Revisiting Spontaneous Ignition of Solids with Diminishing Reaction Rates

Xiao Dong Chen
Dept. of Chemical and Materials Engineering, City Campus
Graeme C. Wake
Industrial Mathematics Group, Division of Science and Technology, Tamaki Campus
The University of Auckland, Auckland, New Zealand

Chemisorption of oxygen by reactive solid surfaces is exothermic and is known to be responsible for the initiation of spontaneous heating of materials like coal, char, and oil containing natural products. As a unique feature of such a process, the rate of oxygen chemisorption depends on the active surface area and diminishes as less reactive area becomes available, such as the studies by Winmill (1913–1915), Graham (1914–1917), Schmidt and Elder (1940), Stott (1959), and Mejdoub and Delfosse (1989). It is therefore important to account for this effect correctly so that a realistic prediction of the temperature-time profile during spontaneous ignition can be achieved. Several sophisticated mathematical model analyses have been carried out to deal with such an effect and produced the corresponding critical parameters for ignition (Boddington et al., 1980, 1982; Lacey and Wake, 1983). However, these analyses have incorporated directly the time-dependence of the rate of exothermic reaction into the energy balance to solve it for the simultaneous temperature evolution over time and these are conceptually incorrect.

In this note, we would like to provide a quantitative comparison between the correct treatment of the mathematical model and the published work (Boddington et al., 1980, 1982; Lacey and Wake, 1983).

A brief summary of the related mathematical models is provided.

Energy Balance Involving Diminishing Rate of Exothermic Reaction

The energy balance that governs the one-dimensional process of the spontaneous-heating of solid (an infinite slab geometry) may be written as follows (Bowes, 1984) (no internal convective heat transfer is allowed and the reactant depletion is ignored).

$$C_p \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + Q \rho A \exp(-E/RT); 0 < x < r, t > 0 \quad (1)$$

where the lefthand side is the local rate of enthalpy change in the solid; the first term on the righthand side is the conductive heat transfer in the solid, and the last term is the heat generation term of the lumped exothermic *reactions* without the reactant depletion. C_p is the specific heat capacity of bulk solid per unit mass (J/kg·K), ρ is the bulk density of the solid (kg/m^3), T is the local temperature (K), t is time (s), k is the thermal conductivity of solid (W/m·K), x is distance (m), and r is the half-width of the slab (m). Q is considered as the heat of reaction per m^3 of oxygen consumed at standard-temperature-pressure condition (J/m^3). A is the rate constant with a unit of 1 m^3 oxygen consumed by one kg of solid within 1 s (m^3/kg·s). E is the activation energy (J/mol).

Typical boundary conditions can be set up as:

$$\text{at } x = 0, \partial T/\partial x = 0; \text{ from symmetry at center} \quad (2a)$$

$$\text{at } x = r, -k\partial T/\partial x = h(T - T_a), T = T_s; \text{ Newtonian cooling.} \quad (2b)$$

h is the convective heat-transfer coefficient (W/m^2·K). If the rate of reaction diminishes, due to the *diminishing availability* of reactive sites, as more oxygen is chemically absorbed by the solid, one may express the pre-exponential factor or the reaction frequency factor A as the following (Stott, 1959; Mejdoub and Delfosse, 1989; Stott and Murtagh, 1971; Stott and Quan, 1974).

$$A = A_o f(O_{ab}) \quad (3)$$

or (Boddington et al., 1980, 1982; Lacey and Wake, 1983)

$$A = A_o g(t) \quad (4)$$

Correspondence concerning this article should be addressed to X. D. Chen.

where Q_{ab} is the previous oxygen chemisorption having a unit of 1 m^3 oxygen per kg of solid (m^3/kg) and $f(O_{ab})$ is a dimensionless function of O_{ab} which decreases as O_{ab} increases; O_{ab} would be the integral of the rate equation of oxidation over the reaction period of concern; t is the time of reaction (s), and $g(t)$ is the time dependency of the reaction rate and reduces with time. These two equations give the same message that the reaction rate diminishes as reaction time prolongs.

