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A Theory on the Mechanism of an Outbreak of Spontaneous Combustion of Coal I

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Contents

I. Preface	249
II. Low-Temperature Oxidation Tests	250
(1) Experimental Apparatus and Procedure	250
(2) The Coal Samples	251
(3) Experimental Procedure	251
(4) Results of the Experiment	252
III. The Induction of a Theory of Occurrence of Spontaneous Combustion of Coal	253
(1) Curves of Perfect Dissipation of Heat	253
(2) Curves of Perfect Accumulation of Heat	254
(3) The Initial Oxidation Rate $\left(\frac{d\Omega}{d\theta}\right)^0$ and Values of k	257
(4) The Establishment of a Theory of the Outbreak of Spontaneous Combustion of Coal	258
IV. The Expansion of the Theory to the Quantities not used in Experiment	263
(1) Expansion to the Larger Particles	263
(2) Expansion to Low-Temperature	264
V. Application to Underground Conditions	265
VI. Conclusion	267
Bibliography	268

I. Preface

There have been few published reports which treat quantitatively the phenomenon of generation of heat in oxidation in the early period of spontaneous combustion, though many experiments and studies concerning it have been undertaken hitherto. Insofar as the present writer knows, only G. S. Scott¹⁾ discussed it in his paper.

In this paper, it is proposed to give quantitative evidence of the phenomenon of generation of heat in oxidation in the early period based on experiments on oxidation under constant low-temperature of coal from the Mitsubishi Oyubari colliery in Hokkaido, the results of which have suggested a theory on the outbreak of spontaneous combustion of coal. In other words, a theory has been formulated concerning its outbreak based upon the results of laboratory experiments.

The error of oxidating test on coal materials is very great at low-temperature in the use of rough particles which are the true conditions in coal mines. The writer expands his experimental results with his theory, so that he is able quantitatively to measure the conditions. Consequently this theory is believed to be applicable to other kinds of coal from other mines through similar experiments.

II. Low-Temperature Oxidation Tests

Up to this time the oxidation rate and the relationship between the gases produced by oxidation and its temperature at various temperatures have been obtained by experiments on low-temperature oxidation, so as to get some solution of the problem of spontaneous combustion of coal.

The results of a number of similar studies on the subject have been published; some of them are as follows: Parr and Milner²⁾, Parr and Hobart³⁾, Tideswell and Wheeler⁴⁾, Winmill⁵⁾⁶⁾⁷⁾⁸⁾ and Graham⁹⁾, etc.

In the present experiments the apparatuses are basically the same as those of above mentioned investigators. The consequent oxidation rate is utilized to design the general formula of the heat generation.

(1) Experimental Apparatus and Procedure

The apparatus for determining the rate of oxidation coal is shown in Figure 1.

First the quantity of dried air is measured, and then it is dried up through drying agent and soda lime. Carbon dioxide (CO_2) is drawn off from dried

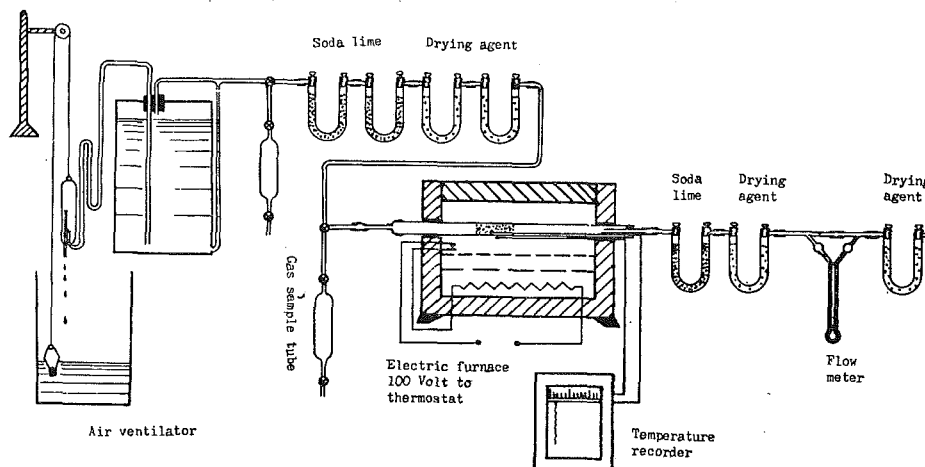


Fig. 1. Low-temperature oxidation apparatus

air and then the dried air minus CO_2 is led into the coal to be tested within the glass tube in the furnace.

The oxidized gases are taken with sampling tubes at random intervals. The effluent gases which have completed oxidation are sucked into ventilator through the air pipe. The volume, temperature and pressure of the residual gas in the ventilator bottle were measured, and the gas was analyzed.

When necessary, the effluent gases are led through drying agent and soda lime, the resulting out water and the CO_2 of effluent gases are measured.

The air ventilator is so prepared as to admit a certain amount of air constantly and to enable exact measurement of the gas.

(2) The Coal Samples

The samples used for the test, were from Oyubari colliery. After they were taken in the pit, the samples were put into containers filled with methane gas as soon as possible. After some of the samples were crushed into needed size, they were kept cool in air-tight glass vessel, and the experiment was carried out as soon as possible.

