Improving Lime's Reactivity Towards Flue Gas Desulfurization by using Fly Ash, Bottom Ash and Waste Activated Sludge

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ABSTRACT

Lime reactivity was improved by blending it with either fly ash, bottom ash or waste activated sludge (W.A.S). The reactivity was tested using a pH-stat apparatus which simulates wet flue gas desulfurization (FGD). Temperature, solid to liquid ratio and stirring speed were varied in addition to lime to additive ratio in optimization tests. Design expert's central cubic design was used in the design of experiments to aid with regression analysis. Temperature had the highest effect whereas W.A.S was the best additive then fly ash and finally bottom ash. The results were confirmed by the use of fixed bed apparatus where the best sorbents from each additive was tested in dry FGD. In a bid to explain the results, BET surface area analysis was used where the sorbent from the blend of lime and W.A.S had the highest improvement in surface area.

Keywords: Lime, Pozzolan, Reactivity, Surface area

INTRODUCTION

South Africa is a comparatively energy intensive country. It is ranked 16th in the world in terms of the total amount of primary energy consumption, of which 75% of the total national energy needs is provided by coal (Pretoria, 2001). Coal, when combusted, release air pollutant which are harmful to the environment. Sulfur dioxide (SO_2) is one of these pollutants and of which is a prerequisite for acidic rain. This rain cause havoc both to the environment, vegetation and animals, humans included. Gauteng Highveld, where South Africa main coal-burning power stations are concentrated, is one of the most polluted areas in the world. In this region, annual emissions of SO_2 are estimated to reach 57 ton/km² (Dintchev etal, 1998). In 2005, coal accounted for 27% of world energy consumption. It is projected that there will be a 65% increase in world coal consumption by 2030 (Energy, 2008). For instance, in South Africa, three old coal-firing power stations (Camden, Grootvlei and Komati) with a combined capacity of 3800 megawatts are being reinstated and two new ones (Medupi and Project Bravo with 4800 and 5400 megawatts capacity respectively) being constructed to meet the increasing demand of electricity (Energy, 2010).

To beat the increase in acidic rain brought by increase in coal combustion, researchers strive to improve Flue Gas Desulfurization (FGD) methods. Improvements from

traditional limestone FGD processes have been possible through calcinations and hydration of the limestone. Additional improvement through use of hydration agents and pozzolanic materials has further increased the efficiency of FGD processes. Due to the demand of better FGD sorbents in terms of cost, efficiency and environmentally friendly end product, a lot of research is still on-going in this discipline. In this research, fly ash, bottom ash and waste activated sludge (W.A.S) are used to enhance the reactivity of slaked lime. These additives are waste products of power plants (fly ash and bottom ash) and sewage and industrial waste-water treatment plants (W.A.S). The use of these additives have two environmental benefits i.e. reduction of landfill (normally they are disposed off as landfill) and indirectly reduction of SO_2 in air which ultimately results in reduction of acid rain.

MATERIALS AND EQUIPMENT

Natural limestone was mined in South Africa whereas fly ash and bottom ash were provided by South Africa electric power producer (ESKOM) while W.A.S was provided by the Pretoria sewage treatment plant. The raw samples were crushed, ground and sieved to a particle size of utmost 200 μm. The limestone was further calcined in an electric furnace at 900 °C for 4 hours. The chemical analysis of the calcined limestone and the aditives is shown in table 1.

Table 1: chemical analysis of the materials

Compound	Percentage Present			
	Quick Lime	Fly Ash	Bottom Ash	W.A.S
Calcite	5.02	-	-	14.29
Quicklime	75.54	7.36	8.34	-
Alumina silicates	9.55	79.65	80.83	47.56
Hematite	1.78	5.99	5.10	-
Others	8.10	6.99	5.73	38.15

