Simulation of a Maximum Storage Amount of Coal for Preventing Spontaneous Combustion and Degradation in Quality[†]

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Abstract

The temperature rise curve due to the natural oxidation of a coal deposit was numerically simulated for a coal bed having a 'spherical' geometry. The maximum temperature occurred at the center of the bed when oxygen was fully supplied within the bed and near the surface when oxygen decreased due to the process of the reaction. The rate of temperature rise was significantly affected by the activation energy and frequency factor of the coal. Furthermore, the measurement of the moisture adsorbed on the oxidized coal samples showed that the loss in mass due to oxidation increased remarkably at temperatures above 120°C. In assuming the limiting temperature in coal storage to be 120°C, a maximum allowable amount of coal storage was estimated for various kinds of coal under the conditions of neither spontaneous combustion nor significant loss in mass.

1. Introduction

The problems faced in long-term coal storage include quality degradation due to natural oxidation and spontaneous combustion due to heat accumulation and temperature rise. The degree of heat accumulation in coal depends on physical factors, including the coal storage method, coal storage quantity, coal particle size and ambient temperature, along with the reactivity of coal. If the heating velocity of the inside of the coal surpasses the speed at which it radiates heat into the atmosphere, oxidation speed rises gradually as the coal layer temperature climbs until it reaches ignition temperature, leading to spontaneous combustion. In coal storage, therefore, there is a maximum

allowable coal storage size depending on heat income and outcome. Previous studies concerning the spontaneous combustion of coal dealt with powdered coal inside a coal mine, coal crusher or similar environment with emphasis put on estimating the ignition conditions for the sake of security^{1,3,5,7)}. However, considering that the basic composition of coal and its content ratio of oxygen and other matter of the functional group change gradually due to oxidation even at lower temperatures than the ignition temperature¹⁰⁾, we believe it important to design such large-capacity coal storage equipment that prevents mass loss and quality degradation as well as spontaneous combustion. This paper aims to evaluate the maximum allowable storage amount (maximum critical size) that satisfies the above requirements. More specifically, this paper aims to evaluate the maximum storage amount by:

- allowing for the effect of coal particle diameter, oxygen density and coal reactivity on heat accumulation and temperature rise; and

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- empirically studying the relationship between oxidation and mass loss.

2. Theory

2. 1 Basic equations expressing a temperature rise

The shape of coal deposits depends on the coal storage method. Solving the heat balance equations and material balance equations of some shapes of coal deposits are very difficult. This paper excludes factors related to the shape of deposits and assumes the simplest shape: spherical deposits. Sphere diameter, we believe, gives rough guidelines for determining silo diameter and storage height in the case of a silo storage method, and for determining storage height in the case of an outdoor storage method.

On the assumptions listed below, the temperature rise process of a spherical body can be expressed as in Eqs. (1) ~ (3).

Assumption 1) Coal and its ambient gas share the same temperature.

2) Heat and mass transfers due to convection are neglected. Heat is transferred by conduction and radiation, while oxygen is transferred by molecular diffusion.

3) Moisture transfer and resulting heat transfer are neglected.

$$C_v \frac{\partial T}{\partial t} = k_e \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) + \rho_b (-\Delta H) \frac{\partial X_1}{\partial t} \quad (1)$$

$$\frac{\partial C}{\partial t} = \vartheta \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - \frac{\rho_b}{\epsilon} \frac{\partial X_1}{\partial t} \quad (2)$$

$$\frac{\partial X_1}{\partial t} = A \cdot \exp \left(-\frac{E_a}{RT} \right) \cdot P_{O_2}^n; P_{O_2} = RCT \quad (3)$$

where T , C and X_1 mean the temperature, oxygen concentration and the molar amount of oxygen consumed per unit mass of coal, at time t and location r . Oxygen consumption rate $\partial X_1 / \partial t$ is commonly expressed at Eq. (3) as a function of Arrhenius' rate constant and oxygen partial pressure^{5,11,12}. At the center of the sphere ($r = 0$), the boundary conditions of the above equations are:

$$\frac{\partial T}{\partial r} = 0, \quad \frac{\partial C}{\partial r} = 0 \quad (4)$$

At the sphere surface ($r = D/2$), oxidation

occurs so slowly that we assumed:

$$T = T_a, \quad C = C_a \quad (5)$$

where T_a and C_a refer to ambient temperature and concentration.

