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Kinetic Studies of the Desulphurization of a Nigerian Coal Sample Using Sulphuric Acid and Hydrogen Peroxide

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Abstract:

The kinetics of desulphurization of Onyema coal with hydrogen peroxide and sulphuric acid solutions was studied in this work. The influence of temperature, concentrations of hydrogen peroxide and sulphuric acid as well as particle size, were studied. It was found that the dissolution curves for total sulphur follow the kinetic model of the shrinking core model, with diffusion through the product layer as the rate-determining step. The calorific value of the coal sample was relatively unaffected. The desulphurization reaction followed the pseudo-first order kinetics. The process activation energy, enthalpy, entropy and free energy are $-11.19 \text{ kJ mol}^{-1}$, 8.43 kJ mol^{-1} , $-22.32 \times 10^{-2} \text{ kJ mol}^{-1}$, and $74.97 \text{ kJ mol}^{-1}$ respectively. The negative activation energy indicates a complicated process mechanism. The positive free energy can be attributed to the steric hindrance by large aromatic rings present in the coal. The findings from the experimental tests showed that the desulphurization process of coal was best achieved with hydrogen peroxide stabilized with dilute sulphuric acid. The reaction kinetics can be described by the semi-empirical model:

$$1 - \frac{2}{3} X_B - (1 - X_B)^{2/3} = 0.467 C_{[H_2SO_4]}^{-0.133} (H_2SO_4 / H_2O_2)^{-0.110} (p)^{-0.304} \exp(-1345/T) t.$$

Keywords: Coal, kinetics, sulphuric acid, hydrogen peroxide, desulphurization

1. Introduction

Coal is the world's most abundant and widely distributed fossil fuel. It is a global industry that makes a significant economic contribution to the global economy (Anudhyan, 2009). Throughout history, coal has been used as an energy resource, primarily burned for the production of electricity and heat, and is also used for industrial purposes, such as refining metals. Coal is a common source of carbon and is composed primarily of carbon along with variable quantities of other elements chiefly hydrogen, sulphur, oxygen, and nitrogen (Excerpts from Rock Talk, 2005; Blander, 2011; & Pathak, 2014). Much of the world's coal contains hazardous concentrations of sulphur (Excerpts from Rock Talk, 2005). Coal and fuel oils have the largest content of sulphur (Lenior, 2009). Coal combustion is known to release the highest levels of pollutants such as sulphur oxides (SO_x), nitrogen oxides (NO_x), particulates and trace elements. During the burning of sulphur containing fuels at high temperatures with oxygen concentrations typical of combustion, sulphur combines with carbon, hydrogen and oxygen to form sulphur dioxide (SO₂), sulphur trioxide (SO₃), sulphur monoxide (SO), carbon sulphide (CS) – carbon disulphide (CS₂), carbon monosulphide (CS), carbon subsulphide (C₃S₂), methane (CH₄), carbonyl sulphide (COS), hydrogen sulphide (H₂S), elemental sulphur (S) and diatomic molecular sulphur (S₂) (Lenior, 2009). According to the Integrated Pollution Prevention and Control, Joint Research Centre (2006), another aspect of sulphur species and particularly H₂S is its toxicity to life and environment. Chemical desulphurization of coal is a hydrometallurgical process, typically heterogeneous that aims at reducing the quantity of sulphur dioxide released into the atmosphere during coal utilization processes. The knowledge of the kinetics is crucial for the design and development of these processes. Quantitative modelling of reactive solids behaviour in liquids is a big challenge. The reaction mechanism can be a very complex one, often comprising several unknown elementary steps. The structure and structural changes of the solid material are also often difficult to determine. Kinetics and mass transfer effects are coupled in the determination of the intrinsic kinetics (Grénman, et. al, 2011). In most hydrometallurgical processes, high level of extraction is achievable at high oxidation potential (Adebayo, et. al, 2003). Kinetic studies have been carried out using various coal desulphurisation techniques in a bid to achieving an affordable and effective method of coal sulphur removal. Vestal & Johnston, (2006) in their study used a non-isothermal desulphurization technique to satisfactorily determine theoretical interpretations, and

identify sets of chemical reactions which are responsible for desulphurization. Amer, (2011) in another study found that the dissolution curves for pyritic sulphur followed the kinetic model of the shrinking core model, with diffusion through the solid product of the reaction as the controlling stage which is apparently a heterogeneous process on the pyrite surface. Fois, et. al, (2012) in a kinetic study of a sub-bituminous by sequential leaching with potassium hydroxide followed by hydrogen peroxide reported a high efficiency of sulphur reduction for relatively large particle sizes without reduction in the calorific value.

2. Materials and Method

2.1. Coal Sample Collection and Preparation

Coal samples used were obtained from the Nigerian Coal Corporation (NCC) Enugu. The coal samples originated from the Onyema coal mining field in Enugu state of Nigeria. The physico-chemical properties of the coal samples, the bulk density and heat value were analyzed after crushing with a Corona hand mill and screened into various mesh sizes, and stored in well-labelled air tight containers.

2.2. Preparation of Leaching Solutions

The Sulphuric acid and hydrogen peroxide used were of analytical grade and were used without further purification. Standard solutions were prepared from the stock solutions with adequate volume of distilled water and stored in well labeled containers. The peroxide-sulphuric acid mixture was in the ratio of 70 mL H₂SO₄: 30 mL H₂O₂ and was freshly prepared and allowed to cool each time prior to usage.

2.3. Batch Experiments

The batch experiments were carried out in a 250 mL agitated beaker with a 100 mL working solution. 20 g of coal sample of +70 mesh size (210 μm) was added to the working solution at 80 °C. The pulp was agitated at regular intervals of 10 rotations per minute (rpm) every 5 minutes. The effect of H₂SO₄ concentrations (0.1, 0.3, 0.5, 1.0 and 6.0 M), H₂SO₄ with 10 % H₂O₂, particle sizes (+20, +40, +70, +100, +200 mesh sizes), and temperatures (25 °C, 60 °C, 80 °C, and 100 °C) were studied. At predetermined intervals (15, 30, 45, 60 and 90 minutes) the pulp was filtered to recover the sample, followed by washing of the residue with copious amount of warm distilled water, oven dried at 40 °C, for 1 hour and then stored in a well labelled air tight container. The determination of total sulphur in the residue was done with sulphur and carbon analyzer (SC-144DR) fitted with a sulphur detector.