When strong acids like sulfuric acid or hydrochloric acid are used in the pH-stat, the reaction mechanism is close to that on a wet FGD plant equipped with air oxidation of the bisulfite ion (Siagi & Mbarawa, 2009). Recently, ASTM developed a standard test method for the determination of total neutralizing capability of dissolved calcium and magnesium oxides in lime for FGD (ASTM C: 1318-95). This method recommends an acid titration procedure. Figure 1 below shows the experimental apparatus used. 1.5 g of the sorbent was dissolved into 200 ml of distilled water. The solution was put in a water bath set at 60 °C with a resolution of ±1 °C. The solution was agitated by a stirrer rotating at 225 rev/sec. The pH in the beaker was measured by a pH electrode inserted in the solution and connected to a pH 200 controller supplied by Eutech Instruments with a resolution of ±0.01. A 1 M solution of HCl was titrated accordingly and the reactivity was determined from a recording of the volume of HCl added versus time. Each experiment was done at least twice and the average of the results taken.
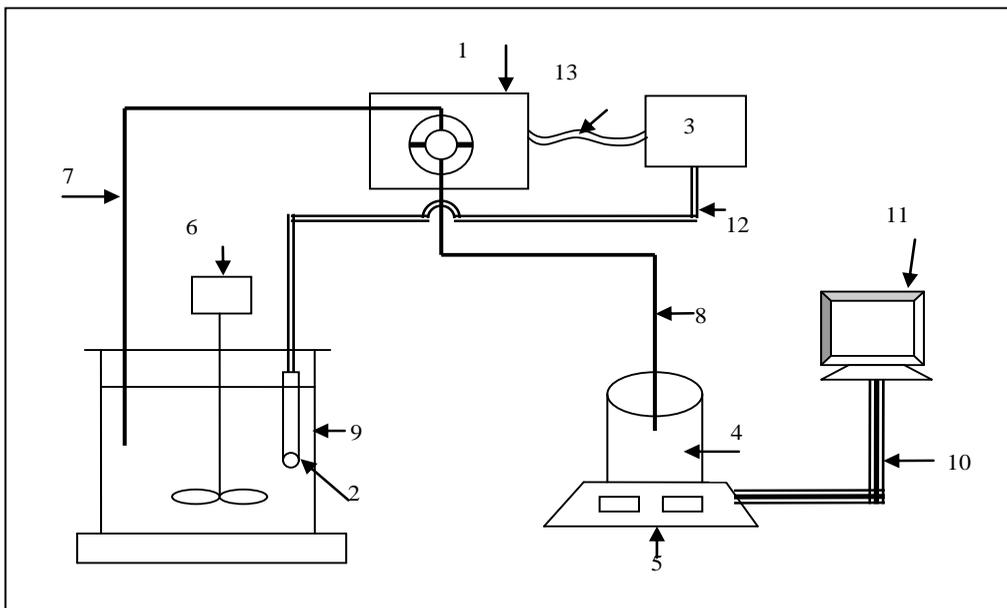
Figure 1: A schematic drawing of the experimental set-up. (1) Peristaltic pump, (2) pH electrode, (3) pH controller, (4) Acid solution Beaker, (5) Electronic balance, (6) Stirrer, (7,8) Plastic tubing, (9) Reaction vessel,(10) RS232 Cable, (11) Computer work station, (12) wiring for pH electrode, (13) Connection between pump and controller.

Models used to describe the heterogeneous non-catalytic solid-fluid reaction mechanism fall into three main categories(Marta, 2005):

- Grain models,
- Pore models and
- Deactivation models

The grain model is relatively simple and largely used to describe heterogeneous non-catalytic solid-fluid reaction. This model assumes that the porous solid is made up of small non-porous grains, and each of these grains is converted according to the shrinking unreacted core model. In shrinking unreacted core model, spherical particles making up the grains, are converted at a rate depending on the limiting step on which as derived and explained in (Levenspiel, 1999);

- If the chemical reaction is the rate-limiting step

$$\frac{t}{\tau} = \left[1 - (1-x)^{1/3}\right] \qquad (1)$$

Where the reactivity will be given by a plot of [1-(1-x)^(1/3)] versus time .

- If the diffusion through the product layer is the rate-limiting step

$$\frac{t}{\tau} = \left[3 - 3(1-x)^{2/3} - 2x\right] \qquad (2)$$

Where the reactivity will be given by a plot of [3-3(1-x)^(2/3)-2x] versus time .

- If the mass transfer through fluid film is the rate limiting step

$$\frac{t}{\tau} = x \qquad (3)$$

Where the reactivity will be given by a plot of x versus time.

Due to the nature of the experiments, the product layer will constantly be dislodged from the surface by the agitation therefore there will be minimum resistance due to diffusion through the product layer and thus it won't be the rate limiting step. Similarly, due to the

fact that the fluid media is liquid in nature, mass transfer through fluid film will have a minimum effect on the overall reaction, therefore it won't be the rate limiting step. Furthermore, a lot of literature with similar experiments states that this type of reaction is chemically controlled (Maina & Mbarawa, 2011). Hence the reactivity constant was calculated by assuming that these reactions were chemically controlled.

Mixtures of operatives affecting reactivity were varied statistically to bring out the effect of each operative clearly. In total all the operatives investigated were temperature, lime to aditive ratio, solid to liquid ratio and stirring speed. Table 2 below shows the maximum and minimum values of each operative. Design of experiments using design expert software was used in these experiments for regression analysis. Response surface methodology (RSM) is a statistical method in design expert that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions. A standard RSM design called the central composite design (CCD) is suitable for investigating linear, quadratic, cubic and cross product effect of the operatives. It also helps to optimize the effective parameters and provide a lot of information with a minimum number of experiments as well as to analyze the interaction between the parameters. In addition, the empirical model that relates the response to the operatives is used to obtain information about the process. CCD comprises a two level full factorial design ($2^4 = 16$), eight axial points and six center points. The center points were used to determine the experimental error and the reproducibility of the data. Alpha (α) value, which is the distance of axial point from the center, was fixed at 2 to make the design rotatable. The experiment sequence was randomized in order to minimize the effects of the uncontrolled factors. Each response of the reactivity was used to develop a mathematical model that correlates the reactivity to the absorbent preparation operatives through first order, second order, third order and interaction terms, according to the following third order polynomial equation:

$$Y = b_0 + \sum_{j=1}^{4} b_j x_j + \sum_{i,j=1}^{4} b_{ij} x_i x_j + \sum_{j=1}^{4} b_{jj} x_j^2 + \sum_{k,i,j=1}^{4} b_{kij} x_k x_i x_j + \sum_{j=1}^{4} b_{jjj} x_j^3$$

