VARIATION IN THE LOWER ZONES
OF THE OXFORD CLAY

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ABSTRACT

By the employment of suitable sampling and analytical methods a marked degree of vertical variability is shown to exist in two exposures of Oxford Clay. Very little of this variation was apparent on visual examination of the strata. Some lateral variation exists between the two exposures, which are thirty miles apart, but this is on a relatively minor scale.

Trends for the vertical variation have been determined and these are in the main common to both areas. The lowest beds are high in organic content and low in acid-soluble lime, whilst higher up in the succession the amount of organic material diminishes and the percentage of lime increases. When examined in greater detail these trends are found to be more complex: they are the resultant of innumerable small scale sedimentary cycles. Thermal methods of analysis have shown that the organic material present in the lowest sixty feet or thereabouts of the Buckinghamshire succession, differs considerably in its ignition range from that found in the next twenty feet. In some respects the characteristics of the higher-level combustible resemble those of lignite. D.t.a. examination suggests that the clay mineral illite is dominant in all layers of the succession in Buckinghamshire. Some montmorillonite may be present in certain of the higher zones either as a simple impurity or in the form of an interlayering with the illite.

The effects of some aspects of these variations on the processes of Fletton brickmaking are discussed.

GEOLOGY

The Oxford Clay accounts for up to six hundred feet of strata forming the lower part of the Upper Jurassic in England. The outcrop, which varies in width from about twenty miles to as little as three miles, follows a diagonal course stretching from Scarborough in Yorkshire to Weymouth in Dorset. There is an overall formational dip of a few degrees to the South East. The lithology of the Oxford Clay includes dark-coloured bituminous clay shales in the lowest sixty or seventy feet, followed by more plastic, more homogeneous, lighter-coloured clays higher up. Concretionary limestone doggers, concentrated in definite bands, and impure stratified limestones, are of frequent occurrence throughout the succession. The Kellaways
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beds, a predominantly sandy series of strata, underlie the Oxford Clay and at the junction between the two there is a very well developed shell band, which for all practical purposes can be considered to be the base of the Oxford.

A substantial brickmaking industry has developed during the last seventy years in four areas along the middle of the outcrop. The particular type of brick made, called the Fletton, accounts for a third of the brick requirements of the United Kingdom. Ideally, only the bituminous shale is used in the production of these bricks, partly because it is physically suited to a dry grinding process and to the manufacture of brick shapes by a simple pressing technique, and partly because the proportion of combustible matter helps in the firing stage.

The exposures which have been examined are in two of the brick-making centres, one in Bedfordshire and one in Buckinghamshire, although by no means all the clay horizons investigated are, or would be, used in Fletton brick manufacture.

CLAY SAMPLING

Two methods of sampling an exposure are possible.

Spot sampling, which involves taking a relatively small amount of material from a definite height in the succession and assuming it to be more or less representative of the surrounding strata.

Bulk sampling, which means taking a continuous “scrape” of the strata between specified heights.

Whilst both sampling methods can be applied to the cores recovered from a drilling unit, it is obviously much easier to take spot samples when sampling an actual exposure, such as a quarry face.

A comparison was therefore made, in the first instance, of both methods of sampling applied to the same clay face. Calorific values obtained on the samples have been plotted in Figs. 1 and 2 against their original position in relation to the basal shell band. Fig. 1 shows the results from spot samples and Fig. 2 those from bulk samples. Although both Figs. show the same trend of variation up the clay deposit, considerably less scatter is exhibited by the results obtained on bulk samples, and this is significant. The broad spread given by the spot samples suggests the presence of a large degree of variability within the compass of comparatively small stratal thicknesses. Bulk sampling, on the other hand, only reflects the larger scale variation existing between the stratal thicknesses represented by the sampling length or “module.” Since this work was undertaken
Fig. 1—Relationship between calorific value and stratigraphical succession: spot samples in a Bedfordshire exposure.

Fig. 2—Relationship between calorific value and stratigraphical succession: bulk (5ft.) samples from same exposure as spot samples in Fig. 1.
with the primary object of determining the major trend lines of variation, the bulk sampling technique was used in the main. Initially the sampling module was ten feet, but later it was considered that this could usefully be shortened to five feet.

**D.T.A. Examination**

Figure 3 gives a series of thermal analysis curves obtained on samples from the Buckinghamshire succession. Prior to examination all the clays were treated in peroxide in order to eliminate exothermic peaks from the organic material present which would otherwise have obscured the clay reactions.