3. Theory

3.1. Leaching Kinetics

The Pseudo-first order, pseudo-second order and shrinking core models were used to study the desulphurization kinetics of the coal samples and to describe the reaction mechanism.

3.1.1. Pseudo-first Order Rate Law

For a reaction of the form $A \rightarrow$ products, the linear form of the pseudo-first order rate law (at $t = 0$, $[A] = [A]_0$) takes the form:

$$\ln[A] = k_1 t + \ln[A]_0 \quad (1)$$

where $[A]_0$ and $[A]$ are the initial and final reactant concentrations, k is the apparent rate constant and t is the time. A plot of $\ln [A]$ against time will be a straight line, with slope $-k_1$ and intercept $\ln[A]_0$

3.1.2. Pseudo-second Order Rate Law

The linear of the pseudo-second order rate law (at $t = 0$, $[A] = [A]_0$) takes the form:

$$\frac{1}{[A]} = k_2 t + \frac{1}{[A]_0} \quad (2)$$

A plot of $\frac{1}{[A]}$ against time will be a straight line, with slope k_{2nd} and intercept $\frac{1}{[A]_0}$.

3.1.3. The Un-reacted Shrinking Core Model

The overall desulphurization process may be described by the un-reacted shrinking core model proposed by Levenspiel, (1972). The following equations were developed to describe these mechanisms (Grénman, Salmi & Murzin, 2011; Yang & Zhang, 2013; Kanervo, 2013):

1. Diffusion through liquid film control: $X_B = k_1 t$;
2. Chemical reaction control: $1 - (1 - X_B)^{1/3} = k_2 t$;
3. Diffusion through porous ore matrix control: $1 - \frac{2}{3} X_B - (1 - X_B)^{2/3} = k_3 \cdot t$;
4. Mixed control: $1 - (1 - X_B)^{1/3} = \frac{k_1 k_2}{k_1 + k_2} \cdot \frac{c_0 M}{R_0 \cdot \rho_B}$

where k_1 , k_2 , k_3 are constants for different control steps, respectively. X_B , t , c_0 , R_0 , ρ_B and M represent the coal leaching rate, leaching time, initial concentration of leaching reagent, initial radius of the ore particle, mole density of the ore particle and mass of the ore particle, respectively.

If a shrinking sphere mechanism is assumed, (i.e. for a chemically controlled reaction) $1 - (1 - X_B)^{1/3}$ is plotted as a function of time for the experimental data and if the plot gives a linear correlation, the assumption is considered to be correct. Analogously, $1 - \frac{2}{3} \cdot X_B - (1 - X_B)^{2/3}$ against time can be plotted for the data if a shrinking core model is assumed (i.e., for mass transfer across a porous product layer). If the model assumption is considered to be correct, values can then be obtained for other parameters such as E_a and k' by fitting the model to experimental data (Grénman, Salmi, & Murzin, 2011; Ajemba & Onukwuli, 2012; Yang & Zhang, 2013; Kanervo, 2013).

3.3. Activation energy and thermodynamics

The Arrhenius and the Eyring-Polanyi equations were used to describe the thermodynamic process of the reaction (Winzor & Jackson, 2006; Keusch, 2009).

$$K = A \exp\left(\frac{-E_a}{RT}\right) \quad (\text{Arrhenius}) \quad (3)$$

$$k = \frac{k_B}{h} \cdot T \cdot \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \quad (\text{Eyring-Polanyi}) \quad (4)$$

From the integrated Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (5)$$

The linear form of the Eyring-Polanyi equation is given by:

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{RT} - \frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} \quad (6)$$

The relationship between the transition state equilibrium constant and the change in Gibbs free energy of the transition state is given by:

$$\ln k^\ddagger = - \frac{\Delta G^\ddagger}{RT} \quad (7)$$

where k = rate constant; A = Pre-exponential factor; E_a = Activation energy ($\text{kJ} \cdot \text{mol}^{-1}$); R = Universal Gas Constant = 8.3145 J/mol K ; T = absolute temperature; k_B is Boltzmann's constant, and h is Planck's constant; ΔS^\ddagger = activation entropy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); ΔH^\ddagger = activation enthalpy ($\text{kJ} \cdot \text{mol}^{-1}$), ΔG^\ddagger = Gibbs free activation enthalpy ($\text{kJ} \cdot \text{mol}^{-1}$).

ΔG^\ddagger was calculated using the following equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (8)$$

4. Results and Discussion

4.1. Proximate and Ultimate Analyses

Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	Bulk density (g/cm^3)
3.6	14.3	35.4	48.7	0.71

Table 1: Proximate analysis of Onyeama coal samples (AR Basis)
(AR = As Received)

The moisture content required for good coking coal is 1.5 % However, the Central Fuel Research Institute, India (CFRI) stipulated a range of 1-4 % The moisture content value recorded in the Onyeama coal sample herein is within the stipulated range (Chukwu, et. al, 2012) which eliminates the tendencies of lengthening the time of heating, increasing of the consumption of the coal (Afonja, 1996). The low ash content signifies pliability, low tendency to produce slag, low susceptibility to form clinker and indicates higher calorific value, which gives best quality for combustibility (Anudhyan, 2009). Lower ash content is an essential requirement for coke making coals (Akpabio, 1998). The fixed carbon of the Onyeama coal sample indicates that it will favour coke production (Anudhyan, 2009) (Diez, Alvarez, & Barriocanal, 2002; Chukwu, et al, 2012). Volatile matter includes the components of coal which are expelled at high temperature in the absence of oxygen, except for water and is a key health and safety concern as coals high in volatiles have an increased risk of spontaneous combustion. "The volatile matter in coal samples from Onyeama mine are classed as high-volatile bituminous" (Chukwu et. al, 2012, Fatoye & Gideon, 2013). The results agree with the reports of (Okolo, 1988; Fatoye & Gideon, 2013) who observed that "Nigerian coals have high volatile matter and as such are potential sources of energy and feedstock for the chemical and allied industries."