(4)

Where Y is the predicted reactivity, b_0 is the first (or intercept) term, b_j is the linear effect, b_{ij} is the first order interaction effect, b_{jj} is the squired effect, b_{kij} is the second order interaction effect, b_{jjj} is the cubic effect, x_i, x_j and x_k are coded operatives and n, the number of operatives in this case 4. Significance of the second-order model as shown in equation 4, was evaluated by analysis of variance (ANOVA). Insignificant coefficients were eliminated after the f (fisher)-test and the final model was obtained. Additional experiments were carried out to verify the predicted model and the associated optimal conditions.

Table 2: Range of operatives

Name	Units	Low	High
Temperature	deg C	40	80
Lime to diatomite ratio (lime mass in 1.5 g sorbent)	g	0	1.5
Solid to liquid ratio (volume of distilled water per 1.5 g sorbent)	ml	100	300
Stirring speed	rev/sec	100	350

To further compare the effect of additives on lime, sorption capacity and BET (Brunauer-Emmett-Teller) surface area analysis of sorbents with the highest reactivity from each additive was performed. Prior to sorption capacity and BET surface area analysis, the

sorbents underwent a thorough mixing process with respect to the optimum lime to additive ratio. Hydration process then followed, in that, 10 g of the sorbents were mixed with 100 ml of distilled water and placed in a water bath at 60 °C for 4½ hours. The resulting slurry was filtered and dried in an oven at 100 °C for 16 hours to produce a dry solid. It was then ground, milled, and sieved to a particle size of utmost 200 μm.

A laboratory-scale fixed bed reactor was used to simulate dry FGD and calculate sorption capacity. The reaction zone is contained in a 0.009 m inner diameter stainless steel tube fitted in a furnace for isothermal operation. 0.2 g of the sorbent material was packed in the center of the reactor supported by 0.03 g of glass wool. The reactor is heated up to 87 °C. A nitrogen gas (N_2) stream was passed through a humidification system consisting of two 750 ml conical flasks immersed in a water bath at a constant temperature to produce 50% humidity ratio depending on the partial pressure of the steam. This humidified stream was allowed through the reactor for 10 minutes to humidify the sorbent. Humidified sorbents are more effective for desulfurization because, SO_2 is hydrated by the adsorbed water molecules on the sorbent surface before reacting (Siagi, 2008). After humidification, the nitrogen gas was mixed with a stream of 1500 ppm of sulfur dioxide gas. The total flow rate was set at 300 ml/min. At exit, the flue gas composition was continuously monitored by an IMR 2800P flue gas analyzer with readings taken at an interval of 20 seconds. A blank run was initially tested with glass wool only in the reactor. Afterwards, the sulphation test was run with the hydrated sorbent loaded. The experiment was done at least twice and the average of the results taken. The total sorbent utilization (sorption capacity) was given by (Marta, 2005):

$$mol\ SO_2\ retained \Big/ mol\ sorbent = \left(A_{bl} - A_{exp}\right)C_0 10^{-6}\ \frac{\varphi_\upsilon}{23652}\ \frac{M_{sorbent}}{m_{sorbent}} \qquad (5)$$

Where A_{bl} is the area under the blank run, A_{exp} is the area under the reaction curve, C_0 is the inlet concentration of SO_2 (ppm), φ_v is the volumetric flow rate (ml/min^{-1}), 23652 is a volumetric constant depending on the operation conditions, $M_{sorbent}$ is the molar mass of the sorbent used and $m_{sorbent}$ is the mass of the sorbent.

For the surface area analysis, BJH (Barret, Joyner and Halenda) was applied to obtain the pore-size distribution from nitrogen desorption data. Adsorption measurements were performed on a micrometrics ASAP 2020 Surface Area and Porosity analyzer by the principle of physical adsorption. High purity nitrogen (99.99%) was used. The pore-size distribution is represented by the derivative $d(V_p)/d(d_p)$ as a function of pore diameter, where, V_p is the pore volume and d_p is the pore diameter. The samples were degassed before being used and characterized using a low temperature (- 196 °C) nitrogen adsorption isotherms measured over a wide range of relative pressures.