We performed numerical calculations of Eqs. (1) ~ (3) based on Eqs. (4) and (5). The constants used in these calculations are as follows. We calculated oxygen mass diffusivity based on Fujita's²⁾ equation and set specific heat at $C_v = 963 \text{ J/(kg} \cdot \text{K)}^{4,12}$, and heat of coal oxidation reaction at $\Delta H = -3.7 \times 10^5 \text{ J/mol}^{11}$. Effective thermal conductivity k_e was obtained from the equation⁶⁾ for estimating the effective thermal conductivity of packed bed with no fluid flow. For these calculations, we set the void fraction of coal deposit ϵ at 0.4, heat radiation factor (emissivity) at 0.9 and coal thermal conductivity at $1 \text{ kJ/(m} \cdot \text{h} \cdot \text{K)}^{12}$, and assumed the gas as air. In the same matter as Iki and Higuchi *et al.*⁴⁾, we neglected changes in k_e due to temperature and used effective thermal conductivity at 60°C. Our calculations revealed that k_e rose as coal particle diameter d_p climbed. An example: k_e when $d_p = 5 \text{ cm}$ is about 2.7 times the k_e when $d_p = 0.1 \text{ cm}$. This finding indicates that more heat is radiated into the ambient atmosphere as the particle diameter of coal deposits increases.

2. 2 Estimation of parameters related to coal reactivity

When a coal sample is enclosed in a heat-insulated apparatus containing oxygen, the sample temperature will rise gradually due to oxidation. Assuming that this apparatus has a heater and can be so controlled as to make ambient gas temperature remain the same as the sample temperature, the resulting rise in sample temperature is due merely to oxidation-induced heat generation of the coal itself. Based on Eqs. (1) and (3), the above procedure can be expressed as:

$$C_v \frac{dT}{dt} = A \exp \left(-\frac{E_a}{RT} \right) \quad (6)$$

where

$$A = A^* \rho_b (-\Delta H) \cdot P_{O_2}^n \quad (7)$$

Assuming that the apparent frequency factor when air (oxygen partial pressure $P_{O_2,i}$) is used as the gas is A_0 , the following holds:

$$A = A_0 (P_{O_2}/P_{O_2,i})^n,$$

$$A^* = A_0 / \{ \rho_b (-\Delta H) P_{O_2,i}^n \} \quad (8)$$

Apparent frequency factor A , apparent activation energy E_a and exponent n of oxygen partial pressure are obtained^{4,5,12)} by determining temperature rise curve (T vs t) with an experimental apparatus, with different oxygen partial pressures, which satisfies Eq. (6) and whose oxygen consumption can be neglected. Onizuka *et al.*¹²⁾ conducted experiments on large quantities of coal and revealed:

- (1) The temperature rise speed dT/dt has an inflection point at about 120°C, above and below which the reaction mechanism differs;
- (2) The apparent frequency factor changes according to the sample particle diameter and can be expressed as $A \propto d_p^{-(0.35 \sim 0.65)}$; and
- (3) The dependency of oxygen partial pressure is $n=0.44 \sim 0.74$.

For the purpose of this report, we also conducted similar experiments on five representative types of coal with different atomic ratios H/C and O/C. The result was that $n \approx 0.4$ and that changes in apparent frequency factor due to d_p were as shown in Fig. 1 in the low temperature range covered in our study. Our result almost agrees with Onizuka *et al.*'s results. Based on the above, we conducted simulation using $n=0.6$ and assuming A vs. d_p as follows:

Fig. 1 Variation of frequency factor with particle diameter

$$A \propto d_p^{-0.5} \text{ or } A = A_B \left(\frac{d_p}{d_{p,B}} \right)^{-0.5} \quad (9)$$

where $d_{p,B}$ and A_B refer to standard particle diameter and known apparent frequency factor. As is evident from Fig. 1, particle diameters used were about 1 mm at the most so that we still do not at all know how applicable and precise Eq. (9) is with regard to grain-type coal with diameters of several centimeters, which is in question in actual coal storage. Since no other appropriate evaluation method is now available, we used Eq. (9) also for grain-type coal. Equation (9) indicates that the apparent frequency factor drops, resulting in a fall in the heat generation speed, as the particle diameter increases. We carried out the calculations in the following order:

- (1) converting apparent frequency factor A_B (reports 4, 12) of coal with a particle diameter of d_B derived from air oxidation into comparable A_B value of coal with a desired particle diameter using Eq. (9); and
- (2) (with the former A_B value set at A_0), evaluating A and A^* on the basis of Eq. (8).

