Investigating the Pozzolanic Potentials of Cowdung Ash in Cement Paste and Mortars

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Abstract
This paper reports on the investigation into the pozzolanic potentials of cowdung ash. Cowdung was calcined at a temperature range of 400-500℃, sieved through 212µm sieve and characterized using chemical and physical methods. Cement paste and mortar were produced using CDA as cement replacement at 0, 5%, 10%, 15%, 20%, 25% and 30%. Standard consistency, soundness and setting time test were conducted on the blended cement paste, while compressive strength test was conducted on the hardened mortar samples after curing for 7, 28, 60 and 90days. The sum of SiO_2, Al_2O_3 and Fe_2O_3 in CDA exceeds the 70% minimum specified by ASTMC 618-12. The test results revealed that addition of CDA to cement paste prolonged the setting time and increased standard consistency, while the compressive strength decrease with increase in CDA and increase with curing age. One way ANOVA conducted on the strength results indicates that there was no statistically significant difference between control mortar (0% CDA) and those containing up to 15% CDA. Linear regression model developed to predict compressive strength with cowdung ash and curing age as predictors was highly significant.
Keywords: Cement, Compressive strength, Cowdung ash, Mortar, Pozzolana, Regression model, Setting times.

1. Introduction

Concrete is one of the most widely used construction material worldwide and there is an increase in the production of concrete to meet the ever-increasing demand for housing and other infrastructure. Cement, which is the main binder in the production of concrete, mortar, sandcrete blocks and other cement products, is very expensive particularly in developing countries [1]. The exorbitant and steadily increasing cost of cement has made concrete, mortar, sandcrete blocks and other cement products expensive and consequently increasing the cost of construction of houses and other infrastructure that uses cement.

Besides the exorbitant cost of cement, its production requires very high temperatures of about 1500℃ which requires enormous amount of energy which is expensive to attain and maintain [2]. The activities of cement producing companies have depleted the natural environment and huge amount of poisonous gases such as CO_2, NO_x, e.t.c are released into the atmosphere causing environmental pollution. These gases are also responsible for depletion of the ozone layer which is responsible for global warming [3].

All the aforementioned challenges have necessitated the need to intensify the search for supplementary cementitious materials (SCMs) for utilization as partial substitute for cement. Several notable researchers have proven that the utilization of SCMs like Sawdust Ash (SDA), Rice husk Ash (RHA) as partial replacement of cement in concrete and mortar is successful [4]-[5]. The use of SCMs has also been established as one way of reducing the amount of CO_2 emissions and embodied energy usage associated with in cement production [6].

Cowdung is the undigested residue of plant matter which has passed through the animals (cow) gut. It has been reported that the faecal material is rich in nitrogen, calcium, carbon, potassium and phosphorus [7]. A full grown well fed cow produces between 10-15kg of cowdung per day which contains about 28% water in its fresh state and 34% ash when calcined[8]. The world cattle population is estimated at 1.4 billion [9]. Nigeria has an estimated cow population of 16 million and is expected to produce an estimated 264,000tons of cowdung per day [10]. In many parts of the world, cowdung is predomominantely used as green manure for farming. It is also used with adobe in brick production, insect repellant and more recently used to produce biogas for electricity and heat generation. It can be duely noted that despite its application in the aforementioned areas, its production outweighs the usage [11]-[12].

Reference [13] studied the effect of cowdung ash in cement paste and concrete. Their results reveal a decrease in compressive strength with increasing ash content. Workability, Setting times and Standard Consistency increased as the CDA content increases. Another study also investigated the possibility of using CDA as partial cement replacement material in the production of concrete [14].Their findings showed that cement replacement with CDA beyond 10% adversely affected its compressive strength. All the aforementioned study did not cure concrete specimens beyond 28days which is essential for assessing the pozzolanic potentials of CDA. Therefore, the aim of this study is to investigate the pozzolanic potentials of CDA with a view on the possibility of using it as a cement replacement material in mortar production.

2. Material and Methods

The cow dung used for this study was collected from four (4) different cow excreta points between Yelwa and Birshi- Miri in Bauchi State, North East Nigeria. It was sundried, pulverized and calcined by controlled burning at a temperature range of 400-500℃. After cooling, the resultant ash was grinded into finer particles using mortar and pestle and was sieved using a 212µm sieve. Ashaka brand of Ordinary Portland cement was used for the study. River sand used for the study was obtained from a stream at bayara in Bauchi. The sand is free from deleterious materials and falls within zone 2 of BS 882(1979) classification chart with a bulk density of 1528kg/m^3 and a specific gravity 2.62. Pipe born water fit for drinking was used for the study and as such no test was conducted on the water.

