



Title	A Study on the Early Detection of Spontaneous Combustion of Coal : The Application of Gas Analysis to the Detection of Heatings
Author(s)	Hashimoto, Kiyoshi
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 11(4), 479-496
Issue Date	1963-03
Doc URL	http://hdl.handle.net/2115/37833
Type	bulletin (article)
File Information	11(4)_479-496.pdf



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A Study on the Early Detection of Spontaneous Combustion of Coal

The Application of Gas Analysis to the Detection of Heatings

Kiyoshi HASHIMOTO

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I. Preface

An oxidation experiment of coal at a constant temperature was carried out for the purpose of theoretical studies on the application of the result of gas analysis to the early detection of spontaneous combustion of coal.

Hitherto, numerous publications on methods for the early detection of spontaneous combustion from the results of gas analysis have been reported: these include simple component such as CO, CO₂, CH₄, C₂H₄ etc., and the values of CO/O₂, CO₂/O₂, CO/CO₂, CO/CO + CO₂ etc. A decisive method, however, has not yet been set forth.

The oxidation experiments in this paper were carried out in parallel with experiments conducted for the establishment of the theory of spontaneous combustion reported previously^{1,2)}. Gas analysis were regularly made. Based on the results a theoretical investigation on the early detection of spontaneous combustion of coal was done.

The changes of gas components, in accordance with the advance of oxidating time, were shown by gas analysis following the experiments of oxidation under a fixed temperature, and the cause of discrepancies was studied. The results show that the possibility of errors was much higher in the procedure of early detection of spontaneous combustion than expected.

The results of gas analysis notwithstanding the possibility of errors are useful for the early detection of spontaneous combustion of coal, but may not be useful for the "diagnosis" of the progressing change during combustion.

II. The Apparatuses and the Method of the Experiments

The apparatuses are the same as were used when the theory of spontaneous

combustion was studied. Therefore in this paper the data on the gases in the former experiments are included.

In these experiments oxidation temperature was kept under 150°C , inasmuch as the use of the result of gas analysis is for the early discovery of spontaneous combustion.

Above 150°C the heat generation of coal by oxidation suddenly becomes active, and there exists the possibility of a rise in temperature. Therefore it is imperative for the early detection of spontaneous combustion of coal by gas analysis that the characteristics of gases produced by oxidation be as low temperature as possible.

The gas samples taken through the experiments of oxidation at a constant low-temperature were analyzed by Orsat gas analytical apparatus. Originally, this apparatus was not high in its accuracy, but has since been so improved as to be useful for gas analysis, making a precise analysis of O_2 , CO_2 and CO possible. The Orsat method which is the easiest to handle is particularly effective, in making a series of analysis in parallel to oxidation experiments.

Many gas samples taken in the underground in natural surroundings, however, are diluted by other gases or air after it has passed through the heated zone, but in a laboratory the gases from oxidation are used without any attenuation by air or other gases after they have passed through coal particles. Therefore in establishing a theory concerning the early detection of spontaneous combustion and discussing it, the Orsat method is reliable. In the examination of CO Kitakawa's CO gas detector, the color comparison method, is referred to.

CO in the oxidated gas at 75°C and 50°C could not be found except for a trace of it, but this means that it does not exist at the unit up to 0.00%. It is regrettable that the author was unable to determine the presence of CO in oxidated gases passed through the coal particles at 75°C and 50°C . The existence of CH_4 and H_2 were not examined, but were included in N_2 , owing to the impossibility of analyzing the same at a thermal temperature under 150°C .

III. Results of the Experiment

Figure 1 shows an example of the relation between the generation rate of CO_2 , the quantity of CO_2 generated by 100 grams of coal within one hour, and its oxidation time. Table 1 shows by average the relation between the generation rate of CO_2 and the oxidation time at every 10 hours of oxidation.

According to this table the generation rate of CO_2 decreases as the time passes, and increases as the size of the grain becomes smaller. These relations are shown by the average in Figure 2. Figure 3 shows the logarithm of the generation rate of CO_2 in Figure 2.

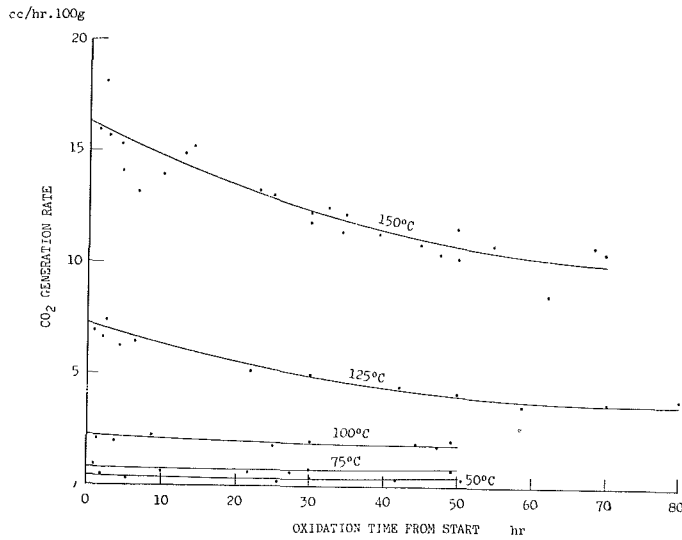


Fig. 1. The relation between CO₂ generation rate and oxidation time, particle size 20-28 mesh

Figure 3 leads the following common formula.

$$\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}_2} = \left(\frac{d\Omega}{d\theta}\right)_{\text{CO}_2}^0 e^{-k_1\theta} \tag{1}$$

where $\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}_2}$: CO₂ generation rate
 $\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}_2}^0$: initial CO₂ generation rate
 k_1 : coefficient
 θ : oxidation hour

The following relation among the initial CO₂ generation rate $\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}_2}^0$, the coefficient k_1 and the temperature t shows Figure 4. Figure 4 leads the following experimental formula.