The sizes of the particles were 20-28 mesh, 28-35 mesh, 35-48 mesh, 48-65 mesh, 65-100 mesh and under 100 mesh. When the air current went through the coal under 100 mesh, the finely crushed coal was unstable and accurate results could not be expected. When the particles were big, the experimental error was big, although the amount of the air current was decreased. Consequently most of the present experiments were carried out with particles between 20 mesh and 100 mesh in size.

(3) Experimental Procedure

One hundred grams of the dried sample was carefully put into a glass pipe, which was inserted into the electric furnace.

To get a high degree of correctness of the result of the oxidation of the coal in an air under a certain temperature, the following methods were adopted.

- i) The air pipe containing a certain size of the particles was prepared so that constant temperature could be maintained; through it the air at required velocity was passed by means of the ventilator.
- ii) Care was taken to gather the effluent gases without changing the velocity of the current.
- iii) The gas analysis was carried out by means of the Orsats method. The concentration of O_2 , CO_2 and CO was measured. Then the volume of O_2 consumed in a given time, and the produced CO_2 , CO and H_2O were measured.

- iv) The quantity of O_2 absorbed into the coal was measured under natural temperature and pressure of $0^\circ C$ and 760 mm after its oxidation rate had been estimated was corrected by the concentration of O_2 and N_2 derived from the analysis. The average quantity of O_2 could be decided by calculation based upon the relation between the oxidation rate per hour and the time.

First the average quantity of absorbed O_2 was obtained by replacing the air in the air ventilator bottle with water and analyzing the gas. In this procedure, however, the experiment was interrupted and was complicated by the double gas analysis. To avoid this complication, the above mentioned methods were adopted, which have led to more correct results.

(4) Results of the Experiment

An example of the result of the experiment is shown in Figure 2.

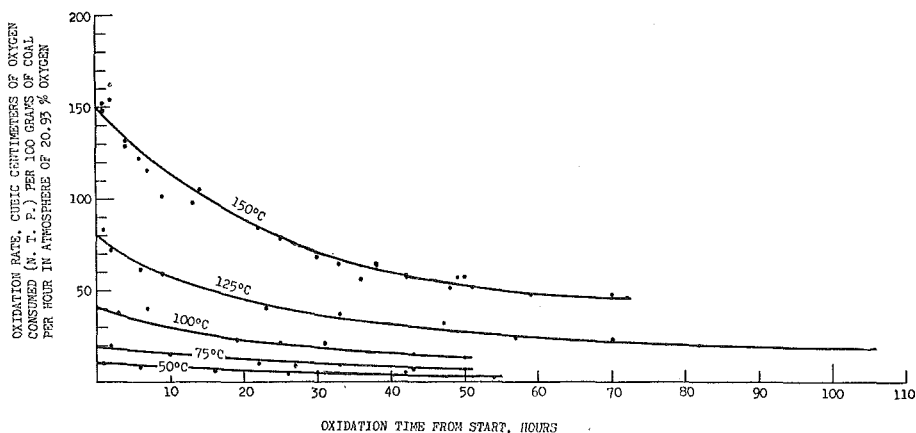


Fig. 2. Oxidation of Oyubari coal, size 20-28 mesh ; temperature, $150^\circ C$, $125^\circ C$, $100^\circ C$, $75^\circ C$, $50^\circ C$

In the early period of the experiment, particularly at the high temperatures of $150^\circ C$, $125^\circ C$ etc., the temperature of the coal was apt to rise because of rapid O_2 absorption, but the heat was wholly dissipated by the air and through the glass pipe. An experiment of oxidation under a constant temperature is a method to get curves of the decreasing oxidation rate when the heat liberated by oxidation is wholly dissipated.

Figure 3 shows the relationship among the quantity of the absorbed oxygen, the oxidation rate and the temperature, attributed to the relationship shown above. (Fig. 2)