2.1 Characterization of cowdung ash, CDA

Characterization of the cowdung ash was done by Physical and Chemical methods. Chemical analysis of the ash was done by X-ray Fluorescence (XRF) spectrometer (Axios Cement Panalytical B.V 7602 Ea Almelo the Netherland). The loss on Ignition and Blaine fineness of CDA was determined in accordance with BS 4550: Part 3: 1978 specification, while the specific gravity of CDA is determined in accordance with ASTM C188-1995. The chemical and physical properties of CDA and Cement are presented in Tables 1 and 2 respectively.

2.2 Test on CDA/OPC Blended Paste.

2.2.1 Standard Consistency of CDA/OPC blended Paste.

The Standard consistency of the blended paste was determined as per ASTM C 143-1978. CDA of 0,5,10,15,20,25 and 30% was used to replace cement. Table 3 shows the result of Normal consistency test on the blended cement.

2.2.2 Setting times and Soundness of CDA/OPC paste.

Fresh pastes were prepared using the standard consistency results obtained. Cowdung ash (CDA) was used as cement replacement at 0, 5%, 10%, 15%, 20%, 25%, and 30%. Setting times and Soundness tests were conducted of each of the seven (7) mixes. The tests were performed in accordance with BS 12(1978) specification. The test results are presented in Table 3.

2.3 Test on Mortar

To study the effect of CDA on the properties of Mortar, the strength activity index (SAI) and compressive strength test were conducted on mortar containing CDA at 0,5,10,15,20,25 and 30% by weight of cement.

2.3.1 Strength Activity Index (SAI)

This is the ratio of 20% replacement levels of cement with CDA to the control expressed as a percentage. The Strength Activity Index (SAI) test was conducted in accordance with ASTM C 311-12.The test for strength activity index is used to determine whether the pozzolan will result in an acceptable level of strength development when used with hydraulic cement in concrete. The test result is present in Table 4

2.3.2 Compressive Strength of OPC/CDA Mortar.

To study the effect of CDA on the compressive strength of mortar, a mix ratio of 1:2.6 was used. The mix had cement content of 300kg/m^3, fine aggregate of 776kg/m^3 and a water binder ratio of 0.55. Seven (7) different mixes were used containing CDA as cement replacement levels of 0,5,10,15,20,25 and 30 percent. Three cubes were crushed at the end of each curing period using the compressive strength test digital machine (TQ SM 100) and the average crushing strength recorded. A total of 84 mortar cubes of 50mm were cast and cured for 7, 28, 60 and 90days.

3. Results and Discussion

3.1 Chemical Composition of CDA.

The results of Chemical analysis of Cowdung ash is presented in Table 1. The result reveals that the constituents of CDA are similar to those of Ordinary Portland cement but with varying quantities. For instance, PC contained more of the main oxides of CaO, Al_2O_3, and Fe_2O_3 than CDA. This implies that with increasing CDA in the blend with cement, there will be reduction in tricalcium silicate (C_3S), tricalcium aluminates (C_3A) and Tetracalcium Aluminoferrite (C_4AF) (calculated using Bogue formula). These compounds are largely responsible for initial setting and early strength development [15]. It can also be seen that as expected amorphous silica forms more than 60% of each of the four CDA samples analyzed. The sum of the oxides of Silicon, Iron and Aluminum is 76.91% which exceeds the 70% minimum specified for pozzolana by ASTM C618-12. The combined alkali (Na_2O+K_2O) in CDA is 3.5%, which is low and thus reduces the possibility of the destructive aggregate alkali reaction which causes disintegration of concrete [16]. The SO_3 of 1.36% present is below the 4% maximum specified by ASTM C 618-12. This indicates that CDA may improve durability and prevent unsoundness when used in mortar and concrete [17].

