# Determination of Kinetic Parameters in Coal Weathering Processes

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## ABSTRACT

Three different methods were employed to measure the degree of aerial oxidation in coal and the resulting oxidation/weathering indices were applied to obtain kinetic parameters of aerial oxidation processes. The index (i.e., slurry pH, Free Swelling Index, weight gain) values were subjected to kinetic analysis based on power-law Arrhenius type reaction model. The results show that activation energy of the aerial oxidation in 20-290°C is in the range of 12-16 kcal/mol and the agreement among three techniques is remarkable. The first order kinetic model is suitable in describing low temperature aerial oxidation process, except in the FSI case where the zero order expression is the best one.

## INTRODUCTION

It has been confirmed in coal utilizing industry that aerial oxidation exhibits detrimental effects on many coal properties such as caking ability, flotability, extractibility, char strength, char reactivity, and calorific value. Except a few cases like the prevention of agglomeration of feed coal powder in the gasifier feeding zone, these oxidation effects cause financial losses and operational hazards. Among examples of operational hazards, self heating in coal stockpiles and the resulting spontaneous ignition are the most noticeable cases demonstrating the necessity of fundamental understanding on low temperature aerial oxidation processes. In addition, increased tendency to generate fines by aerial oxidation ends up to cause environmental pollution in areas around coal stockpiles

Considering the magnitude of detrimental effects by aerial oxidation even at the ambient temperature, some ways to determine the degree of oxidation should be developed. In the past, many attempts have been made: for example, direct measurement of oxygen content increase in coal, ratio of certain wavelengths from FTIR results, measurements of changes in swelling property by dilatometer or Gieseler plastometer, application of pyrolysis mass spectrometry and multivariate data analysis technique. However, most of these measurements require expensive instruments or special expertise in operation.

In this paper, three relatively simple indices (slurry pH, Free Swelling Index(FSI), weight gain) which can be measured in industry without special instrumentation are shown to illustrate the applicability in measuring the degree of aerial oxidation as well as in determining activation energy of the low temperature aerial oxidation process.

## EXPERIMENTAL

## Coal Samples

Three coals were used as follows: Adaville #4 (subbituminous) coal for pH measurements, Hiawatha #1 (high volatile bituminous) coal for FSI measurements, and Upper Freeport (medium volatile bituminous) coal for mass gain experiments. Conventional characterization data on the three coal samples are listed in Table 1.

## Laboratory Coal Oxidation

The apparatus used for carrying out oxidation experiments consisted of a glass reactor (104 mm in length and 37 mm o.d. with a sintered glass frit distributor at the bottom) fitted with Swagelok fittings at each end and an effluent line connected to a bubble flowmeter to check the gas flow rate. The 14–16 g of sieved (–60 mesh) coal in the reactor produced a bed height of ca. 3 cm. The reactor was then placed in a convection oven. Detailed description of the apparatus and experimental procedure have been reported elsewhere [1]. Weathering experiment in the coal stockpile for a pH value is also described in ref 1.

## Free Swelling Index (FSI) determination

The Free Swelling Indices of the oxidized and non-oxidized (fresh) coal were determined according to the ASTM standard method D-720. Briefly, the method involves heating 1 g of –60 mesh coal powder contained in a special crucible in an oven at 800°C and then comparing the resulting coke button with a series of standard shape to which indices are assigned.

## Slurry pH measurement

The pH measurements were performed with a Mettler DL40RC titrator. Coal slurries were made by pouring 0.5 g coal samples into disposable polystyrene beakers, followed by adding 10 ml of deionized water (>1.0 Megohms–cm resistivity) after which the slurry was stirred with a clean glass bar while squashing any agglomerated coal particles with the bar. Finally, 30 ml of deionized water were added to make the final volume of the slurry 40 ml in order to ensure total immersion of the electrode. It should be pointed out that some coals, e.g. Adaville seam coals, are readily wetted without producing any agglomerates, whereas other coals, e.g. some high volatile bituminous and higher rank coals, are hardly wetted unless squashed for 3–4 min. In order to obtain reproducible pH readings, it is important that the final slurry should not have any visible agglomerates.

## RESULTS AND DISCUSSION

### Coal Slurry pH Changes with the degree of aerial oxidation

Figure 1 shows changes of the slurry pH values with aerial oxidation time. As might be expected, coal samples oxidized at higher temperatures produce more acidic functional groups and thus exhibit faster decrease in pH values with time. Detailed discussion on the effects of aerial oxidation/weathering on pH slurry is shown elsewhere [1]. Here, main concern is what will be the kinetic parameters of oxidation/weathering processes estimated by oxidation indixes. Weathering in this paper is defined as the oxidation process occurring in the coal storage pile where coal is in a humid condition, while oxidation refers to the laboratory experiments without any environmental effects. As will be discussed in the following FSI case and as was reported in the slurry pH values [1], humidity has negligible effect on

oxidation behavior at least when measured by FSI or by slurry pH.

