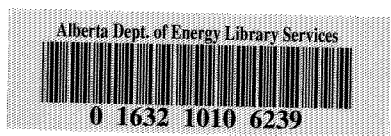


Information Series 66
STORAGE OF COAL SAMPLES

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Information Series 66 STORAGE OF COAL SAMPLES

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PREFACE

Exploration for coal is often conducted in remote areas from which coal samples can only be obtained at high cost. Since all lands disturbed by an exploration program must nowadays be reclaimed on completion of the program unless almost immediate development is contemplated, resampling may be difficult as well as expensive. Having regard for the requirements of a comprehensive coal testing program, it is therefore generally necessary to store coal samples for extended periods of time under conditions in which they suffer little or no quality deterioration.

This review outlines how coal samples up to, say, 5 tons may be conveniently stored, and summarizes what physical and chemical changes coal can undergo when improperly kept. Particular attention has been given to oxidation and loss of moisture during storage.

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1. MOISTURE CONTENT CHANGES AND SIZE DEGRADATION

In its natural state within a seam, coal is always more or less completely saturated with water; and mined coal, when exposed to air, will therefore tend to lose moisture until an equilibrium between it and the ambient atmosphere has been established. If the relative atmospheric humidity then increases, the coal will reabsorb moisture; and this cycle of desorption and reabsorption of moisture can be repeated many times.

During drying, desorption of moisture from the external surfaces of a coal lump will always be faster than desorption from its interior; and, since desorption is accompanied by some volume shrinkage, it will create internal stresses that cause the lump to disintegrate. Similar stresses are set up during reabsorption of moisture, which will also be faster at the surface than in the interior, and so lead to differential expansion. The disintegration is usually termed "decrepitation" or "slacking" and will, among other matters, substantially increase the total surface area which the coal presents to air.

As well as causing slacking, absorption of moisture by coal will generate considerable heat - the heat of wetting sometimes being as high as 22 calories/g or 40 btu/lb. Unless this heat is quickly dissipated, the temperature of the coal will accordingly rise and accelerate deterioration of the coal (see below).

2. OXIDATION

While losing or absorbing moisture when exposed to air, coal will also chemisorb oxygen and so become increasingly "oxidized." There is still some uncertainty about the chemical mechanisms which this process entails; but it is generally agreed that the first stages of oxidation create active peroxide complexes at the coal surface which subsequently decompose to yield water and oxides of carbon and to leave oxygen-bearing functional groups (such as hydroxyl, carboxyl, carbonyl, ethers, enols and anhydrides). Further oxidation appears to cause progressively more extensive molecular degradation, forming so-called humic acids which, in turn, degrade into simpler molecular species (and ultimately water soluble coal acids).

Because oxidation is a surface reaction, its rate under otherwise constant conditions will depend upon the rate at which oxygen can diffuse into a coal lump and this, in turn, is largely determined by the surface area of the coal to which oxygen can have access.

In this connection, it is important to note that rates of oxidation depend also on temperature - generally doubling with every 10°C rise in temperature - and that oxidation is itself an exothermic reaction which generates heat (14,100 btu/lb. of carbon oxidized to carbon dioxide). Accumulation of this heat of reaction and/or the heat of wetting (see above) in the coal mass will consequently lead to progressively faster oxidation and cause so-called autogenous heating which may, ultimately, end in "spontaneous" ignition of the coal.

3. CHEMICAL AND PHYSICAL CHANGES DUE TO MOISTURE CONTENT CHANGES AND OXIDATION

In some instances even more important than autogenous heating, however, is the fact that oxidation and changes in moisture content will affect the chemical and physical properties of the coal.

Quite generally, low-rank coals (such as lignites and subbituminous coals) will slack (or decrepitate) much more quickly and extensively than coals of higher rank. As already noted, such slacking results from changes in moisture content, and the tendency towards slacking is consequently closely related to the so-called bed moisture or capacity moisture content of the coal. Figure 1 illustrates this and shows the statistical correlation between the slacking index and the bed moisture content. One observes that the slacking index (1), defined as the proportion of -0.265 in. material formed when a +1.05 in. coal is alternately air-dried and rewetted by immersion in water for one or more cycles, is small and for all practical purposes insignificant among coals with less than ~10% bed moisture content (2), but that it increases very rapidly thereafter (Figure 1).

