6) local flue gas temperature history (θ). In the kinetically controlled reaction regime, already shown to be true for particle sizes under 2.0 μ m, and if sampling is taken below the dewpoint, then the water insoluble capture can be represented by a Lagrangian formulated function $g(T, \varphi, \tau)$, in gm Na₂O/gm sorbent, given as:

$$g(T, \varphi, \tau) = \int_0^{\tau} R_g(\varphi, \theta(t)) dt \quad 3$$

where $R_g(\varphi, \theta)$ is particle global reaction rate in gm Na₂O/gm-sorbent-sec. Strictly, R_g is a function of local alkali concentration, and some structural parameter term. Both are variables that are changing continuously with extent of capture. If the alkali

concentration is not in excess with respect to sorbent particle density, and if the initial alkali partial pressure is constant at the point of sorbent injection, then the reaction rate term is only a function of dimensionless alkali- sorbent equivalence ratio. No assumption is made, so far, on the exact nature of this reaction rate function, or how it varies with the changing gas phase alkali concentration that changes after injection. It is the shape and form of the global capture function, g , that is to be investigated by the use of approximating graduating functions within the experimental domain. One implicit assumption, however, is that at point of injection, the partial pressure of the alkali gas phase species is the same for all samples. Since the residence time (τ) only depends on point of injection, and hence an implicit function of T , Equation 3 becomes:

$$g(T, \varphi, \tau) = g(T, \varphi) = \int_T^{T_{dwypt}} R_p(\varphi, \theta) \phi(\theta) d\theta \quad 4$$

where $\phi(\theta)$ is a time to temperature transformation function specific to the combustor flow characteristics and combustor temperature profile.

Table A.5-A.7 (Appendix) show water insoluble capture at different sorbent injection temperatures and different sodium to sorbent loading ratio. The experimental runs were carried under same running conditions of a flue gas environment of 250 ppmv sodium with excess sulphur (~ 700 ppmv). Detailed analysis of this case will be presented here. Other runs of sodium alone and sodium with chlorine follow the same format and only the results are presented at the end of this section. The feed conditions from which these experimental data were obtained is given in Table A.8 (Appendix).

The sorbent injection point was varied between port 2 and port 6 corresponding to a temperature range between 1300°C and 850°C. A total of 29 impactor samples were taken in this case.

Fitting of Model $g^*(T, \varphi)$, for Sodium with Sulfur Runs

The experimental capture results $g(T, \varphi)$ can be approximated to some function $g^*(T, \varphi)$, within the experimental domain, such that:

$$g(T, \varphi) \approx g^*(T, \varphi) + \varepsilon \quad 5$$

and ε is a random error from experimental measurements. Figure 1 shows a plot of the experimental domain (T, φ) covered by the capture data. A response surface developed is only applicable within the region *jointly* covered by the experimental results and care must be taken not to extrapolate its use outside the domain. The bulk of the data is seen to be found in the vicinity of alkali-sorbent equivalence ratio of $\varphi=0.25$. This is more of a characteristic of the sorbent feeder and not by design. Our purpose was to cover as wide a range as practically possible by changing sorbent flowrate and sorbent injection temperatures. The injection temperature is first rescaled around the mean injection temperature (approximately 1000°C).

$$T^* = \frac{T(K)}{1273} \quad 6$$

Taking the error on the water insoluble capture data to be random, and so normally distributed, capture can then be approximated by a first or second order polynomial. The data was fitted to a second order polynomial as given in Equation 7.

Figure 1: Response surface experimental domain in terms of sorbent injection temperature (T) and alkali/sorbent equivalence ratio (ϕ) for Na, Na & Cl₂ and Na & SO₂ experiments.

$$g_i^* = \beta_0 T_i^{*2} + \beta_1 T_i^* + \beta_2 T_i^* \varphi_i + \beta_3 \varphi_i^2 + \beta_4 \varphi_i + \beta_5 + \varepsilon_i$$