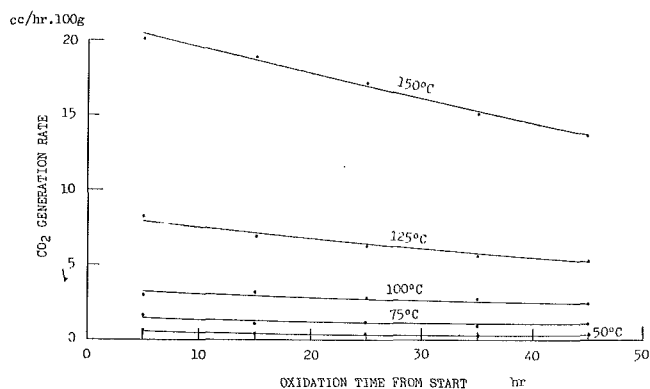
$$\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}_2}^0 = 0.075 e^{0.038t - 0.012\theta} \tag{2}$$

$$k = e^{-4.42} = 0.012 \tag{3}$$

$$\therefore \left(\frac{d\Omega}{d\theta}\right)_{\text{CO}_2} = 0.075 e^{0.038t - 0.012\theta} \tag{4}$$

TABLE 1. The relation between CO₂ generation rate and oxidation time from start

Temperature of oxidation (°C)	Particule size (mesh)	Oxidation time from start (average at every 10 hours of oxidation)					Mean value
		0-10hr	10-20hr	20-30hr	30-40hr	40hr-	
150	20-28	15.76	15.14	12.91	11.72	10.80	13.27
"	28-35	19.49	15.05	15.64	14.07	12.49	15.35
"	35-48	22.96	22.95	19.71	15.57	14.55	19.15
"	48-65	22.89	22.46	19.31	17.44	16.00	19.62
"	mean value	20.48	18.90	16.89	14.70	13.49	16.88
125	20-28	6.36	5.43	4.51	4.86	3.72	4.98
"	28-35	7.69	6.62	5.55	4.27	3.58	5.54
"	35-48	7.61	5.02	5.49	5.76	4.66	5.53
"	48-65	9.42	7.43	6.42	6.53	5.60	7.08
"	65-100	10.14	9.91	8.22	7.38	6.49	8.42
"	mean value	8.24	6.89	6.04	5.58	4.81	6.31
100	20-28	20.20	1.80	1.70	1.98	2.05	1.91
"	28-35	2.47	2.30	2.21	1.99	2.02	2.20
"	35-48	2.67	2.84	2.67	2.65	2.31	2.63
"	48-65	3.63	3.43	3.12	2.61	2.04	2.97
"	65-100	4.93	4.65	2.68	3.02	2.59	3.78
"	mean value	3.14	3.01	2.68	2.45	2.21	2.70
75	20-28	0.73	0.67	0.59	0.78	0.71	0.69
"	28-35	1.13	1.22	0.94	0.86	0.79	0.99
"	35-48	1.83	1.20	1.24	1.19	1.06	1.31
"	48-65	1.91	1.62	1.38	1.33	1.28	1.50
"	65-100	2.03	1.64	1.49	1.38	1.37	1.58
"	mean value	1.52	1.27	1.13	1.11	1.04	1.22
50	20-28	0.29	0.24	0.16	0.16	0.16	0.21
"	28-35	0.33	0.33	0.23	0.22	0.20	0.16
"	35-48	0.36	0.29	0.28	0.27	0.19	0.28
"	48-65	0.52	0.30	0.29	0.27	0.23	0.32
"	65-100	0.62	0.54	0.54	0.45	0.41	0.50
"	mean value	0.42	0.34	0.30	0.27	0.23	0.32

Fig. 2. The relation between CO₂ generation rate and oxidation time from start (average)

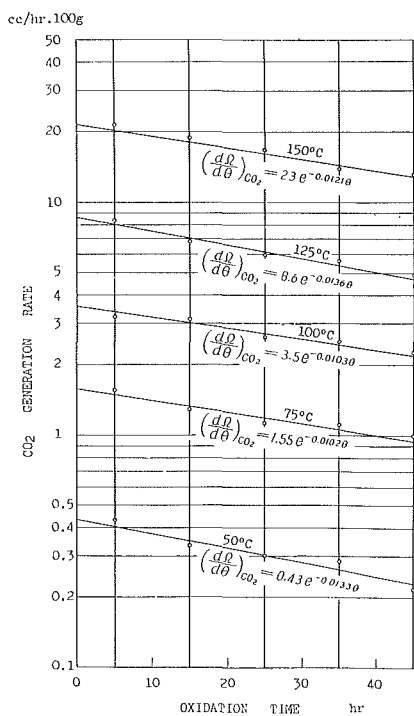


Fig. 3. The relation between CO₂ generation rate and oxidation time from start (experimental value)

Thus Figure 5 is led forth. According to Figure 5 the curves of the CO₂ generation rate are in parallel, and consequently the CO₂ generation rate of the Oyubari coal at a certain temperature is equal to that of the coal oxidated for 82.5 hours at a temperature 25°C higher than the former. In other words, $\frac{25(^\circ\text{C})}{82.5(\text{hr})} = 0.303(^\circ\text{C/hr})$. The result of this experiment shows that CO₂ generation rate becomes constant only when the rising rate of temperature is 0.303°C/hr. (In the case of gases underground at the coal mine site the rise of temperature does not always take place at a certain density of CO₂, because other gases produced by oxidation enter.)

Figure 6 shows an example of the relation between CO generation rate (CO quantity produced by 100 grams of coal in one hour) and oxidation time from start. Table 2 shows the relation between the generation rate and the oxidation time by

the averages at every ten hours of oxidation time.

According to this table the CO generation rate decreases as the oxidation time passes, and increases as the size of grain becomes smaller and the temperature rises. Figure 7 shows the relations among these by average.