3.2 Physical Properties of Cowdung ash (CDA) and Ordinary Portland cement (OPC).

The comparison of the physical properties of OPC and CDA is shown in Table 2. The specific gravity of CDA is about 20% less than that of PC. This implies that more volume of CDA will be required to replace an equal weight of Cement. CDA is seen to be finer than OPC and will certain increase the surface area of cementitious materials available for hydration. The loss on ignition (LOI) of cowdung ash is 12.28%, which exceeds the maximum of 10% specified by ASTM C618. The concern of the high LOI of CDA is that it may affect the reactivity of the cowdung ash in mortar or concrete and may increase the water requirement of the concrete or mortar due to the presence of impurities [18]. The pH of CDA is 9.5, this value shows that the CDA is neither Acidic (pH<7.0) nor alkaline (pH>11) but neutral (pH of between 7-9). This implies that CDA can be used in concrete without affecting its durability [19].

3.3 Standard Consistency of CDA/OPC Paste.

The effect of cement replacement with CDA on standard consistency of the OPC/CDA blended paste is shown in Figure 1. The result showed that the standard consistency increases as the CDA content increases. There was an increase of 3.2%, 17.7%, 24.20%, 41.9%, 48.4% and 54.8% in water required to achieve standard consistency at 5%, 10%, 15%, 20%, 25 and 30% CDA addition respectively. This trend may be due to the finer particles of CDA which are finer than those of cement and consequently increase the surface area available for contact with water thereby increasing the water demand of the OPC/CDA blended Paste [20]. This means that with the addition of more and more CDA, an increasing amount of water in required to achieve the desired consistency.

3.4 Setting Times of OPC/CDA Paste

Setting times (Initial and final) test results conducted on the OPC/CDA paste are presented in Table 3 and Figure 2. It can be observed that both initial and final setting times increase as the percentage of CDA in the blended cement increases. This means that the addition of CDA causes a retardation of the setting times of the blended cement. This trend may be attributed to the ability of CDA to delay the hydration of cement and consequently prolong the setting times [21].Therefore CDA has the potential to decrease the heat of hydration (of cement) which is beneficial for use in hot weather (high temperature) concrete works. This observation was also made by [22].

3.5 Soundness of OPC/CDA Paste.

The purpose of the soundness test is to assess the possible risk of late expansion due to hydration of uncombined calcium oxide and/or magnesium oxide. Table 3 shows the result of soundness test on the blended cement. Soundness is an important property as it is essential that after setting of the cement paste or concrete, there should be no appreciable expansion or change in volume [23]. The result reveals that incorporation of CDA decreased the expansion from 2.0mm(for control sample) to 0.85mm(for 15% CDA). The values of soundness obtained fall within the acceptable limit specified by BS 12(1978). This implies that CDA may be used for applications as cementitious material without recourse to delayed expansion.

3.6 Strength Activity Index (SAI)

Strength Activity index test is often used to determine if the supplementary cementitious material will result in an acceptable level of strength development when used in conjunction with hydraulic cement. The result of this test is presented in Table 4. Strength activity index of CDA was determined to be 77.6% which exceeds the 75% minimum specified by ASTM C 618 for pozzolana.

3.7 Compressive Strength of OPC/CDA Mortar.

The result of compressive strength test on the OPC/CDA blended cement mortar is presented in Table 5 and shown in Figures 3 and 4. The result reveals that the compressive strength decreases as the CDA content increases. For instance, 5% CDA gave 91%, 82%, 91% and 92% of the compressive strength of the control specimen at the end of 7, 28,60 and 90 days of curing respectively. Similarly, 10% CDA gave 85%, 77%, 76.2% and 88% of the compressive strength of the corresponding control specimen at the end of 7, 28,60 and 90 days of curing respectively. Similar trend was observed for other CDA levels of replacement. This behavior may be attributed to the reduction of the strength forming compounds (C_3S and C_3A) in the blended cement through partial replacement of cement with CDA. However, it can be observed from Figure 4 that compressive strength increases as the curing period is prolonged irrespective of the amount of CDA used as cement replacement. It can be seen that the increment in strength is more appreciable at the later curing ages (i.e. 60 and 90 days) than at the early curing periods of 7 and 28days. For instance the compressive strength of 5% CDA cured for 7days was 11.51N/mm^2.This value increased by 35%, 79% and 101% at the end 28days, 60days and 90days respectively. Similarly, the compressive strength of 10% CDA after 7 days was 10.72 N/mm^2 also increased by 34%, 61% and 106% at the end of 28days, 60days and 90days respectively. An explanation to this trend may be due to the pozzolanic activity of CDA. During hydration, the Calcium Hydroxide (CH) produced reacts with the silica from CDA over time to form the more stable Calcium Silicate Hydrates(C-S-H) which is responsible for the appreciable strength gain at the end of 60 and 90days[24]. It has been reported by several researchers that incorporation of pozzolanic materials into cement reduces the CH formation (which promotes micro cracking) and enhances formation of C-S-H, which promotes later strength gain [25].