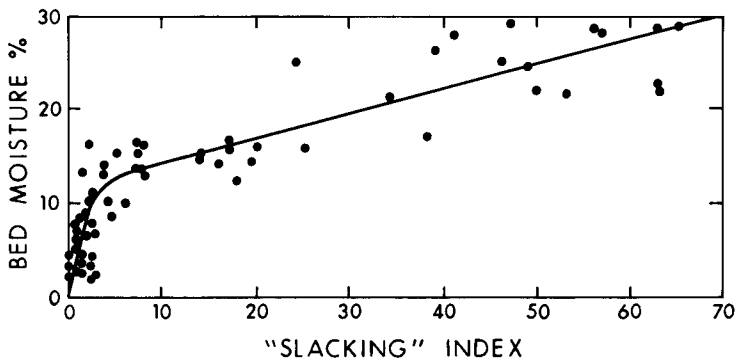


Figure 1 The variation of a slacking index with bed moisture contents (after Yancey, H.F., Ref. 2)

Where coals liable to extensive slacking are stockpiled, slacking will therefore produce large quantities of fines; and since this will usually lead to some size segregation in the stockpile, the effect of slacking will be to create increasingly more surface for oxidation as well as further changes in moisture content and further degradation. In practice, it is therefore important, when stockpiling coal, to minimize drying, wetting and oxidation of the coal; and this can be achieved by careful construction of the pile (see below). Smaller samples of coal can be prevented from slacking and heating due to wetting by storing them under conditions of constant humidity or, more simply, under water.

Like the slacking index, the reactivity towards oxygen - in effect, the rate at which coals will oxidize - decreases with increasing rank; and atmospheric oxidation thus becomes negligible among anthracites. It is, however, most important to recognize that even with low reactivity and consequently very small oxygen uptakes, certain coals can suffer catastrophic quality losses.

In general, the calorific value (or heat content) of a coal will decrease in direct proportion to the amount of oxygen taken up by it through oxidation. But this decrease will also depend on the rank of the coal. Low-rank coals with carbon contents between 70 and 80% (calculated on a dry, ash free basis) will thus, on average, lose ~190 btu/lb. (3) for each 1% increase in oxygen contents, and high-rank coals with carbon contents between 85 and 92% d.a.f. will show an average loss of ~240 btu/lb. (4) for each 1% increase in oxygen. High volatile bituminous coals stored in sealed cans tend, on average, to lose less than 0.3% of their initial calorific value during the first 2 months of storage, and 1-1.5% after 5 months (5).

Because aliphatic and alicyclic structures in coal, which give rise to "volatile matter" when the coal is heated, are particularly sensitive centers for attack by oxygen, oxidation will result in the formation of significant quantities of carbon monoxide and dioxide, and in distinctly lower carbon and hydrogen contents of the coal. In the case of coals with carbon contents in the range 70-84% d.a.f., each 1% increase in oxygen lowers carbon and hydrogen contents by an average ~0.82% and ~0.14% respectively (3). But whether an oxidized coal will, on analysis, show more or less total volatile matter than the corresponding fresh coal depends upon the amount of oxygen taken up by the coal as well as upon the forms which it assumes in the coal, and cannot, therefore, be predicted. In the case of high volatile bituminous coals stored in cans, volatile matter showed an average decrease of approximately 1.2% d.a.f. after 5 months of storage, and fixed carbon, calculated on a d.a.f. basis, increased by the same amount over this period (5).

The increased concentration of oxygen-bearing functional groups (-OH, -COOH, etc.) resulting from oxidation also tends to increase the

moisture-holding capacities of oxidized coals.

From a practical standpoint, it is particularly important to bear in mind that increases in oxygen contents of about 1% suffice to totally destroy the caking properties of prime metallurgical coals. The manner in which oxygen does so is still uncertain, and little is known about why oxidative destruction of caking properties should occur at widely different rates in otherwise closely similar coals. However, a good indication of the sensitivity of Western Canadian coking coals to oxidation, as reflected in changes of their caking properties, is afforded by Figure 2. In connection with this diagram, it should be observed that other methods of monitoring - for example, measurements of dilatation - are generally less sensitive than the Gieseler fluidity and more sensitive than the Free Swelling Index (FSI).