Ultimate analysis of the Onyeama coal sample (wt %)	
Carbon	69.4
Hydrogen	6.55
Nitrogen	1.37
Sulphur	0.32
Oxygen (by difference)	19.76
Moisture	2.6
Calorific value (kcal/kg)	6100

Table 2: Ultimate analysis of the Onyeama coal sample (wt %) (AR-Basis)

4.2. Effect of H_2SO_4 Concentration

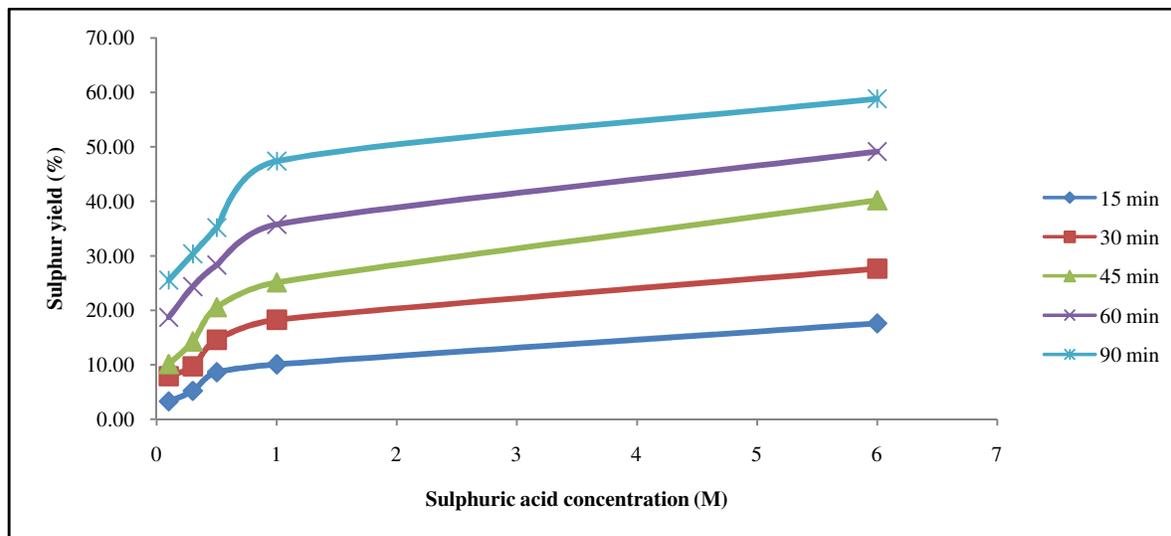


Figure 1: Plot of percentage sulphur yield against H_2SO_4 concentration at variable time, showing the effect of H_2SO_4 concentrations on the sulphur yield.

The dissolution curves illustrated in Figure 1 showed that increase in the concentration of the acid resulted in significant increase in the yield of sulphur. This suggests that sulphuric acid has significant effect on desulphurization of coal. "It is also possible that some elemental sulphur formed during the reaction could adsorb to the surface of the coal particles" (Chuang, 1979). This adsorbed sulphur on the coal sample and will be detected as un-dissolved sulphur. Despite washing the reaction residue with copious amounts of warm water, there is still a tendency that some amount of the free sulphur will not be washed off as sulphur is not soluble in water.

4.3. Effect of H_2SO_4 Concentration with 10 % H_2O_2

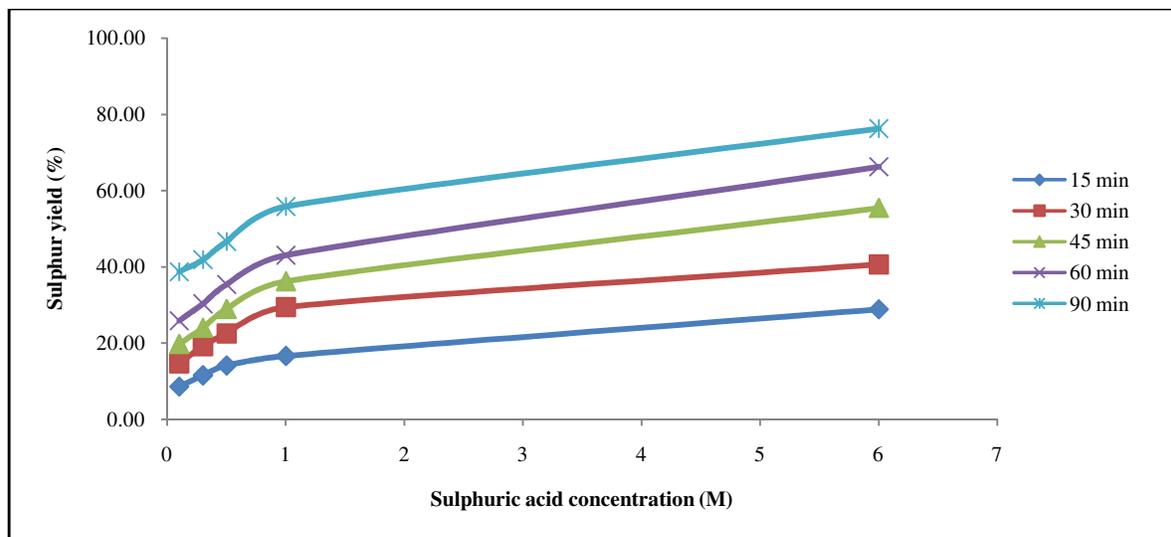
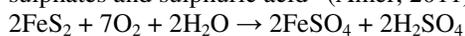


Figure 2: Plot for percentage sulphur yield against different H_2SO_4 concentrations with 10 % H_2O_2 at different times, showing the effect of different H_2SO_4 concentrations with 10 % H_2O_2 on the sulphur yield.

