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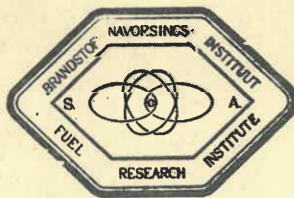
FUEL RESEARCH INSTITUTE
OF SOUTH AFRICA.

BRANDSTOF-NAVORSINGS-INSTITUUT
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SUBJECT :
ONDERWERP: SPONTANEOUS HEATING OF COAL – SUMMARISED EXTRACTS

FROM THE LITERATURE.

DIVISION :
AFDELING : CHEMISTRY.

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C O N T E N T S.

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

REPORT NO. 9 OF 1950.

SPONTANEOUS HEATING OF COAL - SUMMARISED EXTRACTS FROM THE LITERATURE.

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1. Introduction:

The problem created by the spontaneous heating of coal has been receiving attention for more than 100 years and many investigators have worked on problems directly or indirectly associated with this phenomenon.

The volume of literature on the subject is very large indeed, and, in an effort to summarize the findings of the more recent workers in this field, the object has been to provide present and future investigators at the Fuel Research Institute of South Africa with extracts which will be reasonably comprehensive and up to date (literature up to January, 1950, has been consulted).

An excellent review of the existing literature and data on this subject was published in 1928 by Davis and Reynolds 18) and the present report should be regarded as being merely supplementary to their work, and entirely incomplete without it. While studying the more recent literature it was found that many workers had covered more or less the same ground as their predecessors and had arrived at similar conclusions. It was decided that such publications should not be excluded in drafting the present report even if it might lead to apparent repetitions of statements contained in the report of Davis and Reynolds.

Frequent references are made in this report to work done at the Institute and to reports that have been written here.

2. Determination of the Relative Tendency of a Coal to Heat Spontaneously:

According to Special Report No.5 of the D.S.I.R. - Fuel Research 21) there was (in 1929) not yet a satisfactory method available for determining the liability of a coal to spontaneous combustion, and the impression gained from the present survey of the literature is that in spite of substantial progress that has been made in recent years in the understanding of all the phenomena involved, the problem has not been simplified appreciably. The ideal formula or test for assigning to a coal an absolute or relative quantitative value for its liability to spontaneous combustion must take into consideration such a number of possible variables that it seems a task impossible to achieve at this stage. A statistical approach, as made in the case of the report mentioned above 21), certainly holds out promise and is one to be commended.

The rank of a coal is normally regarded as a fairly reliable, general indication of its relative tendency towards spontaneous combustion. The lower the rank the more liable the coal. Besides the usual proximate and ultimate analyses the maximum inherent moisture content of a coal yields evidence of its rank. Methods of determining the maximum inherent moisture content of coals have been investigated and described by various workers 60).

It is stressed that coal will not regain its original inherent moisture capacity after prolonged drying in atmospheres of lower humidity than about 75%.

There is a close relationship between the maximum inherent moisture content, and the internal surface and heat of wetting characteristics. The determination of these properties is well covered in a recent publication of the B.C.U.R.A. 6) and in subsequent papers 5), 19). Values found for the heat of wetting (methyl alcohol) for British coals ranged from about 1.2 to 25 cal./gram of dry, ash-free coal. (The liberation of heat per square metre of coal surface is approximately 0.095 calories).

According to Scott and Jones 57), the inflection point," of a coal (i.e. the temperature at which liberation of carbon monoxide when heated in air becomes appreciable), and its relation to the ignition temperature is probably related to the tendency of the coal towards spontaneous combustion. An inflection point for anthracite (non-liable) of $376^{\circ}C$ and for sub-bituminous coal (definitely liable) of $141^{\circ}C$ was found.

The oxidizability, content of volatile matter and ignition temperature of a Georgian SSR coal were found to characterize it as safe, and yet numerous mine fires were experienced. However, the low C and high H content increase the coal's ability to absorb O. Thus the coal is not spontaneously inflammable, yet quite dangerous 13).

Methods based on analytical data, e.g. hygroscopic water, disposable hydrogen and oxygen iodine value, etc., or on behaviour with oxidising agents e.g. H_2O_2, $KMnO_4$, O_3

etc. are unreliable for determining the spontaneous inflammability of coal according to von Walther and Bielenberg 71).

The oxidising power of a coal which has undergone a certain degree of weathering is a guide in this respect. The oxidising power is taken to be due to peroxides formed and a knowledge of the peroxide content of an oxidised coal is therefore helpful. Various workers have studied this aspect and a more complete summary of this phase of the problem has been prepared at the Institute 28). The action of coal on a photographic plate in the dark described by Haslam 31) is possibly related to this phenomenon as the presence of oxygen in the surrounding atmosphere was found to be essential for the action to take place.

The oxygen/........

The oxygen absorption characteristics of coals have been studied by many workers. Winnill 75) was, undoubtedly, the real pioneer in this respect. Some of his findings were as follows:-

1. For coal containing no pyrites the heat liberated by the absorption of 1 ml. of oxygen (N.T.P.) is 2.1 calories, and for pyrites it is 4.3 calories.

2. Low ignition point is not, ipso facto, an indication of liability to spontaneous combustion, although these phenomena very often run parallel.

3. Low rank coals liberate more CO_2 on absorption of O than higher rank coals.

4. (a) If the oxygen absorption capacity of a coal (~60 mesh size) is below 200 ml. oxygen (N.T.P.) in 96 hrs. (in an atmosphere of air) at 30°C the coal is regarded as not liable to fire. Coals liable usually absorb well over 300 ml.

(b) If the absorption is between 200 and 300 ml. and the coal contains pyrites, some of which is in a fine state of division the coal is termed: "Suspected to be liable to fire, particularly if stored in warm climates."

5. The oxygen content of a coal is, by itself, no guide to the absorbing capacity, e.g.

% O in coal.	ml. O_2 absorbed by 100 gms. of coal in 96 hrs. at 30°C
8.93	623
8.63	133
8.25	453

Lategan 39) determined the oxygen absorption and also 'relative ignition point' characteristics of Witbank coals and concluded that they were non-liable to spontaneous combustion under existing conditions of storage and transport.

More recently Schmidt and Elder 56) have conducted a series of very informative experiments on the atmospheric oxidation of a series of coking coals at temperatures below 100°C. They found that under thermostatic conditions:-

(a) the characteristic rates of oxidation of coals increased with increasing volatile matter content.

(b) the rate of oxidation decreased rapidly as the coal consumed oxygen, being inversely proportional to the ¼th root of the amount of oxygen consumed.

(c) the rate was proportional to the 0.61 power of the oxygen concentration in the gas phase.

(d) the logarithm of the amount (X) of oxygen consumed varied linearly with the logarithm of the time (T) of oxidation, or, expressed mathematically:-

$$\log X = \log C + b \log T$$
$$\text{or } X = CT^b$$

where C and b are constants, and the rate of reaction (R) is given by the expression:-

$$R = \frac{dX}{dT} = CbT^{b-1}$$

They further found that the variation of oxidation rate with temperature was approximately as predicted by the Arrhenius equation:

$$\frac{d \ln R}{dT_K} = \frac{E}{1.986 \ T_K^2}$$

or $2.303 \log_{10} \frac{R_1}{R_2} = \frac{E}{1.986} \left\{ \frac{1}{(T_K)_2} - \frac{1}{(T_K)_1} \right\}$

where $(T_K)_1$ and $(T_K)_2$ are reaction temperatures in °Kelvin, R_1 and R_2 are reaction rates at the two temperatures $(T_K)_1$ and $(T_K)_2$, respectively, and E is the energy of activation in cal./mol.