Application of the slurry pH in Figure 1 as an oxidation/weathering index yields an activation energy of 10-16 kcal/mol in the 26-150°C range (see Table 3), depending upon the assumed reaction order. Judged from correlation coefficient of the Arrhenius plot (1/T vs. ln k), the first order power-law model describes the oxidation/weathering behavior best. The oxidation/weathering products (e.g., carbonyl and carboxylic groups) are believed to originate from reactions of oxygen and water with coal moieties. The reactions basically involve mass transport processes such as adsorption, desorption of oxygen and water molecules. Thus, reaction order of oxidation/weathering processes must be close to 1.0 and activation energy should be below ca. 15 kcal/mol which are characteristics of mass transport processes. The result in Table 3 confirms these arguments. With increase in reaction order, the fitness of data to kinetic model deteriorates. In summary, the first order kinetic model with activation energy of ca. 14 kcal/mol is the best expression of the low temperature oxidation process when measured by slurry pH.

*FSI Changes by aerial oxidation*

FSI values at various oxidation conditions are summarized in Table 2 and one case at 80°C is shown in Figure 2. The results in Figure 2 illustrate that moisture in air negligibly influences the oxidation/weathering process, at least when estimated by FSI oxidation index. Slurry pH was also reported not to be influenced by moist environment [1].

One noticeable point in Table 2 is that FSI value is not as sensitive in the initial stage of aerial oxidation as the slurry pH or weight gain. However, kinetic value estimated (15 kcal/mol) is more or less close to those values (12-14 kcal/mol) obtained from kinetic estimations using slurry pH and weight gain. Kinetic value is rather slightly higher in the FSI case and the zero order kinetic expression is the best one in this case, compared to slurry pH and weight gain cases.

FSI is a fundamental property in caking coals and the value is easily obtainable in industry. Considering the simplicity of FSI measurement technique, the agreement of estimated activation energy with the values from other two techniques is remarkable.

*Mass Changes by aerial oxidation*

The mass of coal continuously changes during aerial oxidation. The observed change in mass is a balance between the mass gain due to the oxygen uptake and the mass loss due to the evolution of volatile products. The ratio of the oxygen consumption to the volatile production depends upon coal constitution and aerial oxidation conditions (mainly upon oxidation temperature).

In order to eliminate the disturbing effect of the continuous moisture loss on the mass determination, isothermal measurements are required. Before oxidation experiments, moisture is generally removed by evacuating the sample or by heating the sample while flushing with inert gas. Care must be taken to avoid contact with air, otherwise the mass of the fresh coal (reference point) will be uncertain. Figure 3 shows the mass gain of a medium volatile bituminous coal oxidized in a thermogravimetry system at constant temperature. The samples oxidized at lower

temperatures up to 260°C show continuous gain in mass up to several hours. At higher temperature (285°C), however, after a rapid increase in mass the mass profile passes through a maximum. The temperature at which the decline of mass occurs appears to be dependent on coal rank. The mass of a subbituminous coal produced a maximum point at 175°C [2], while the decline in mass takes place at 250°C for a high volatile bituminous coal [3]. In Figure 3, the decrease in mass occurs within a few hours. In lower oxidation temperatures, the decline in mass never occurs. Swann and Evans [4] reported no further increase in mass after about 45 days at 70°C for a brown coal. According to a gas analysis result, the oxidation does not cease at this point, but the mass of oxygen consumed equals the mass of volatile products evolved from the coal.

Table 5 illustrates estimated activation energies at different apparent reaction orders. The first order expression is the best one and the resulting activation energy is ca. 13 kcal/mol.

## CONCLUSIONS

- Instead of employing complicated instruments, simple three methods were applied to obtain oxidation/weathering index. All three methods illustrate applicability in estimating the degree of oxidation/weathering.
- Estimated activation energies from three methods agree reasonably at 12-16 kcal/mol and the aerial oxidation/weathering process can be modeled as a first order process, except in the case measured by FSI (zero order).
- Estimated activation energies obtained from three different rank coals show similar values, although different oxidation/weathering indices were applied. The similar activation energy values demonstrate that coal rank appears not to be an important factor governing the low temperature oxidation process.
- Moisture does not exhibit significant influence in oxidation indixes. Therefore, the index obtained under dry-air conditions can be extrapolated to coal stockpile samples under humid condition.