RESULTS AND DISCUSSION

Optimization process of various operatives affecting the reactivity of sorbents was analyzed by design of experiments in design expert software. Table 3 shows the experimental design matrix and response of the experiments in terms of the reactivity constant. The maximum reactivity achieved by using fly ash, bottom ash and W.A.S were 0.0003022, 0.0002955 and 0.0003244 per second, respectively. From these results, it is seen that W.A.S produced the best sorbents in terms of maximum reactivity.

A sorbent made of a blend of lime to W.A.S was tested in the fixed bed reactor and a sorption capacity of 0.239 mols of SO_2 per mol of sorbent was achieved. The author in (Ogenai, 2009) used the same lime and fly ash and bottom ash as the ones used here, and

in their results, the sorption capacity of their best blends with similar operating values and conditions as the one used here was 0.191 and 0.183 mols of SO_2 per mol of sorbent respectively. Without any additive, lime sorption capacity was found to be 0.107 mols of SO_2 per mol of sorbent. Furthermore, the W.A.S blend sorbent made here had a BET surface area value of 26.9 m^2/g while the similar fly ash and bottom ash blend sorbents in (Ogenai, 2009) had BET surface area values of 21.3 and 20.4 m^2/g. Lime without any additive had a surface area of 5.6 m^2/g. This proves that sorbents made from W.A.S are superior to those of fly ash or bottom ash and, sorbents with additives had higher qualities than sorbents without additives. It was also noted that increase in surface area was the cause of increase in reactivity and sorption capacity.

Table 3: Design of experiments matrix and its response

		VARIABLES				RESPONSE (Reactivity Constant)		
Run	Block	A: Temperature °C	B: Lime weight g	C: Vol of Water ml	D: Stirring Speed RPM	Fly Ash Per Sec	Bottom Ash Per Sec	W.A.S Per Sec
1	Block 1	60	0.75	200	225	0.00028674	0.00025244	0.00030238
2	Block 1	50	1.125	250	287.5	0.00026276	0.00024107	0.00028905
3	Block 1	70	1.125	150	287.5	0.00029297	0.00028732	0.00032147
4	Block 1	60	0.75	200	225	0.00028776	0.00025354	0.00030320
5	Block 1	50	1.125	150	162.5	0.00022111	0.0002093	0.00029266
6	Block 1	70	0.375	250	287.5	0.00029646	0.00028032	0.00030885
7	Block 1	50	0.375	250	162.5	0.00022006	0.00021834	0.00027506
8	Block 1	70	1.125	250	162.5	0.00027664	0.000277	0.00031538
9	Block 1	50	0.375	150	287.5	0.0002444	0.00023467	0.00028322
10	Block 1	70	0.375	150	162.5	0.00026977	0.00025846	0.00030887
11	Block 2	70	0.375	250	162.5	0.00027536	0.0002701	0.00030872
12	Block 2	50	0.375	150	162.5	0.0002136	0.00020634	0.00028221
13	Block 2	70	1.125	150	162.5	0.00027178	0.00026861	0.00031688
14	Block 2	50	1.125	250	162.5	0.00024105	0.00022267	0.00028875
15	Block 2	70	1.125	250	287.5	0.00030215	0.00029117	0.00031300
16	Block 2	60	0.75	200	225	0.00028727	0.00025299	0.00030143
17	Block 2	70	0.375	150	287.5	0.00029181	0.00027877	0.00031069
18	Block 2	50	1.125	150	287.5	0.00025849	0.000236	0.00029546
19	Block 2	50	0.375	250	287.5	0.00025145	0.00023916	0.00028124
20	Block 2	60	0.75	200	225	0.00028827	0.00025394	0.00030413
21	Block 3	60	0	200	225	0.00024786	0.00022957	0.00026255
22	Block 3	60	0.75	300	225	0.00027941	0.0002578	0.00029260
23	Block 3	60	0.75	200	350	0.00029824	0.00028724	0.00030538
24	Block 3	60	0.75	100	225	0.00026847	0.00024399	0.00030844
25	Block 3	60	1.5	200	225	0.00026722	0.00024354	0.00027346
26	Block 3	40	0.75	200	225	0.00019203	0.00019259	0.00027213
27	Block 3	60	0.75	200	225	0.00028677	0.00025434	0.00030288
28	Block 3	60	0.75	200	225	0.00028877	0.00025464	0.00030476
29	Block 3	80	0.75	200	225	0.00029095	0.00029553	0.00032440
30	Block 3	60	0.75	200	100	0.0002507	0.00024748	0.00029806

The increase in surface area was attributed to the complex calcium alumina silicates products which have superior surface area. The type of alumina silicates available in the additives dictates the amount of the reactive product being formed, therefore, W.A.S superiority might have being caused by the fact that it had more fine, hydrous and

amorphous alumina silicates than the other additives. Bottom ash had more alumina silicates than fly ash and W.A.S, but as it was seen in (Ogenai, 2009), these alumina silicates were in agglomerate and crystalline form compared to those in fly ash and W.A.S which are in amorphous form and thus more reactive.