Values of E found for the temperature range 30°C to 99.3°C were about 11,000 cal./mol., corresponding to a factor of increase in the reaction rate of about 1.7 for each 10°C rise in temperature.

Also, for the coals tested, higher rates of oxidation tended to be compensated for by lower friabilities, so that both these factors (opposing as they are) had to be considered when assessing the relative storing qualities of coals.

According to Davis and Byrne 17) the temperature of preliminary drying of coal (in an inert gas) should not exceed 140°C. Such drying should not be extended over an excessive period, since the colloidal nature of the coal may be altered, affecting its ability to absorb oxygen.

In estimating the tendency of coal to self-inflammation Oreshko 47) placed a 1 - gram coal sample in a perforated metal cup suspended from a calibrated quartz spiral, and heated in an electric furnace while a stream of oxygen passed through. Weight changes of the sample were determined from the extension of the spiral while temperatures were recorded with thermocouples. Results were plotted, showing weight changes, temperature of sample and temperature of furnace for different rates of oxygen feed and temperature rise. The maximum and minimum temperature points of the weight curves did not change with variations in physical factors (rate of heating, rate of O feed, and size of coal) but depended only on the chemical and physical nature of the coal. Since the minimum temperature varied little for different coals, the maximum temperature could be utilised to characterize the tendency of coals to self-inflammation. The method was more complicated than the Erdmann method (Chem. Abs. 17, 1705) but yielded more objective results.

In studying/.......

In studying the effect of oil-treatment on the oxygen absorption capacity of coals Ambrose and Gaspari 1) measured the absorption by a manometric method and found the method very satisfactory.

The 'ignition point' or 'relative ignition point' of coal is often used for assessing liability to spontaneous combustion 39), 18), 71), 21). The main objection against this is that the ignition point lies far above the ordinary temperatures where spontaneous combustion begins to assume appreciable proportions. There has apparently been good progress lately with improving methods of determining ignition temperatures 58), 48), 36), but it is not known whether this has been applied in the field of the spontaneous combustion investigation.

The adiabatic calorimeter is apparently the most promising tool available so far for determining the relative tendencies of different coals to heat spontaneously as it simulates most closely the actual large scale, spontaneous heating phenomena. Winmill has also pioneered this type of investigation, and was followed by Davis and Byrne 16).

Very comprehensive details about the spontaneous firing characteristics of brown coal, brown coal briquettes and brown coal semi-coke, covering mainly adiabatic calorimeter tests on these substances have been described by von Walther and Bielenberg 72) in 1927 and Rosin 54) in 1928.

Workers in Japan 7) treated the oxidation of coal as a gas reaction as follows:-

$$\ln k_1 + a\,{}^1\!/_{T_1} = \ln k_2 + a\left({}^1\!/_{T_2}\right) = C$$

where k_1 and k_2 are velocity constants corresponding to the absolute temperature T_1 and T_2 respectively, while a and C are characteristic constants of the reaction. The reaction velocity is always proportional to the velocity constant and the following equation was derived:-

$$\ln \frac{d\theta}{dt} + a/\theta = C, \text{ or } \frac{d\theta}{dt} = K e^{-a/\theta}$$

where θ is the characteristic curve of the coal and $K = e^c t$

can be calculated from the above equation by substituting the experimental values of a and K. The time required to fire spontaneously is calculated by the formula:-

$$t = {}^1\!/_K \int_{\theta_1}^{\theta_2} e^{a/\theta}\, d\theta,$$

and the value obtained will coincide with practical experiences. The danger of spontaneous combustion in coal mines can be known in advance by tracing the curve shown by the formula $\int e^{a/\theta}\, d\theta - \theta.$

According/........

According to Makarov and Oreshko 42) the rate of spontaneous heating V of coal as determined in an adiabatic calorimeter is given by the parabolic equation:-

$$V = \ell (t - m)^2 + a^1$$

in which

t = initial temperature

ℓ = a constant = 12.3×10^{-5}

and m and a^1 are the co-ordinates of the apex of the parabola.

The experimental value found for 'm' is called the "critical temperature of spontaneous heating of the coal." At temperatures below this 'critical' point the rate of heating, a^1, is constant, being lower than a certain critical value. Above it the rate increases with temperature.

In further adiabatic calorimeter studies by the same authors 43) oxygen was supplied in amounts of 0.6 - 5.15 c.c. per gram per minute at temperatures between 100 and 150°C. The spontaneous heating curves obeyed (within the limits of experimental error) the equations:-

$$\bar{w} = a + bt, \text{ and } w_t = C e^{-A/RT},$$

where $\bar{w}$ = average velocity of spontaneous heating, a, b and C are constants, and t is the temperature of the coal. The second equation expresses the relation $w = \phi(T)$ better than the first, and gives a theoretical explanation of the spontaneous heating of the coal from the point of view of Semenov's theory of explosive reactions. With a change of velocity of the oxygen supply A remains constant (= 7000 cal./mol.).

Dependence of the velocity of spontaneous heating of coal under adiabatic conditions on the velocity of the oxygen current is given by

$$w = \ell V/(m + V)$$

At 100°C the constant m = 0.15 c.c./gm./min. and the constant ℓ = 0.36 gm./min.

The theoretical basis for this equation is taken from the adsorption theory of heterogeneous gas functions. Velocity of spontaneous heating of coal increases sharply in the region of oxygen velocities of from 0 - 2 c.c./gm./min. At velocities of 2.5 - 5.15 c.c./gm./min. the velocity of spontaneous heating is practically constant and is 96 - 97% of its maximum value at the given temperature. This region of velocities of the gas current is the most convenient for the investigation of spontaneous heating processes of coal.

In experiments conducted by Oreshko 46) oxygen was passed through a heat insulated pile of dry coal and the temperature (θ) measured. It was found that:-

$$\text{Rate of heating} = \frac{d\theta}{dt} = C e^{-A/R\theta}$$

where t = time and C and A are constants. The lower the initial temperature of the coal (40°C - 100°C) the smaller is C. Approximate values of A found were:-

/........

$$2.7 \text{ kg.Cal. at } \theta < 80^\circ C \text{ (approx.)}$$

$$\text{and } 7 \text{ " " " } \theta > 85^\circ C$$

Hence the mechanism of the oxidation suffers a change when a temperature of about 80 - 85°C is exceeded.

Other workers 12) employed a differential thermocouple and photographic registration of thermal curves by means of the Kurnakov pyrometer. They noticed two endothermal effects in the heating curves of coals. The endothermal effect of the removal of water was superimposed by an exothermal effect of the oxidation of the coal. The exothermal effect appeared before the completion of the second endothermal wave, i.e. the process of intensive oxidation began before all water had been removed completely.