## REFERENCES

1. Yun, Y. and H.L.C. Meuzelaar, *Fuel Processing Technology* 1991, *27*, 179-202.
2. Cronauer, D.C., R.G. Ruberto, R.S. Silver, R.G. Jenkins, I.M.K. Ismail, and D. Schlyer, *Fuel* 1983, *62*, 1116-1123.
3. Mahajan, O.M., M. Komatusu, and P.L. Walker, Jr., *Fuel* 1980, *59*, 3-10.
4. Swann, P.D. and D.G. Evans, *Fuel* 1979, *58*, 276-280.

## Table 1. Conventional Characterization Data on Coal Samples

| Seam | Rank | Moisture(%) | VM(%) | FC(%) | Ash(%) | S(%) | C.V.(Btu/lb) |
|------|------|-------------|-------|-------|--------|------|--------------|
| Adaville #4 | subbit. | 18.6 | 36.0 | 42.6 | 2.8 | 0.3 | 10460 |
| Hiawatha #1 | hvb | 3.5 | 41.4 | 42.4 | 12.7 | 0.5 | 13786 |
| Upper Freeport | mvb | 0.7 | 29.0 | 60.2 | 10.1 | 1.9 | 13853 |

Note: subbit. (subbituminous); hvb (high volatile bituminous); mvb (medium volatile bituminous)

Table 2. FSI Values at Various Oxidation Conditions on Hiawatha #1 hvb Coal

| Oxidation Temp. (°C) | 20 | 40 | 40 | 50 | 60 | 80 | 150 | 150 | 150 | 150 |
|---|---|---|---|---|---|---|---|---|---|---|
| Oxidation Duration(days) | 90 | 7 | 33 | 10 | 4 | 2 | 15 min | 30 min | 60 min | 120 min |
| FSI | 2.5 | 2.5 | 1.5 | 1.5 | 1.5 | 1.5 | 3.0 | 2.5 | 1.5 | 1.0 |

Note: FSI of unoxidized sample: 3.5

Table 3. Activation Energy Estimated from Slurry pH Values at Different Reaction Orders

| Reaction Order | T (°C) | k x 10³ | Corr. Coeff.ᵃ | E (kcal/mol) |
|---|---|---|---|---|
| 0 | 26<br>60<br>100<br>150 | 29.51<br>1260<br>740<br>8200 | -0.9064 | 10.00 |
| 1 | 26<br>60<br>100<br>150 | 1.284<br>11.17<br>149.1<br>1021 | -0.9986 | 13.78 |
| 2 | 26<br>60<br>100<br>150 | 0.452<br>12.40<br>97.91<br>1087.8 | -0.9964 | 15.50 |
| 3 | 26<br>60<br>100<br>150 | 3.277<br>11.74<br>72.27<br>1493.2 | -0.9779 | 12.25 |

k: reaction rate constant, E: activation energy
ᵃ 1/T vs. ln k

Table 4. Activation Energy Estimated from FSI Values at Different Reaction Orders

| Reaction Order | Corr. Coeff.ᵃ | E (kcal/mol) |
|---|---|---|
| 0 | -0.9953 | 15.15 |
| 1 | -0.9291 | 16.54 |
| 2 | -0.9070 | 17.03 |

ᵃ 1/T vs. ln k

Table 5. Activation Energy Estimated from Weight Gain Values at Different Reaction Orders

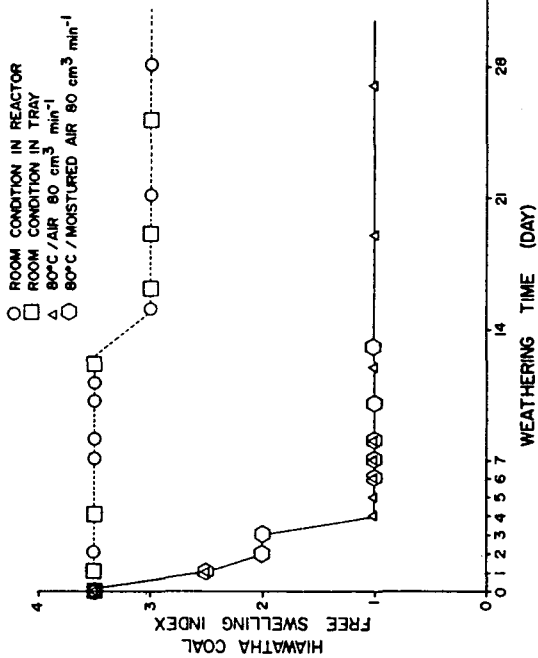| Reaction Order | T (°C) | k | Corr. Coeff.ᵃ | E (kcal/mol) |
|---|---|---|---|---|
| 0 | 150<br>210<br>260<br>285 | 0.143<br>0.758<br>0.814<br>4.240 | -0.9268 | 10.04 |
| 1 | 150<br>210<br>260<br>285 | 0.04<br>0.241<br>0.906<br>1.609 | -0.9996 | 12.84 |
| 2 | 150<br>210<br>260<br>286 | 5.43<br>86.70<br>3326.5<br>619.2 | -0.9240 | 19.97 |