The least square polynomial fit results are shown in Table 1. Also shown in the same table are the standard errors associated with each term, the partial t^* test statistic, and the tabulated t distribution at 10%, 5%, and 1% significance levels. These results were obtained from the SPSS-X (1986) computer package. The package employs the methods of orthogonal polynomials. Computer packages that makes use of orthogonal formulation are particularly useful in that they can handle problems that exhibit multi collinearity between variables. A detailed discussion of the problem of multi collinearity in regression problem is discussed in detail by Neter (1983). It is to be noted that the type and nature of a multiple regression fit so derived depends on whether or not the independent variables included in the model are (1) correlated among themselves and (2) correlated with any other independent variables that are related to the dependent variable but omitted from the model. In the present study, for instance, it is known that residence time is one variable that determines capture. However, it has not been included in the model explicitly. The existence of thermodynamic dewpoints within the experimental domain may lead one to question how valid an assumption that continous capture functions exist. The argument we have put forward is that capture only takes place above the dewpoint and that the dewpoint acts as a unique reaction cutoff point. This argument has been supported by our thermodynamic equilibria studies (earlier report). Experimental results did not show that any such discontinuities existed in our system. Indeed, when sorbents were inject at port 6 at a temperature of 800°C in the presence

of excess SO_2 (which was below the dewpoint ($\sim 850^\circ\text{C}$) negligible capture was found instead the bulk of sodium was water soluble.

Table 1: Second order regression results for sodium capture response surface in an excess SO_2 environment.

Tabulated percentiles of the t distribution at 10%, 5%, and 1% significance levels				
$t(0.95,23) = 1.71$		$t(0.975,23)=2.07$		$t(0.995,23)=2.81$
Coefficient		Value	std. err	t^*
β_0	T^2	-0.360 ± 0.263	0.153	2.36
β_1	T^*	0.754 ± 0.577	0.336	2.25
β_2	$T^*\varphi$	0.372 ± 0.094	0.055	6.78
β_3	φ^2	-0.061 ± 0.055	0.032	2.02
β_4	φ	-0.274 ± 0.122	0.071	3.86
β_5		-0.383 ± 0.318	0.185	2.07

Test of Fit

Two statistical tests of significance were considered separately. These are; the t-test statistic for regression coefficients, and the overall F test statistic for the existence of a regression. A detailed discussion on the interpretation and use of such tests is given by Box (1987). Table 1 show both the standard error of estimate and the partial t^* test statistic for each coefficient. The partial t, tests in turn, whether or not each coefficient is uniquely not equal to zero.

The t^* statistic is defined as:

$$t^* = \frac{\beta_k}{s(\beta_k)} \quad 8$$

where $s(\beta_k)$ is the standard error associated with the estimation of the coefficient β_k .

The parameter estimate range, at 95 % confidence interval, is then given as

$$\beta_i = \beta_i \pm t(0.975, n-p) \times s(\beta_i) \quad 9$$

The t test conclusion at 95 % confidence limit is:

$$\begin{aligned} \text{If } |t^*| \leq t(0.975, n-p), \beta_i &= 0 \\ \text{If } |t^*| > t(0.975, n-p), \beta_i &\neq 0 \end{aligned} \quad 10$$

Where n is the number of data points, and p is the number of fit coefficients, β s. The results in Table 1 show that all the coefficients, at 95 % confidence limit, were not equal to zero. When a partial t test is used on a two variable quadratic model, there may exist two reject possibilities: (1) All the coefficients related to one variable e.g. temperature, equals to zero, (2) Only one of the coefficients associated with a variable (say the quadratic term or the linear term) equals to zero. The first case, all coefficients related

to a variable equal to zero, does not necessarily mean the effect of the variable can be neglected from the model. There may still exist a strong correlation. The reason for this is that partial t tests only considers the marginal contribution of each term of the independent variable. Given that the other variables are included in the model, further tests have to be done before a conclusion is made. The second case, that is one of coefficients related to a variable equals to zero, is more interesting as it points that either the linear or the quadratic term with respect to a variable say temperature can be dropped out from the model. The decision to drop or maintain a term, however, will depend on the actual system under study.