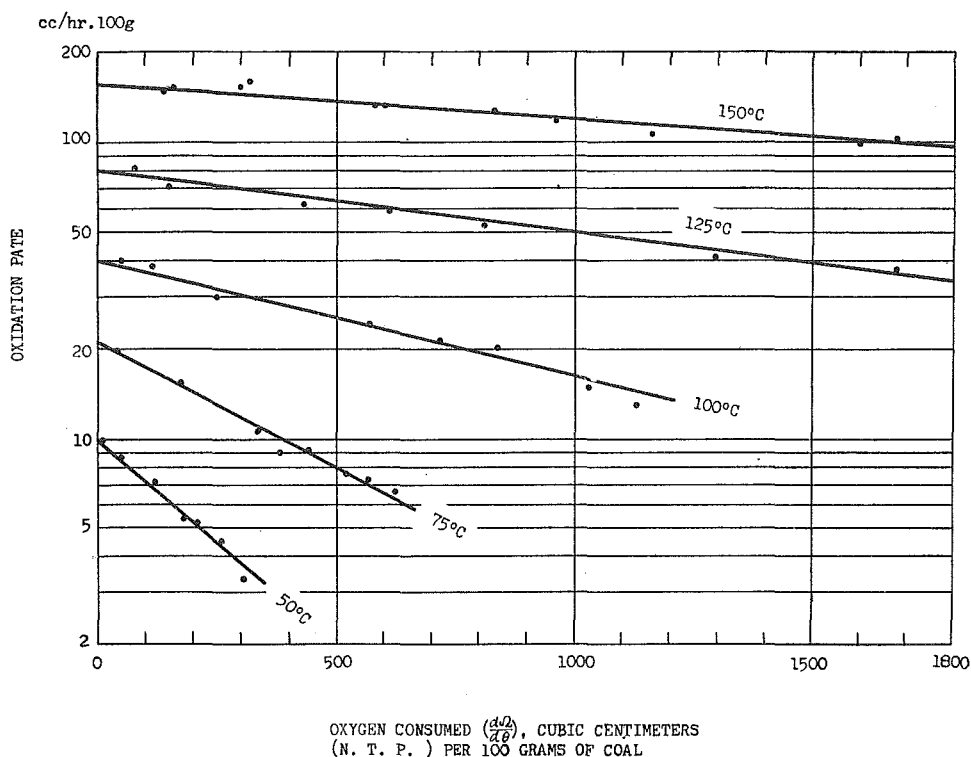


Fig. 3. Oxidation of Oyubari coal, size 20-28 mesh; temperature, 150°C, 125°C, 100°C, 75°C, 50°C

III. The Induction of a Theory of Occurrence of Spontaneous Combustion of Coal

(1) Curves of Perfect Dissipation of Heat

The relationship between the oxidation rate and the quantity of the absorbed oxygen—the curves of perfect dissipation of heat—obtained through the experiment of oxidation of coal under constant low-temperature is shown by the following general formula.

$$\frac{d\Omega}{d\theta} = f\left(\frac{d\Omega}{d\theta}\right)^0 e^{-k\Omega} \quad (1)$$

where $\frac{d\Omega}{d\theta}$: oxidation rate
 $\left(\frac{d\Omega}{d\theta}\right)^0$: initial oxidation rate

- k : exponential constant
 f : size factor
 Ω : the quantity of previously consumed oxygen

(2) Curves of Perfect Accumulation of Heat

The subject of this section is the change of oxidation rate when the heat liberated is perfectly accumulated. It is necessary for one to know how many calories are produced when the coal absorbs 1 cc of oxygen and to know the specific heat of the coal.

The direct determination of the heat liberated by low-temperature oxidation has been made by Lamplough and Hill¹⁰, who found a mean value of 3.3 calories per cubic centimeter of oxygen consumed for a minus 30 mesh coal at normal temperatures, and by Scott¹¹, who found 4.7 calories for fresh anthracite. The latter's method was adopted for this study. Consequently for the theoretical basis one should refer to his paper. For the mean specific heat

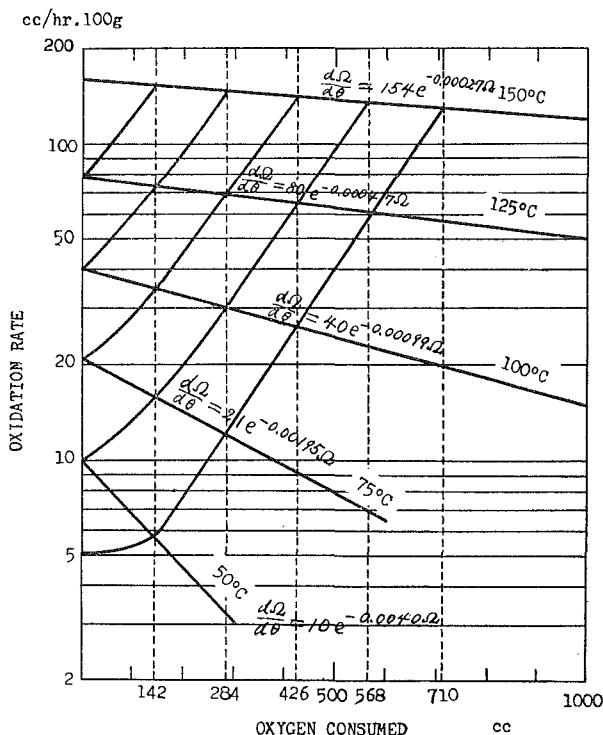


Fig. 4. Oxidation rate vs. quantity of oxygen consumed; size 20-28 mesh

of the coal, 0.25 cal was used.

Table 1 was compiled by making use of Scott's method.

The calories of Oyubari coal emitted when 1 cc of oxygen is absorbed in low-temperature oxidation were found to have a mean value of 4.4 cal/cc.

When 100 grams of the coal is taken,

$$\frac{x \times 4.4}{0.25 \times 100} = 1$$

$$x = 5.7 \text{ cc/}^\circ\text{C. coal 100 g}$$

In every absorption of 5.7 cc of oxygen, the temperature for 100 grams coal rises by 1°C . Consequently in every absorption of 142 cc of oxygen, the increase is 25°C . Therefore in Figure 4 when one draws a line passing the crossing of the lines of every 142 cc and the curves of the perfect dissipation of heat of every 25°C , one can get the curves of the perfect accumulation of heat, the changing curve of the rising heat and the oxidation rate in the curves.