The dissolution curves illustrated in Figure 2 showed that increase in the concentration of the acid resulted in significant increase in the yield of sulphur. At acid concentration of 6.0 M the yield rose to about 76 % in 90 minutes of leaching which is 18 % higher than the sulphur yield when sulphuric acid was used alone. This suggests that sulphuric acid has significant effect on desulphurization of coal. The effect of the acid was due to the increase in the redox potential of the oxidant. This means that hydrogen ion concentration increases the redox potential of H_2O_2 , which consequently increases the rate of the reaction. "With increasing acid concentration and high toxic conditions the pyritic and organic sulphur forms in the coal are oxidized to sulphate, which appears as ferrous and ferric sulphates and sulphuric acid" (Amer, 2011).



(9)

4.4. Effect of Particle Size

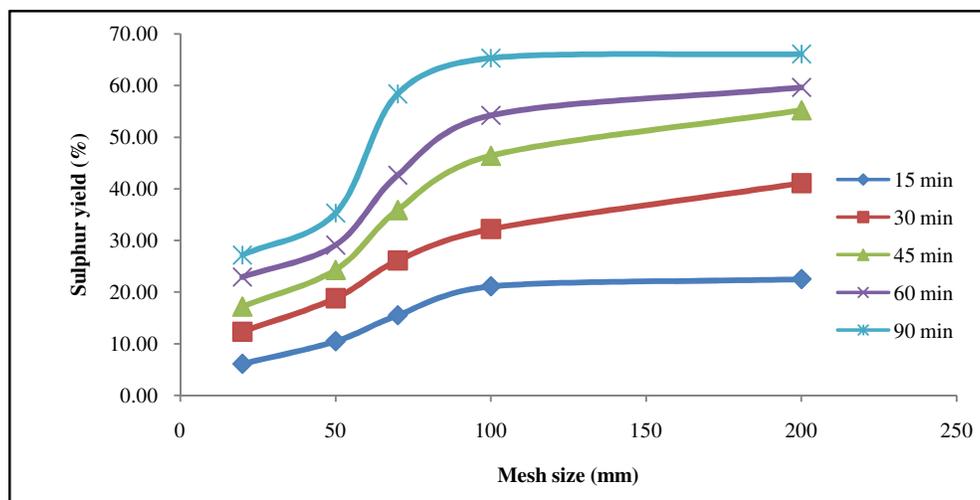


Figure 3: Plot for percentage sulphur yield against different particle sizes at different times using 20 % H_2O_2 and 0.1 M H_2SO_4 , showing how particle size affects the yield of sulphur.

From Figure 3 above it is evident that particle size influences the extraction rate in a number of ways. The smaller the size, the greater is the interfacial area between the solid and liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is hindered, and separation of the particles from the liquid and drainage of the solid residue are made more difficult. Desulphurization is found to increase with decrease of the particle size until an optimum point when the particle size will be too small to permit effective solid–solution contact. As agitation time increases, size of particles decreases due to collision of impeller of agitator with particles, this exposes more surface area, thereby increasing rate of leaching (Baruah & Khare, 2007). But after optimum residence time, particles get smaller in size and finer, possibly causing formation of slime. Hence rate of leaching decreases. The resulting reduction in the size of the coal particles would be accompanied by an increase in surface area which would lead to progressive reduction in the rate as the reaction proceeded. The simplest explanation of this is that leaching is accompanied by an increase in surface roughness which compensates for the reduction in surface area. Microscopic examination of some pyrite crystals present in coal subjected to desulphurization revealed degree of surface etching which provides a support for this interpretation (Amer, 2011).

4.5. Effect of Temperature

The Figure 4 below shows that the rate of extraction is proportional to the temperature. As the temperature of the system increases, rate of leaching increases due to more easy diffusion of solvent into and out of coal particles amounting to enhanced desulphurization. The formation of sulphuric acid was favoured at the expense of elemental sulphur with increasing temperature (Amer, 2011).

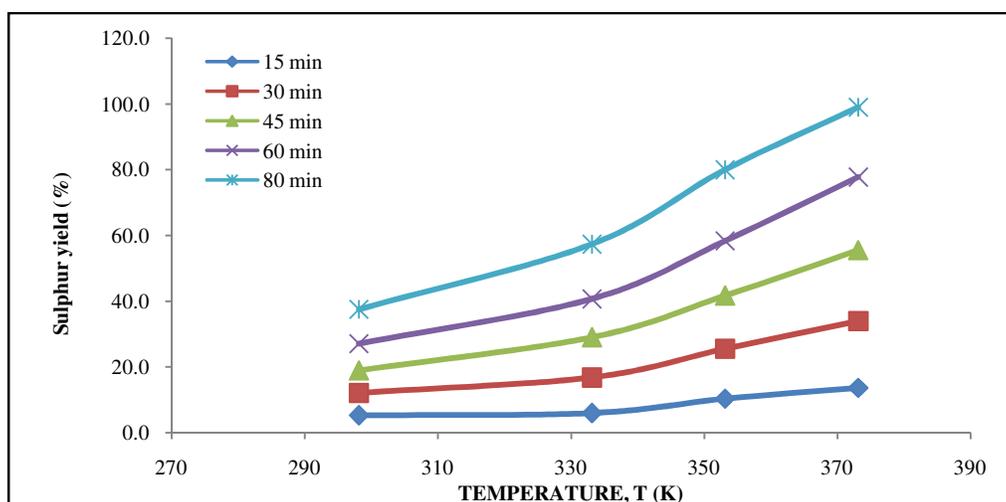


Figure 4: Plot for percentage sulphur yield against temperature when coal samples of 70 mesh size were treated with 100 mL 20 % H_2O_2 and 0.1 M H_2SO_4 at different times.

4.6. Integrated Rate Law Model

H ₂ SO ₄ concentration	Pseudo-first order		Pseudo-second order	
	R ²	k (min ⁻¹)	R ²	k (L.mol ⁻¹ .min ⁻¹)
0.1 M	0.897	0.027	0.673	-0.003
0.3 M	0.923	0.023	0.738	-0.002
0.5 M	0.955	0.018	0.836	-0.001
1.0 M	0.945	0.020	0.803	-0.001
6.0 M	0.969	0.015	0.882	-0.000

Table 3: Pseudo-first order and pseudo-second order kinetic models for coal leaching at different H₂SO₄ concentrations.