Whereas the partial t test statistic was used to test whether or not the fit coefficients equals to zero, an analysis of variance test was used to test whether or not there exists a regression relation between experimental capture results and regression predicted capture. An analysis of Variance(ANOVA) results is shown in Table 2. Also shown on the same table is the coefficient of multiple regression R^2 , the sum of squares due to regression (SSR) and that due to error (SSE). The test statistic for the analysis of variance is defined by F^* , which is the ratio of mean sum of squares due to regression to the mean sum of squares due to error. The decision rule is given as:

If $F^* \leq F(0.95, p-1, n-p)$, conclude no correlation

If $F^* > F(0.95, p-1, n-p)$, conclude a correlation

Table 2: Analysis of Variance results for least square fit of Table 1

Analysis of Variance for Na & SO ₂ system					
Source of Variation	Sum of squares	degree of freedom	Mean sum of squares	F [*]	R ²
Regression	0.0129	(p-1)= 5	0.0026	55.5	0.923
Error	0.0011	(n-p)= 23	0.00005		
Total	0.0140	n-1 = 28			
# points:	29	Std err:	0.0068	Reject level F(0.975,p-1,n-p)= 3.15	

Table 2 shows our present fit F^* to be 55.5 as compared to the tabulated reject level $F(0.975, 5, 23) = 3.15$. The coefficient of regression is 0.92. Judging from the results of F^* and that of the coefficient of multiple regression R^2 , it can be concluded that the regression fit closely predicts capture response. Figure 2, shows a plot of experimental capture against the regression model capture good agreement is shown. Residuals (calculated as the difference between experimental capture and the regressed capture) is shown plotted against independent variables T and ϕ respectively in Figure 3. The residual plot shows that there is no bias, or systematic trends, in the departures of the residuals from zero with respect to any of the independent variables. It is concluded that the residuals are normally distributed about nought, a pre-requisite for the use of the least square method that required that all errors associated with experimental results are random.

Figure 2: Experimental water insoluble capture of sodium in excess SO₂ (~ 700ppm) plotted against polynomial regression model of Table Sodium level was at 250 ppm.

Figure 3: Residuals from second degree model of capture plotted against independent variables T and ϕ for Na/S runs. A normal distribution of the residuals about zero is shown

Comparison of Experimental and Regression Surfaces

In dealing with multidimensional fits, it is conceivable that two very different surfaces in space can share same plots. In the case of our system, the response surface is a three dimensional surface and hence it can be plotted out using conventional software. Once a response surface is plotted in a three dimensional plot, non mathematical judgement can be made by comparing a three dimensional plot generated by the experimental data and that generated by the regression fit. In systems of more than two independent variables, such surfaces can not be plotted in which case care must be taken in interpreting the regression results.

Figure 4 and Figure 5 show experimental and model three dimensional response surface of sodium capture against injection temperature and equivalence ratio. Selected experimental values are posted on Figure 4. A peak alkali capture in the range of 0.11-0.12 gm Na_2O /gm sorbent was recorded corresponding to a maximum sorbent utilization of 45%. It is also shown that within the experimental domain, the polynomial fit closely describes the capture response surface of alkali capture against sorbent injection temperature.

It should be noted that the response surface analysis was adopted so that the effect of sorbent injection temperature and that of alkali/sorbent loading ratio could be studied simultaneously. With a model surface in hand, effect of sorbent injection temperature at a fixed equivalence ratio can be derived.

Figure 4: Experimental water insoluble sodium capture (Na/S runs), plotted against dimensionless sorbent injection temperature and alkali/sorbent equivalence ratio. Data points are posted on surface

Figure 5: Model water insoluble sodium capture in an excess SO_2 environment plotted against dimensionless sorbent injection temperature and alkali/sorbent equivalence ratio (ϕ)

Is a Response Surface Adequately Estimated?

As was pointed in the last section, the problem with multi dimensional surfaces is that, it is conceivable that different response surfaces can share same planes within a confined region. It is with this in mind that care must be taken not to extrapolate such fitted response surfaces. Another source of misinterpretation is to make predictions outside the scope of the model by looking at the levels of the independent variables singly. In multiple regression, it is particularly easy to lose track of the region since levels of both independent variables jointly define the region. Thus, one cannot merely look at the ranges of each independent variable. In this regard we have used three dimensional plots for both our experimental results and our model surfaces for visual guideline on the regions of applicability of fit. The questions still to be addressed are "when is a fitted function sufficiently well estimated to permit useful interpretations?". "Should adequacy of fit be judged on the size of F and R^2 alone?", "If so how large an F is necessary?". An argument presented by Wetz (1973) suggests that the calculated F should be at least larger than tabulated F by a factor of 10. Table 2 shows that this criteria was satisfied. However, the final acceptance of a regression model is subject to the judgement of the experimentalist. The use of randomly obtained replicate data to test a regression model is another useful tool to adopt. We have used this in the case of the sodium in excess chlorine runs to show that replicate runs did also agree with the regression prediction. The final acceptance of a regression model is not based on one source of evidence but on the sum total of the piece of evidence put together.