According to this the CO generation rate is represented by the following equation.

$$\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}} = \left(\frac{d\Omega}{d\theta}\right)_{\text{CO}}^0 e^{-k_2\theta} \tag{5}$$

where

$\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}}$: CO generation rate

$\left(\frac{d\Omega}{d\theta}\right)_{\text{CO}}^0$: initial CO generation rate

k_2 : coefficient

θ : oxidation hour

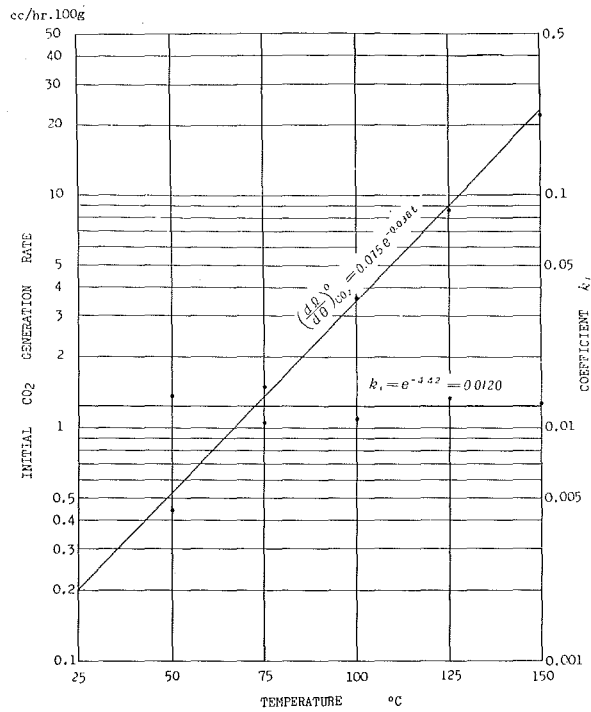


Fig. 4. Values of k_1 and $(\frac{dQ}{dt})_{CO_2}^0$

Figure 8 shows the relationship between the generation rate of CO which is logarithm, and oxidation time from start. This suggests the possibility of the calculation of the generation rate of CO produced by oxidation at the lower temperature.

Moreover the following relation between the coefficient k_1 of the CO₂ generation rate and the coefficient k_2 of the CO within the scope of the experiment under 150°C is :

$$k_1 < k_2$$

and the lower the temperature becomes, the greater its difference is.

As a matter of fact the density of CO and CO₂ can be acquired as a result of the analysis of gases in the underground, but the quantity of air leakage cannot be calculated. Consequently, it is impossible to know the generation rate of CO and CO₂.

Under a certain condition the high density of CO and CO₂ indicates a higher temperature, if the air leakage is assumed to be almost constant. In

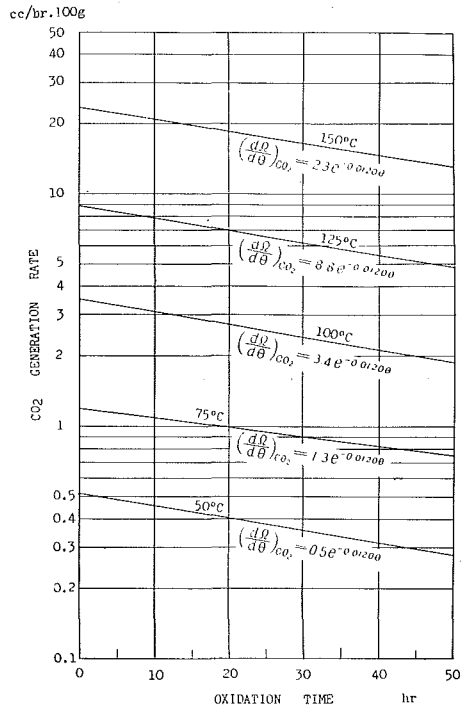


Fig. 5. The relation between CO₂ generation rate and oxidation time from start (theoretical value)

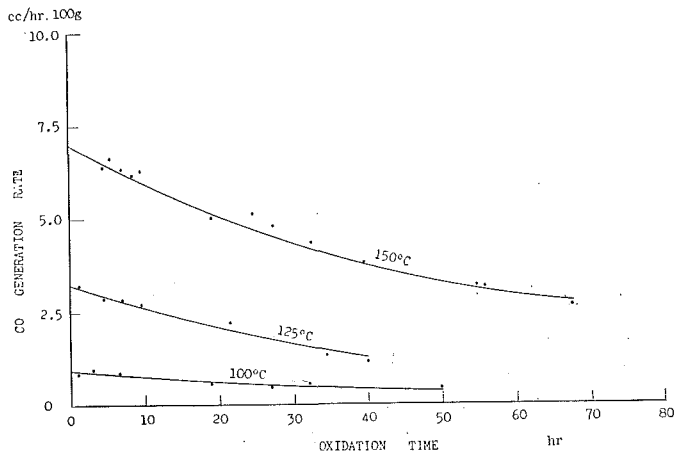


Fig. 6. The relation between CO generation rate and oxidation time (particle size 28-35 mesh)

TABLE 2. The relation between CO generation rate and oxidation time from start

Temperature of oxidation (°C)	Particle size (mesh)	Oxidation time from start (average at every 10 hours of oxidation)					Mean value
		0-10hr	10-20hr	20-30hr	30-40hr	40hr-	
150	20-28	5.00	4.19	3.76	3.55	2.69	3.84
"	28-35	6.89	4.96	5.12	4.11	3.10	4.83
"	35-48	7.49	7.80	6.26	4.92	3.58	6.01
"	48-65	8.44	8.53	7.13	5.55	4.57	6.85
"	mean value	6.96	6.37	5.57	5.53	3.48	5.35
125	20-28	1.95	1.71	1.47	1.44	0.95	1.50
"	28-35	2.89	2.43	1.97	1.33	1.15	1.95
"	35-48	3.01	1.86	1.65	1.35	1.60	1.89
"	48-65	3.51	2.48	2.23	1.88	1.75	2.37
"	65-100	3.74	3.07	2.77	2.33	2.04	2.79
"	mean value	3.02	2.31	2.02	1.67	1.49	2.10
100	20-28	0.69	0.58	0.57	0.54	0.42	0.50
"	28-35	0.88	0.58	0.50	0.46	0.50	0.59
"	35-48	0.95	0.63	0.49	0.50	0.38	0.59
"	48-65	1.24	0.91	0.70	0.63	0.44	0.78
"	65-100	1.63	1.64	1.21	0.86	0.65	1.20
"	mean value	1.08	0.86	0.69	0.59	0.48	0.74