From statistical point of view, there are three tests required to evaluate the model, these are, significance of factor test, R-squired test and lack of fit test. The significance test was indicated by the Fisher variance ratio (the F-test value) and its associated probability (Prob>F). The model equations were evaluated by F-test ANOVA which revealed that these regressions are statistically significant at 95% confidence level. As a general rule the greater the F-value is from unity, the more certain it is that the empirical model describe the variation in the data about its mean and the estimated significant terms of the adsorbent preparation operatives are real. The values of prob>F which are 0.05 or less indicate significance. Quadratic models were suggested to be the best because their prob>F were less than 0.05 (<0.0001). By using multiple regression analysis, the response (reactivity constants) obtained in table 4 were correlated with the four operatives studied using the polynomial equations shown in equations (5, 6 and 7) after excluding the insignificant terms identified using Fisher's test method.

Fly Ash: $Y_1 = 2.876 \times 10^{-4} + 2.341 \times 10^{-5}A + 4.282 \times 10^{-6}B + 3.495 \times 10^{-6}C + 1.276 \times 10^{-5}D - 1.153 \times 10^{-5}A^2 - 7.513 \times 10^{-6}B^2 - 3.413 \times 10^{-6}C^2 - 3.281 \times 10^{-6}D^2 - 2.735 \times 10^{-6}AB - 1.965 \times 10^{-6}AD$ (5)

Bottom Ash: $Y_2 = 2.536 \times 10^{-4} + 2.542 \times 10^{-5}A + 3.122 \times 10^{-6}B + 3.666 \times 10^{-6}C + 9.883 \times 10^{-5}D - 2.149 \times 10^{-6}A^2 - 4.025 \times 10^{-6}B^2 + 3.676 \times 10^{-6}D^2 - 1.62 \times 10^{-6}AB - 1.928 \times 10^{-6}AD - 1.903 \times 10^{-6}CD$ (6)

W.A.S: $Y_3 = 3.031 \times 10^{-4} + 1.337 \times 10^{-5}A + 3.983 \times 10^{-6}B - 2.628 \times 10^{-6}C - 7.559 \times 10^{-6}B^2$ (7)

Where A, B, C and D are as defined in table 4. The coefficient of the full regression model equation and their statistical significance were determined and evaluated using design expert software. Positive sign before terms indicate synergistic effect, while negative sign indicates antagonistic effect. The coefficients of the operatives in equations (5, 6 and 7) represent the magnitude of the effect the variable have on reactivity. This is also supported by the F value of the variable in the ANOVA analysis. The higher the coefficient, the higher the F value and the higher the effect of the operative in the reactivity. The first term, which represents the average reactivity for the sorbents made from each additive, shows that W.A.S had better sorbents than the other additives. R values are very high for the model (0.9982 for fly ash, 0.9995 for bottom ash and 0.9889 for W.A.S) therefore the variability of the responses could accurately be explained by the mathematical models of equations (5, 6 and 7). On the other hand, the values of R^2 for the models are 0.9964 for fly ash, 0.9991 for bottom ash and 0.978 for W.A.S, which implies that 99.64%, 99.91% and 97.8% of the total variation in the reactivity responses are attributed to the experimental operatives studied as stipulated by the models respectively. The models are further supported by the low value of their respective standard deviations (2.514, 1.153 and 3.387×10^{-6} respectively), the high value of Adequate Precisions (56.47, 117.19 an 25.48 respectively) and the closeness between their respective Adjusted R-squired and Predicted R-squired (0.9925 and 0.9722 for fly ash; 0.9982 and 0.9953 for bottom ash; and 0.9544 and 0.8833 for W.A.S).

The lack of fit test compares the residual error to the experimental error (pure error) from replicated design points. It is this test which was used to select the quadratic models over the linear models, whereby both of them had model Prob>F values of less than 0.05 (< 0.0001) but the lack of fit test for the linear models were significant whereas the lack of fit

test for the quadratic models were insignificant with F-values of 7.86, 4.41 and 7.46 for fly ash, bottom ash and W.A.S sorbents respectively. This implies that lacks of fit are not significant relative to their pure errors. Plots of predicted results and actual (experimental) results (fig 2 a, b and c) further validates the mathematical model due to their linearity with the line of unit slope (perfect fit with points corresponding to zero error). These plots prove that the models describe the connection between the operatives and output adequately within the range of the operatives being studied. Extra experiments at different operation conditions confirmed the accuracy of these models.