ᵃ 1/T vs. ln k

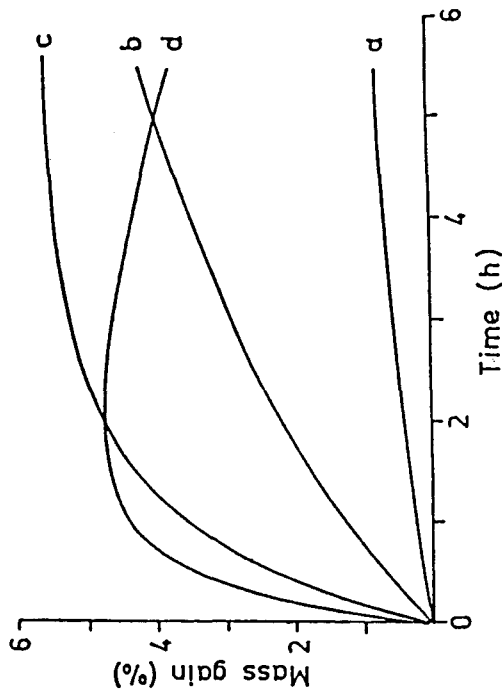Figure 2. Free Swelling Index value of Hiawatha #1 high volatile bituminous coal at different oxidation conditions.

Figure 3. Mass changes of a Upper Freeport medium volatile bituminous coal, oxidized at constant temperatures: (a) 150°C; (b) 210°C; (c) 260°C; (d) 285°C
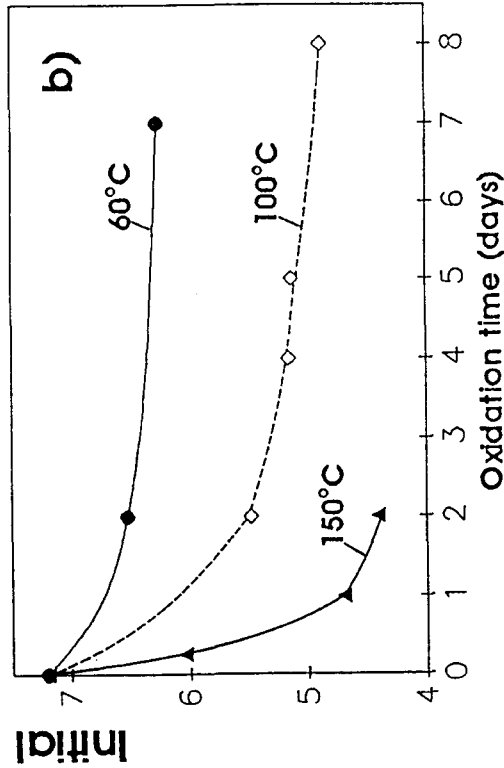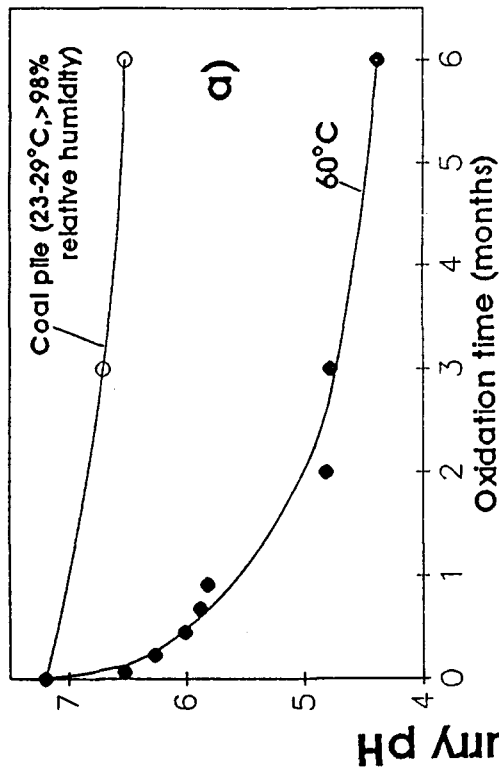
Figure 1. Slurry pH vs. oxidation duration at different oxidation temperatures for Adaville #4 subbituminous coal.