Full details of an adiabatic calorimeter and tests carried out in it are given in a recent publication by Elder and co-workers 24). An interesting conclusion drawn is that both the behaviour in the adiabatic calorimeter and the rate of oxygen consumption at 212°F in air arrange a series of coals in the same order of tendency towards spontaneous heating. The wellknown relation between rank of a coal and tendency towards spontaneous heating was further confirmed, and data for the increase in reaction rate with increase in temperature, and decrease in this rate with increase in oxygen already consumed by the coal were obtained. The authors concluded that the rate of oxidation (of fresh coal) was proportional to the oxygen concentration in the reacting atmosphere raised to the power 0.66, and to the cube root of the (external) surface area. Mineral constituents or ash acted as inert diluents and decreased the relative tendency. The presence of appreciable amounts of moisture tended to reduce the relative tendency due to the high specific heat and latent heat of evaporation of water. To eliminate these effects during experiments the coals were therefore dried at 212°F in nitrogen before testing.

Adiabatic calorimeter tests are at present being undertaken at the Fuel Research Institute and the results will be combined and correlated with the results of "bunker" tests (which may be regarded as adiabatic calorimeter tests on a semi-large scale, simulating practical conditions) carried out at the Bluff, Durban, and oxygen absorption tests also at present being conducted at the Institute.

3. Factors Promoting or Retarding
    Spontaneous Heating:

    A. Physical Factors:

Hood 32) concluded that the factors most concerned in the spontaneous heating of coal are:- temperature at time of storage, freshness of coal surface, dissipation of heat generated and access of oxygen.

Winmill 75) was probably the first worker to demonstrate that the amount of oxygen consumed by coal was dependent on the size or particle diameter, in other words, on the external surface area which is proportional to the reciprocal of the particle diameter for the same amount of coal. His results, however, also demonstrated that this was not a simple direct relationship, but that at least a certain amount of internal surface must be available for reacting with the oxygen. As stated above Elder and co-workers 24) concluded that the rate of oxidation was

approximately proportional to the cube root of the external surface area of the coal. Two very important factors to be considered are therefore:-

1. The screen analysis of a coal, the amount of fines present and the degree of segregation of these fines.

2. The potential capacity of coal to produce fines on being handled, in other words, the friability.

The Fuel Research Institute has from time to time carried out surveys of screen analyses of various South African coals, and screen analyses on nuts exported are regularly carried out, the results being available in the Institute's records.

On the friability of South African coals there have been two publications 70), 38), and further data will be available soon when the final report on the weathering characteristics of South African coals becomes available 29).

The internal surface available to the action of oxygen is closely connected with such properties as rank, maximum inherent moisture and heat of wetting. These properties have already been discussed above but it may be added that the National Chemical Laboratory of the C.S.I.R. is conducting investigations of these properties on South African coals at present.

The heat generated by the absorption of 1 ml. of oxygen (N.T.P.) was found by Winmill 75) to be 2.1 calories for coal and 4.3 calories for pyrites.

It is held by Turner and Sinkinson 69) that the adsorption of carbondioxide by coal is an important factor in the production of the initial temperatures necessary for its spontaneous combustion.

Blaskett 4) demonstrated the potential heating effect of water condensation on coal by passing air saturated with water through a low rank coal for 4 minutes - the moisture content increased from 5% to 6¾% while the temperature rose from $20^{\circ}C$ to $39^{\circ}C$.

The same author believes that coal is more likely to heat to the point of ignition if piled in hot weather than if piled in cold weather, in fact a matter of a few degrees difference may be significant. Further, if both CO_2 and O_2 are present, the CO_2 being much more readily adsorbed than the O_2, would in consequence appreciably retard the rate of oxidation of the coal, and not merely serve as a diluent of the oxygen.

The author believes that the tendency to spontaneous heating within a pile of stored coal can be assessed, approximately, by the expression:-

$$\frac{R H^2}{a}$$

where R = initial rate of oxygen consumption.

H = height of pile

and a = k/DS

where k = thermal conductivity of coal pile
     D = density of coal pile
     S = specific heat of coal pile.

To reduce the tendency of heating within the pile, 'R' and 'H' should be kept as small as possible while 'a' should be large.

'R' is dependent on the coal type, but its value is increased with increase in fineness of the coal, with initial storage temperature and with abundancy of the oxygen supply.

'a' Appears to be mainly dependent on the specific heat of the coal and hence on the moisture content. A higher moisture content leads to decreased values of 'a' while there is an additional danger of condensation in drier parts of the pile.

The permeability K of a bed, i.e. the rate of flow/unit pressure gradient (cm./sec.) is dependent on its porosity ϵ (vol./wt.) according to the expression:-

$$K = \frac{constant}{S_0^2} \times \frac{\epsilon^3}{(1-\epsilon)^2} ,$$

where S_0 is the specific surface/unit volume of solid, and is therefore proportional to $\frac{1}{d}$, d being the diameter of particles. Thus

$$K = constant_2 \times d^2 \times \frac{\epsilon^3}{(1-\epsilon)^2}$$

Loosely piled, uniformly sized coal shows a porosity of something over 0.5, while, when well packed down ϵ would be less than 0.4. With this range of ϵ the function $\frac{\epsilon^3}{(1-\epsilon)^2}$ shows a 3 to 4 fold variation, i.e. the permeability of loosely packed coal can be reduced to approximately $\frac{1}{4}$ of its original value by packing down.

The thermal conductivity of a pile of coal increases with increasing apparent density.

With restricted air supply, air-flow has a negligible effect on heat dissipation (only about 1/400th of the heat generated).

At a higher temperature the reaction rate falls off more rapidly with time than at a lower temperature, and this compensates, somewhat, for the increased reaction rate at higher temperature.

According to Taylor 62) the rate at which an air current has to move through a heap of coal in order to cause spontaneous heating is of the order of 9 inches a day.

Dunningham and Grumell 22) maintain that the "self-heating of a coal heap is.........directly correlated to wind pressure. For the first step, the development of high temperature in a mass of interior coal, wind is necessary. Heating therefore occurs only on the sides exposed to prevailing winds."

Winds are more responsible for air movements through, and heating in large coal piles than is the stack effect, according to Drewry 20).

Certain/.......

Certain vitrains have been found to be unduly susceptible to spontaneous heating, the theory being the liberation of CH_4 caused by tremendous pressures accompanying earth movements, resulting in the addition of oxygen to restabilize the compounds. The other components of the coal do not appear to be affected similarly 9).

The relationship between selfignition of coal beds and their petrographic constitution has been investigated by Pohl 52) who concludes that as a result of the high specific ignition temperature of fusain it can never be the cause of fire when not in contact with vitrain. The latter, undoubtedly, plays a very important role. Fusain may, however, act as a catalyst due to its fineness and high absorbing power for oxygen. Durain plays a part of secondary importance only. (See also under: B. Chemical Factors)

B. Chemical Factors:

The effects of the concentration and availability of oxygen, the possible role of the formation of peroxides and the part played by the weathering of coals on their spontaneous heating have already been mentioned above and very little remains to be added.

The concensus of opinion is still that the role of pyrites in this phenomenon is a minor one.

Barkley 3) states that in a coal pile rain or water may increase the rate of oxidation of pyrites by supplying the necessary water and (or) washing off oxidation products. The pyrites is also accused of disintegrating coal (thus producing fresh surfaces) through being oxidised to bulkier products.