As most of these empirical equations have been obtained by correlating the results from laboratory scale isothermal experiments, among them Eq. 4 is a popular expression. In general, the function $g(t)$ may be written as follows

$$g(t) = 1/t^{\alpha},\ \alpha > 0 \tag{5}$$

or even more generally,

$$g(t) = 1/(t + t_{pr})^{\alpha},\ \alpha > 0 \tag{6}$$

where t_{pr} is a parameter of the diminishing reaction rate law which makes a finite rate of reaction at $t = 0$ and may also be interpreted as the prior reaction time; α is an empirical constant usually found in the range of 0.2–0.7, as summarized by Lacey and Wake (1983).

So far, the rigorous mathematical analyses provided in several prominent scientific journals, such as those by Boddington et al. (1980, 1982), and Lacey and Wake (1983), have incorporated either Eq. 5 or 6 into the energy balance (1) and solved the resulted equations numerically. For instance, once Eq. 6 is incorporated in Eq. 4 and then substituted into Eq. 1, one obtains the following

$$C_p \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \frac{Q \rho A_o}{(t + t_{pr})^{\alpha}} \exp(-E/RT);$$

$$0 < x < r,\ t > 0 \tag{7}$$

Despite the complex mathematics involved in these analyses, the physics that this time-dependent energy balance represents is not conceptually correct, having been derived empirically using isothermal data of oxidation rates without regard to the detailed physiochemical process where a changing temperature vs. time is of the concern.

This may be reasoned as follows:

From Eqs. 4 and 6, one can work out the oxygen absorbed by solid O_{ab} as a function of time t at a constant temperature by simple integration as below

$$O_{ab} = \frac{A_o e^{-\frac{E}{RT}}}{1 - \alpha} \left[(t + t_{pr})^{1-\alpha} - (t_o + t_{pr})^{1-\alpha} \right] \tag{8}$$

where t_o is the time at which an experiment starts. These experiments are isothermal and are commonly adopted in practice for determining the oxidation kinetics, i.e., A_o, E, and α.

One can then plot O_{ab} vs. t as shown qualitatively in Figure 1. This figure shows that the oxygen absorption by solid O_{ab} increases as reaction proceeds at two constant temperatures starting from the same raw materials. If the experiment starts from $T = T_1$ for an initial period and then suddenly the temperature is increased to T_2, the reaction must continue following the route B → D (from the same oxygen absorption level) rather than the route B → C (from the same timing). The simulations carried out using Eq. 6, however, have taken the route (B → C) and are therefore conceptually incorrect. In the mathematical analyses published (Boddington et al., 1980, 1982; Lacey and Wake, 1983), the dimensionless form of the energy balance has been used. It should be noted that the differences in the final predictions of temperature-time profile, between two pathways B → C and B → D, may not be too great if one uses sufficiently small numerical steps in T except when the inflammation occurs.

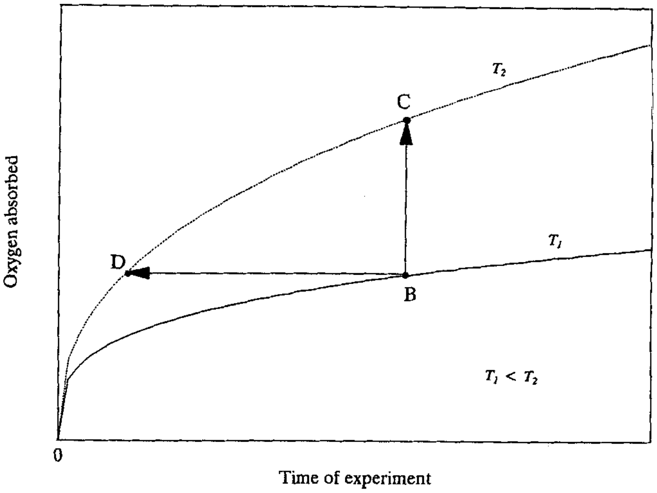

Figure 1. Qualitative demonstration of reaction routes: oxidation history dependency.

Since the current objective is to quantify the practical difference that could have occurred between using Eq. 6 and using Eq. 3, the dimensional equations are adopted and solved numerically.