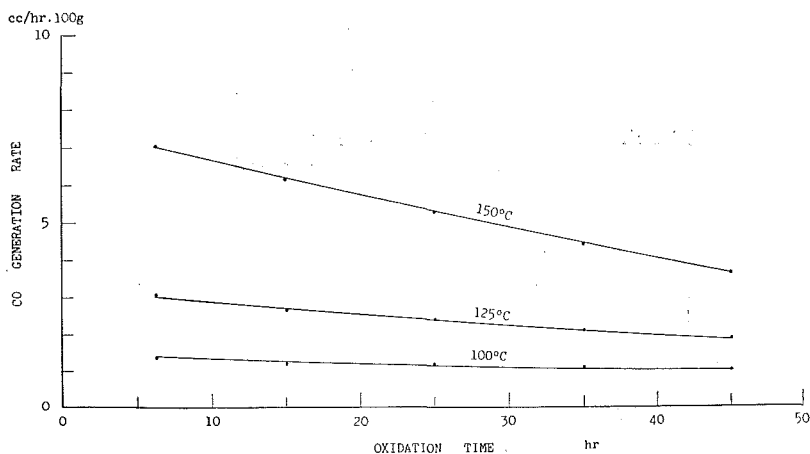


Fig. 7. The relation between CO generation rate and oxidation time (average)

general, however, the higher the temperature rises, the more the leakage of air increases, which is particularly remarkable in the cases of steep pitching seams and the thick seams. Therefore, the rise of temperature gives the dilution of the density of gases, from the point of view of air leakage. The increase of density of CO suggests a greater danger than it is assumed to be, for the generation rate of CO has a tendency to decrease as the time elapses in the experiments of oxidation at a constant temperature.

Moreover, the values of density of CO and CO₂ obtained from this analytical method appear to be smaller than the true values, due to the diluted gases by other oxidation gas or air after oxidation. This tendency is feasible in actual coal mines sites. The rate of dilution by air cannot be known only by the density of CO and CO₂.

Consequently, in order to detect the spontaneous heat of coal by the density of CO and CO₂, the samples of gases must be taken at a place where the rate of dilution by air is considered to be about constant. This, however, is nearly impossible because of the characteristic status of the ventilation in the underground.

In Figure 9, an example of the relation among CO₂/O₂ value (CO₂ produced/O₂ absorbed) and the oxidation time and the oxidation temperature, is shown.

Table 3 shows the relation between the value of CO₂/O₂ and the oxidation time by the average at every ten hours of the oxidation time. Figure 10 shows these relations by the average.

According to the results of the experiments of oxidation at a constant temperature, the relation between the value of CO₂/O₂ and the oxidation time θ is as follows.

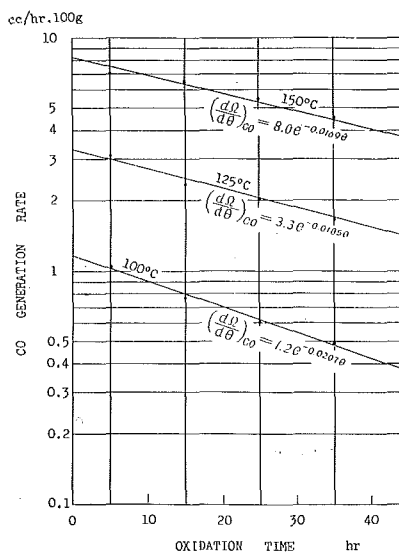


Fig. 8. The relation between CO generation rate and oxidation time

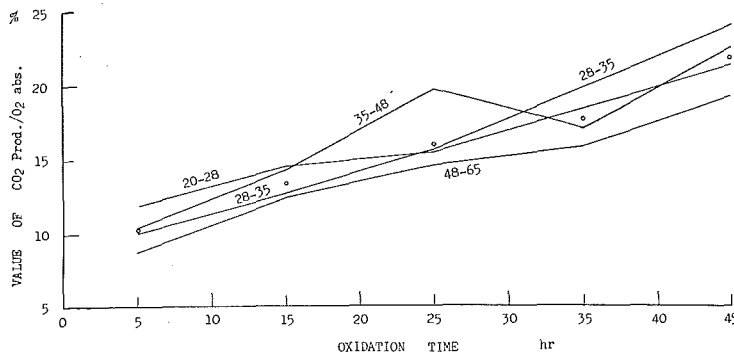


Fig. 9. The relation between CO₂/O₂ value and the oxidation time temperature 150°C, ○ mark is the mean value

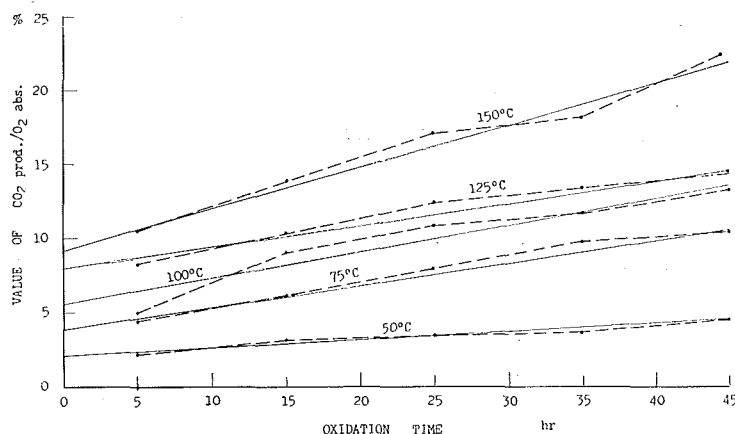


Fig. 10. The relation between CO_2/O_2 value and the oxidation time (average)