3. Results and discussion

3. 1 Temperature rise simulation

Figure 2 shows the results of numerical calculations, based on Eqs. (1) and (3), of the

Fig. 2 Temperature histories of spherical coal deposit in simulated natural oxidation under constant oxygen concentration

temperature rise with an equal oxygen concentration in all portions of the well-ventilated coal deposits. The target coal is Joban coal mentioned in the previous report⁴⁾. We set particle diameter d_p as 1 cm; deposit initial temperature T_o and ambient temperature T_a as 20°C; and deposit diameters as (I) $D = 2.6$ m and (II) $D = 2$ m. $2r/D$ means a dimensionless version of the distance from the deposit center. When $D = 2$ m, temperature rises slightly but heat generation speed equals heat radiation speed at a low temperature ($dT/dt = 0$), resulting in no occurrence of spontaneous combustion. When $D = 2.6$ m, after heat generation speed surpasses heat radiation speed and nears 100°C, heat is rapidly accumulated and temperature rises quickly ($dT/dt > 0$), leading to spontaneous combustion. Both temperature and the temperature rise rate maximize at the sphere center. Figure 3 gives an example of the case in which the oxygen content in the deposit of the same coal as in Fig. 2 is consumed and decreases as reaction proceeds. The oxygen concentration curve indicates that oxygen declines gradually over time, because oxygen consumption rate surpasses oxygen resupply speed due to molecular diffusion. Figure 3, therefore, shows no such exponential-function-

Fig. 3 Temperature and oxygen concentration histories in simulated natural oxidation

like rise as in Fig. 2. However, it does indicate temperatures surpassing coal ignition temperature (about 200 ~ 220°C). This finding shows that the coal storage size used here is inappropriate. Figure 4 shows the results with the coal particle diameter set at double that used in Fig. 2 and 3 and the deposit diameter D set at 10 m. An increase in particle diameter and a resulting decline in reaction rate due to a drop in apparent frequency factor [Eq. (9)] and oxygen consumption cause the temperature to rise slowly despite the large deposit diameter ($D = 10$ m) and its high heat accumulation effect. After 3,000 hours, however, the intra-layer maximum temperature reaches 135°C. The position at which the temperature is maximized is, unlike in Figs. 2 and 3, near $2r/D = 0.75$ nearer to the deposit surface. Near the center of the sphere, reaction slows down as oxygen quantity declines so that, we believe, temperature is maximized nearer to the surface from the center. Some existing papers^{8,9)} already report that temperature may diverge ($dT/dt > 0$) near the surface of spontaneous-ignitable powder when it is exposed to a high-temperature atmosphere. Figure 4 indicates that a similar phenomenon occurs when such material contacts ordinary ambient temperature. This shows that spontaneous ignition and quality degradation cannot be prevented suf-

Fig. 4 Temperature and oxygen concentration histories in simulated natural oxidation for a large coal deposit

ficiently by detecting the temperature at the center of deposits alone.

3. 2 Changes in coal pores due to oxidation

Even before the ignition temperature is reached, oxidation brings about changes in basic composition and a loss in coal¹⁰⁾. To confirm this, we examined the rise due to oxidation in amount of water adsorbed on the coal sample (80 ~ 100-mesh), shown in Fig. 1 E, which was left in a constant-temperature drier containing enough air. More specifically, we conducted the experiment in the following order:

- (1) shutting up an oxidized sample, together with a saturated salt water solution having a constant vapor pressure, in a desiccator in a vacuum state;
- (2) leaving the desiccator in a 20°C constant-temperature water bath for a certain period of time, until adsorption reaches its equilibrium; and
- (3) determining the amount of water absorbed V [m³/g·coal] on the basis of the rise in sample weight.

Similarly, we measured V using different types of saturated salt water solution with various vapor pressure p . Figures 5 and 6 indicate the results (adsorption isotherms) plotting the

above V value with regard to relative vapor pressure p/p_0 (p_0 is the saturated vapor pressure of 20°C water). Figure 5 indicates the effect of oxidation temperature on adsorption isotherms on samples oxidized for one day. No considerable rise is seen in the amount of water absorbed at temperatures below 110°C. In the case of samples at 140°C or more, on the other hand, the amount of water absorbed climbs considerably. This shows that, here, oxidation proceeds faster than at temperatures below 110°C, thus considerably promoting the loss of mass and the development of micropores. The above results, as mentioned in clause 2.2, correspond to the report that the oxidation mechanism generally differs above and below about 120°C¹²⁾.