Fit for Sodium Only Runs.

Experimental runs in which sodium, at a gas phase concentration of 250 ppm, in the absence of chlorine and sulphur were carried out to serve as base capture case. Other conditions such as sorbent injection points, sample point, mass flowrates etc, were similar to those described in the previous section. A summary of the water insoluble sodium capture results is given in Table A to A.1 (Appendix). Data analysis follows similar procedure as has been presented for sodium with excess sulfur. Water soluble sodium capture in this case is best described by Equation 12:

$$g^* = -0.144T^{*2} + 0.265T^* + 0.1637\varphi - 0.1630\varphi^2 - 0.0896\varphi - 0.124 \quad 12$$

for $0.1 < \varphi \leq 1.0$ and $0.9 \leq T^* \leq 1.27$.

Table 3 shows the analysis of variance for the fit model of Equation 12. Notable results on table are: $F^* = 77.6$, $R^2 = 0.94$, and tabulated $F(0.975, 4, 21) = 3.2$ which more than satisfies the criteria for F^* to be at least ten times larger than the tabulated F . Figure 6, Figure 7 and Figure 8 summarizes the results of regression fit when compared with experimental data.

Table 3: Analysis of Variance results for least square fit of equation 12.

Analysis of Variance for Na system					
Source of Variation	Sum of squares	degree of freedom	Mean sum of squares	F*	R ²
Regression	0.0261	(p-1)= 4	0.0065	77.6	0.937
Error	0.0018	(n-p)= 21	0.00008		
Total	0.0279	n-1= 25			
# points:	26	Std err:	0.0092	Reject level F(0.975,p-1,n-p)= 3.15

Figure 6: Experimental water insoluble capture of sodium (base case) plotted against polynomial regression model results. Sodium level was at 250 ppm.

Figure 7: Experimental water insoluble sodium capture (Sodium alone) plotted against dimensionless sorbent injection temperature and alkali/sorbent equivalence ratio (ϕ). Selected data points are posted on surface.

Figure 8: Three dimensional model of sodium capture in sodium only environment, plotted against dimensionless sorbent injection temperature and alkali/sorbent equivalence ratio(ϕ)

Fit for Sodium with Excess Chlorine Runs

Sodium capture results for runs in which sodium level was kept at 250 ppm Cl_2 was at ~ 700 ppm (1400 ppm Cl) are summarized in Table A 5.3 to Table A 5.5 (Appendix). The second order regression polynomial that fitted the data is given as:

$$g^* = -0.124T^{*2} + 0.235T^* + 0.120T^* \phi - 0.0566\phi^2 - 0.097 \quad 13$$

The level of numerical significance of the linear term with respect to equivalence ratio was small and hence dropped. Table 4 show the analysis of variance results for the polynomial fit.

Table 4: Analysis of variance for a sodium capture in a combustor environment with excess chlorine (equation 5.13)

Analysis of Variance for Na & Cl ₂ system					
Source of Variation	Sum of squares	degree of freedom	Mean sum of squares	F*	R ²
Regression	0.00868	(p-1)= 4	0.0022	55.5	0.923
Error	0.00036	(n-p)= 16	0.00002		
Total	0.00904	n-1= 20			
# points:	21	Std err:	0.0048	Reject level F(0.975,p-1,n-p)= 3.6	

A summary of the results are shown in Figures 9-11. The results show that capture sensitivity to sorbent injection temperature is reduced in comparison to the sodium - SO_2 system. replicate runs were carried out that were not used in development of the regression model. These results are plotted in Figure 9 as well.

Figure 9: Plot of polynomial regression model against experimental results of sodium capture in a flue gas environment of $\text{SR}=1.2$, and sodium concentration of 250 ppm. Chlorine level was at 400-500 ppm

Figure 10: Experimental water insoluble sodium capture in an excess Cl_2 environment, plotted against dimensionless sorbent injection temperature and alkali/sorbent equivalence ratio.