(a)

(b)

(c)
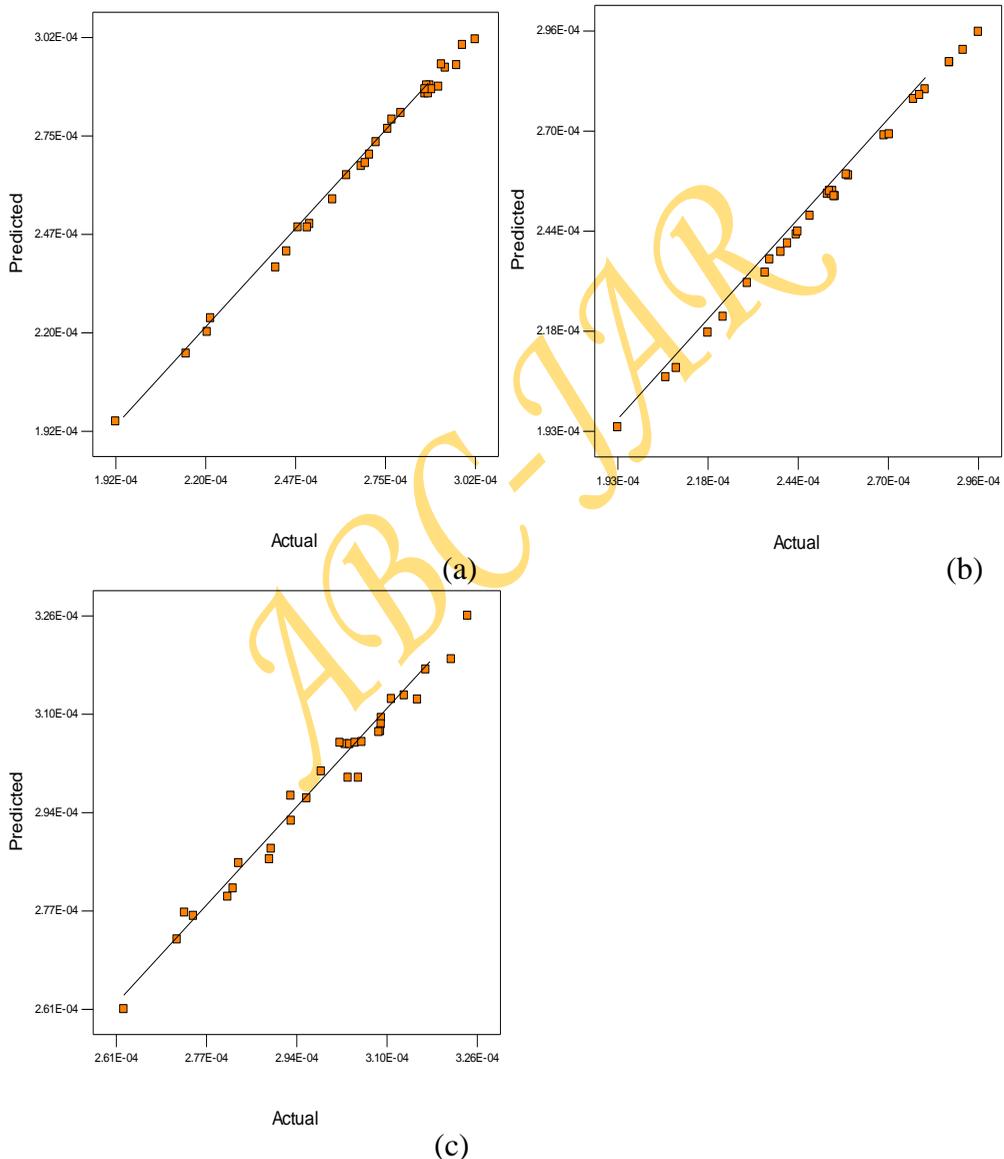
Figure 2: Model Predicted reactivity responses versus Actual (Experimental) reactivity responses in per sec. (a) Fly ash, (b) Bottom ash and (c) W.A.S.

Fig 3, 4 and 5 are 3D plots of interaction between operatives and their effect to reactivity for fly ash, bottom ash and W.A.S blended sorbents respectively. The X and Y-axis values of these figures are the real values. These response surfaces facilitate a straight-forward examination of the effects the operatives exert on the reactivity of the sorbent, especially with respect to the other operatives or in conjunction with them. The interactive effect of these operatives is very important in optimization process. Due to the fact that design experts uses axial points (alpha range of -1 to +1) to analyze the results, axial points value range was used in these diagrams instead of end point value range so as to give a clear interactive reactivity response. The units of the variables and response are as shown in table 2 and 3. Part (a) shows the response surface of the reactivity with varying temperature (A) and lime to additive ratio in terms of amount of lime in a 1.5 g of sorbent (B), the other two variables were held constant at their mid-levels. Part (b) shows the response surface of the reactivity with varying solid to liquid ratio presented by volume of distilled water per 1.5 g of sorbent (C) and stirring speed (D), temperature and lime to additive ratio being held at their mid-levels.