It appears that the main mineral present is of illite type. Calcium carbonate is the dominant impurity, and the percentage present increases markedly with sampling height above formation base. The small endothermic reactions at about 680°C which are given by some of the more calcareous samples suggest a possible degree of montmorillonite interlayering.
ACID-SOLUBLE LIME CONTENT

Figure 4 plots the percentage of acid-soluble lime determined on samples from both Bedfordshire and Buckinghamshire as a function of the sampling height in the two successions. (Lime is expressed as CaO although it is, of course, present as the carbonate). The pattern of variation is similar in the two areas, although the thicknesses of strata making up each part of the pattern show differences. The lowest beds are characterised by a low percentage of lime—about $2\frac{1}{2}\%$ CaO in the lowest 20 or 30 feet in Buckinghamshire and $3\frac{1}{2}\%$ CaO in the lowest 15 feet in Bedfordshire. In the overlying strata the percentage of lime increases until in both exposures a maximum is reached. Thereafter a fall in lime percentage ensues for a short distance, but this is soon replaced by a steady increase in the higher strata.

In the process of brickmaking, lime percentage is a major factor in determining colour, weight, porosity and size of the fired product.
Fig. 5—Firing shrinkage curves showing effect of acid soluble lime percentage. Curve 2 is from Kellaways sand, all others from Oxford clay. All heights given refer to distance from basal shell band.
It has a particularly important effect on firing shrinkage. This is demonstrated by the curves in Fig. 5 which trace firing shrinkage as a function of temperature for samples containing varying amounts of lime. Thus, clays containing a small amount of lime (say 0 to 5%—Fig. 5, curves 1 to 3) are characterised by a high firing shrinkage which begins at a temperature of about 900°C and proceeds at a high rate. The rate of shrinkage is accelerated as the temperature is increased. Because of the relatively high average rate, the time of "soaking" (i.e., the length of time during which the maximum firing temperature is maintained) is of considerable importance in determining total shrinkage. Bricks made from these clays have low porosity and a strong red coloration. Clays with only a moderate amount of lime (say 5% to 14%—curves 4 and 5) have a lower firing shrinkage which may start well below 900°C. The rate of shrinkage is also reduced, so that a long soaking period has less effect on the final level of shrinkage than it has in the case of low-lime clays. The increased weight loss, which accompanies the higher lime percentage due to loss of carbon dioxide, results in a lighter brick of higher porosity. The colour of the brick ranges from pink to yellowish-pink. Oxford Clay containing a high percentage of lime (say 14% to 18%—curves 6 and 7) produces bricks of high porosity and low density. Colour ranges from yellow to white.

**Calorific Value**

An important factor in the economics of the Fletton brick industry is the extent to which the bituminous material in the best shales aids the firing process. Quite small variations in the amount present in the clay can markedly affect kiln firing performance. Thus it is important to know the distribution of the fuel throughout the succession. The obvious approach is to examine the clays in a calorimeter. This method is very useful, but has certain limitations. Precautions must be taken to adapt the experimental method to the relatively low calorific values encountered (King, 1953) and even then a threshold is found at about 200 calories per gram: samples with calorific values less than this cannot be induced to fire at all in the apparatus.

Subject to these reservations, a useful picture can be built up of calorific value in relation to the stratigraphical succession. Fig. 6 shows how the levels of calorific value remain more or less stable in the lowest beds of the succession both in Bedfordshire and Buckinghamshire (though it will be noted that the actual levels in the two
areas differ by about 100 calories per gram). This stable level is succeeded by a gradual rise in the higher beds until a maximum is reached—some forty feet above the base of Buckinghamshire and thirty feet above in Bedfordshire. Higher up still the calorific value falls, eventually to a level below the calorimeter threshold. Accumulation of organic-rich sediment is thickest in Bedfordshire. Basically, the trends in the two areas are again similar, the differences being

![Diagram](image)

**Fig. 6**—Relationship between calorific value and stratigraphical succession: Bedfordshire and Buckinghamshire exposures compared. (Samples originating more than 75 feet above the base of the Bedfordshire exposure fail to ignite in the Mahler-Cook calorimeter).

only in the actual thicknesses of beds comprising each part of the sedimentation cycle and in the precise levels of calorific value attained.

Gross calorific value in itself does not, however, give a very satisfactory picture of the type of carbonaceous material present. A better approach is by the use of what may be termed "low sensitivity d.t.a." For most of the samples the exothermic reactions from the
bituminous material present are relatively large in proportion to the clay mineral "peaks." Hence, if the d.t.a. sensitivity be damped, these fuel exothermics can be studied in detail. Various methods can be used to reduce the sensitivity: in this particular case it was found that the best method was to dilute the sample with the reference material (calcined kaolinite) since this both lengthened thermocouple life and promoted more ready oxidation of the packed sample.