H ₂ SO ₄ concentration	Pseudo-first order		Pseudo-second order	
	R ²	k	R ²	K
0.1 M	0.944	0.020	0.802	-0.001
0.3 M	0.963	0.016	0.862	-0.001
0.5 M	0.969	0.015	0.882	-0.001
1.0 M	0.971	0.014	0.892	0.000
6.0 M	0.979	0.012	0.919	0.000

Table 4: Pseudo-first order and pseudo-second order kinetic models for coal leaching at different H₂SO₄ concentrations and 10% H₂O₂.

Particle size	Pseudo-first order		Pseudo-second order	
	R ²	k	R ²	k
20 Mesh	0.958	0.017	0.845	-0.001
50 Mesh	0.972	0.014	0.895	-0.001
70 Mesh	0.962	0.016	0.859	-0.001
100 Mesh	0.973	0.014	0.897	0.000
200 Mesh	0.981	0.011	0.929	0.000

Table 5: Pseudo-first order and pseudo-second order kinetic models for coal leaching for different particle sizes.

Temperatures	Pseudo-first order		Pseudo-second order	
	R ²	k	R ²	k
25 °C	0.890	0.025	0.691	-0.002
60 °C	0.86	0.028	0.633	-0.002
80 °C	0.856	0.025	0.659	-0.001
100 °C	0.805	0.024	0.635	-0.001

Table 6: Pseudo-first order and pseudo-second order for different temperatures when coal samples of 70 mesh size were treated with 100 mL 20 % H₂O₂ and 0.1 M H₂SO₄.

4.7. The Un-reacted Shrinking Core Model

Process parameter	Kinetic equation			
	1 - (1 - X _B) ^{1/3} = k ₁ . t(chemical reaction control)		1 - $\frac{2}{3}$. X _B - (1 - X _B) ^{2/3} = k ₂ . t(product layer diffusion control)	
H ₂ SO ₄ conc. (M)	k ₁	R ²	k ₂	R ²
0.1	0.0208	0.938	0.249	0.974
0.3	0.0200	0.937	0.332	0.963
0.5	0.0170	0.937	0.332	0.975
1.0	0.0198	0.953	0.451	0.988
6.0	0.0174	0.913	0.486	0.955
Process parameter	Kinetic equation			
	1 - (1 - X _B) ^{1/3} = k ₁ . t(chemical reaction control)		1 - $\frac{2}{3}$. X _B - (1 - X _B) ^{2/3} = k ₂ . t(product layer diffusion control)	
H ₂ SO ₄ conc. (M) with 10 % H ₂ O ₂	k ₁	R ²	k ₂	R ²
0.1	0.018	0.980	0.363	0.999
0.3	0.016	0.965	0.356	0.995
0.5	0.016	0.955	0.379	0.990
1.0	0.016	0.920	0.439	0.972
6.0	0.016	0.914	0.547	0.947

Table 7a: The Un-reacted shrinking core model for reaction controlled (1 - (1 - X_B)^{1/3} = K₁ . t) and diffusion controlled shrinking-core (1 - $\frac{2}{3}$. X_B - (1 - X_B)^{2/3} = K₂ . t) models.

Process parameter	Kinetic equation			
	$1 - (1 - X_B)^{1/3} = k_1 \cdot t$ (chemical reaction control)		$1 - \frac{2}{3} X_B - (1 - X_B)^{2/3} = k_2 \cdot t$ (product layer diffusion control)	
Particle size (mesh)	k_1	R^2	k_2	R^2
20	0.016	0.886	0.265	0.946
50	0.014	0.890	0.293	0.949
70	0.018	0.950	0.491	0.990
100	0.017	0.911	0.511	0.953
200	0.015	0.780	0.475	0.838

Process parameter	Kinetic equation			
	$1 - (1 - X_B)^{1/3} = k_1 \cdot t$ (chemical reaction control)		$1 - \frac{2}{3} X_B - (1 - X_B)^{2/3} = k_2 \cdot t$ (product layer diffusion control)	
Temp. (°C)	k_1	R^2	k_2	R^2
25	0.026	0.971	0.461	0.999
60	0.032	0.959	0.708	0.999
80	0.033	0.965	0.931	0.999
100	0.035	0.949	1.135	0.994

Table 7b: The Un-reacted shrinking core model for reaction controlled ($1 - (1 - X_B)^{1/3} = K_1 \cdot t$) and diffusion controlled shrinking-core ($1 - \frac{2}{3} X_B - (1 - X_B)^{2/3} = K_2 \cdot t$) models.

From the R^2 values in table 7a and 7b above, it can be seen that the desulphurisation process followed the SCM for diffusion through product layer. A plot of the natural logarithm of the rate constants against their various parameters can be used to obtain the E_a and reaction orders as show in figures 5 to 8 below.