Teichmann 65), working on samples of coal and pyrites obtained from various South African collieries, failed to detect any marcasite in his samples and found that moist oxygen at 105°C. produced only a small amount of oxidation over a period of six weeks. The rate of oxidation of pure pyrites is appreciably less than when pyrites is associated with coal.

According to Davies 15) coal pyrites concentrates are quite liable to spontaneous firing when in piles of over 10 ft. in height. Apparently there is a very marked difference in the behaviour of pyrites from different sources. Some show no tendency to spontaneous firing or disintegration on weathering. Other varieties break down to powder within a few days. Some oxidise to the ferric state and others to the ferrous state. The nature of impurities, and particularly the physical form of their association with the pyrites may account for this variation in behaviour.

It is also possible that bacteria which have been identified in many mine drainage waters, and which are responsible for the oxidation of sulfuritic materials, including pyrites 66), play an important part in the phenomena mentioned above.

According/......

According to Taylor 62) there is no justification for believing that a low-sulphur coal would necessarily store better than a high-sulphur one.

The mixing of powdered pyrite with powdered coal has been shown to result in a retardation of oxygen absorption of the mixture. High ash in a sample has a similar diluting effect if the ash is low in iron oxide. If the iron oxide is high, oxidation is promoted 11).

It has been demonstrated that by drying a coal its oxygen absorption capacity is reduced.^{x} Oxidation becomes more rapid with increasing water content until a certain maximum is reached, after which additional water has a retarding effect 11). In this connection it is interesting to compare the effect of water on the combustion of carbon at higher temperatures. Dried carbon, even at incandescent heat burns slowly, yielding mainly carbon monoxide. Moist carbon burns at a much lower temperature, yielding mainly carbon dioxide 67).

The above should also be viewed in the light of the inversion of the $CO:CO_2$ liberation ratio occurring at $70 - 80^{\circ}C$, CO_2 preponderating above this temperature range. The breakdown of the hydroperoxide (formed during the oxidation at low temperature of coal in the presence of water vapour) at this temperature is accompanied by a marked increase in the rate of reaction of the coal with air or oxygen, and this phenomenon is of profound importance in the whole problem of spontaneous combustion 37), 35).

Phenolic radicals are regarded by Tronov 68) to be the most readily oxidizable parts of molecules comprising the humus components of coals. He has advanced an explanation of the mechanisms involved in the low temperature attack of atmospheric oxygen on these radicals, and of the formation of the oxides of carbon.

According to Taylor 62) "the liability of a mixture of coals is that of the most liable constituent under the conditions prevailing; there seems to be a wide-spread belief that the circumstances are aggravated by some kind of interaction between the constituents of the mixture, but this is out of the question."

Regarding the above remark about the dominating effect of "the most liable constituent," Davis and Reynolds 18) concluded that the behaviour of a sample of coal could not be 'computed' from that of the individual petrographic constituents, although they all contribute to self-heating in storage. A comparable position has been found to exist with regard to ignition temperatures, where small additions of a highly reactive coal to a less reactive one has an effect of lowering the ignition temperature of the mixture out of proportion with the percentage added 58).

'Opencast' coals appear to be particularly liable to spontaneous combustion 53). Chemical and (or) physical alterations of the coal substance related to a certain degree of sub-surface weathering may be the cause of this behaviour.

It has/........

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^{x} This has been confirmed during oxygen absorption tests carried out at the Institute.

It has been reported that selfignition is in certain instances promoted by the presence of alkaline water derived from weathered minerals of the covering rock layers 14a). On the other hand it is held that a greater initial concentration of acid favours the development of marcasite in preference to pyrite during formation 14b). (See also Section 5, 'Prevention of Spontaneous Combustion')

4. Deterioration of Coal on Storage:

Contrary to widespread belief loss of calorific value on storage is negligible, provided there has been no spontaneous heating. If this occurs, obviously the coal can deteriorate to any extent, depending on the extent of heating or combustion that has occurred.

If heating is only slight such deterioration as is practically appreciable is limited to disintegration by weathering and loss of coking power, which occurs fairly rapidly especially with small coal.

The consequent higher proportion of small coal and loss of coking power causing a loss of coherence in the fire bed may cause a greater loss of unburnt material, but this should not be confused with loss of calorific value 62).

An approximate indication of the amount of deterioration (presumably in respect of calorific value) with time for British coals is given by Taylor 63) as follows:-

Years of Storage.	Percentage Deterioration.
1	0.8
3	2.0
5	3.0
10	4.0
25	5.0

Deterioration on storage is dependent on the rank of the coal, being the least and slowest for the high rank coals like anthracite, and increasing in amount and rate towards the lignite ranks.

Hard coals deteriorate much less than soft ones, and cannel coals are particularly durable in this respect.

Increased friability results from weathering, and this is usually concentrated in the outer layers of a stack 63).

The coking value of a coking coal is very likely to be destroyed completely in 3 years, and it is recommended that a coal for coking purposes should never be stored for longer than 1 year 63). The deterioration of a coking coal in storage is accompanied by a marked increase in the breeze content of the coke made from it 33).

According to Spooner and Mott 59), however, coals of over 86 per cent carbon content (Parr basis) (i.e. high rank coals) are not liable to deteriorate on storage for periods of 6 months. Silkstone coal (carbon 85 - 86%, hydrogen 5.7%) gives a harder coke when coked in coke ovens after 5 months storage and this coal can be stored for 11 months as slack without any deterioration to the coal.

The volatile matter content of coal is only slightly decreased by storage. Undue heating in a stack may, of course, result in excessive loss of volatile matter 33).

Both the airdry moisture content and the oxygen content increase on storage of the coal. The rank of the coal is an important factor in determining the magnitude of the increase 33).

A very informative contribution on the effects of storage, without rise in temperature, has been made by Scarf and co-workers 55). They concentrated to a large extent on the effect of size of the stored coal on the rate of change of its various properties.

Parry and Goodman 50a) have shown that sub-bituminous coal can be stored for long periods in closed bins minimising moisture changes, without suffering much degradation. If stored in the open, or in a ventilated bin, degradation and deterioration can be serious, however.

Barkley 3) quotes an average yearly heat loss of 0.1 percent for 'fireproofed' piles (storage period 14 months) as against 0.9% for 'unfireproofed' piles (storage period 4½ months) (In the case of the latter spontaneous heating had occurred in spots.) The coal tested was low-moisture coal of about 35% volatile matter.

The increase in surface moisture of coal stored in the open may increase by as much as 10% in bad weather, resulting in a decrease in effective heat generation of about 1%. Even so the extra cost of providing extensive covered storage for coal stocks is not justified 51).

5. Prevention of Spontaneous Combustion:

The liability of coal to spontaneous ignition is a very relative and indefinite conception and likewise the prevention of spontaneous heating is usually not achieved by the application of a single, simple formula. The complexity of the phenomena involved, is perhaps best illustrated by quoting Stoek and co-workers 61):-
"It is probably true that all varieties of bituminous coal have been stored without fire resulting, and equally true that all varieties of coal have fired when stored."