Figure 11: Three dimensional regression model of sodium capture in sodium and excess chlorine environment, plotted against dimensionless sorbent injection temperature and alkali/sorbent equivalence ratio(ϕ)

SUMMARY

- Response surface experimentation approach, using a variable sorbent injection point design, together with statistical regression has successfully been combined to generate continuous alkali capture functions. The use of a response surface to extract rate kinetics of sodium induced corrosion on a combustor test rig was previously reported by Lowell et al (1982)
- The results can now be combined to analyze the effect of sorbent injection temperature, chlorine and sulfur on sodium capture. A sodium to sorbent equivalence ratio of $\varphi=0.45$ is selected for this comparative analysis. This is because the equivalence ratio of 0.45 is jointly covered by all the experimental data. Figure 12 shows a comparative plot of sodium capture plotted against sorbent injection temperature. Taking the sodium alone as base case, the effect of chlorine is seen to reduce capture by as much as 30%. This result is consistent with the impactors that were taken under similar conditions were compared.
- Extrapolation of the experimental results show that the alkali dewpoints is probably around 700°C for sodium alone and sodium with chlorine cases, and around 850°C for sodium with sulfur case. These results are summarized in Figure 13.

Figure 13: Comparative effect of Cl and S on sodium capture plotted against sorbent injection temperature at $\phi=0.45$

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APPENDIX A

Table A Response surface results for sodium alone

Sodium capture by Kaolinite: Na Acetate only runs										
Run No	Injection Temp(C)	Sample Temp(C)	ER(ϕ)	Sample Qty(mg)	Flow Rate (gm/min)	Total alkali capture.		Water insoluble capture		
						%Na st1-7	%Na (ins)	Impactor Av (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
111	1284	639	1.978	8.3	371	31.9	13.0	0.072	0.11	0.1095
112	1284	682	0.8943	19.9	371	83.6	44.7	0.1117	0.11	0.1151
113	1284	803	0.5675	34.8	371	85.8	61.1	0.0969	0.14	0.0998
114	1284	803	0.5024	47.0	371	86.6	76.8	0.0812	0.12	0.0909
116	1284	916	0.4448	21.7	371	84.8	62.7	0.0779	0.10	0.0814
121	1043	639	0.2151	58.0	448	89.0	62.9	0.0378	0.03	0.0464
122	1043	682	0.1634	69.3	448	90.2	65.1	0.0297	0.03	0.0342
123	835	639	0.3114	42.7	448	77.6	52.1	0.0453	0.04	0.0496
124	835	639	0.1626	50.5	448	72.2	33.4	0.0173	0.01	0.0253
151	988	695	0.2033	42.1	480	91.7	65.9	0.0374	0.06	0.0433
152	1125	695	0.6377	14.4	480	89.1	60.8	0.1082	0.12	0.1064
153	895	695	0.3892	21.0	480	84.8	70.2	0.0763	0.07	0.0667
154	842	695	0.3230	31.9	480	89.0	70.2	0.0633	0.06	0.0521

APPENDIX A

Table A.1 Response surface results for sodium alone

Sodium capture by Kaolinite: Na Acetate runs										
Run No	Injection Temp(C)	Sample Temp(C)	ER	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ins)	Impactor (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
241	991	728	0.0868	41.6	474	79.3	53.0	0.0128	0.01	0.0149
242	1112	728	0.1086	62.3	474	93.2	64.4	0.0195	0.03	0.0163
243	1112	728	0.1441	63.5	474	94.7	76.6	0.0303	0.04	0.0263
244	1244	728	0.3320	26.6	474	97.2	77.9	0.0722	0.10	0.0625
245	1244	728	0.3170	20.9	474	97.1	79.2	0.0701	0.09	0.0592
271	1236	728	0.5576	23.5	474	94.6	69.5	0.1082	0.16	0.0984
272	1236	728	0.5070	27.9	474	98.5	50.0	0.0707	0.09	0.0922
341	1023	600	0.1484	20.0	474	99.6	82.7	0.0343	0.04	0.0307
342	1023	600	0.1444	18.9	474	99.0	87.9	0.0354	0.04	0.0297
343	878	600	0.0922	25.0	474	95.5	84.3	0.0217	0.02	0.0148
344	878	600	0.0965	66.9	474	97.9	89.0	0.0240	0.02	0.0157
345	825	600	0.0931	31.8	474	92.6	86.1	0.0220	0.02	0.0115
346	825	728	0.0904	25.7	474	90.6	82.9	0.0209	0.02	0.0110