3.8 Statistical Analysis on the Compressive Strength results.

The statistical analysis on the compressive strength was carried out using the Minitab Statistical software (Minitab 15). One-way analysis of variance (ANOVA) at 5% level of significance was carried out on the compressive strength data. The purpose of the one way ANOVA is to determine whether there is a statistically significant difference between the means of compressive strength at different CDA additions. The results are presented in Table 6. The significance level for CDA additions of 5%, 10% and 15% were 0.549, 0.351, and 0.154 respectively. These values are more than the selected level of significance of 5%(P=0.05). Therefore, there is no statistically significant difference in compressive strength between control mortar (0% CDA) and those containing up to 15% CDA ($p>0.05$). The P-values (significance level) at 20%,25% and 30% CDA reveals that there is a statistically significant difference in compressive strength when compared with the control samples($p<0.05$). This implies that no more than 15% CDA may be used as cement replacement in the production of Mortar.

Linear regression model was fitted based on the compressive strength results test data. The cowdung ash and curing period are considered as the independent variables (source of variation) while the compressive strength is the dependent variable.

The computation of the regression analysis is presented in Table 7 and the regression model is given by :

$$f_c = 14.6 + 0.112a - 0.380b \quad (1)$$

R^2=95.8% Where a and b are curing period and cowdung ash content respectively. From the P values obtained from the regression analysis, it can be seen that the cowdung ash and curing period have significant effect on the compressive strength of mortar ($P<0.05$) and thus are useful predictors of the regression model. The coefficient of variation of the fitted model given in equation one (1), i.e. R^2 is 95.8%. This implies that 95.8% of variation in the compressive strength is explained by the regression model with curing age and CDA content as variables. This shows a perfect correlation and the generated model is highly significant.

5. Conclusion

The following conclusion can be drawn from the results of the study:

1) Based on the chemical composition, cowdung ash can be classified as a class N pozzolan according to ASTM C618-2012 specification
2) The Strength Activity Index of CDA is 77.6% which exceeds the 75% minimum set by ASTM C618-2012 and thus CDA can be used as a Supplementary Cementitious Material for mortar and Concrete Production
3) Due to the moderate Calcium carbonate content in CDA (22.4%-23.6%), it has potential for application as raw feed in cement production.
4) More water is required to achieve the standard consistency as the amount of CDA increases.
5) The use of CDA as cement replacement in mortar has the potential to reduce the risk of late expansion.
6) Incorporation of CDA prolonged the initial and final setting times of the blended cement paste by a range of 12%-59% and 3%-44% respectively; hence it has the potential to be used as a set retarder in hot weather concrete works.
7) Compressive strength decreases as the CDA content increases and increases as the curing period is prolonged.
8) With strength as a criterion, CDA of no more than 15% can be used to produce good and quality mortar and concrete.
9) Cowdung ash addition of no more than 15% resulted in significant long-term increase in compressive strength.
10) The compressive strength is related to the CDA content and Curing age by the expression: $f_c = 14.6 + 0.112a - 0.380b$,Where a and b are curing period and cowdung ash content respectively.
11) The coefficient of variation of the regression model of 95.8% is high; therefore cowdung ash and curing age are useful predictors of the proposed regression model.

