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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 64-101

CENTRAL TECHNICAL
JAN 5 1965
C-10/IR64-101
GEOLOGICAL FILES

**EFFECT OF KILN ATMOSPHERE UPON THE
FIRED COLOUR OF HIGH-LIME BRICK**

by

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MINERAL PROCESSING DIVISION

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COPY NO. 6

NOVEMBER 26, 1964

IR 64-101

01-17989796

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Mines Branch Investigation Report IR 64-101

EFFECT OF KILN ATMOSPHERE UPON THE FIRED COLOUR
OF HIGH-LIME BRICK

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K. E. Bell*

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SUMMARY OF RESULTS

At the request of Domtar Construction Materials Ltd., controlled atmosphere firings of high-lime brick were conducted to determine the effect of kiln atmosphere upon fired colour. Kiln atmospheres tested ranged from moderately oxidizing (estimated 25% excess air), through neutral, to moderately reducing (estimated 70% of theoretical air),

Under oxidizing conditions, the fired bricks were pink or red at temperatures below vitrification. Fired in neutral or reducing atmospheres, the test specimens were buff-greyish at the lower temperature, clear buff at normal maturing temperatures, and greenish when vitrified. The vitrification temperature was progressively lower with increasing degree of reduction, indicating a requirement for co-regulation of temperature and atmosphere to obtain uniform, clear buff colours.

The composition of the kiln atmosphere was markedly affected by CO_2 liberated from the brick, rendering atmosphere control by conventional flue-gas analysis of doubtful value; probably the best method would be by $\% \text{O}_2$ and $\% \text{Combustibles}$ measurements on gas samples obtained from within the heart of the brick setting.

When wick tested, the "oxidized" specimens showed heavy, dark-red efflorescent stains, the "neutral" and "reduced" specimens showed small concentrations of dark-brown efflorescent stains, particularly at the corners and edges. In addition, the specimens showed slight to moderate white efflorescences. These were notably less on the "reduced" specimens.

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INTRODUCTION

A request was received from Mr. Y. R. Anderson, Chief Ceramic Engineer, Domtar Construction Materials Limited, Cooksville, Ontario, for an investigation of the effect of kiln atmosphere upon the fired colour of high-lime brick.

Samples of unfired brick, Panel No. 303 L-16 (16% limestone addition), were supplied from the company's plant at South Gloucester, Ontario. The samples were assigned Laboratory No. 1506.

PRELIMINARY TESTS

Preliminary studies were carried out to determine the nature of the gases evolved by the ware during firing and their effect upon kiln atmosphere, and to aid in establishing suitable firing schedules and finishing temperatures. The material was analysed by thermogravimetric (TGA) and differential thermal (DTA) methods. The TGA weight-loss curve and DTA thermogram are shown in Figure 1.

The sample showed a total loss at 1000°C (1832°F) of 11.6% of original weight. The predominant gaseous products liberated during heating can be deduced to include:

- (1) 212 to 285°F; water vapour from adsorbed water not removed during drying at 220°F; weight loss about 0.4%.
- (2) circa 650°F; CO₂ from the oxidation of carbonaceous material; weight loss about 0.1%.
- (3) 825 to 1330°F; evolution of water vapour from the structural breakdown of clay mineral material; loss of about 2.9% of original weight of sample.
- (4) 1350 to 1700°F; loss of CO₂ from calcite and dolomite components (includes some high-temperature water from micaceous clay minerals); about 7.9%.

The evolution of such large quantities of CO₂ from the ware made it impractical to regulate kiln atmospheres on the simple basis of theoretical CO₂ control. The preferable method of control would have been through measurement and regulation of the O₂ and combustibles, but no suitable equipment was available. Atmosphere control was in fact achieved through measurement and control of O₂ and CO, measured by standard Orsat apparatus. The