Taylor 62) states:- "It is wellknown that anthracite, dry steam coal and cannel are not liable to heat spontaneously. While there are differences in the liability of other coals to heat spontaneously, it is safer to regard them all as suspect; for none can be reliably expected to be exempt from the danger, and such differences as there are between them are not very marked in practice."

The following data, cited by Lowry 40) illustrates the great importance of conditions of oxidation:-

Observed rate of oxidation.		1	3
Condition 1:- Temperature of oxidation		60°F	84°F
Condition 2:- Size of coal particles	(1 inch	18 mesh	
	(¼ "	48 "	
Condition 3:- Oxygen in air, %.		3.5	20.9
Condition 4:- Time since oxidation started	)coarse coal	4 months.	12 hrs.
	)fine "	2.9 days.	12 "

By altering each of the conditions from the values stated in the middle column to those stated in the third column, the rate of oxidation of a sample of coal would reveal, approximately, a 3-fold increase, so that all the changes in conditions listed taken together could cause an 81-fold increase in the rate of oxidation, which would over-shadow in importance the comparatively small difference between different coals.

Coal is rendered absolutely safe by the exclusion of all ventilation, but this is expensive, especially when a large amount of coal has to be kept in stock. Generally, it may be taken for granted that the less the precautions that have to be taken against spontaneous heating, the less expensive the storage of coal will be. In practice this usually results in a compromise between amount spent on safety measures taken, and risk run of experiencing spontaneous heating.

Spontaneous heating and firing is not limited to stored coal, but is quite common in underground workings, often occurring in crushed or broken coal from pillars left as roof support or from roof coal or seams overlying a worked-out seam. The prevention of spontaneous combustion by the use of steel arches as road supports has been described by MacGregor and Temperley 41).

Pohl 52) suggests that the method of exploitation may be a contributory cause of underground fires. The introduction of the long-wall method of mining with pneumatic stowage has resulted in the elimination of underground fires in certain cases.

Obviously certain types of coal would posess better storing qualities than others. The two most important characteristics to be considered are rank and friability. Coals of relatively high rank are preferred on account of their lower moisture content, absorption of oxygen, slacking tendencies and general deterioration on storage. These coals are also invariably the better quality coals so that the ratio-therms per cu.ft. (or per ton) of coal stored is an optimum.

Hard, dull, anthracitic, splint and cannel coals and anthracite are safer to store than soft, bright, bituminous, sub-bituminous and lignitic coals 64).

Although a high rank coal may be preferable this does not, apparently, preclude low-rank coals from being safely stored. Parry 49) reports that "a large power plant in Texas stores thousands of tons of lignite in open pits for emergency use. An earthen pit 20 to 30 feet deep, with tight sidewalls, is filled with lignite and the top is levelled. This is a very cheap method of storing reserve fuel. Spontaneous combustion does not occur because all air is excluded from bottom and sides."

Further details of the successful storage of sub-bituminous slack coal in open pits is provided by Goodman and co-workers 50b).[x]

Large coal deteriorates more slowly than a smaller size of the same coal, due to a smaller total exposed surface in the case of the former, and from this point of view it is therefore preferable to store large coal 64).

The advantages of low friability, as a result of which the formation of fines on handling is minimized, are self-evident.

It has been demonstrated that safe storage of large amounts of coal can be achieved by providing suitable and adequate ventilation 22), but the weight of evidence seems to be against this practice, and the other extreme, viz. exclusion of all ventilation or reducing it to a minimum is usually aimed at in modern installations. Whether ventilation is resorted to or eliminated, the course adopted must be pursued with the greatest thoroughness.

Both deterioration and spontaneous ignition can be avoided by under-water storage. At least one American plant has facilities for storing as much as 300,000 tons of coal under water 40). It is, however, a fairly expensive method of storing 50b) and unless fines are removed before storage drainage of the water on taking up the coal again is not very satisfactory 3).

Both the rate of deterioration and the probability of spontaneous ignition can be decreased by storing coal in compacted layers. Coal can be laid down in 2 - 4' layers by spreading with a bulldozer, thus eliminating to a large extent the segregation of sizes. By compacting, the bulk density of broken coal can be increased from 45 - 50 lbs. per cu.ft. for loosely piled coal to 65 lbs./cu.ft. 40). The success of the method seems to indicate that the decreased availability of oxygen through decreased air circulation, more than compensates for the increased area of fresh coal surfaces caused by breakage. Compacting can also be done with a roller.

The principle of decreased air circulation has been further applied in the use of a layer of paper between layers of coal. This method has proved successful where it was necessary to store a coal that was especially sensitive to oxidation 40).

Storage of coal in an open pit in the earth is similar to storage under water, except that the use of the water is avoided. Segregation during laying of the coal should be avoided and the coal should preferably be spread and compacted with a bulldozer tractor. The coal should be level on top

and not/........

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[x] According to a private communication received at the Institute from the U.S.A. (see letter of 3rd March, 1950 in Secretary's file No. 4/7/1/2) the safe storage of sub-bituminous coal (35 - 40 percent moisture) above ground, without having to dig or construct expensive pits, has now been worked out. Piles of well over one-hundred thousand tons can be formed, provided that: (a) the coal is laid down in layers and very well crushed and compacted (b) segregation of sizes is avoided, and (c) the angle of rise at the edges of the pile is held between 17 and 20 degrees.

A report on the investigation and method recommended is to be issued in the near future by the U.S. Bureau of Mines.

and not be higher than the sides of the pit. The sides of
the pit should be in good condition and impervious. A
further precaution with such piles in a pit is to provide
a protective capping as described hereunder 3).

Covering a large coal pile with a layer of very fine
coal (say 12" thick) and then with a layer of lump coal
(say nuts) to reduce subsequent erosion,forms an efficient air-
tight coating which inhibits spontaneous heating.

An asphalt coating is a very efficient means of
preventing the diffusion of air into the interior of a mass of
coal and has often served as a last resort to arrest
spontaneous heating. Any cracks developing in the coating x
should, ofcourse, be mended so as to maintain a perfect seal.

Cut-back asphalts, road tar and asphalt emulsions have
been used for capping coal piles, but Barkley 3) recommends the
latter as being superior to the others.

Other capping materials tried, but apparently with less
success, have been portland cement with coal dust for the
aggregate, and even plaster of paris 3).

A capping is less liable to crack as a result of settling
of the pile if care is taken to compact the coal adequately
before the capping is applied.

The conclusions and recommendations of the many writers
on the subject is suitably summarized by Lowry 40) as follows:-

"1. Storage area should be level, firm, well drained, and
free of fences, piers, etc.

2. Decreased height of storage piles results in decreased
probability of spontaneous ignition, since (a) the effective
resistance to heat flow is lower, so that the heat of oxidation
can be dissipated with less rise in temperature, (b) lower piles
tend to decrease the amount of segregation of sizes when coal is
piled carelessly, and (c) it is easier to remove "hot spots" when
they occur.

3. Segregation of sizes should be avoided since many fires
occur near the boundaries of zones of coarse coal that apparently
act as chimneys for conducting air into the pile.

4. Preferably coal should not be piled in hot weather since
many fires apparently are due to this cause.

5. Coals from different sources should not be stored in a
common pile.

6. A shipment of coal that is especially wet should not be
piled with other coal.

7. Care should be taken to keep out extraneous material,
which may cause fires, even in anthracite, which is not ordinarily
subject to spontaneous ignition.
                                              8. After/.......