Further Derivations to Obtain Conceptually Correct Energy Balance for a Process of Changing Temperature

To simplify the model analysis in the current work, taking a practical example, i.e., freshly mined and crushed coal and assuming that t_{pr} is 0, at a constant temperature from Eq. 8 the relationship between the oxygen absorption O_{ab} and time of reaction ($t > t_o$) may be modified as

$$O_{ab} = \frac{A_o e^{-\frac{E}{RT}}}{1 - \alpha} [t^{1-\alpha} - t_o^{1-\alpha}] \tag{9}$$

where t_o demonstrates any preoxidation that has occurred during laboratory sample preparation which may be considered as minimum. From the above equation, we also obtain

$$t = \left[\frac{O_{ab}(1 - \alpha)}{A_o e^{-\frac{E}{RT}}} + t_o^{1-\alpha} \right]^{1/(1-\alpha)} = G(O_{ab}, T) \tag{10}$$

where G is the above function of oxygen absorption O_{ab} and temperature T. In fact, $g(t)$ in Eq. 5 can be transformed into a function $f(O_{ab})$ if t is replaced by the above equation. In reality, this would mean that the rate of oxidation is correlated to the amount of oxygen consumed as an isothermal experiment proceeds. The oxidation rate equation, when neglecting oxygen concentration depletion, can then be rewritten as

$$\frac{\partial O_{ab}}{\partial t} = A \exp\left(-\frac{E}{RT}\right) = A_o g(t) \exp\left(-\frac{E}{RT}\right) = A_o \exp\left(\frac{E}{RT}\right) g[G(O_{ab},T)] \quad (11)$$

The lefthand side is positive as the amount of oxygen absorbed O_{ab} always increases as time increases at a constant temperature. More precisely, one has

$$\frac{\partial O_{ab}}{\partial t} = A_o G(O_{ab},T)^{-\alpha} e^{-\frac{E}{RT}} \quad (12)$$

As such, during the development of spontaneous ignition process, the conceptually correct energy balance becomes

$$C_p \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \frac{Q \rho A_o}{G(O_{ab},T)^{\alpha}} \exp(-E/RT); \qquad 0 < x < r, t > 0 \quad (13)$$

This equation has to be solved in conjunction with Eq. 12.

In order to further simplify the situation while still achieving the aim of the current study, only the adiabatic condition with uniform initial temperature is considered. One would then obtain the following set of equations which can be solved for the temperature-time profiles for given A_o and other physiochemical properties

$$\partial T/\partial O_{ab} = Q/C_p \quad (14)$$

and

$$\partial O_{ab}/\partial t = A_o G(O_{ab},T)^{-\alpha} e^{-E/RT} \quad (15)$$

Equation 14 indicates that the temperature increases as the amount of oxygen absorbed increases in this adiabatic case. O_{ab} may be regarded as another time scale defined in Eq. 15. In this case, one can obtain the explicit relationship between T and O_{ab} as below

$$T = (Q/C_p) O_{ab} + T_o \quad (16)$$

or

$$O_{ab} = (Q/C_p)^{-1}(T - T_o) \quad (17)$$

Substitution of the above equation into Eq. 15, gives

$$dT/dt = Q A_o C_p^{-1} G^{-\alpha} e^{-E/RT} \quad (18)$$

where T is now independent of position. From Eq. 7 which was used in previous analyses one has

$$dT/dt = Q A_o C_p^{-1} (t + t_{pr})^{-\alpha} e^{-E/RT} \quad (19)$$

A FORTRAN program has been written to solve the above two equations numerically.

Numerical Results and Discussion

The explicit finite difference method (Incropera and DeWitt, 1990) has been used with a time increment of 1 s (a typical heating process would be of hours if not days). This has been found to be appropriate for the high accuracy of the predictions reported here.

The physiochemical properties used in our computations (using fresh coal as an example) were: an activation energy of $E = 65$ kJ/mol as shown by Schmidt and Elder (1940), Q is 12×10^6 J/m^3 O$_2$ consumed (Stott, 1959), A_o is 7.2×10^4 m^3 O$_2$/kg·s (this gives an oxygen consumption rate similar to that reported in Stott (1959)), and C_p is 1,000 J/kg·K. t_o is assumed to be 0. $\alpha = 0.2$ and 0.23 respectively were chosen, which are at the lowest end of the range for α. This would show the effect of the diminishing rate on ignition on the conservative side. To avoid singularity at $t = 0$ for $G^{-\alpha}$ in Eq. 18, which is when a heating starts, O_{ab} is assumed to be 1×10^{-8} m^3 O$_2$ per kg of coal. This is reasonable, because in reality any exposure of a fresh sample to air for however short a period before heating would give an initial nonzero value of O_{ab}.