Figure 6 shows the effects of oxidation period on adsorption isotherms at 75°C (low-temperature side) and 140°C (high-temperature side) on oxidized coal samples. At 75°C, the amount of water absorbed did not increase to a considerable extent even after about a one-month oxidation period, showing a very slow rate of oxidation. At 140°C, on the other hand, mass loss proceeded considerably with the passage of time. To prevent excessive quality degradation and mass loss, therefore, we should inhibit temperature from becoming so

Fig. 5 Effect of oxidation temperature on adsorption isotherms of water vapor at 20°C on coal samples oxidized for one day

Fig. 6 Effects of oxidation temperature and time on adsorption isotherms of water vapor at 20°C on oxidized coal samples

Fig. 7 Effects of particle diameter and oxygen concentration on a maximum critical size in coal storage

Fig. 8 Effect of coal reactivity on a maximum critical size in coal storage

high level that leads to considerable coal loss during the required storage period. Although, strictly speaking, the upper limit temperature in storage T_c , we believe, varies according to the type of coal, we assumed $T_c = 120^\circ\text{C}$ in the subsequent part of our study.

3. 3 Estimation of maximum storage amount

We evaluated the maximum diameter D_c of spherical coal deposit which satisfies the following requirements:

- Temperature should not reach ignition temperature, and quality should not drop;
- Storage period is set at t_c ;
- No point in the layer should exceed 120°C .

Figure 7 shows the maximum critical size as a function of coal particle diameter, where $T_c = 120^\circ\text{C}$ and $t_c = 2,000$ hrs. (about 83 days). The

coal sample is the same as that used in Figs. 2 ~ 4. The upper side region of each curve in the figure provides hazardous sizes for coal storage. The figure shows two cases:

- the case in which oxygen concentration is constantly of the same composition as that of the air; and
- the case in which oxygen is consumed and decreases due to the reaction.

As d_p increases, the maximum critical size rises. As mentioned before, this is presumably due to a rise in effective thermal conductivity (i.e., an increase in heat radiation effect) as d_p increases, while the apparent frequency factor drops (i.e., heat generation slows down). The figure shows that, when oxygen consumption is allowed for, ordinary-sized deposits having d_p of about 3 cm or more rarely lead to spontaneous ignition or mass loss. In the case of outdoor storage, deposits are compacted to prevent the air from flowing in due to convection. This method is effective, as indicated by the above results. If it is guaranteed that no air will enter the deposits, we can estimate the storage size by preparing similar drawings according to the type of coal. However, it is still possible that some cause or other may lead to the formation of an air passage in the coal deposits. To prevent such a risk, designers should predict the maximum critical size on the safety side, i.e., under such a condition that air is resupplied sufficiently. This condition alone applies to the subsequent part of our study.

3. 4 Effect of coal reactivity on maximum critical size

Onizuka *et al.*¹²⁾ conducted experiments on large quantities of coal and reported apparent activation energy E_a and apparent frequency factor A converted on the basis of particle diameter $74\mu\text{m}$. Of their various types of coal, we chose five characteristic types of coal and calculated their respective maximum critical sizes D_c . The results are shown in Fig. 8. D_c varies greatly according to the difference in type of coal, i.e., the difference in E_a and A . The factor E_a , we believe, generally exercises more influence than A .

3. 5 Determination of maximum critical size using a dimensionless term

We conducted a dimensional analysis of fac-

tors related to the maximum critical size and obtained the following dimensionless term:

$$X = \frac{QT_c}{C_v(T_c - T_o)}$$

$$Y = \left\{ \frac{k_e D_c^2 \cdot (T_c - T_o)/D_c}{QD_c^3/4} \right\}^{-0.5}$$

$$= \left\{ \frac{4k_e(T_c - T_o)}{QD_c^2} \right\}^{-0.5}$$

$$\eta_1 = \frac{T_c}{T_c - T_o}, \quad \eta_2 = \frac{T_a}{T_c - T_o}, \quad \eta_3 = \frac{T_o}{T_c - T_o}$$

$$\eta = \eta_1 \cdot \eta_2 \cdot \eta_3 \quad (10)$$

where T_c , upper limit temperature in storage, was set at 120°C. Q refers to the average heat generation speed defined by the following equation:

$$Q = \frac{1}{T_c - T_o} \int_{T_o}^{T_c} (C_v \frac{dT}{dt}) dT$$

$$= \frac{1}{T_c - T_o} \int_{T_o}^{T_c} A \exp(-E_a/RT) dT \quad (11)$$

X and Y^2 are amounts proportionate to (amount of heat generated/amount of heat accumulated) and (heat radiation speed/heat generation speed)⁻¹ respectively until time t_c . Assuming various types of coal¹²⁾ and particle diameters, we calculated maximum critical size D_c and then determined X and Y . The results are indicated in Fig. 9. $\eta = 33.7$ holds on the assumption of $T_a = T_o = 20^\circ\text{C}$ and $\eta = 70$ holds on the assumption of $T_a = T_o = 40^\circ\text{C}$. Interestingly, the X vs Y curve scarcely depends on t_c and is expressed as a single curve when the maximum storage period t_c ranges from 1,000 hrs. (about 42 days) to 3,000 hrs. (125 days = 4 months). Use of Fig. 9 enables us to estimate the maximum deposit size, which is the subject

Fig. 9 Dimensionless plot for the estimation of D_c

of our present paper, without performing numerical calculations of differential equations.