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x   The only other two remedies that remain in cases when
   uncontrollable spontaneous heating is occurring in a pile of
   coal is complete flooding, or removal of the hot coal from the
   seat of trouble and cooling it.

8.   After storage the temperature of a pile should be
determined regularly by means of thermometers in previously
installed pipes, or by thrusting down iron rods and feeling
the rods on withdrawal.   The extremely local nature of "hot
spots" makes it necessary to test at points on 10- to 20-foot
centres;   if temperatures of 140 to 150°F are found, danger is
impending, and the temperature of the coal near these points
should be taken on 5-foot centers;   even so, it is possible
to miss "hot spots," and combustible gas indicators have been
used successfully for their detection.

9.   If coal at a temperature above 150°F is found it
should be dug out and used immediately or wet down thoroughly
and repiled by itself.   Water should be sprayed on the large
piles only as a last resort.

10.   The following heights of storage piles are
recommended as safe: fine coal over 18 percent volatile
matter, up to 4 yards;   large coal over 18 percent volatile
matter, up to 6 yards;   fine coal below 18 percent volatile
matter, up to 6 yards;   and large coal below 18 percent
volatile matter, up to 8 yards."

          Regarding 8 above, it may be added that temperatures
should also be taken at different depths from the surface
at the same spot, and all temperatures should be recorded so
as to be able to follow the trend of temperature variations 44).

          The design of an armoured thermometer, especially
suitable for testing temperatures in coal dumps has been
described in the literature 2).

          Naturally all sources of external heat, e.g.
steampipes, chimneys, etc., should be avoided in coal piles.

          To combat wind effects in assisting spontaneous
combustion in a pile of coal it is recommended that the
stack should be built up so that its longer side is in the
direction of the wind 44).

          Coal that has once heated and then cooled is safer
to store than the same coal freshly wrought 64).

          Sized coal, with fines removed, will give much
less trouble from heating than unsized coal, the relatively
small amount of coal surface developing only a small amount
of heat which can be readily dissipated.   Coal of one size
is better than a mixture of sizes, and sized coal should not
be stored on a foundation of fine coal 61).

          Bins, bunkers and silos can provide safe storage
places provided they are free from air leaks.   The discharge
chute of a bunker requires particular attention for air leaks.
When emptying them, all old coal from corners, etc., should be
cleaned out before charging with fresh coal 3).

          Spontaneous combustion in open heaps of coal not
exceeding about 200 long tons is very rare indeed, but this
200 ton limit is considerably reduced if the coal is stored
in a bunker providing air leakage from the sides and (or)
bottom 62).

Fires have been put out by expelling air from the
pile with carbon dioxide gas used in frozen or liquid form.
The air must be kept out of the pile long enough to allow
appreciable cooling, or heating may re-develop after
disappearance of the carbon dioxide. For some conditions
the use of carbon dioxide may provide a delay in the burning 3).
The use of carbon dioxide is, however, not attractive,
economically.

Flue gases have been suggested and tried as a means
of maintaining an inert atmosphere in a mass of coal, but
no details are available 62).

Reverting again to the question of height of piles
Taylor states 62): "Limiting the height of a coal stack is
often suggested," (as a preventive measure) "and eight feet
is perhaps one of the lower commonly suggested limits. But
it is by no means safe. It represents a compromise between
economic use of the stocking site and a reduced likelihood
of spontaneous combustion; all that can be said of it is
that it is better than ten feet or twelve feet. It is
possible, but not certain that four feet is a safe limit;
five feet is not."

As mentioned earlier, Blaskett 4) suggests a formula
for assessing the relative tendency to spontaneous heating
within a pile of coal. In his formula this tendency is
proportional to the square of the height of the pile,
indicating again the necessity of avoiding appreciable heights
when stacking coal where access of air is unavoidable.

Special circumstances may, however, bring about that
the 'safe height' is exceeded to an appreciable extent. In
this connection Taylor, e.g., states 63):- "A crane and grab
is not only useful as a rapid means of stacking coal; it
enables the seat of trouble to be got at most quickly. On
this account the mere possession of a crane and grab influences
the safe height of stacking."

The same author also describes the building up of
stacks of coal in stages or layers, e.g. a 5' layer of coal
is laid down, and at 9- monthly intervals further 1½' layers
are added.ᵡ The oxygen absorbing capacity of a layer of
coal is reduced to a very low level during the 9 months of
exposure to air, so that the "safe height" is considerably
increased.

Spontaneous combustion usually occurs within four
weeks to four months after stacking. A coal that is eight
months old can be regarded as safe if there is no heating in
the heap, or if what heating there is is not increasing 30).

In fair sized closed bunkers it is much better to
charge the bunker from a number of openings in the cover than
from a single one. Less trimming is required, and
segregation is reduced by eliminating the formation of a
single large conical heap. Similarly, if the bunkers are

of the/......

ᵡ
Convenient schemes and plant for laying down
stocks of coal are illustrated by Pope 53) and
Goodman and co-workers 50b).

of the self-emptying type, withdrawal should preferably be done from a number of outlets, and the bottoms should slope at an angle of not less than 45° with the horizontal 51).

Regarding the export of South African coal there are several reports dealing with cases of reputed spontaneous combustion and investigations thereof 25a).

The coaling appliances at Union ports are notorious for the amount of breakage caused to coal handled by them 25b) and this factor is certainly not to be ignored where cases of spontaneous heating of South African export coals have occurred.

Furthermore, the spontaneous heating that might occur, e.g. in a ship's cargo, will in the majority of cases probably be negligible, provided the interval of time between the time of commencement of loading the coal into the veesel, and off-loading at the destination is reduced to a minimum. Thus the abnormally long delay in completing the loading of a vessel was probably one of the contributing factors in a case of spontaneous heating recently experienced at Lourenco Marques 27).*

Tests carried out by the Institute on board ship in 1944 revealed that spontaneous combustion was appreciably reduced by sealing a hold full of coal instead of ventilating it in the usual manner. The recommendations made in the report describing these tests 26) have, however, apparently not yet been put into practice. The findings of the British D.S.I.R. 21) yield ample support to the view that there seems to be scope for improvement in the practice of shipping coal.

Other more or less artificial methods of 'curing' coal (or brown-coal coke) of its liability to spontaneous combustion have been suggested, and some of these methods are actually being practiced. They include:-

A. Three/..........

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*   Inadequate trimming of the conical heap of coal formed in a hold during loading operations is probably another contributory cause of spontaneous heating experienced in the coal export trade. It has been observed that the tendency is to trim as little as possible, with the result that segregation of different sizes is appreciable.

A.   Three methods recommended by Rosin 54)
for brown-coal coke, viz.:-

(i) Artificial alteration of the brown-coal
coke by treatment with air at controlled temperature
whereby its affinity towards oxygen is largely reduced. ☒

(ii) Saturation with carbon dioxide. When
this is afterwards exchanged for air very little heating
results.

(iii) Treatment of coal with magnesium or
ammonium chloride.

(Other chemicals found by Russian workers to reduce,
considerably, the amount of oxygen absorbed by coal are:
SF_6, $CaCl_2$, $Ca(HCO_3)_2$ and sodium silicate 8).