The response surfaces have different variation depending on the type of additive and the specific operatives being varied. For fly ash blended sorbents, all the operatives had a weak sinusoidal type of behavior towards the reactivity. Temperature and stirring speed had the largest effect on the reactivity of these blends as shown in fig 3 (a) and (b) respectively, where there is a large variation of reactivity with these operatives. Large temperature and stirring speed effects were also depicted by the model equation (5) where their linear coefficients were the highest. Similar behavior was observed with bottom ash blends in terms of temperature and stirring speed. Equation (6) also supported these observations concerning bottom ash blends. For W.A.S blends, only temperature had a major effect on the reactivity. Stirring speed and interaction effects on the reactivity weren't pronounced enough to be of use in these sorbents.

Temperature effect, which was the highest in all additives, has been reported to affect chemical reactions. Temperature has been found to increase reaction rates by either increase in activation rate or decrease in diffusion resistance. The strong effect of temperature can be a suggestion that chemical reaction is the rate limiting step (Ghosh etal, 1995). The authors in (Siagi & Mbarawa, 2009) stated that diffusion controlled processes are characterized by being slightly dependent on temperature while chemical controlled processes are strongly dependent on temperature. This statement is further supported by authors in (Ekmekyapar etal, 2008). Increasing the temperature is known to increase the rate of diffusion of molecules across external boundaries and internal pores owing to the decrease in viscosity of solutions. The enhancement of reactivity might be also due to increase in chemical interaction between the reactants, creation of new active sites, increase in mobility of reactants and increase in porosity and total pore volume at higher temperatures. The increase in pore volume and porosity might be due to temperature involvement in release of low-molecular weight reactants from the matrix structure resulting in pore development and porosity which increases the reaction surface area, resulting to higher reactivity (Hu etal, 2006). As it was seen earlier in this section, sorbent surface area plays a crucial role in its reactivity.
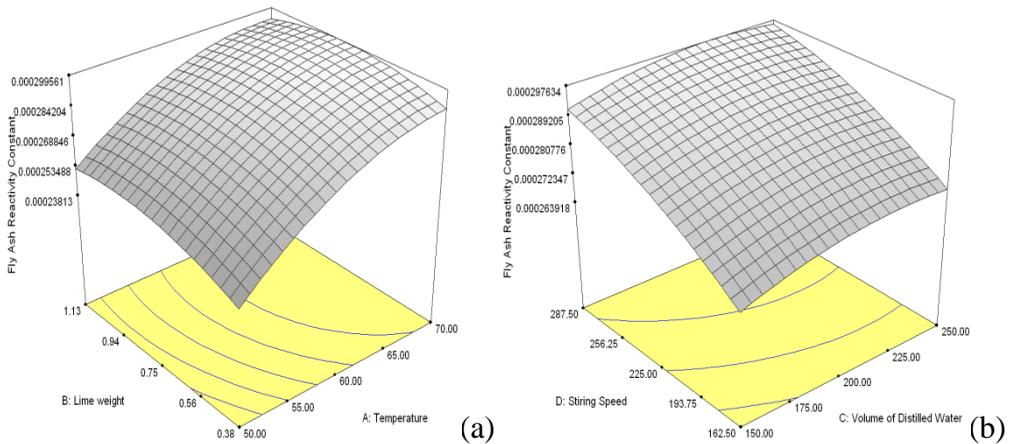
Figure 3: Interactive effect of fly ash operatives on the reactivity (a) temperature and lime to fly ash ratio, (b) liquid to solid ratio and stirring speed.
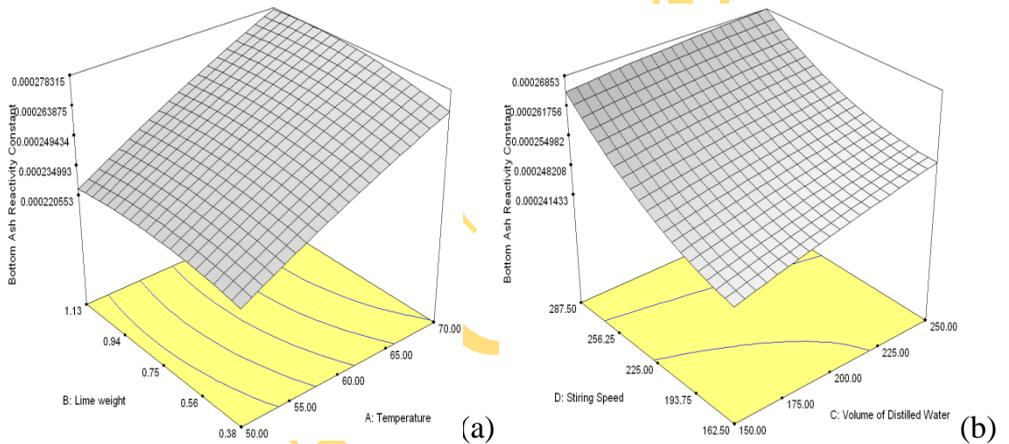
Figure 4: Interactive effect of bottom ash operatives on the reactivity (a) temperature and lime to bottom ash ratio, (b) liquid to solid ratio and stirring speed.
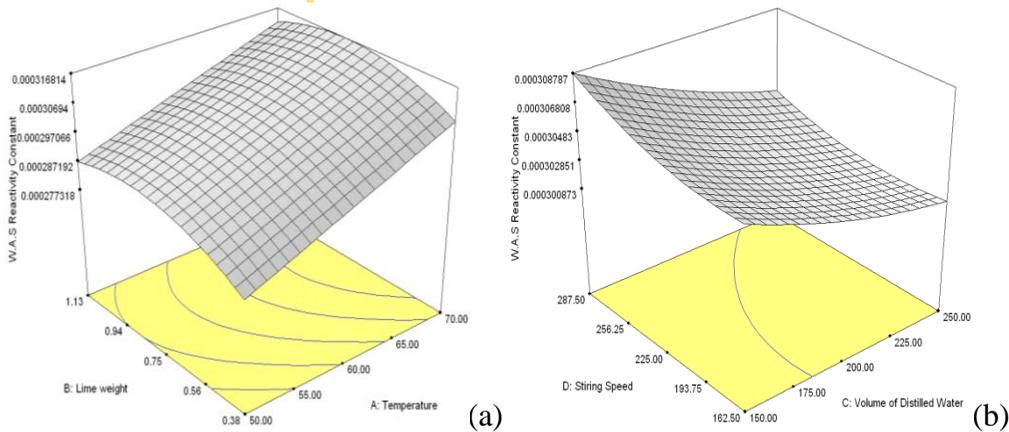
Figure 5: Interactive effect of W.A.S operatives on the reactivity (a) temperature and lime to W.A.S ratio, (b) liquid to solid ratio and stirring speed.