Figures 2 and 3 show two comparisons between the correct model (i.e., Eq. 18) and the incorrect model (i.e., Eq. 19) when $\alpha = 0.2$ and 0.23, respectively. The significant differences have occurred in the time to reach ignition in these two cases. The current model tends to give a shorter time to ignition (some tens of hours). This indicates the importance for one to use the correct model as far as the prediction of time-to-ignition

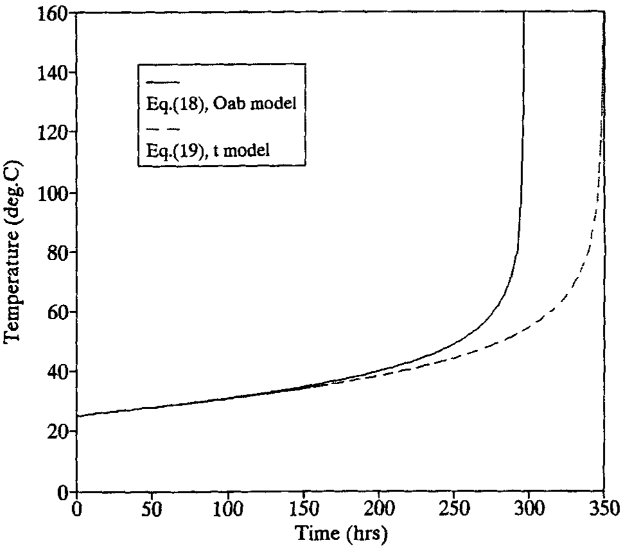

Figure 2. Temperature-time profiles predicted with α = 0.2 using: Eq. 18 (correct model) vs. Eq. 19 (incorrect model).

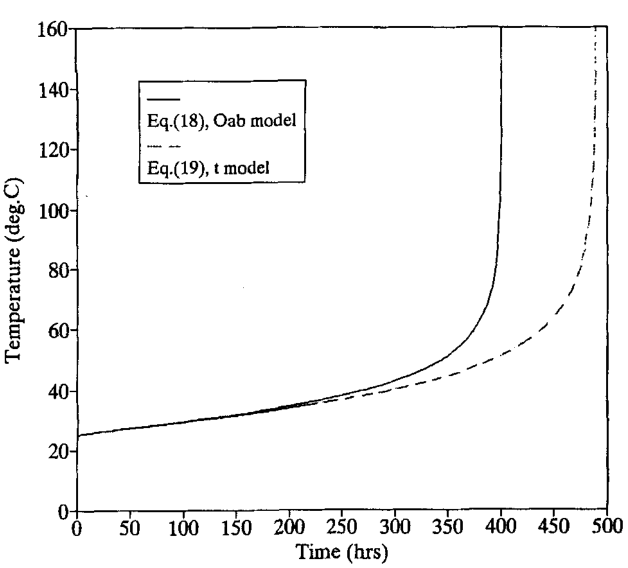

Figure 3. Temperature-time profiles predicted with $\alpha = 0.23$ using: Eq. 18 (correct model) vs. Eq. 19 (incorrect model).

is concerned. As such, although the rate Eq. 4 may be adequately fitted to the experimental results of isothermal tests it must not be directly incorporated into the energy balance. A transformation of such a time-dependency as suggested from Eqs. 9 to 12 may be used to obtain an oxidation history dependency for the oxidation rate equation.

Notation

A_o = reaction frequency factor without time or preoxidation dependency, $m^3(kg \cdot s)^{-1}$
Bi = Biot number
G = a function of preoxidation history (O_{ab} and T)
R = universal gas constant, = 8.31 J $(mol \cdot K)^{-1}$

Subscripts

a = ambient
ab = oxygen absorption
c = critical parameter
o = initial value; reaction frequency factor without time or preoxidation dependency
s = solid boundary

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