B.   The Fleissner method for drying lignite 23) is
a remedy against the disintegration of the lignite on
exposure to the atmosphere and hence against spontaneous
combustion.   The drying is effected by a treatment in
saturated steam at about 15 atmospheres pressure (i.e. 200°C).
The cooling has to be carefully controlled to overcome the
risk of spontaneous ignition at this stage.   The final
product is reported to be much less liable to spontaneous
combustion than the original material.

C.   Dedusting and dustproofing of coal has many
advantages, amongst them also the lessening of liability
to spontaneous combustion.   Numerous literature references
to this process will be found in Chemistry of Coal
Utilization 40), and others are listed by Wilkens 74) and
Walters 73).   The principle underlying dustproofing is
the spraying of non-drying agents like petroleum oil, oil
emulsions etc. (possibly also solutions of hygroscopic salts
or other substances) to agglomerate and fix the dust
particles.   Clogging of pores and filming of the surfaces
results in reduced ability of the coal to react with
atmospheric oxygen.

According to Ambrose and Gaspari 1) the greatest
effect is obtained by the first $\frac{1}{2}$ - 1 gallon of oil used per
ton of coal.   There is very little advantage in using more
than 2 gallon/ton.   Sizes below about 10 mesh cannot be
treated economically as they require too much oil.

D.   According to Olin 45) the carbon dioxide
liberated under moist conditions by a mixture of aluminium
sulphate and calcium carbonate is quite effective in
combating spontaneous combustion.   The dosage is 1.5 lb./ton
of coal (-2" slack) costing 3.5 cents/ton treated.

E. Briquetting/.....

☒

According to a private communication received at
the Institute this treatment is actually applied with
success to certain Polish export coals which are
particularly liable to spontaneous combustion.

The same treatment in the 'Jalousie' apparatus has
also been described by Jappelt 34).

E.   Briquetting fine coal with a weather proof binder is a very effective means of combating spontaneous combustion. e.g. The active surface of a brown coal dust was estimated to be 350 sq. metres/kg., whereas that of the briquette made from the dust was 0.07 sq. metres/kg.   Such briquettes are not liable to spontaneous combustion 10).

6.   <u>Some Data on Costs and Economics:</u>

Very useful guidance in respect of the cost of constructing storage space for different quantities of coal and under different conditions is provided in Fuel Efficiency Bulletin No. 49, 44), and further details on the construction of open pits are given by Goodman and co-workers 50b). According to these authors water-tight concrete storage pits varying in capacity from 6,000 tons to 13,000 tons normally cost from 13,000 dollars to 29,000 dollars.

According to Parry 49) it costs 20 - 50 cents/ton in the U.S.A. to store coal under water.

Barkley 3) considers asphalt emulsions (40% water) to be superior to all other materials for providing air-tight coverings to piles of coal.   The material costs 6 - 12 cents/ (U.S.) gallon, and a gallon will treat about 1 to 2 square yards of surface to a thickness of $\frac{1}{16}$" to $\frac{1}{8}$".   For larger piles this would be equivalent to about 0.1 to 0.2 gallon/ton.   The total cost for capping will depend on the dimensions of the pile, and might range from a few cents up to 10 cents/ton. One 72,000 ton pile was covered at a total cost (labour and materials) of about $2\frac{1}{2}$ cents/ton.

According to Taylor 62) the cost when using road tar should not exceed 6d./ton and may even be less than 3d., while as much as 15% of the cost may be recoverable in the fuel value of the tar when picked up with the coal.

The Ministry of Fuel and Power 44) recommends that: "As deterioration is most marked in the earlier period of storage stored coal should not be used while fresh supplies are available.   In this way loss is kept to a minimum because a new lot of fresh coal is not continually being exposed. Also, second handling of the coal is reduced.   Over a long period, however, coal may deteriorate considerably in size, forming a large proportion of dust.   It is thus usually advisable to take coal from stock every five years or so and replace with fresh coal."

There would be two exceptions to the above, viz. (a) where total exclusion of air was provided for, e.g. storage under water, in airtight bins, under an airtight tar capping, etc.   In such cases the quality of the coal would be assured for much longer periods and, economically, it would be desirable to store longer, if possible, (b) in the case of coking coal it would probably be necessary to use the coal within, say, one year, on account of the loss of coking power, unless exclusion of air is again provided for.

<div align="right">

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PRETORIA.

12th April, 1950.

7. Literature References.

1). Ambrose, H.A. and Gaspari, H.J.R., Coal Age, 42, p.p. 252 - 4 (1937).

2). Anon, Eng. and Chem. Digest, 1, No.3, p.p. 114 - 6 (1949).

3). Barkley, J.F., "The Storage of Coal," U.S. Bur. Min., Inf. Circ. 7235 (1943).

4). Blaskett, D.R., "Spontaneous Heating of Coal." Ore-Dressing Investigations - Joint Investigations of the (Australian) C.S.I.R. and the South Australian School of Mines and Industries. Reports from the Bonython Lab., New Series No.179, C.S.I.R. No. 164 (1947).

5). Bond, R.L. and Maggs, F.A.P., Fuel, 28, 169 and 172 (1949).

6). B.C.U.R.A., "The Ultra Fine Structure of Coals and Cokes," London (1944).

7). Chemical Abstracts, 23, 5299[7] (1929).

8). Chemical Abstracts, 34, 8285[1] (1940).

9). Chemical Abstracts, 35, 1599[9] (1941).

10). Chemical Abstracts, 36, 3657[5] (1942).

11). Chemical Abstracts, 38, 3446[4] (1944).

12). Chemical Abstracts, 39, 1974[1] (1945).

13). Chemical Abstracts, 41, 4291b (1947).

14)(a) Chemical Abstracts, 41, 7753i (1947).
   (b) see: Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 14, p.207 (1947 reprint) Longmans, Green and Co., London.

15). Davies, D.T., J. Inst. Fuel, 21, 301 (1948).

16). Davis, J.D. and Byrne, J.F.,- see reference 18), p. 22.

17). Davis, J.D. and Byrne, J.F.,Ind. Eng. Chem. 18, p.p. 233 - 6 (1926) and Chem. Abs., 20, 1136[2] (1926).

18). Davis, J.D. and Reynolds, D.A., "Spontaneous Heating of Coal," U.S. Bur. Min. Tech. Pap. 409 (1928).

19). Dresel, E.M. and Griffith, M. Fuel, 28, p.p. 193 - 9 (1949).

20). Drewry, M.K. Chem. Abs., 31, 6848[6] (1937).

21). D.S.I.R. - Fuel Research - Special Report No.5. "Fires in Steamship Bunker and Cargo Coal," London (1929).

22). Dunningham, A.C. and Grumell, E.S. J., Inst. Fuel, 10, p.p. 170 - 7 (1936-7).

23)(a) Fleissner, Trans. Fuel Conf., World Power Conf., London, Vol. 1, 328 (1928).
   (b) Lavine, Gauger and Mann, Ind. Eng. Chem., 22, 1347 - 60 (1930).
   (c) U.S. Patents 1,632,829 and 1,679,087

24). Elder, J.L., Schmidt, L.D., Steiner, W.A. and Davis, J.D., "Relative Spontaneous Heating Tendencies of Coals." U.S. Bur. Min. Tech. Pap. 681 (1945).