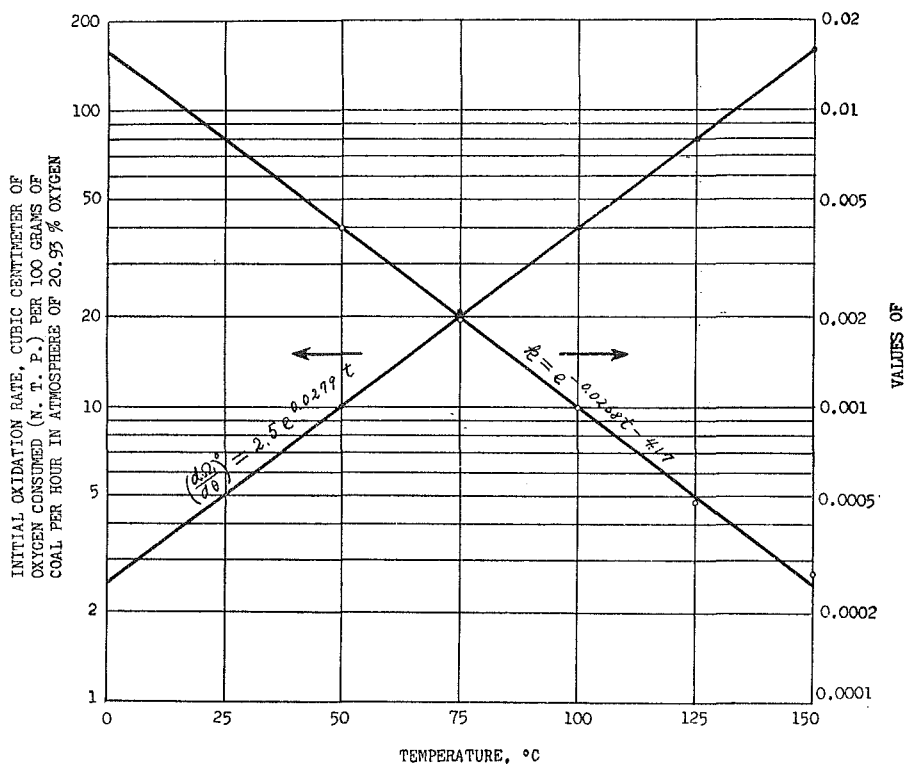


Fig. 5. Values of k and $\left(\frac{dQ}{dt}\right)^0$; size 20-28 mesh

(3) The Initial Oxidation Rate $\left(\frac{d\Omega}{dt}\right)^0$ and Values of k

The initial oxidation rates at different temperatures are shown in Figure 5.

For comparison, the samples were brought to the same initial condition with respect to the quantity of oxygen consumed and were as fresh as possible. The related formula may be as follows:

$$\left(\frac{d\Omega}{dt}\right)^0 = Ce^{at} \quad (2)$$

where $\left(\frac{d\Omega}{dt}\right)^0$: initial oxidation rate
 t : temperature °C
 a : coefficient
 C : a constant
 e : base of the Napierian logarithms

For the 20-28 mesh Oyubari coal shown in Figure 5, the equation is

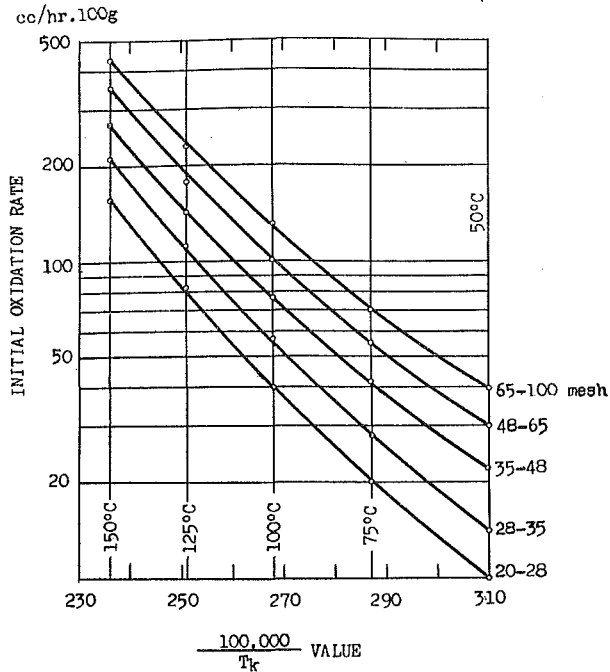


Fig. 6. Variation of initial oxidation rate with the reciprocal of the absolute temperature

$$\left(\frac{d\Omega}{d\theta}\right)^0 = 2.5 e^{-0.0279\theta} \quad (3)$$

Values of k plotted against temperature are also shown in Figure 5.

$$k = e^{-0.0268\theta - 4.17} \quad (4)$$

Many investigators plot the logarithm of the rate against the reciprocal of the absolute temperature in conformity with the theoretical equation of Arrhenius. For the samples tested by the present author, the relationship over the range shown agrees better with the above equation than with the Arrhenius equation. The results are plotted in Figure 6; they agree with Porter-Ralston's¹¹⁾ and Scott's¹⁾ conclusions.