APPENDIX A --continued

Table A.2 Response surface results for sodium with excess chlorine

Run No	Sodium capture by Kaolinite in the presence of excess chlorine:Na ~ 250 ppm, Cl ₂ ~ 700 ppm.									
	Injection Temp(C)	Sample Temp(C)	ER(ϕ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ins) st1-7	Impactor (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
201	980	728	0.1918	39.1	474	90.3	74.6	0.0400	0.05	0.0345
202	980	728	0.0760	137.1	474	89.2	71.2	0.0151	0.02	0.0227
203	1123	728	0.1143	56.1	474	91.9	70.6	0.0226	0.03	0.0257
204	1123	728	0.2674	25.7	474	85.9	54.0	0.0403	0.06	0.0425
205	1202	728	0.2469	21.3	474	91.8	65.5	0.0451	0.06	0.0394
206	1202	728	0.2210	28.8	474	92.7	68.3	0.0422	0.04	0.0365
207	1278	728	0.1955	24.3	474	82.0	55.5	0.0303	0.04	0.0314
208	1278	728	0.4454	14.3	474	65.2	42.9	0.0533	0.11	0.0588
231	933	728	0.1471	94.5	474	90.9	76.2	0.0313	0.03	0.0296
232	1148	720	0.0841	150.6	474	93.0	70.1	0.0218	0.03	0.0215
233	1211	720	0.1559	68.9	474	93.4	70.4	0.0307	0.04	0.0287
234	1012	720	0.1075	99.2	474	89.4	78.2	0.0235	0.03	0.0261
221	1211	720	0.3897	29.6	474	71.1	46.3	0.0504	0.06	0.0540

APPENDIX A --continued

Table A.3 Response surface results for sodium with excess chlorine

Sodium capture by Kaolinite in the presence of excess chlorine: Na ~250 ppm, Cl ₂ ~700 ppm.										
Run No	Injection Temp(C)	Sample Temp(C)	ER(ϕ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ins) st1-7	Impactor (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
301	1349	679	3.1740	9.1	474	27.9	11.8	0.1044	0.12	0.0968
302	1349	679	1.5150	10.7	474	40.0	21.3	0.0900	0.11	0.0968
303	1196	679	0.3682	24.7	474	75.1	48.4	0.0498	0.06	0.0521
304	1196	679	0.2914	34.0	474	60.1	31.0	0.0489	0.08	0.0443
305	947	679	0.2302	18.3	474	89.0	62.9	0.0405	0.05	0.0376
306	947	679	0.2014	22.5	474	84.9	60.5	0.0340	0.04	0.0350
291	1236	724	0.3753	35.5	474	93.2	78.5	0.0522	0.09	0.0524
292	1236	724	0.4137	33.8	474	94.6	74.5	0.0561	0.12	0.0562
321	1000	690	0.2185	24.9	474	70.1	56.0	0.0342	0.04	0.0373
322	1000	690	0.2355	25.3	474	84.3	79.2	0.0521	0.06	0.03893
323	1000	690	0.1789	61.9	474	86.0	76.0	0.0380	0.04	0.0310
324	1230	690	0.5006	6.8	474	67.6	57.3	0.0801	0.09	0.0640
325	1230	690	0.4595	7.9	474	69.7	61.6	0.0670	0.09	0.0604

APPENDIX A --continued

Table A.4 Response surface results for sodium with excess chlorine

Sodium capture by Kaolinite in the presence of excess chlorine:Na ~250 ppm, Cl ₂ ~700 ppm.										
Run No	Injection Temp(C)	Sample Temp(C)	ER(ϕ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ins) st1-7	Impactor (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
326	910	690	0.3145	8.0	474	65.8	56.1	0.0493	0.05	0.0436
327	910	690	0.2465	16.5	474	73.4	67.7	0.0466	0.04	0.0382
331	850	690	0.3144	158.0	474	63.3	57.5	0.0505	0.05	0.0419
332	850	690	0.3952	7.0	474	63.5	42.9	0.0474	0.06	0.0462
333	940	690	0.5764	4.6	474	50.9	26.6	0.0428	0.07	0.0591
334	940	690	0.7146	3.6	474	48.9	24.0	0.0479	0.07	0.0628
335	1130	690	0.2608	649.7	474	90.9	64.9	0.0472	0.04	0.0434
336	1130	690	0.7456	3.6	474	48.2	37.3	0.0776	0.06	0.0766