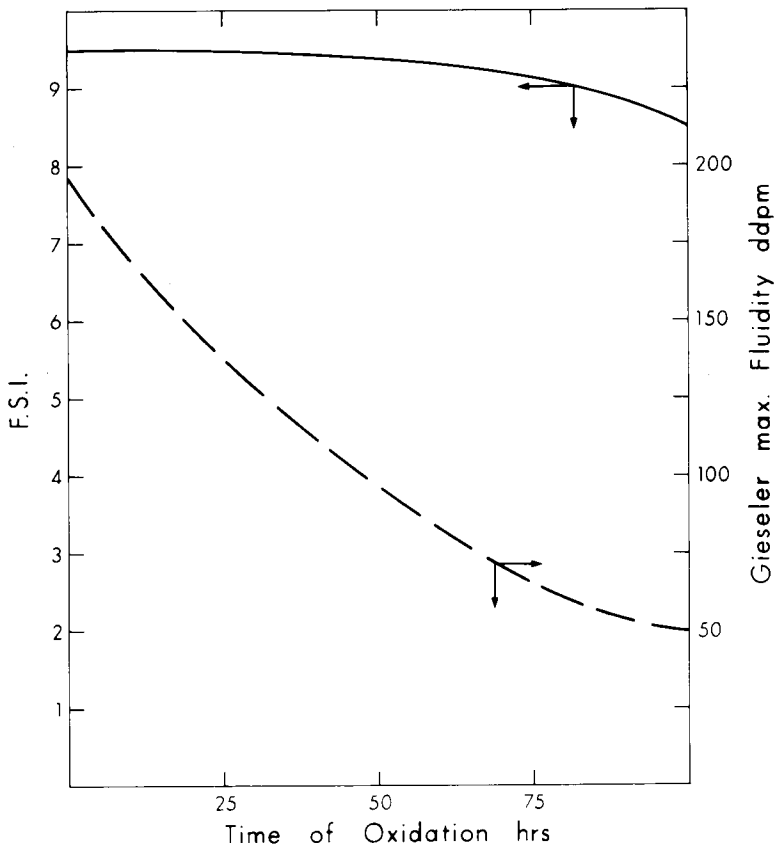


Figure 2 Change of FSI and Gieseler maximum fluidity with time of oxidation with air at 70°C

Results obtained in these laboratories suggest that Western Canadian prime coking coals, when sized to -60 mesh and stored in fairly thin layers under normal laboratory conditions, will show an average reduction of the FSI by 1 unit per 8 months of storage, and a loss of 10-20% in the Gieseler fluidity after 1 week.

The change in caking properties resulting from oxidation can also be monitored by coke oven performance and the change in coke quality. As a rule, cokes made from "weathered" or oxidized coal will be characterized by lower tumbler stability, lower coke size and a higher yield of coke breeze. Improvements in coke quality after mild oxidation are usually only observed with high fluidity coals which are not found in Western Canada.

To prevent oxidation of coal samples, it is suggested that the temperatures during storage be kept as low as possible (though above 32°F) and that the sample be stored in an oxygen-free or substantially oxygen-free atmosphere, or under water. Antioxidants (e.g. hydroquinones, amines, etc.), added to the coal, have little effect and, where of some benefit, will not afford protection against oxidation for more than a few months.

4. STORAGE METHODS

Both oxidation and slacking can be almost entirely eliminated by storing the coal under water. However, when stored in this manner in the open, water in the pores of the coal lump will freeze during winter and, through accompanying expansion, greatly weaken or disintegrate the coal. Some difficulty may later also be experienced in removing water from fine coal.

Coal stockpiles, in order to be "safe" - i.e. suffering minimal oxidation, slacking and size segregation - must be carefully constructed in accordance with procedures based on practical experience. Air circulation through a pile will generally increase the danger of autogenous heating through generation of local - typically meandering - hot spots. Fluctuations in ambient temperature and barometric pressure can cause significant expansion or contraction, often noticeable by continuous "breathing" at the surface of the pile. And the presence of foreign materials such as straw, wood, oily rags, will not only tend to increase air circulation but also create danger of ignition as a result of their own characteristic rates of oxidation.

In the case of relatively small storage piles, reasonable protection against deterioration can be gained from spraying the surface of the pile with petroleum products (or aqueous emulsion of hydrocarbons), fatty acids

or milk of lime. Alternatively, the pile may be covered with several inches of tightly packed coal fines or with wet straw, or drying out may be slowed by regular (and frequent) watering of the pile. However, these latter methods are not entirely satisfactory and can, indeed, in themselves create hazards. Furthermore, such measures affect the analytical parameters of the coal sample.

Storage in closed airtight containers will eliminate slacking and oxidation since the available supply of oxygen will be quickly used up and a constant humidity will be reached. Properties of coals stored in closed containers under an inert gas (such as nitrogen or carbon dioxide) will in fact not change over long periods of time. However, the disadvantages of storage in closed containers are the relatively high cost of containers and of their maintenance, and the fact that the method is generally restricted to small samples.

As an alternative, especially where larger quantities of coal are involved, recourse may be made to storage in bins or bunkers. For satisfactory storage, care must be taken to ensure that foreign materials (such as wood, oily rags, etc.) are excluded and that size segregation is minimal. Difficulties experienced with storage in bins or bunkers arise usually from air flow through improperly closing gates or lids or, in the case of bunkers, through slits or cracked walls. Parry (6) has described bins particularly suitable for storage of subbituminous coals and given details of their performance.

SUMMARY

Qualitative and quantitative aspects of changes of coal characteristics due to weathering have been outlined. In addition, some indication has been given of the circumstances under which weathering can occur and the measures to be taken for the prevention of deterioration of coal samples.

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