Special precautions have to be taken in the design of the apparatus to ensure an adequate air supply to the reaction block. Heady (1952), making no special provision for air supply, seems largely to have suppressed combustion reactions. Stott and Baker (1953) found it necessary to employ a positive piped air stream impinging on the sample. In the apparatus used in the present work (Fig. 7) the ceramic reaction crucible is encased in a well-ventilated canister machined out of Nimonic 75: heating is by radiation only—the canister being supported axially in a vertical tube furnace on two Nimonic rods. The ventilation holes are light-trapped to prevent direct radiation striking the inner crucible. With this arrangement convection provides a considerable air-flow which can be controlled by varying the closure of the furnace ends. Oxidation conditions have proved in practice to be reproducible satisfactorily.

A parallel method of investigating the fuel content is that of differential thermogravimetry. D.t.g. and d.t.a. curves, if obtained using similar linear rates of heating, can be compared, though when the

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**Fig. 7**—D.t.a. arrangement used to obtain low sensitivity d.t.a. curves. Spring tension on the control couple ensures location of the crucible.
respective sample sizes and sample packing differ, as in this case, (loose packed 2 g sample for d.t.g.; 0.2 g, d.t.a. sample) the comparison should not be pursued too far. Figure 8 gives two series of curves, all of which were obtained on samples from the deposit in Buckinghamshire. In comparing the curves, two points are immediately apparent:

1. The combustible material in the lowest 57 feet of the deposit produces one pattern of exothermic peaks, whilst that in the higher beds produces a different pattern.

2. There is a lag between the temperatures for corresponding peaks on the weight loss curves and the d.t.a. curves. The temperature of combustion is always higher than that of the weight loss but the gap between the two narrows as the reaction temperature increases. The carbonaceous matter present in the lower 57 feet of beds shows typically two main exothermic peaks. The first peak is the greater of
the two and lies between 300°C and 325°C. The second peak is at around 400°C. A third peak may be present in the 450° to 475°C region, but is not exhibited in all cases. The type of combustible in the beds above 57 feet is characterised in the d.t.a. curves by the same peak at around 325°C, followed by a higher-temperature second peak at 450°C, but in this case the second peak is bigger than the first. The 400°C peak of the samples from lower down in the succession is absent.

For comparison, an exothermic d.t.a. curve for lignite, which constitutes a very minor visible impurity in the Oxford Clay, is also given. This corresponds more closely to the second type of combustible, but shows in addition a further small peak at 530°C.

Neither of the samples from above 57 feet fired in the calorimeter. Thus it may be that the presence in a sample of a relatively large percentage of material which burns at around 325°C favours its ignition in the bomb calorimeter. Comparison of d.t.a. peak areas is an obvious way of estimating calorific values which lie below the ignition threshold of a conventional calorimeter.

Several factors would be expected to cause the lag which has been observed between corresponding peak temperatures in the d.t.g. and d.t.a. curves.

1. Sample packing, which, as was noted above, differs widely.
2. The fact that a fuel fraction may well distill off for quite a time before it builds up a high enough concentration for combustion to occur.
3. The flash point of a fraction may be higher than its distillation range.

The differences in grouping of exothermic reactions shown by the various clay layers may have considerable practical importance. The process of firing Fletton bricks in continuous kilns is unusual in that, ideally, no coal is added until the bricks are up at their full firing temperature. The combustible present in the raw material, in conjunction with preheating air from cooling bricks, should alone suffice to raise the temperature of the bricks. Coal should only be required to maintain the fire at peak temperature for a period of time long enough to develop adequate strength in the bricks (i.e., during the "soaking" period to which reference was made earlier). Both the amount and the type of combustible present in the raw material will to a large degree determine whether or not this desirable condition is attained in practice. Obviously the gross calorific value of the raw material must be more than sufficient to provide the heat required
in the rising temperature stage. In addition, the heat must be available in the appropriate temperature range. If all the combustible present were a high temperature form burning at, say 700°C, the bricks would not ignite at all, and the peculiar Fletton firing process could not then be applied: hence the vital importance of the low temperature fuel.

The clay faces dug for the manufacture of Fletton bricks do not always provide material with properties which meet these requirements. As a result, the firing process must sometimes be altered to suit the material—a most undesirable procedure as it almost always entails a reduction in the speed of firing and hence of the kiln output. On the other hand if a precise knowledge is available of the actual type of fuel deficiency in any one clay pit, or part of a pit, it is possible to devise ways of altering the characteristics of the raw material supply to conform to the firing process.

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REFERENCES

Heady, H. H. 1952. _Amer. Min._, 37, 804.
King, R. 1953. _Chem. and Ind._, 41, 1074.