TABLE 3. The relation between CO_2/O_2 value and oxidation time from start

Temperature of oxidation (°C)	Particle size (mesh)	Oxidation time from start (average at every 10 hours of oxidation)					Mean value
		0-10hr	10-20hr	20-30hr	30-40hr	30hr-	
150	20-28	11.60	14.24	15.88	18.21	20.86	16.16
"	28-35	9.90	12.61	15.96	19.60	23.23	16.26
"	35-48	10.20	14.08	19.43	16.91	22.00	16.52
"	48-65	8.34	12.48	14.75	15.83	18.92	14.06
"	mean value	10.01	13.35	16.51	17.64	21.25	15.75
125	20-28	9.28	10.09	10.89	12.92	17.23	12.08
"	28-35	9.28	10.58	11.87	11.00	10.26	10.60
"	35-48	7.31	9.10	14.71	14.29	14.03	11.89
"	48-65	7.07	9.09	11.28	14.57	14.30	11.26
"	65-100	6.23	10.01	10.94	12.76	13.53	10.69
"	mean value	7.83	9.77	11.94	13.11	13.87	11.30
100	20-28	5.56	7.41	7.87	9.69	14.52	9.01
"	28-35	4.93	9.12	7.34	9.89	11.71	9.00
"	35-48	4.95	8.65	12.89	15.38	16.40	11.65
"	48-65	4.89	11.18	12.70	11.33	12.50	10.52
"	65-100	4.67	7.05	10.44	10.22	9.70	8.42
"	mean value	5.00	8.68	10.65	11.30	12.97	9.72
75	20-28	4.06	4.19	6.09	8.29	9.41	6.41
"	28-35	4.43	8.11	7.14	7.79	8.29	7.15
"	35-48	6.52	7.96	10.85	11.54	12.13	9.80
"	48-65	5.04	7.19	8.37	8.98	9.58	7.83
"	65-100	3.57	4.32	7.18	11.33	13.27	7.93
"	mean value	4.72	6.35	7.93	9.59	10.54	7.82
50	20-28	2.98	3.37	2.99	3.13	4.23	3.34
"	28-35	2.83	4.08	4.11	4.48	5.32	4.16
"	35-48	1.81	2.91	3.28	3.65	4.26	3.18
"	48-65	2.53	2.34	2.86	3.38	4.09	3.04
"	65-100	2.68	3.92	4.76	4.76	6.33	4.49
"	mean value	2.57	3.32	3.60	5.88	4.85	3.64

$$\left(\frac{\text{CO}_2}{\text{O}_2}\right) = a_1 + b_1 \theta \quad (6)$$

where $\left(\frac{\text{CO}_2}{\text{O}_2}\right)$: the value of CO_2/O_2

a_1 : a coefficient

b_1 : a coefficient

θ : the oxidation hour

Thus the equation which appears as a straight line is formed.

According to Table 3, the value of CO_2/O_2 rises when the temperature rises, but the effect of the particle size at the same temperature is not so accurate.

The increase of the value of CO_2/O_2 as time elapses during the low temperature oxidation is the crucial defect in the examination of the temperature rise by the value of CO_2/O_2 .

Morgan^{3,4)} stated that the increase of the value of CO/O_2 and the decrease of that of CO_2/O_2 are manifestations of heating. From the results of the experiments it was determined that the decrease of the value of CO_2/O_2 is not a sign of radiation.

Figure 11 shows an example of the relations among the quantity of produced CO/the quantity of the O_2 absorbed and the oxidation time and the oxidation temperature (100°C).

Table 4 shows by average at every ten hours the relation between the value of CO/O_2 and the oxidation time, which relation is illustrated in Figure 12.

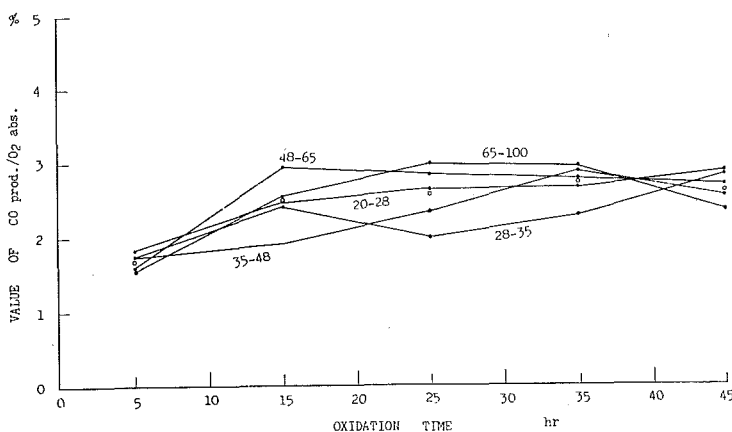
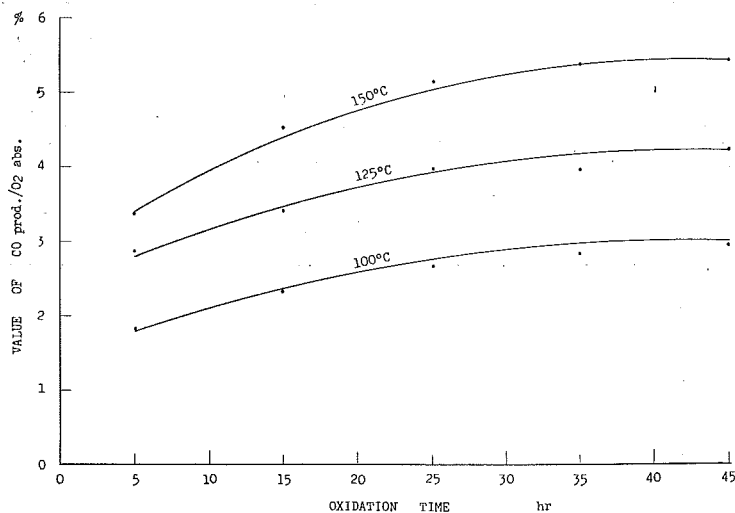