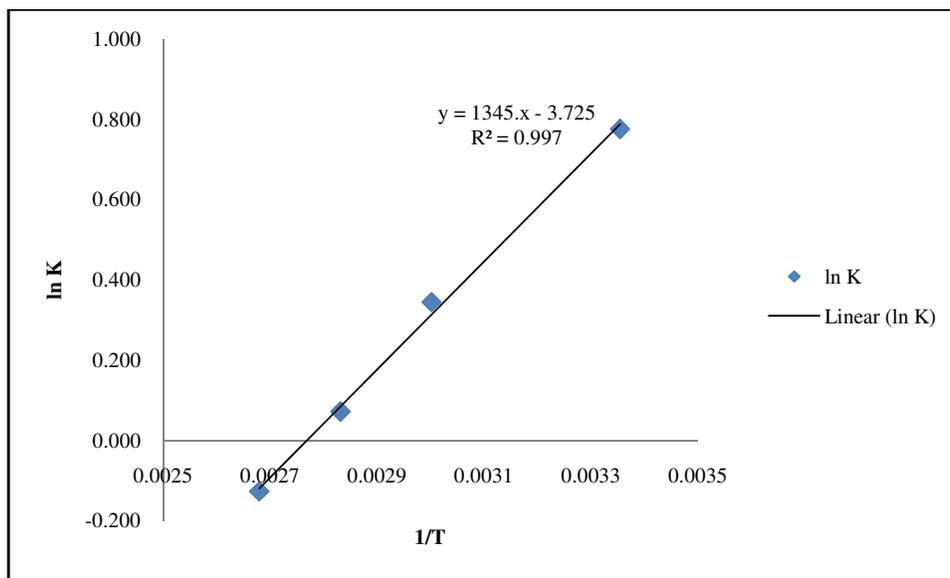


Figure 5: Plot of $\ln k$ versus $1/T$

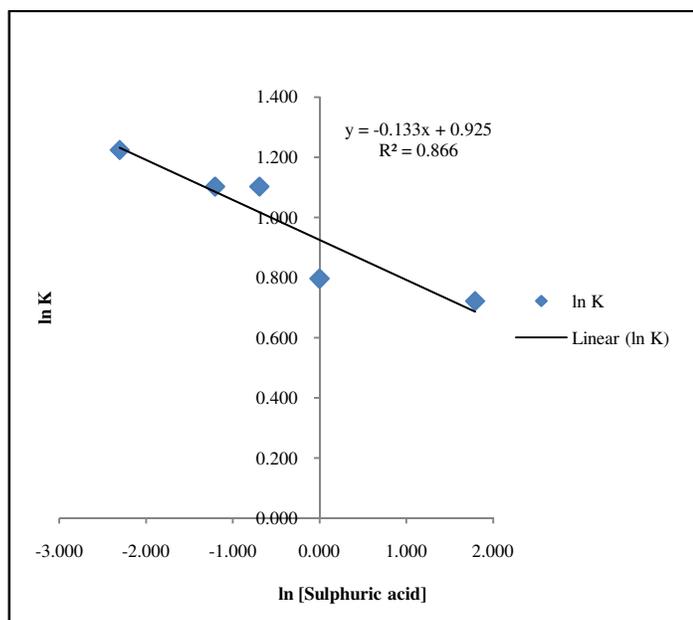


Figure 6: Plot of ln k versus ln [H₂SO₄]

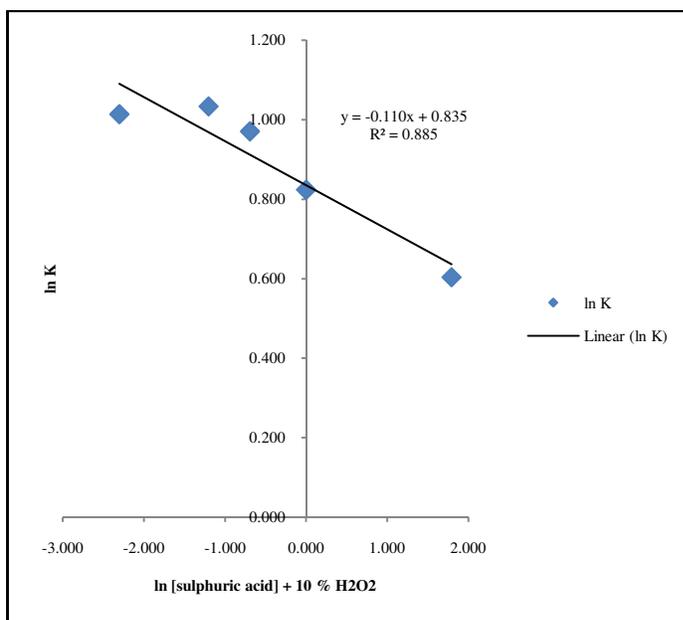


Figure 7: Plot of ln k versus ln [H₂SO₄] with 10 % H₂O₂

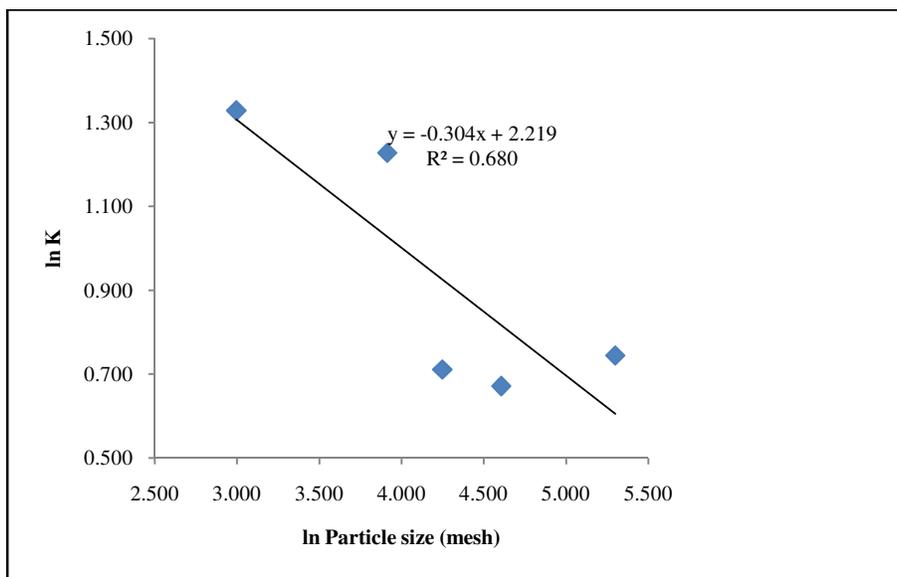


Figure 8: Plot of ln k versus ln particle sizes.