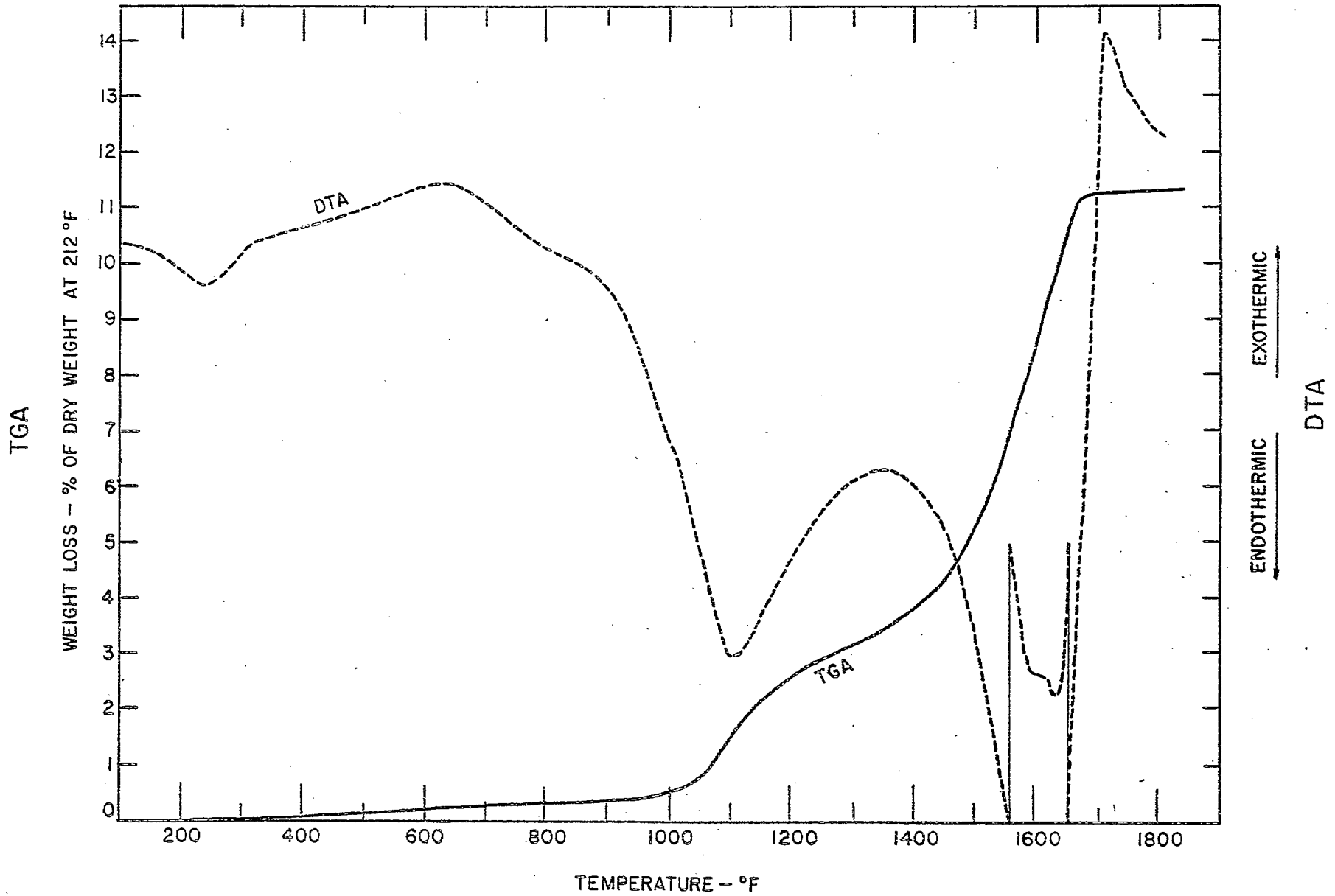


Figure 1. Thermogram and Weight-Loss Curve of High-Lime Material.

evolution of water vapour, of course, presented no measurement error, since any excess condensed upon cooling the gas sample to room temperature for analysis.

To determine suitable firing temperatures and schedules, four half-brick were fired in an electrically heated (Globar) furnace to cone 03 (1987°F) in seven hours. The average absorption (24-hour cold soak) was 9.9% of dry weight, which is considered suitable for this type of ware. During firing, the atmosphere surrounding the brick was sampled periodically and analysed for CO₂, O₂ and CO. Small quantities of CO₂ from the ware were first detected at about 1020°F, and a peak of about 12% CO₂ was reached about 1620°F; the O₂ varied inversely with the CO₂, and no CO was found.

PROCEDURE

Four half-brick were selected at random for each of three main firing tests, one moderately oxidizing, one neutral and the third moderately reducing. The oven-dried half-brick were edge-set in pairs, one pair with the textured faces together, the other with the smooth faces (backs) together. The two stacks were about one inch apart, allowing the thermocouple and the gas-sampling probe to be placed at the centre of the setting.

Gas analyses for CO₂, O₂ and CO were made at intervals of 15 to 20 minutes throughout each firing.