Fig. 11. The relation between the CO/O_2 value and oxidation time (The oxidation temperature: 100°C)

TABLE 4. The relation between the CO/O₂ value and oxidation time

Temperature of oxidation (°C)	Particle size (mesh)	Oxidation time from start (average at every 10 hours of oxidation)					Mean value
		0-10hr	10-20hr	20-30hr	30-40hr	40hr-	
150	20-28	3.68	4.41	4.63	5.49	5.11	4.66
"	28-35	3.54	4.18	4.84	4.94	5.03	4.51
"	35-48	3.35	4.79	6.14	4.32	5.33	4.79
"	48-65	2.09	4.74	5.45	4.89	5.11	4.62
"	mean value	3.37	4.53	5.27	4.91	5.14	4.64
125	20-28	2.85	3.21	3.56	3.83	4.02	3.49
"	28-35	3.50	3.85	4.20	3.44	3.30	3.66
"	35-48	2.63	3.38	4.41	3.97	4.82	3.84
"	48-65	2.59	3.03	3.93	3.97	4.40	3.58
"	65-100	2.29	3.10	3.69	4.19	4.50	3.55
"	mean value	2.77	3.30	3.96	3.88	4.21	3.62
100	20-28	1.87	2.36	2.62	2.64	2.94	2.49
"	28-35	1.73	2.28	2.08	2.28	2.93	2.26
"	35-48	1.77	1.92	2.34	2.88	2.65	2.31
"	48-65	1.66	2.96	2.87	2.73	2.68	2.58
"	65-100	1.60	2.49	2.97	2.92	2.42	2.48
"	mean value	1.73	2.40	2.58	2.69	2.72	2.42

Fig. 12. The relation between the CO/O₂ value and the oxidation time (average)

According to the subsequent results, the value of CO/O₂, during the oxidation at a constant temperature, tends to increase more or less as time goes on, but the rate of increase is not so high.

The following relation is seen between the value of CO/O₂ and the oxidation time:

$$\left(\frac{\text{CO}}{\text{O}_2}\right) = a_2 + b_2 \theta - c_2 \theta^2 \quad (7)$$

where

$\left(\frac{\text{CO}}{\text{O}_2}\right)$: the value of CO/O_2

a_2 : a coefficient

b_2 : a coefficient

c_2 : a coefficient

θ : the oxidation time

If CO gas definitely exists in the underground, the temperature generally shows a rise. Thus, insofar as the experiments of low-temperature oxidation are concerned, the closest relation between the value of CO/O_2 and the temperature generation by oxidation was verified. This agrees with the point of view of Graham⁵⁾, Burrell & Seibert⁶⁾, and Jones⁷⁾.

Figure 13 shows the relation between the value of CO/CO_2 and the oxidation time and temperature. Figure 14 shows the relation between the value of $\text{CO}/\text{CO} + \text{CO}_2$ and the oxidation time and temperature.

According to the result of these experiments both the values of CO/CO_2 and $\text{CO}/\text{CO} + \text{CO}_2$ have a tendency to decrease more or less as the oxidation time continues. These values also tend to have about the same changes, for the generation rate of CO is approximately from 1/3 to 1/5 of the generation rate of CO_2 . Besides, these values do not show any distinctive change as the temperature rises.

Consequently, insofar as these experiments are concerned, the changes of

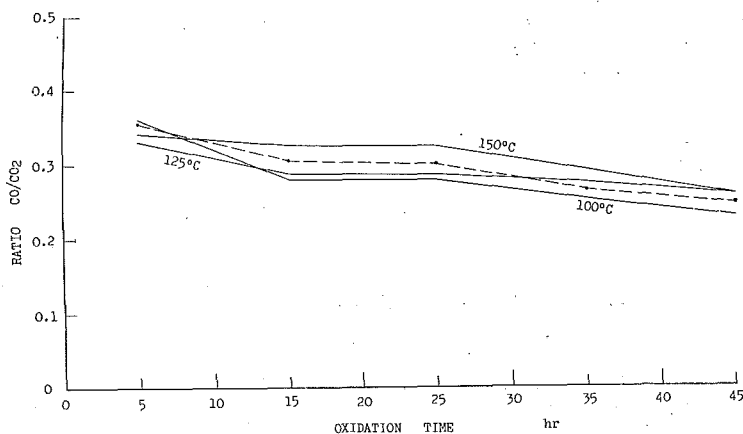


Fig. 13. The relation between the value of CO/CO_2 and the oxidation time and temperature.

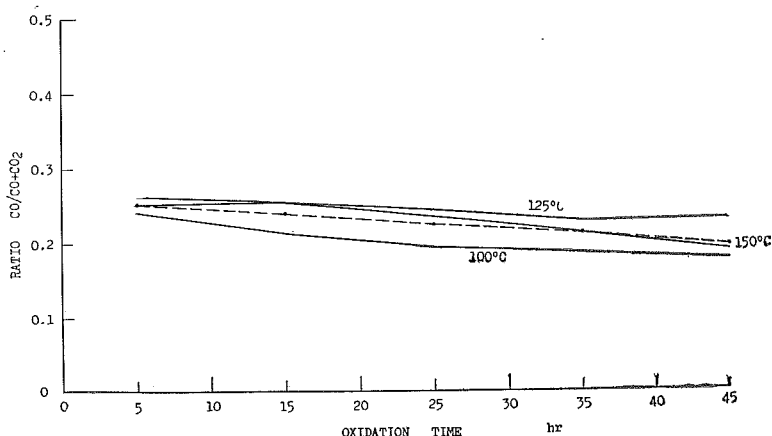


Fig. 14. The relation between the value of $\text{CO}/\text{CO}+\text{CO}_2$ and the oxidation time and temperature.

these values do not have any importance in the early detection of spontaneous combustion of coal.