A semi-empirical model was also developed for the process as follows;

$$1 - \frac{2}{3} \cdot X_B - (1 - X_B)^{2/3} = k' C_{[H_2SO_4]}^a (H_2SO_4 / H_2O_2)^b (p)^c \exp (-Ea/RT) t \tag{10}$$

The variables a, b and c were determined to be -0.133, -0.110 and -0.304 respectively. Substituting these values in equation (10), we obtained an equation that represents the semi-empirical model for the desulfurization kinetics of Onyeama coal:

$$1 - \frac{2}{3} \cdot X_B - (1 - X_B)^{2/3} = 0.467 C_{[H_2SO_4]}^{-0.133} (H_2SO_4 / H_2O_2)^{-0.110} (p)^{-0.304} \exp (-1345/T)t \tag{11}$$

4.8. Effect on Calorific Value

Experimental Variable	Calorific Value
H ₂ SO ₄	5950 cal/g
H ₂ SO ₄ + 10 % H ₂ O ₂	5800 cal/g
Particle size (20 % H ₂ O ₂ + 0.1 M H ₂ SO ₄)	5710 cal/g
Temperature (20 % H ₂ O ₂ + 0.1 M H ₂ SO ₄)	5840 cal/g

Table 8: Average calorific values after treatment

Calorific value before treatment = 6100 kcal/kg

“Higher rank coals show a low reduction in calorific value probably because they contain a lower number of carboxylic and phenolic groups than the lower ranks, which increase the solubilisation of such coals in the acidic mixture” (Carbini, et. al, 1990). Moreover, the effect of the mechanical disintegration following the chemical attack, contributes to losses in calorific value. This disintegration generates the formation of ultra-fine coal particles, a phenomenon less remarkable in the higher rank coals with less porosity where the consequent calorific value loss becomes less considerable.

5. Conclusion

In this study the physical phenomena (kinetics and thermodynamics) accompanying the desulphurization of high-rank sub-bituminous Onyeama coal using sulphuric acid and hydrogen peroxide, and the underlying mechanism were investigated. The effects of leaching agents, concentration of the leaching solution, particle size and temperature were investigated. The rate of sulphur recovery increased with increasing temperature, residence time and decreasing particle size (increase in mesh number). The rate of extraction was shown from the graphical and ANOVA analyses to have a linear relationship with the residence time. It was observed that rate of extraction increased as residence time increased to an optimum. The comparative analysis of the regression coefficient, R^2 values from the integrated rate law model showed that the desulphurization process followed a pseudo-first order kinetics in all, which corresponds with the findings made by Baruah, et. al, (2006) and Borah, Baruah, & Haque, (2001). The Arrhenius and Eyring-Polanyi equations were used to determine the experimental activation energy ($E_a = -11.19 \text{ kJ mol}^{-1}$), enthalpy of activation ($\Delta H^\ddagger = 8.43 \text{ kJ mol}^{-1}$), entropy of activation ($\Delta S^\ddagger = -22.32 \times 10^{-2} \text{ kJ mol}^{-1}$), and Gibbs free energy of activation ($\Delta G^\ddagger = 74.97 \text{ kJ mol}^{-1}$) for desulphurization process. The negative E_a obtained points at a complicated mechanism with distinct intermediate species, and thus does not have any physical meaning; it only indicated that the reaction in question does not fulfil all the conditions for an “apparent” activation energy to be interpreted which is peculiar with heterogeneous reactions. “The non-spontaneous nature of the reaction is mainly due to the steric hindrance by large aromatic rings” (Baruah & Khare, 2007). Apparently, the removal of different sulphur compounds from coal is however best achieved with an oxidizing reagent such as hydrogen peroxide stabilized with dilute sulphuric acid which was verified by the statistical and mathematical tests carried out. The calorific value was relatively not affected by the process considering the degree of desulphurization achieved. The apparent reaction orders obtained were -0.133, -0.110 and -0.304 for H_2SO_4 concentration, H_2SO_4 concentration with 10 % H_2O_2 and particle size, respectively. “The negative signs in the reaction orders signify that an instantaneous increase in the variables will have an inverse effect on the yield” (Davis, 2015). This behaviour will be observed after an optimum time. The reaction kinetics can be described by the semi-empirical model:

$$1 - \frac{2}{3} \cdot X_B - (1 - X_B)^{2/3} = 0.467 C_{[\text{H}_2\text{SO}_4]}^{-0.133} (\text{H}_2\text{SO}_4 / \text{H}_2\text{O}_2)^{-0.110} (p)^{-0.304} \exp(-1345/T)t.$$

6. References

- i. Adebayo A. O., Ipinmoroti K. O., & Ajayi O. O. (2003). Dissolution Kinetics of Chalcopyrite with Hydrogen Peroxide in Sulphuric acid Medium. Department of Chemistry, Federal University of Technology, Akure, Nigeria. *Chem. Biochem. Eng. Q.* **17** (3) 213–218 (2003). Original scientific paper Received: October 19, 2002. Accepted: March 11, 2003.
- ii. Afonja, A. A. (1996). Production of Metallurgical Coke from Non-Coking Coals. In: *Nigerian Coals: A Resource for Energy and Investments*, Afonja, A. A. (Ed.). RMRDC, Abuja, Nigeria, pp: 89-105.
- iii. Ajemba, R. O. & Onukwuli, O. D. (2012). Dissolution kinetics and mechanisms of reaction of Udi clay in nitric acid solution. Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Anambra, Nigeria. *AMERICAN JOURNAL OF SCIENTIFIC AND INDUSTRIAL RESEARCH* © 2012, Science Huß, <http://www.scihub.org/AJSIR> ISSN: 2153-649X, doi:10.5251/ajsir.2012.3.3.115.121.
- iv. Akpabio, I. O. (1998). Thermal properties of some Nigerian coals: *Science forum. J. Pure Applied Sci.*, 1: 87-92.
- v. Amer A. M. (2011). Kinetics of Hydrometallurgical Extraction of Sulphur From Egyptian El-Maghara Coal Deposits. Received December 15, 2009; Reviewed; Accepted July 19, 2010. *Physicochem. Probl. Miner. Process.* **46**(2011)163-172. Journal home page: www.minproc.pwr.wroc.pl/journal/
- vi. Anudhyan, M. (2009). Assessment of Coal Quality of Some Indian Coals. National Institute of Technology, Rourkela, India.
- vii. Baruah, B. P. & Khare, P. (2007). Desulphurization of Oxidized Indian Coals with Solvent Extraction and Alkali Treatment. *Energy Fuels*, 2007, 21 (4), 2156-2164. DOI: 10.1021/ef070087a. Publication Date (Web): 30 June 2007. Downloaded from <http://pubs.acs.org> on May 13, 2009.
- viii. Blander, M. (2011.). Calculations of the Influence of Additives on Coal Combustion Deposits. Argonne National Laboratory. P. 315. Retrieved 17 December 2011.
- ix. Borah, D., Baruah, M. K., Haque, I. (2001). *Fuel*, 80, 1475-1488.
- x. Carbini P., Curreli L., Ghiani M. & Satta F. (1990). Desulphurization of Europeans coal using molten caustic mixtures, Processing and utilization of high sulphur coals III, Eds. Markuvzewski R. And Wheelock T. D., Elsevier, Amsterdam.
- xi. Chuang, K. (1979). Desulfurization of coal by oxidation in alkaline solution. Retrospective Theses and Dissertations. Iowa State University Digital Repository @ Iowa State University. Iowa State University
- xii. Chukwu, C. J., Obasi, N. A., Jauro, A., Ezeribe, A. I., Nwachukwu, C. B. & Putshak`a, J. D. (2012). Physical and Plastic Properties of Three Nigerian Coals. *Asian Journal of Materials Science*, 4: 45-51. DOI: 10.3923/ajmskr.2012.45.51. URL: <http://scialert.net/abstract/?Doi=ajmskr.2012.45.51>.