25)(a) F.R.I. of S.A. Reports Nos. 2 of 1931, 3 of 1931, 4 of 1931, 19 of 1936, 3 of 1943, 6 of 1943 and 7 of 1943.

   (b) F.R.I. of S.A. Reports Nos. 6 of 1931, 9 of 1945 and 1 of 1949.

26). F.R.I. of S.A., Report No. 7 of 1944.

27). F.R.I. of S.A., Reports Nos. 6 of 1948 and 7 of 1948.

28). " " " " " 8 of 1950.

29). " " " Report to be written on completion of investigation.

30). Fuel Efficiency Committee of the Ministry of Fuel and Power."The Efficient Use of Fuel." London (1944).

31). Haslam, G.S., Fuel, 7, p.p. 253 - 7 (1928).

32). Hood, O.P., "Spontaneous Combustion of Coal." U.S. Bur. Min. Inf. Cir. 7074 (1939).

33). Jamieson, J. and Skilling, W.J., Copyright Publ. No. 201/84 of The Institution of Gas Engineers. London (1939).

34). Jappelt, A., Chem. Abs. 24, 710 (1930).

35). Jones, R.E. and Townend, D.T.A., Trans. Faraday Soc., 42 p.p. 300 - 5 (1946).

36). Jonkin, Cohen, Corey and Jain, A.S.T.M. Proceedings, 1948, p.p. 269 - 89.

37). Kramers, W.J., B.C.U.R.A. Monthly Bull., 10, No.12, p.p. 395 - 404 (1946).

38). LaGrange, C.C., Jrl. Chem. Met. Min. Soc. of S. Afr., 47, p.p. 217 - 223 (1946).

39). Lategan, P.N., The S.A. Jourl. of Industries, Dec., 1925.

40). Lowry, H.H., "Chemistry of Coal Utilization," Vol.1, New York (1945).

41). MacGregor, D. and Temperley, S.J., Trans. Inst. Min. Engrs., 100, p.p. 279 - 307 (1940 - 41).

42). Makarov, S.Z. and Oreshko, V.F., Chem. Abs., 35, 8297[8] and 8298[6] (1941).

43). Makarov, S.Z. and Oreshko, V.F., Chem. Abs., 36, 1463[9] (1942).

44). Ministry of Fuel and Power. "The Handling and Storage of Coal." Fuel Efficiency Bull. No. 49. (Aug. 1949).

45). Olin, H.L. Fuel, 16, 257 (1937).

46). Oreshko, V.F. Chem. Abs., 39, 2633[9] and 2634[2] (1945).

47). Oreshko, V.F., Chem. Abs., 43, 2754h (1949).

48). Orning, Mallov and Neff, Ind. Eng. Chem., 40, p.p. 429 - 32 (1948).

49). Parry, V.F., "Questions and Answers on Storage of Coal in the Rocky Mountain Area." U.S. Bur. Min. Inf. Cir. 7214 (1942).

50).(a) Parry, V.F. and Goodman, J.B., "Storage of Sub-bituminous Coal in Bins." U.S. Bur. Min. R.I. 3587 (1941)
    (b) Goodman, J.B., Parry, V.F. and Landers, W.S., "Storage of Subbituminous Slack Coal in Open Pits." U.S. Bur. Min. R.I. 3915 (1946).

51). Pinckheard, J., Jrl. Inst. Fuel, 23, p.p. 4 - 10 (1950)

52). Pohl, H., see Review: Fuel, 16, 249 (1937) and Chem. Abs., 31, 6441[6] (1937).

53). Pope, P.C., "Coal: Production, Distribution, Utilization," p.116, London (1949).

54). Rosin, P., Braunkohle, 27 Jahrgang, Heft 13, 241 - 256; Heft 14, 282 - 292 (1928)[x]

55). Scarf, F., Hall, D.A., and Yearsley, C.W., Trans. Inst. Min. Engrs., 100, p.p. 88 - 118 (1940 - '41).

56). Schmidt, L.D. and Elder, J.L., Ind. Eng. Chem., 32, p.p. 249 - 256 (1940).

57). Scott, G.S. and Jones, G.W., Ind. Eng. Chem., 29, 106 - 8 (1937).

58). Sherman, R.A., Pilcher, J.M. and Ostborg, H.N., A.S.T.M. Bull. No. 112 (1941).

59). Spooner, C.E. and Mott, R.A., Fuel, 16, 96 - 106 (1937).

60)e.g.(a) Stansfield, E. and Gilbart, K.C., Amer. Inst. Min. Met. Engrs., Trans., 101, Coal Division, p.p. 125 - 143 (1932).
    (b) Dulhunty, J.A. Jrl. and Proc. Royal Soc. New South Wales, 81, p.p. 60 - 8 (1947).
    (c) Dunningham, A.C., see Ref. 6), p.p. 57 - 70.
    (d) Bainbridge, J.R., Scanlan, P.G. and Belyea, I., Fuel, 28, p.p. 88 - 90 (1949).

61). Stoek, H.H., Hippard, C.W. and Langtry, W.D., "Bituminous Coal Storage Practice" Eng. Expt. Sta. - Univ. of Illinois, Bull. No.116 (1920).

62). Taylor, R.A.A., "The Spontaneous Combustion of Coal: A Review of Recent Advances." D.S.I.R., Fuel Research Ref. R.S. 31. 20. London (1949).

63). Taylor, R.A.A., "Deterioration of Coal on Storage." D.S.I.R., Fuel Research Ref. No. R.S. 17/3, London (1935).

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[x]   Photostat copy of this article is available in the F.R.I. library.

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64). Taylor, R.A.A., Jrl. Inst. Fuel, 14, p.p. 144 - 7 (1941).

65). Teichmann R.F.J., Jrl. Chem. Met. Min. Soc. of S. Afr., 45, p.p. 141 - 156 (1945).

66). Temple, K.L. Bituminous Coal Research, 9, No.4, p.5 (Oct. - Dec., 1949).

67). Townend, D.T.A., B.C.U.R.A. Monthly Bull., 11, No.10, 420 (1947).

68). Tronov, B.V. Chem. Abs., 37, 1029^4 (1943).

69). Turner, H.G. and Sinkinson, E., Chem. Abs. 21, 2975^2 (1927).

70). Vogel, J.C. and Quass, F.W., Jrl. Chem. Met. Min. Soc. of S. Afr., 37, p.p. 469 - 478 and p.p. 553 - 6, (1937). (See also F.R.I. Repts. Nos. 5 and 30 of 1936).

71). Von Walther, R. and Bielenberg, W., Chem. Abs., 19, 3007^9 (1925).

72). Von Walther, R. and Bielenberg, W., Braunkohle, 26, Jahrgang, Nr. 36, 825 - 829, Nr. 37, 853 - 856 (1927)ℵ

73). Walters, G.W., Coal Age, 53, No.11, 97 (1948).

74). Wilkens, E.T., Jrl. Inst. Fuel, 10, 213 - 220 (1936 - 7).

75). Winmill, T.F., Trans. Inst. Min. Engrs., Vols. 46 to 51 (1913 - 1916).

ℵ   Photostat copy of this article is available in the F.R.I. library.