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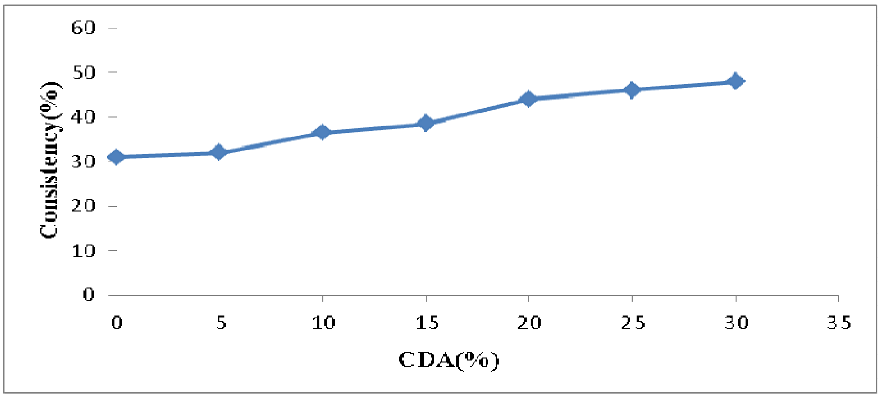

Fig.1: Plot of Standard Consistency versus Cowdung ash (%)

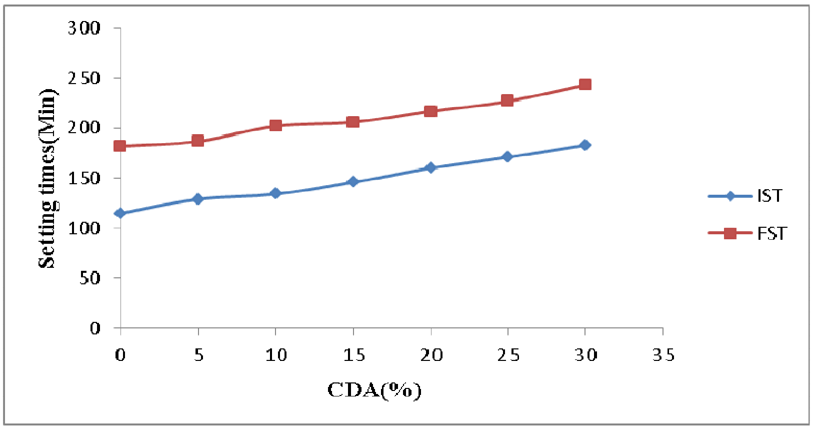

Fig.2: Plot of setting times versus Cowdung ash (%)

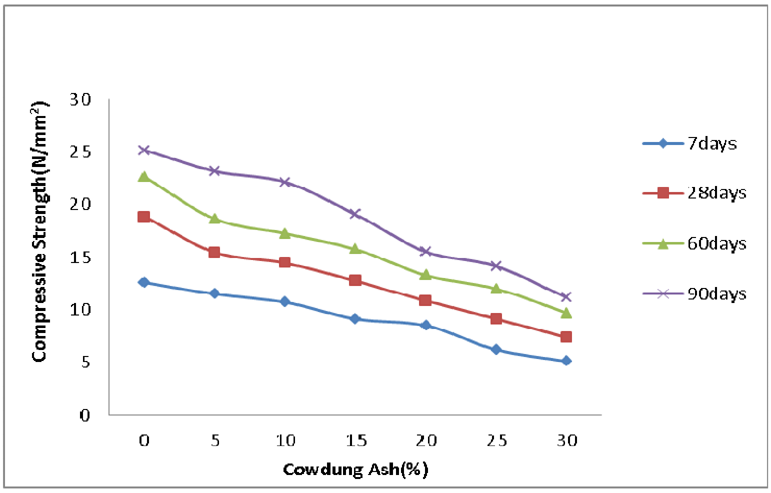

Figure 3: Plot of Compressive strength versus cowdung ash

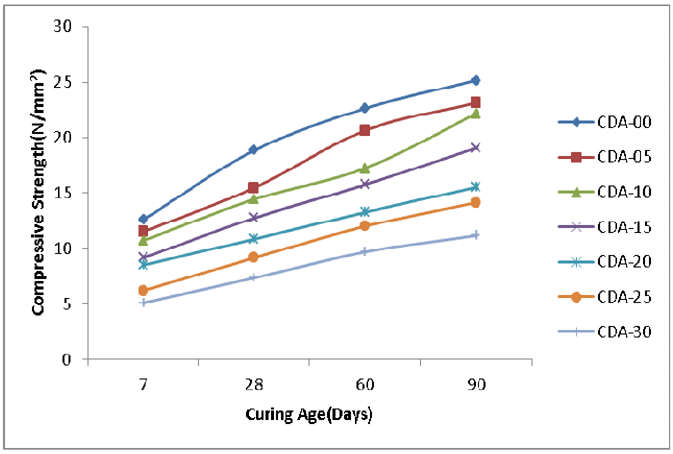

Figure 4: Plot of Compressive Strength versus Curing Age (Days)