The tests were conducted in a small, gas-fired updraft pottery kiln, featuring a single burner of the inspirated-air type. Initial heating was rapid, under oxidizing conditions, reaching about 1100°F in 2 to 2.5 hours. The burner and drafts were then set to provide the desired atmospheric condition, and only minimal adjustments were needed for the duration of the burn. Total firing times were between 6.5 and 7.5 hours. Cones proved unreliable under reducing conditions and finishing was according to temperature: 1985°F oxidizing; 1975°F neutral; and 1965°F reducing. Cooling was at the natural rate of the kiln, overnight.

The exposed surfaces of all of the specimens bore what appeared to be a red stain, heaviest on the oxidized specimens, less pronounced on the reduced specimens. In commercial practice, this phenomenon is usually attributed to improper water-smoking. Thus, the results were set aside and the tests repeated with the initial heating period (to 1100°F) doubled to 4.5 to 5 hours, and with maximum secondary air supplied to sweep the water vapours from the kiln chamber. Each firing was then completed as before, with total times varying between 8.75 and 9.25 hours.

The firing schedules and attendant atmospheric gas analyses are illustrated in the curves of Figures 2, 3 and 4. In Figure 2, featuring a controlled oxidizing atmosphere, the probable levels of O_2 and CO_2 due to combustion (discounting the effect of CO_2 liberated by the ware) are indicated by the dotted lines at about 5 and 9.5%. This is considered to correspond to about 25% excess air under the mixing conditions prevailing at the burner. In Figure 3, neutral atmosphere, the CO_2 due only to combustion is indicated between 11 and 11.5%, which is probably as close to theoretical as possible under the circumstances. The O_2 and CO are essentially zero throughout the controlled-atmosphere stage. In Figure 4, reducing atmosphere, there is no O_2 , CO is 0.2 to 0.4% and the portion of CO_2 due to combustion is about 9.5%, which probably corresponds to about 70% of theoretical air at the burner.

Two specimens from each firing were used to determine absorption (24-hour cold soak), then sectioned longitudinally with a diamond saw. The remaining specimens were subjected to the standard 7-day wick-test for efflorescence.

RESULTS

The average absorption of the specimens fired in an oxidizing atmosphere was 10.4% of dry weight. They were light pink or pinkish buff on the protected surfaces, darker pink to light red on the exposed surfaces. The darkest colour appeared on the portions farthest from the flame, where circulation within the kiln chamber was probably least and the temperature a little lower.

The specimens fired in a neutral atmosphere had an average absorption of 10.8% of dry weight. The protected faces showed a pink "heart" and were buff around the edges; there was a grey-buff intermediate region. The exposed faces were buff, the colder header having a slightly brownish cast and the hotter end showing the first stages of the greenish colour normally associated with over-firing of high-lime materials.

The specimens fired in a reducing atmosphere also had an average absorption of 10.8% of dry weight. The protected faces were buff at the perimeter with a grey-buff central region. The exposed faces were identical with those of the specimens fired in a neutral atmosphere, except that the green coloration was darker, indicating a greater degree of vitrification.

There was no great difference in appearance between the smooth and wire-cut faces that were protected; where "hearts" appeared they were usually slightly more extensive on the smooth faces.