(4) The Establishment of a Theory of the Outbreak of Spontaneous Combustion of Coal

When the logarithmic mean of initial oxidation rates $\left(\frac{d\Omega}{d\theta}\right)^0$ and values

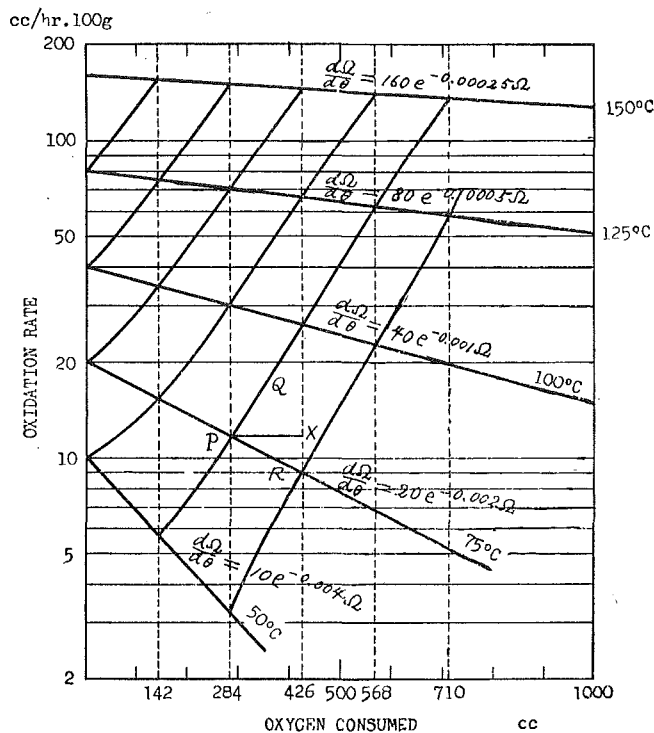


Fig. 7. The theory of an outbreak of spontaneous combustion of coal, size 20-28 mesh

of k are obtained, Figure 4 transforms itself into Figure 7, and the theoretical chart is established.

In Figure 7 the line PX is drawn parallel to the axis of abscissa from an optional point P . At P , 284 cc of oxygen is absorbed up to the given time, the oxidation rate at the point is 11.8 cc/hr. 100 g, and the temperature is 75°C.

When the oxidation at P produces no rising of heat, one must draw a straight line PR . When the heat is perfectly accumulated, the temperature rises and the oxidation goes along the curve PQ . In other words the reaction at an optional point P is the oxidation and the heat generation progressing rightward within QPR .

As the progression of the rate of oxidation in XPR gradually diminishes even when the temperature rises slightly, there is little danger of the onset of spontaneous combustion of coal. In QPX , however, the oxidation rate rises in accordance with rising of the temperature. Thus, the temperature rises slowly at first, but later on it rises so rapidly that spontaneous combustion results.