- xiii. Davis U. C. (2015). Reaction Order 2. Chemwiki: The Dynamic Chemistry Hypertext.
- xiv. Diez, M. A., Alvarez, R. & Barriocanal, C. (2002). Coal for metallurgical coke production: Production of coke quality and future requirements for coke making. *Int. J. Coal Geol.*, 50: 389-412.
- xv. Excerpts from Rock Talk (2005). Volume 8, Number 2.
- xvi. Fatoye, F. B. and Gideon, Y. B. (2013). Appraisal of the Economic Geology of Nigerian Coal Resources. *Journal of Environment and Earth Science*. www.iiste.org ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online) Vol. 3, No.11, 2013.
- xvii. Fois E., Pistis, A. & Lallai, A. (2012). Kinetics of Sulcis Coal Chemical Cleaning Process. *Chemical Engineering Transactions*. Vol. 29, 2012. A publication of The Italian Association of Chemical Engineering Online at: www.aidic.it/cet. ISBN 978-88-95608-20-4; ISSN 1974-9791 DOI: 10.3303/CET1229158.
- xxviii. Grénman, H., Salmi T., & Murzin, D. Y. (2011). Solid-liquid reaction kinetics – experimental aspects and model development. *Rev. Chem. Eng.* 27 (2011): 53–77 © 2011 by Walter de Gruyter • Berlin • Boston. DOI 10.1515/REVCE.2011.500.
- xix. Jauro A. & Chukwu C. J. (2011). Production of Formed Coke from Nigerian Coals. *Petroleum & Coal* ISSN 1337-7027. Available online at www.vurup.sk/pcPetroleum & Coal 53 (1) 22-25, 2011. Chemistry Programme, Abubakar Tafawa Balewa University, Bauchi, PMB 0248, Bauchi, Bauchi State, Nigeria.
- xx. Kanervo J. (2013). Group of Industrial Chemistry. KE-40.4130 Multiphase Reactors November 26th 2013 Fluid-solid reactions.
- xxi. Keusch, P. (2009). Eyring Equation. University of Regensburg.
- xxii. Lenior, T. (2009). Analytical Techniques for the determination of sulphur components in flue gas, fuel gas and natural gas. Literature thesis Chemistry, Analytical Sciences. VU University Faculty of Exact Sciences, Department of Analytical Chemistry & Applied Spectroscopy. De Boelelaan 1083. 1081HV Amsterdam. August 2009.
- xxiii. Levenspiel, O. (1972). *Chemical reaction engineering*. 2nd edition, John Wiley & Sons, Inc., New York, New York. p.578.
- xxiv. Ministry of Mines and Steel Development. (2010). Coal Deposits. Overview of Mineral in Nigeria (2010). Earth group Pte. Ltd. Originally published in 2010 by the Ministry of Mines and steel development under the title Coal Exploration and Power generating opportunities in Nigeria.
- xxv. Okolo, H. C. (1988). Investment Opportunities in the Nigerian Coal Industry. In: Nigeria Coals: Resources for energy and Investments, Okolo, H.C. and M.C. Mkpadi (Eds.). Raw Material Research and Development Centre, Abuja, pp: 132-412.
- xxvi. Pathak, K. (2014). Quality Improvement of Coal. Department Of Mining Engineering, Iit., Kharagpur-721302. Retrieved on 17th Feb. 2014.
- xxvii. Sada, M. M. (2012). Nigeria minister of Mines Presentation at Africa Down Under International Conference, Perth, Western Australia, on Investment Opportunities in Nigeria's Mineral and Metals Sector. Ministry of mines and Steel Development.
- xxviii. Staff Writer, (2010). How we made it in Africa. www.howwemadeit in africa.com/Nigerian_coal_deposits_identified/653
- xxix. Vestal, M. L. & Johnston, W. H. (2006). Chemistry and Kinetics of the Hydro-Desulphurization of Coal. Scientific Research Instruments Corporation, Baltimore.
- xxx. Winzor, D. J. & Jackson C. M. (2006). "Interpretation of the temperature dependence of equilibrium and rate constants". *J. Mol. Recognit.* 19 (5): 389–407. Doi:10.1002/jmr.799. PMID 16897812.
- xxxi. Yang, X. Z. & Zhang, L. (2013). Effects of Reagent Concentration and Particle Size on Diffusion Rate of Mixed Ores with Rare Elements. School of Sciences, Changchun University, Changchun 130022, P.R. China (Received July 23, 2012; in final form March 16, 2013). Vol. 124 (2013) ACTA PHYSICA POLONICA A No. 1.