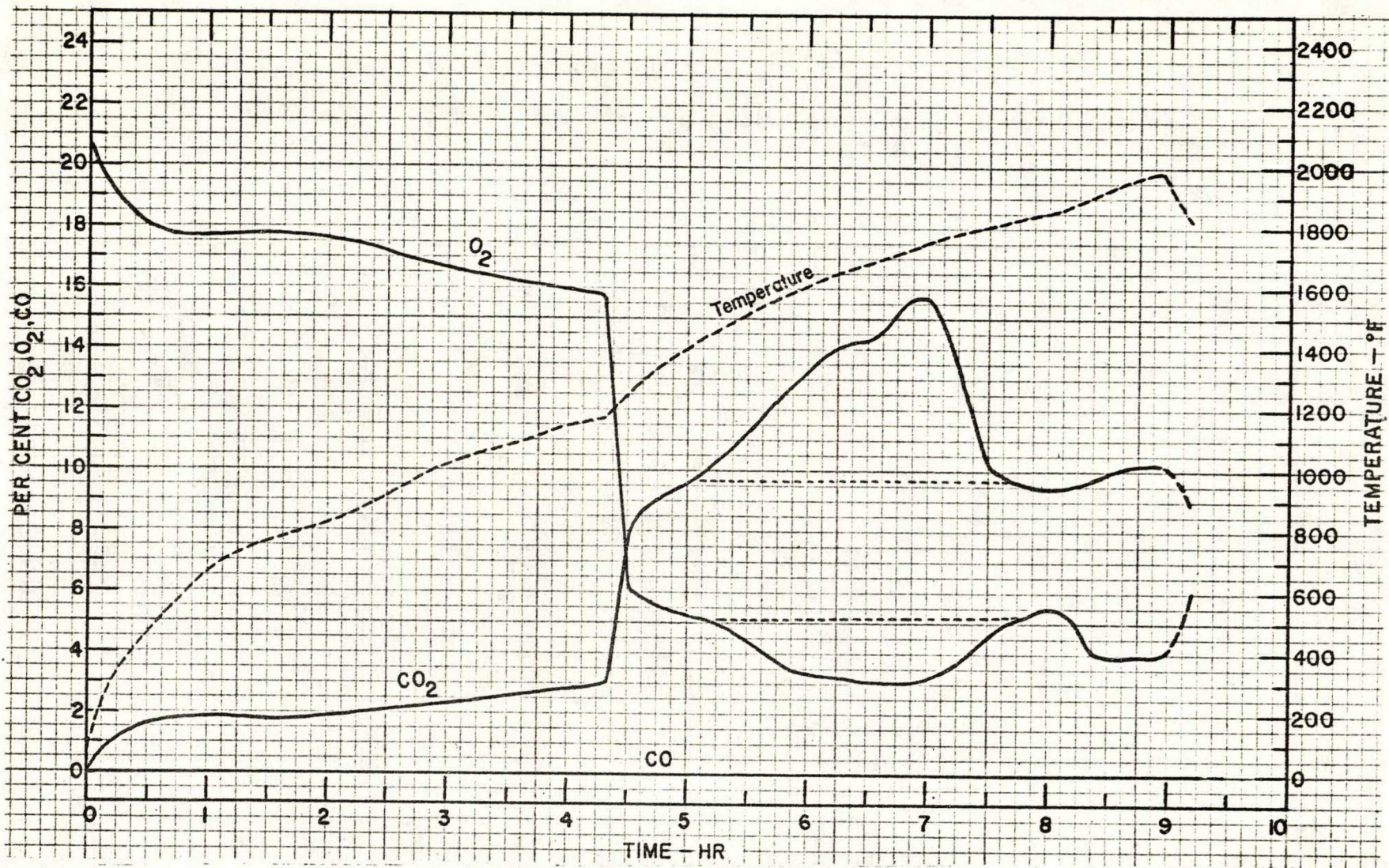


Figure 2. Firing Schedule and Composition of Kiln Atmosphere, Oxidizing Conditions.