4. Conclusion

To study ways to store coal stably for a long period, we simulated a maximum critical size with which coal can be stored without the risk of spontaneous ignition or excessive mass loss due to natural oxidation. With a constant sufficient supply of oxygen, coal temperature was maximized at the center of the deposit. With some decline in oxygen due to oxidation, on the other hand, temperature was maximized near the coal surface. Heat accumulation speed depended largely on activation energy and apparent frequency factor which govern coal reactivity. Measurements of amounts of water adsorbed on oxidized coal revealed that coal mass loss increased considerably at temperatures above 120°C. We, therefore, set the upper limit storage temperature at 120°C. Then, for various types of coal, we calculated their respective maximum storage amounts which must be observed to hold the stored coal below 120°C over a specified storage period. We then indicated the results in a dimensionless manner for engineering applications.

Nomenclature

A	: apparent frequency factor	$[\text{J} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$
A_0	: A at $P_{O_2} = 0.21 \text{ atm} (= 0.021 \text{ MPa})$	$[\text{J} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$
C	: oxygen concentration in gas phase	$[\text{mol} \cdot \text{m}^{-3}]$
C_v	: specific heat	$[\text{J} \cdot \text{m}^{-3} \cdot \text{K}^{-1}]$
D	: diameter of spherical coal deposit	$[\text{m}]$
D_c	: critical value of D in coal storage	$[\text{m}]$
ϑ	: mass diffusivity	$[\text{m}^2 \cdot \text{s}^{-1}]$
d_p	: particle diameter	$[\text{m}]$
E_a	: apparent activation energy	$[\text{J} \cdot \text{mol}^{-1}]$
ΔH	: heat of reaction	$[\text{J} \cdot \text{mol}^{-1}]$
k_e	: effective thermal conductivity	$[\text{J} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{K}^{-1}]$
p/p_0	: relative vapor pressure	$[-]$
r	: radial distance in spherical coordinate	$[\text{m}]$
T	: temperature	$[\text{K}, ^\circ\text{C}]$
T_a	: ambient temperature	$^\circ\text{C}$
T_c	: upper limit temperature in storage	$^\circ\text{C}$
T_o	: initial temperature of coal deposit	$^\circ\text{C}$
t	: time	$[\text{s}]$
t_c	: storage time	$[\text{s}]$
V	: amount of water adsorbed	$[\text{m}^3 \cdot \text{g}^{-1}]$
X_1	: amount of oxygen consumed	$[\text{mol} \cdot \text{kg}^{-1}]$
ϵ	: void fraction of coal deposit	$[-]$

References

- 1) Baum, M.M.: *Combustion and Flame*, **41**, 187 (1981).
- 2) Fujita, S.: *Kagaku Kogaku*, **28**, 251 (1964).
- 3) Iki, S. and K. Higuchi: *J. of the Mining and Metallurgical, Japan*, **89-1025**, 455 (1973).
- 4) Iki, S. and K. Higuchi: *ibid.*, **90-1033**, 175 (1974).
- 5) Kuchta, J. M., V. R. Rowe and D. S. Burgess: Int. Bu. of Mines, PGH., PA. 24815, U.S. Government Printing Office, 1980-603-102/100.
- 6) Kunii, D. and J.M. Smith: *AIChE J.*, **6**, 97 (1960).
- 7) Lawn, C. J., P. J. Street and M. M. Baum: 18th Int. Symp. on Combustion, p. 731 (1981).
- 8) Liang, H. and T. Tanaka: *J. Soc. Powder Technol., Japan*, **23**, 326 (1986).
- 9) Liang, H. and T. Tanaka: *Kagaku Kogaku Ronbunshu*, **13**, 63 (1987).
- 10) Marinov, V. N.: *Fuel*, **56**, 165 (1977).
- 11) Nishikawa, S., T. Nakayama and K. Yoshida: Preprints for 16th Autumn Meeting of The Soc. of Chem. Eng., Japan, SD101, Toyota (1982).
- 12) Onizuka, S. and T. Watanabe: Technical Report by Hitachi-Zosen Co., **43**, 13 (1982).