The increase in reactivity due to the temperature also can be explained by the exponential dependence of the reactivity rate constant in Arrhenius equation reported in literature(Siagi & Mbarawa, 2009). Reactions involving alumina silicates typically start with the digestion of vitreous alumina and/or silica by alkaline water. The dissolved alumina and/or silica will then react with lime to form reactive products. Therefore the increase in reactivity due to temperature can be due to the fact that higher solubility of alumina silicates increases with increase in temperature thus resulting in more pozzolanic products formed. Although at very high temperatures, this effect becomes detrimental probably because temperature, when too high, changes the physical and chemical properties of the reactants (Hu etal, 2006).

Lime to additive ratio as an operative, produce a sinusoidal behavior in relation to sorbent reactivity of all additives tested here. This means that, as the additive is added, reactivity increases until a maximum value is achieved, where the ratio between lime and additive is optimum. A further increase of additive leads to less overall reactivity. This behavior is influenced by the amount of pozzolans available to react with lime. The optimum amount of pozzolans in relation to lime available will produce sorbents with highest reactivity. The ratio of lime to additive generally determines the amount of raw materials available in the preparation mixture for formation of reactive species. As an additive is being added, it provides alumina-siliceous material which reacts with the lime to form complex compounds. As more additive is added, more alumina-siliceous material is available thus more reactive product which leads to more reactivity. The reactivity reaches its peak with an optimum lime to additive ratio, which means that all the available lime reacts with all alumina-silicates. Further increase in the additive began to be detrimental to the reactivity because there will be excess alumina-silicates than the available lime, therefore, less reactive products which ends up with less reactivity. This trend will continue until only the additive is available for reaction thus the least reactivity. This type of behavior has also been reported by other researchers dealing with similar experiments.

Solid to liquid ratio effects were not that pronounced. As the solid to liquid ratio reduce, the reactivity appreciates. The increment of reactivity due to the solid to liquid ratio has been reported in literature (Ekmekyapar etal, 2008). A possible explanation is; increase in the amount of solid per unit liquid volume reduces dissolution rates (Aphane, 2007). Finally, stirring speed had a major effect especially on sorbents made from fly ash and bottom ash. Agitation caused by stirring enhances convective mass transfer between reactants thus promoting the reaction (Xiang etal, 2009). Apart from the effects in the mass transfer, agitation also assists in detaching and removing the product layer therefore greatly reduces resistance due to product layer (DemirkIran, 2009). At high speeds, the turbulence becomes excessive that it impacts negatively on the reaction. On the other hand, very slow stirring speed do not enhance reactivity due to the inability to keep particles in suspension and sustain a realistically homogenous solution (Aydogan etal, 2006), thus an optimum stirring speed is important for maximizing reactivity, though for W.A.S, this operative effect was negligible.

CONCLUSION

W.A.S was found to be more effective in augmenting lime's reactivity when compared to fly ash and bottom ash. This result was confirmed by two different experiments, one using pH-stat apparatus and the other using fixed bed apparatus. BET surface area analysis approved the hypothesis that increase in surface area due to pozzolanic reactions in these sorbents is responsible for improvement of reactivity. Among the operatives, temperature

had the maximum effect, while stirring speed had a high effect in fly ash and bottom ash sorbents but a negligible effect in W.A.S.

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