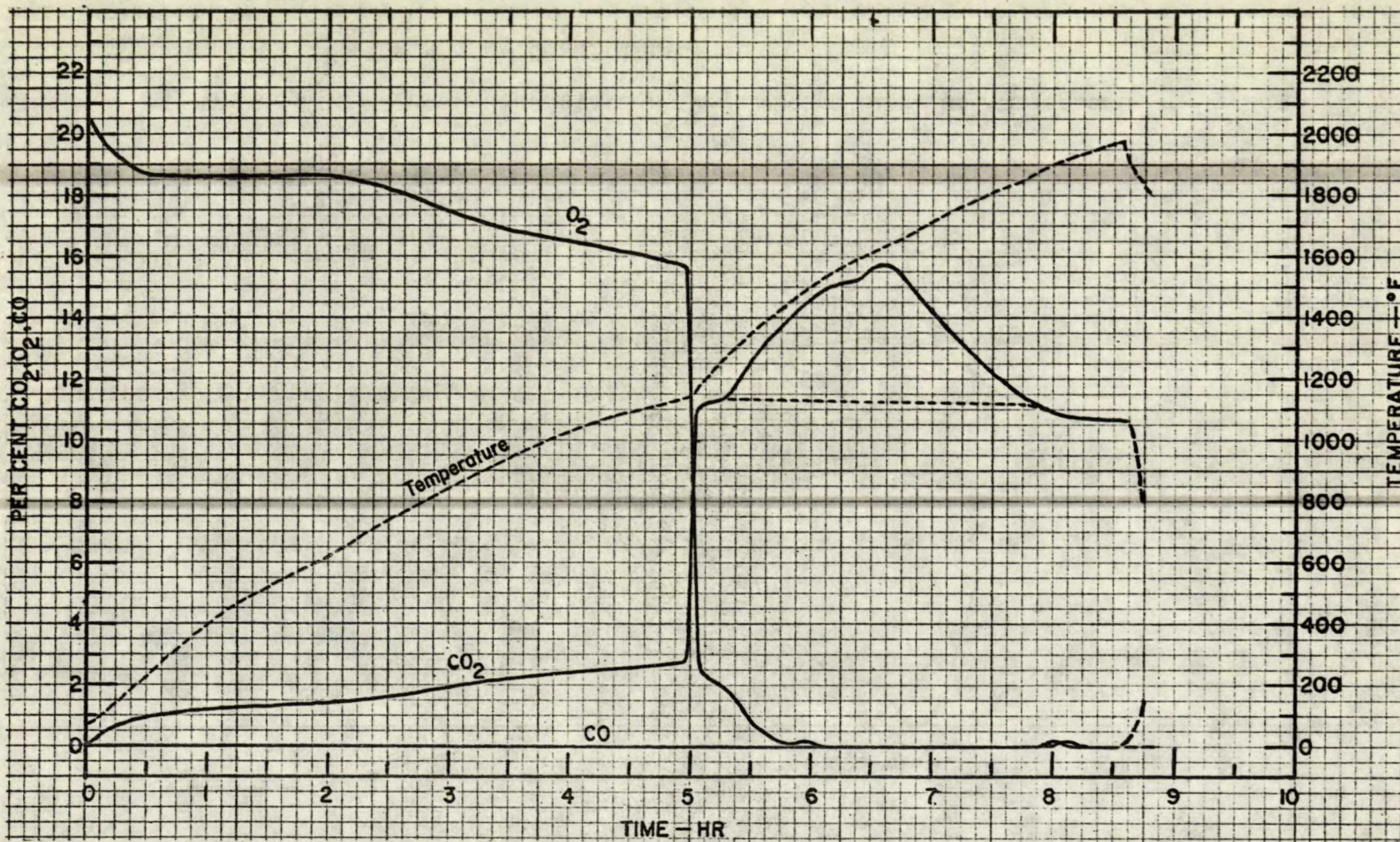


Figure 3. Firing Schedule and Composition of Kiln Atmosphere, Neutral Conditions.