APPENDIX A --continued

Table A.5 Response surface results for sodium with excess SO₂

Run No	Sodium capture by Kaolinite in the presence of excess SO ₂ : Na ~250 ppm, SO ₂ ~700 ppm; SR=1.2									
	Injection Temp(C)	Sample Temp(C)	ER(ϕ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ins)	Impactor Av. (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
161	865	689	0.6157	18.9	475	32.4	10.4	0.018	0.0091	0.0149
162	921	689	0.1472	62.5	475	43.4	19.8	0.0082	0.0031	0.0171
163	1016	689	0.1240	21.6	475	63.8	36.0	0.0125	0.0130	0.0229
164	1152	689	0.2059	25.1	475	79.6	51.0	0.0293	0.0480	0.0364
165	1228	689	0.2149	31.9	475	84.0	56.6	0.034	0.0484	0.0377
166	1301	689	0.2285	48.5	475	89.8	65.1	0.0415	0.0686	0.0377
171	1281	747	0.2636	54.9	475	81.9	52.5	0.0386	0.1100	0.0438

APPENDIX A --continued

Table A.6 Response surface results for sodium with excess SO₂

Run No	Sodium capture by Kaolinite in the presence of excess SO ₂ : Na ~250 ppm, SO ₂ ~700 ppm; SR = 1.2									
	Injection Temp(C)	Sample Temp(C)	ER(ϕ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ins)	Impactor Av. (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
172	1228	747	0.2424	44.8	475	82.6	53.6	0.0363	0.0677	0.0416
173	1174	747	0.2116	52.4	475	81.1	63.2	0.0374	0.0382	0.0374
174	1014	747	0.2196	48.9	475	77.3	54.6	0.0335	0.0349	0.0307
175	910	747	0.1490	98.1	475	78.5	54.9	0.0229	0.0146	0.016
251	1187	670	0.6314	31.7	475	92.8	49.4	0.0871	0.1297	0.0802
252	1187	670	0.6088	8.7	475	84.3	37.3	0.0634	0.0764	0.0785
253	1187	670	0.1838	36.8	475	91.5	59.5	0.0305	0.0419	0.0338
254	1187	670	0.1601	43.1	475	95.7	74.7	0.0334	0.0403	0.0306

APPENDIX A --continued

Table A.7 Response surface results for sodium with excess SO₂

Sodium capture by Kaolinite in the presence of excess SO ₂ ; Na ~ 250 ppm, SO ₂ ~ 700 ppm; SR = 1.2										
Run No	Injection Temp(C)	Sample Temp(C)	ER(ϕ)	Sample Qty (mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ins)	Impactor Av. (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
255	1187	689	0.3478	17.6	475	95.0	57.8	0.0562	0.0594	0.0539
256	1187	689	0.1496	70.1	475	98.7	73.3	0.0306	0.0395	0.0292
261	1298	740	0.3038	18.2	475	94.1	51.5	0.0437	0.0595	0.0496
262	1298	740	0.3658	18.1	475	98.0	57.8	0.0591	0.0797	0.0587
263	1298	740	0.1750	59.1	475	99.1	69.2	0.0338	0.0544	0.029
264	1073	740	0.2126	26.6	475	95.8	75.4	0.0448	0.0374	0.0342
265	1073	740	0.1005	67.9	475	96.1	81.0	0.0227	0.0275	0.0228
266	1167	740	0.1133	52.3	475	93.8	68.5	0.0217	0.0384	0.0245
267	1167	740	0.1235	67.4	475	95.3	74.3	0.0256	0.0233	0.0262
315	1061	694	0.1513	23.8	475	84.7	79.8	0.0337	0.0374	0.0277
316	1216	694	0.2054	17.9	475	88.8	85.7	0.0491	0.0578	0.0365

APPENDIX A --continued

Table A.8 Conditions for base response surface for sodium only, sodium with excess chlorine and sodium with excess sulphur runs.

Condition	Level
Sorbent type	Kaolin clay, Burgess Pigment Co, Ga. 1-2 μ m equivalent modal spherical size
Sorbent injection temperature range	850°C-1300°C
Sorbent sampling point	Port 11
Flue gas environment:	Excess O ₂ (SR = 1.2); 450-480 gm/min
Alkali Solution	Sodium Acetate, 0.2 M, 20 cc/min ~250 ppm Na
Excess Cl ₂ /SO ₂ flowrates:	250 cc/min ambient (21°C, 700 mmHg) ~ 500-700 ppmV

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