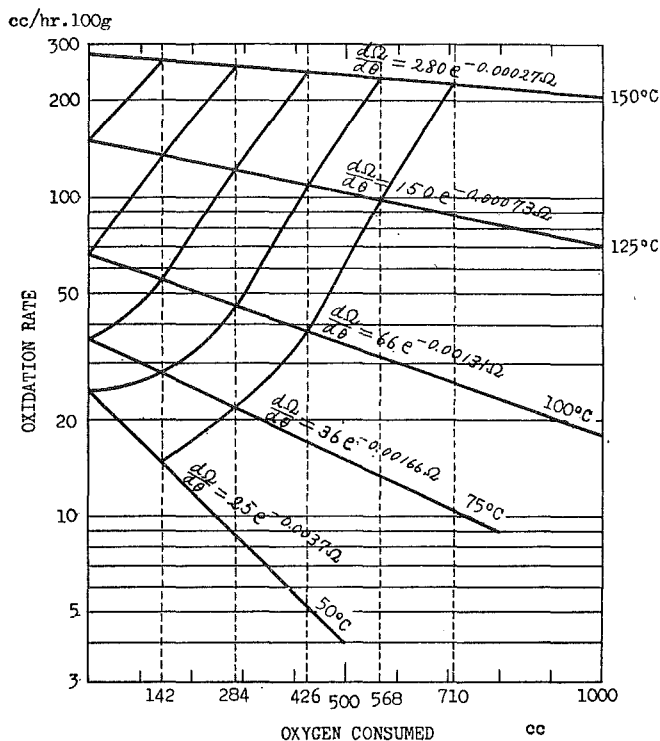


Fig. 8. Oxidation rate vs. quantity of oxygen consumed, size 35-48 mesh

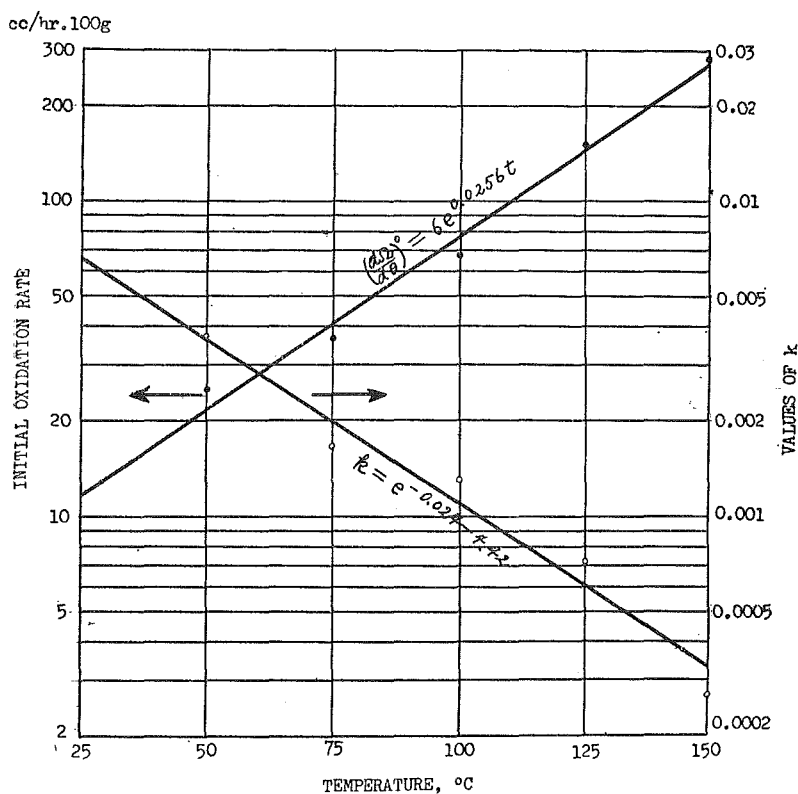


Fig. 9. Values of k and $\left(\frac{d\Omega}{d\theta}\right)^0$; size 35-48 mesh

(It is desirable to mention cases in which supplies of heat are received from other high-temperature coal.)

In Figures 8, 9 and 10 the theoretical charts are drawn on the results of experiments with 35-48 mesh.

The general formula of the perfect heat accumulation curve is as follows:

$$\frac{d\Omega}{d\theta} = \alpha \left(\frac{d\Omega}{d\theta} \right)^0 e^{\beta\Omega} \quad (5)$$

where

$\frac{d\Omega}{d\theta}$: oxidation rate

$\left(\frac{d\Omega}{d\theta}\right)^0$: initial oxidation rate

α : coefficient about the initial temperature

β : coefficient

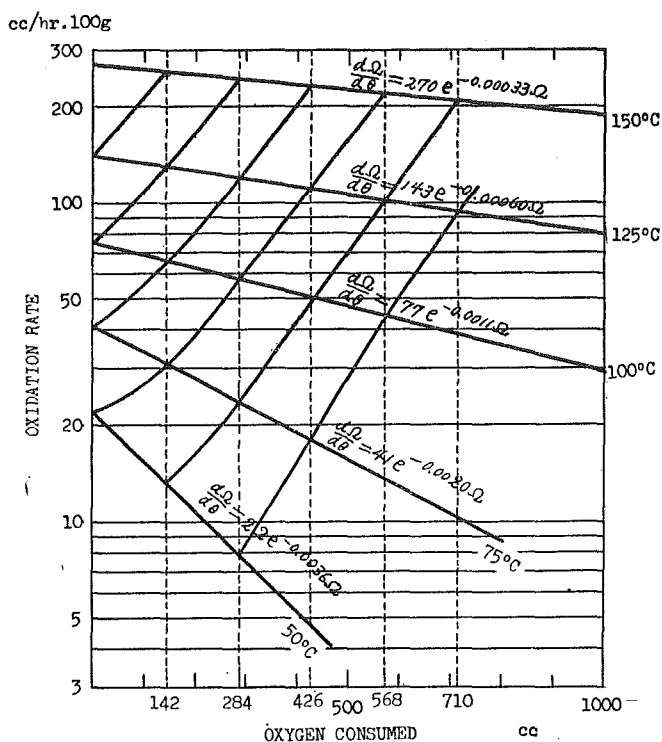


Fig. 10. The theory of an outbreak of spontaneous combustion of coal, size 35-48 mesh

The relationship between the initial temperature and the coefficient α in the perfect heat accumulation curve of the Oyubari lower coal is shown in Figure 11. The numerical value of β is 0.004-0.0063.

Formula (5) is adaptable to change during oxidation at high temperature over 75°C. In the cases of lower temperature, one must depend upon the chart calculation.

In the chart calculation, as is shown in Figure 12, the crossing point of the initial oxidation rate, which is the quantity of O_2 absorbed in the first one hour, and the perfect heat accumulation curve is named A, and then the oxidation rate at A is to be regarded as the subsequent oxidation rate; then the crossing point of this oxidation rate, which is the quantity of O_2 absorbed in two hours, and the perfect heat accumulation curve is named B, and then this oxidation rate at B is regarded as the following oxidation rate; this is repeated again and thus the oxidation rate and the time needed are calculated.