Next, the effects of mixing of the gases produced by oxidation must be considered as the result of diffusion of gases. Mixing gases produced by oxidation is not reasonably considered to cause changes under temperatures of 500°C .

Figure 15 shows an example of the changes of the values of CO/O_2 and CO_2/O_2 when these gases are mixed at a rate of 50 and 50 after values have been calculated at a temperatures of 150°C , 100°C , 75°C and 50°C respectively. (a) shows the oxidation at the beginning, (b) shows that of ten hours later and (c) thirty hours later. Though the highest temperature of the gas is 150°C , the values of CO/O_2 and CO_2/O_2 are shown approximately at 125°C . The values of these are shown at the lower temperature—about 100°C —in Figure 16.

This means that these values show the lower states instead of the higher ones when these gases are mixed with other low temperature oxidation gases, though there is no change in the value when these gases are diluted by pure air. This reveals a crucial defect of the value of CO/O_2 and CO_2/O_2 and so on for the detection of spontaneous heatings in the underground.

IV. Considerations for the Early Detection of Spontaneous Heating

There are two meanings in the early detection of spontaneous combustion of coal: a wide and a narrow one. Narrowly interpreted it is to discover a possibility or a sign of spontaneous combustion, or the combustion itself as early as possible. Widely taken it is not only to discover these points but also to judge the scale or to determine whether it is progressive, unchangeable, or

retreating precisely. These judgements are called the diagnosis⁸⁾.

Now a big theoretical contradiction can be pointed out between the results of Dr. Graham's experiments shown in Table 5 and the value of CO/O_2 for an early detection of spontaneous combustion in the underground which he advocated in his paper.

According to his paper 0.5% of the value of CO/O_2 indicates a warning status and 1.0% indicates an extraordinary one when it is examined in the

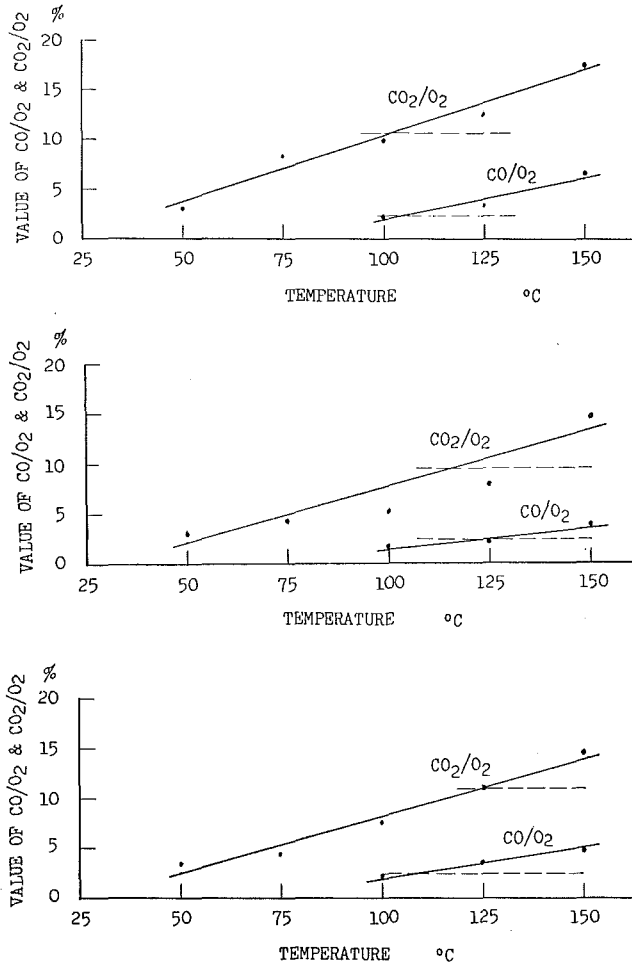


Fig. 15. The changes of the values of CO/O_2 and CO_2/O_2
 (a) The oxidation at the beginning (b) The oxidation at 10 hours later (c) The oxidation at 30 hours later, particle size 20-28 mesh, and mixture ratio 150°C 1, 125°C 1, 100°C 1, 75°C 1, 50°C 1.

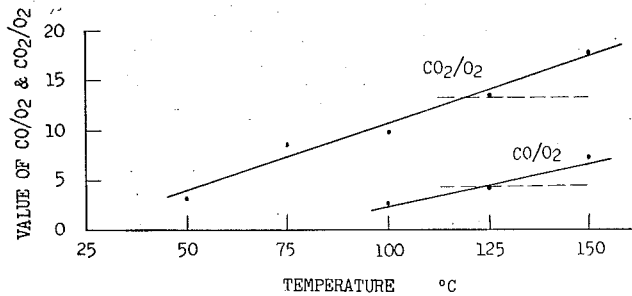


Fig. 16. The changes of the values of CO/O₂ and CO₂/O₂ mixture ratio 150°C 1, 125°C 2, 100°C 3, 75°C 4, 50°C 5.