Table 1: Chemical Composition of Cow Dung Ash (CDA) and Ashaka Portland Cement (OPC)

Oxide Composition	Percentage Composition					
	Source 1	Source 2	Source 3	Source 4	Average	OPC
S_iO_2	69.76	69.65	61.786	61.866	65.7655	20.26
Al_2O_3	4.74	4.27	5.206	3.614	4.4575	6.30
Fe_2O_3	3.18	2.99	3.978	2.502	3.1625	3.26
CaO	13.25	12.55	13.307	12.852	12.98975	65.51
MgO	2.12	2.22	1.779	1.952	2.01775	0.96
SO_3	0.89	1.36	0.705	0.807	0.9405	0.69
K_2O	2.71	2.94	2.674	3.011	2.83375	0.88
Na_2O	0.611	0.56	0.388	0.485	0.511	0.89
P_2O_5	1.37	1.48	1.215	1.466	1.38275	0.25
Mn_2O_3	0.62	0.63	0.565	0.582	0.59925	0.21
TiO_2	0.38	0.34	0.443	0.312	0.36875	0.24
$CaCO_3$	23.64	22.40	23.751	22.938	23.18225	-
$SiO_2+Al_2O_3+Fe_2O_3$	77.68	76.91	70.97	67.982	73.3855	-

Table 2: Physical Properties of Cow Dung Ash (CDA) and Ashaka Portland Cement (OPC)

Property	CDA	Ashaka Cement
Specific Gravity	2.55	3.15
Loss on ignition (%)	12.28	1
Blaine Fineness(m^2/Kg)	338	370
pH	9.5	-

Table 3: Setting Times and Soundness of OPC/CDA Paste.

Mix ID	Standard Consistency (%)	Soundness (mm)	Setting Times(Min)		Retardation relative to control (Min).	
			Initial	Final	Initial	Final
CD-00	31.0	2.0	115	182	0	0
CD-05	32.0	1.65	129	187	14	05
CD-10	36.5	1.00	134	202	19	20
CD-15	38.5	0.85	146	206	31	24
CD-20	44.0	1.5	160	217	39	35
CD-25	46.0	1.5	171	227	56	45
CD-30	48.0	2.0	183	262	68	80

Table 4: Test result of Strength Activity Index at 7days

Mix ID	Compressive Strength(N/mm^2)	Average Comp. Strength(N/mm^2)
CDA-00-01	14.80	
CDA-00-02	14.40	14.61
CDA-00-03	14.64	
CDA-20-01	11.16	
CDA-20-02	11.60	11.32
CDA-20-03	11.20	

$$SAI = \frac{11.32}{14.61} = 77.48$$

Table 5: Compressive Strength test results for OPC/CDA blended Concrete(N/mm^2)

Mix ID	7days	28days	60days	90days
CDA-00	12.61	18.84	22.63	25.16
CDA-05	11.51	15.48	20.64	23.18
CDA-10	10.72	14.44	17.24	22.14
CDA-15	9.16	12.76	15.76	19.06
CDA-20	8.52	10.86	13.28	15.53
CDA-25	6.22	9.17	12.01	14.14
CDA-30	5.13	7.37	9.70	11.18

Table 6: Analysis of one way ANOVA for the Compressive strength results Significance level of 5%

Mix- ID	MeanCompressive Strength	F	P	Remarks
CDA-00	19.810	-	-	-
CDA-05	17.690	0.315	0.595	Not Significant
CDA-10	16.135	1.020	0.351	Not Significant
CDA-15	14.185	2.657	0.154	Not Significant
CDA-20	12.048	6.188	0.047	Significant
CDA-25	10.385	8.533	0.0266	Significant
CDA-30	8.345	14.273	0.0092	Significant

Table 7: Regression Analysis of Compressive strength.

Predictor	Coeff	SE Coeff	T	P	Significance
Constant	14.62	0.5030	29.08	0.000	Yes
a	0.111	0.006863	16.25	0.000	Yes
b	-0.379	0.002164	-17.54	0.000	Yes
Basic ANOVA					
Source	DF	SS	MS	F	P
Regression	2	749.98	374.99	285.96	0.000
Error	25	32.78	1.31		
Total	27	782.76			