In Figure 12 the perfect heat accumulation curve was followed from the

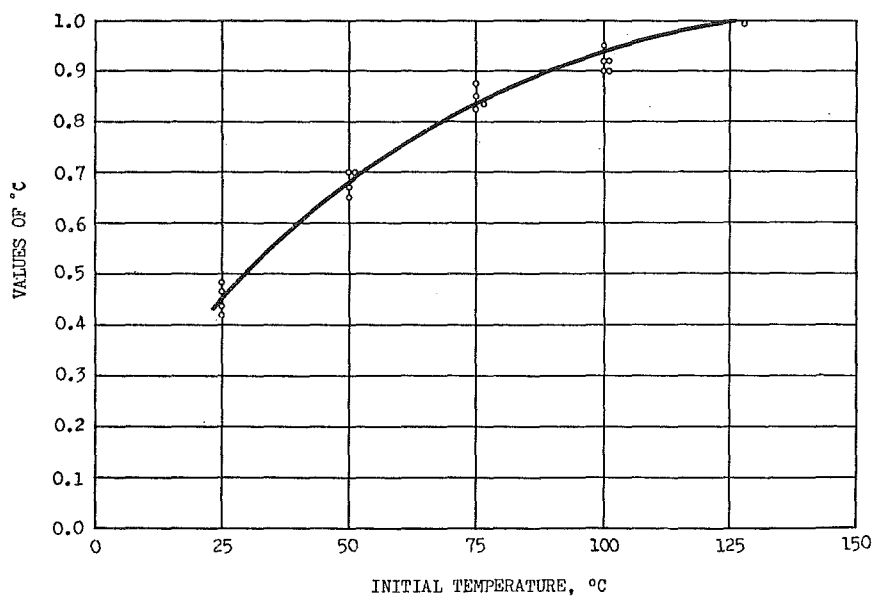


Fig. 11. Initial temperature vs. the coefficient in the perfect heat accumulation curves

case in which the initial oxidation rate is 20 cc/hr.100 g and the first temperature is 75°C. In six hours of oxidation, 100°C was reached.

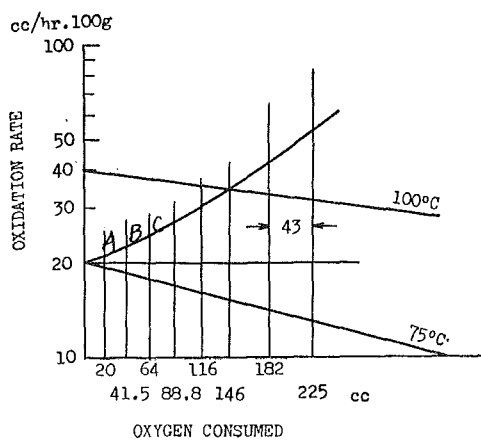


Fig. 12. An example of chart calculation

IV. The Expansion of the Theory to the Quantities not Used in Experiment

The above discussed theory can be expanded to cases in which no actual experimental temperature and grain size were used.

(1) Expansion to the Larger Particles

Figure 13 shows a plot of the initial oxidation rates plotted against mean particle diameter for 50°C, 75°C, 100°C, 125°C. and 150°C.

From Figure 13 it is apparent that a definite relationship exists between particle size and initial oxidation rate. The relationship is shown more clearly, if the logarithmic averages of the rates for each size are plotted against particle size, as in Figure 14. The relationship becomes much smoother when the particle sizes are bigger than 20-28 mesh (0.076 cm). The curves intersect at an angle of 45°. This shows that in the low-temperature oxidation

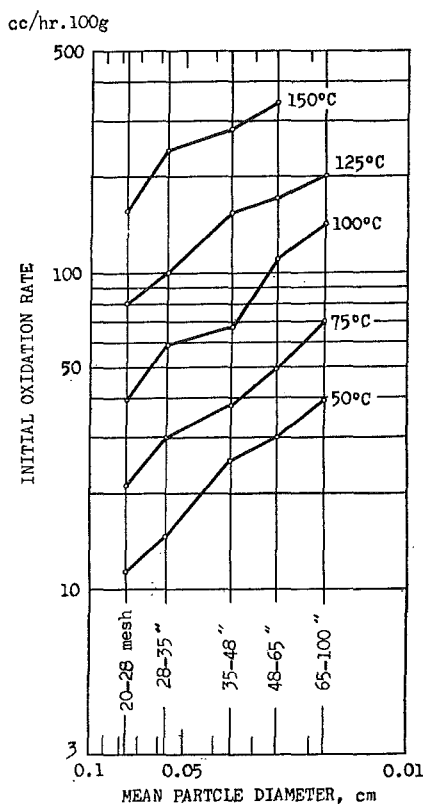


Fig. 13. Initial oxidation rates of coal

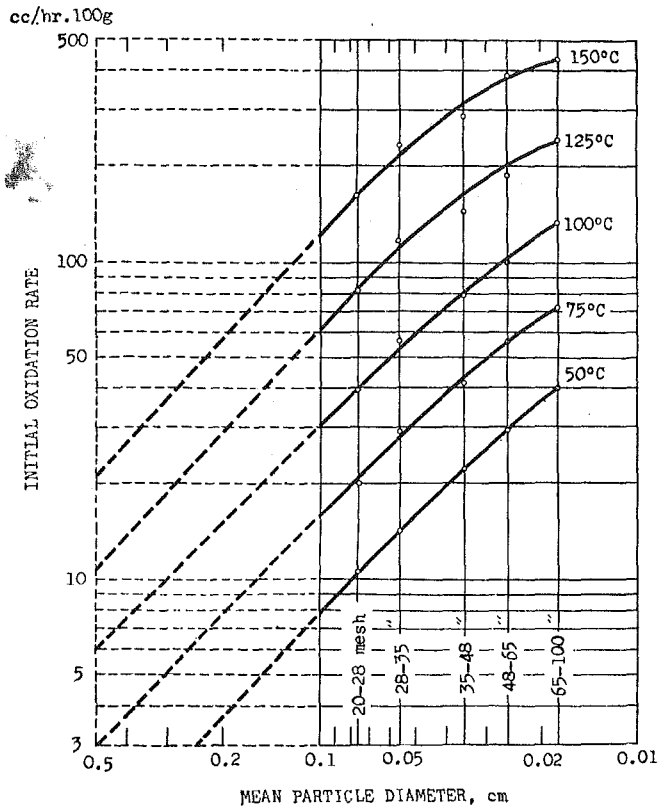


Fig. 14. Logarithmic averages of initial oxidation rates

below 150°C, the initial oxidation rates are in direct proportion to the surface area of the particles.