TABLE 5. The relation between the oxidation temperature and oxidation time (by Graham)

Oxidation temperature (°C)	Oxidation hours (hr)	CO ₂ prod.	CO prod.	CO prod.
		O ₂ abs. (%)	O ₂ abs. (%)	CO ₂ prod. (%)
20	21	—	0.5	—
	145	—	0.7	—
30	24	4.0	0.7	17
	96	12.0	1.0	8
50	24	5.0	—	—
	96	7.0	—	—
70	24	6.0	—	—
	96	11.0	2.0	18
100	48	16.5	2.8	17
	96	15.4	2.6	17
120	24	16.0	4.0	25
	96	23.0	5.0	22
140	24	20.0	6.0	30
	96	36.0	7.0	20

underground, though the results of oxidation experiments show 0.5–0.7% of the value of CO/O₂ at 20°C, and 0.7–1.0% at 30°C.

It is when the temperature of coal is higher than 100°C at the lowest that a coal smell is emitted by the radiation of heat by oxidation, in which case the value of CO/O₂ must be 2.5% or more. That the value of CO/O₂, however, is only 0.5–1.0% even when the underground is in a dangerous conditions, suggests that the gas produced by oxidation is diluted by other causes.

As it is mentioned in the former paper by this author, the value of CO/O₂ does not have any change by dilution by pure air, but has a remarkable change by mixing of other air including “blackdamp”. This will also be proved by

the experiments explained in the preceding chapter.

The result of the analysis of the underground gases gives warning at a very low figures of 0.5–1.0%. In spontaneous combustion the value of CO/O_2 is higher than 0.5%, but on the contrary values higher than 0.5% of the value of CO/O_2 is not always a sign of the beginning of a spontaneous combustion.

It is already forty years since Graham published a method for an early detection of spontaneous combustion, but a decisive method has not yet been discovered. Thus, it is emphasized that this is not because the results of gas analysis are inaccurate, but because the experiments in a laboratory does not represent the conditions in the underground.

As many students considered only about dilution by air or methane, Graham's method by being improved, has been thought to be effective in the early detection of spontaneous combustion in the underground. The value of CO/O_2 , however, gives various figures from the accepted figures to zero, if Graham's method is applied in the underground. This means that the result of gas analysis is in the scope from an ordinary temperature to the maximum.

This paper may have proved that the values of CO/O_2 , CO_2/O_2 , CO/CO_2 , $\text{CO}/\text{CO}+\text{CO}_2$, etc., greatly vary according to the ratio of the mix of high temperature and low temperature oxidation gases.

Thus a diagnosis or an early detection of spontaneous heatings by the values given above is theoretically meaningless. Is an early detection of spontaneous heatings by gas analysis impossible, then? A definite negative answer cannot be given. Yet the evident existence of CO suggests sufficient doubt for spontaneous combustion, and the increase of its density indicates the progression of generation of heat by oxidation. As the gas is diluted by air and other kinds of gases, its numerical value does not indicate the degree of danger of spontaneous combustion, and very often its rising rate gives a far lower figure than that of the real danger.

V. Conclusion

The followings are what have been known in regards to the early detection of spontaneous combustion by gas analysis as a result of the oxidation experiments at a constant temperature.

i) It is ascertained that determining the density of CO and CO_2 is insufficient for the early detection of spontaneous combustion, because of the dilution effect during oxidation.

ii) The increase of the density of CO and CO_2 indicates a state approaching danger, because in oxidation at a constant temperature the density of CO and CO_2 decreases as time elapses.

iii) The value of CO_2/O_2 is not useful in the detection of spontaneous combustion, because it increases with time.

iv) The value of CO/O_2 is considered to be useful, though the value of CO/O_2 increases as time elapses, because the increasing rate is low.

v) The values of CO/CO_2 and $\text{CO}/\text{CO} + \text{CO}_2$ are not so important insofar as an early detection of spontaneous combustion is concerned.

vi) In the present experiment the values of CO/CO_2 and $\text{CO}/\text{CO} + \text{CO}_2$ show about the same changes.

vii) The values of CO/O_2 and CO_2/O_2 greatly change when gases of various temperatures are mixed in, but they do not give the values of CO/O_2 and CO_2/O_2 at the highest temperature. Therefore they have a crucial defect in application for a diagnosis of spontaneous heatings.

Bibliography

- 1) Hashimoto: A Theory on the Mechanism of an Outbreak of Spontaneous Combustion of Coal I. Memoirs of Faculty of Engineering, Hokkaido University, Vol. XI, No. 3.
- 2) Hashimoto: A theory on the Mechanism of an Outbreak of Spontaneous Combustion of Coal II. Memoirs of Faculty of Engineering, Hokkaido University, Vol. XI, No. 3.
- 3) Morgan: Spontaneous Combustion in the Warwickshire Thick Coal. Part 1. The Application of Gas Analysis to the Detection of Heatings. Coll. Guard., Vol. 131, 1926, pp. 251, 252, 316-318.
- 4) Morgan: Spontaneous Combustion in the Warwickshire Thick Coal. Trans. Inst. Min. Eng., Vol. 75, 1928, pp. 346-355.
- 5) Graham: The Gaseous products resulting from Fires and Underground Heatings. Trans. Inst. Min. Eng., Vol. 79, 1929-30, pp. 92.
- 6) Burrell and Seibert: Gas Analyses as an Aid in Fighting Mine Fires. Bureau of Mines, Tech. Paper 13, 1912, pp. 16.
- 7) Jones: Spontaneous Combustion in North Staffordshire. A Record of Air Samples taken during the Combatting of a Gob-Fire. Coll. Guard., Vol. 138, 1929, pp. 2395-2397.
- 8) Graham: The Normal Production of Carbon Monoxide in Coal-Mines. Trans. Inst. Min. Eng., Vol. 60, 1920-1921, pp. 222-231.
- 9) Storrow and Graham: The Application of Gas Analysis to the Detection of Gob-Fires. Trans. Inst. Min. Eng., Vol. 68, 1924-25, pp. 408.
- 10) Hashimoto: Influences of the Shutting off Gob-Fires upon the Gaseous Products. Jour. Inst. Min. Hokkaido, Vol. 13, 1957.