Thus, if 100 grams of fresh coal is taken for the basis of calculation, the initial oxidation rate of 20-28 mesh coal is 40 cc/hr at 100°C, and when the diameter of particles is 0.1 cm, it is 30 cc/hr.

If the coefficient of the particle size is f ,

$$f = \frac{30}{40} = 0.75$$

When the diameter is 0.2 cm, it is 15 cc/hr.

$$f = \frac{15}{40} = 0.375$$

(2) Expansion to Low-Temperature

In Figure 5, one can regard that the initial oxidation rate $\left(\frac{d\Omega}{d\theta}\right)^0$ and value

k are strictly functions of the temperature t . Consequently this theory can be expanded to the low-temperature, the natural temperature, at which determinations cannot be made experimentally.

When the size of particle is 20–28 mesh and the temperature is 25°C at the beginning the perfect dissipation curve is

$$\left(\frac{d\Omega}{d\theta}\right) = 5e^{-0.008\Omega}$$

When this equation is integrated, one obtains

$$\frac{e^{0.008\Omega} - 1}{0.008} = 5\theta$$

By substituting 142 cc for Ω (see Figure 4) and solving for θ ,

$$\theta = \frac{2.114}{0.04} = 52.8 \text{ hr.}$$

This shows it takes 52.8 hours for the above mentioned coal to absorb 142 cc of O_2 for the first time. Moreover one can find the quantity of the absorbed oxygen in a given time assigning a number instead of θ .

V. Application to Underground Conditions

Figure 15 shows the relationship among the oxidation time, its rate, the quantity of the absorbed oxygen, rate of temperature rise, etc., when the temperature of the early period is 25°C, the diameter of particles is 20–28 mesh, 0.1 cm or 0.2 cm. Further, the conditions are altered in the perfect heat dissipation, in the perfect heat accumulation or in case of keeping up the initial oxidation rate.

TABLE 2. Relation among the oxidation time, the quantity of oxygen consumed and the rise of temperature

Oxygen consumed	Every given volume	142	142	142	142	142
	Total volume cc	142	284	426	568	710
Perfect heat dissipation	Temp. °C	25	25	25	25	25
	Time hr	52.8	164.8	510	—	—
Initial oxidation rate maintained	Temp. °C	45	58	65	70	74
	Time hr	28.4	28.4	28.4	28.4	28.4
Perfect heat accumulation	Temp. °C	50	75	100	125	150
	Time hr	28	20	9	4	1.5

Most oxidation phenomena on the surface or in the underground without spontaneous combustion of coal show reaction similar to the perfect heat dissipation. The time necessary to absorb a given quantity of oxygen increases rapidly, while there appears only a slight rise of temperature.

This theory not only explains the problem of spontaneous combustion of coal, but also has made it possible for one to compare the freshness of coal quantitatively at the usual temperature.

It is technically impossible to maintain the oxidation rate in the early period for a long time, through it should be possible theoretically. In this case the velocity of the rising of temperature in every given period, here in 28.4 hours, gradually decreases. Therefore in this kind of reaction, it is impossible for the oxidation to proceed toward spontaneous combustion. Consequently the reaction toward spontaneous combustion is always found in the range between perfect heat accumulation and the maintenance of the initial oxidation rate. In the case of perfect heat accumulation, the time required for the temperature to rise every 25°C decreases along an exponential curve as the temperature rises, which has been shown as a result of the experiments by J. D. Davis and J. F. Byrne¹²⁾ and Miyakawa *et al*¹³⁾. Till now there has been no sufficient explanation about the abnormal rising temperature of a small pile of coal dust produced in mine levels. Some of the investigators tried to explain it as the working of some catalyzer, upon which they did not touch. The present writer attempts to explain it as the oxidation phenomenon close to the perfect heat accumulation.

VI. Conclusion

Experiments have been conducted on oxidation in the constant low-temperature using Oyubari coal in Hokkaido. It has been shown as a result that it is possible to explain the early heat generation phenomenon in the oxidation of coal quantitatively. The basic difference between this theory and the information in Scott's report is that in this theory the oxidation of coal is taken to proceed between the perfect heat accumulation curve and the perfect dissipation curve unless there is supply or withdrawal of heat by other materials.

To make the problem simple no consideration is taken, in this theory, of the quantity of coal. The size of a pile of coal greatly influences the change in oxidation by lowering the oxygen contents, the cooling due to the effects of the outside air, the spread of heat in a pile of coal and so on. These points, however, have little importance in the explanation of the rise of the initial temperature in instances of the spontaneous combustion of coal.

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