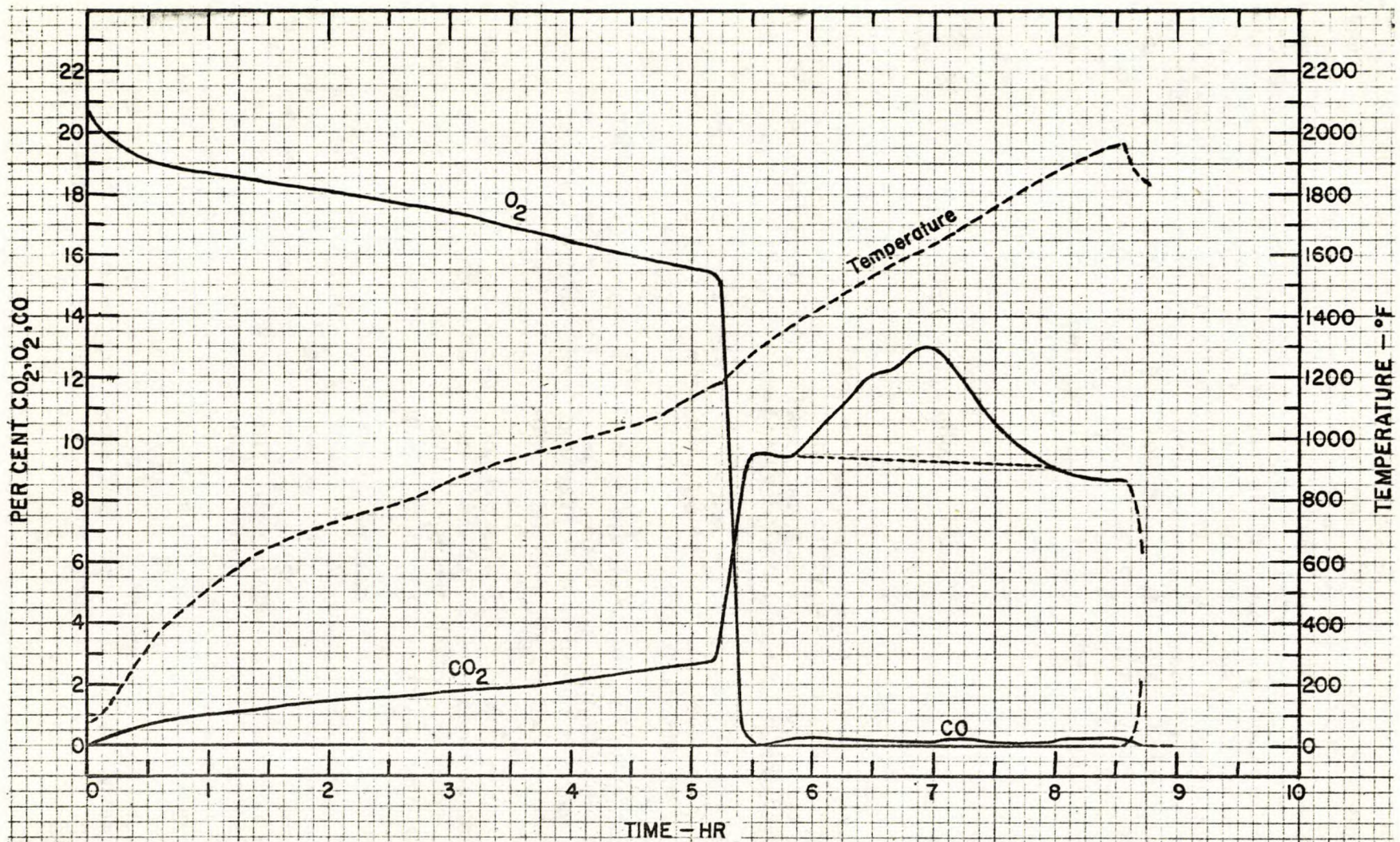


Figure 4. Firing Schedule and Composition of Kiln Atmosphere, Reducing Conditions.

The specimens subjected to the wick test all showed efflorescent tendencies. The efflorescences appeared as a dark stain, most heavily concentrated at the sharp edges and corners of the bricks, the whole being overlain with a whitish sheen. The greatest staining was on the bricks fired in the oxidizing atmosphere, the stain being dark red or dark brownish red over the whole surface of the exposed header. There was little difference in the degree of staining of the bricks fired in neutral and reducing atmospheres - the stain was dark brown, very thin on the flat surfaces and concentrated at the edges and corners. The whitish efflorescence, which appeared to be superimposed upon the dark stain, was heaviest on the specimens fired in the neutral atmosphere and lightest on the specimens fired under reducing conditions.

DISCUSSION

From the appearance of the bricks, particularly the "hearted" areas and cross-sections, and from the reactions known to occur in high-lime clays, it is possible to hypothesize upon the effects of kiln atmosphere on fired colour.

The full gamut of colours (at least five distinct colour zones) appears in the cross-sections of the bricks fired under neutral conditions.

Zone 1, the central core, consists of a light buff matrix with dark coarse particles that lend a greyish cast. Probably this area was never thoroughly oxidized, owing to its distance from the surface, or the iron was reduced during the carbon burn-out period and maintained in that condition by virtue of the evolution of steam and CO_2 , which blocked the pores and prevented the penetration of oxygen. (This zone is absent in the bricks fired under reducing conditions, indicating that they were more strongly oxidized during the heating-up stage).

The core is surrounded by an area of red or reddish-brown coarse particles imbedded in a pink matrix - Zone 2. There is a thin, light buff, halo-like transition stage between the two zones. This is probably a chromatic effect, resulting from the reduction in intensity of the colour of the coarse particles, particularly the smaller ones. Zone 2 shows no evidence of glass, so the reactions have probably proceeded in the solid state according to the manner proposed by West(1). The iron is unreacted and is in the ferric form. It is uniformly distributed, accounting for the even, pink colour of the matrix and it must be very finely divided, perhaps amorphous, and thus free to be transported to a drying surface where it is deposited as a red efflorescent stain.

These first two stages represent the complete colour transitions evident in the bricks fired under oxidizing conditions.

It is most probable that the "neutral" firing conditions were, in fact, mildly reducing. Although no CO was detected in the gas analyses, there was probably some uncombusted fuel present as a result of incomplete mixing at the burner. This is indicated by the greyish buff Zone 3, identical with the central core, and surrounding the pink Zone 2. As before, there is a thin buff transition zone between the pink and greyish areas. The latter, then, has probably been reduced, but the temperature was too low for the iron to react. The adjoining, and hotter, Zone 4, which includes most of the exposed surfaces, is light buff. (According to West, the iron has combined, in the solid state, to form calcium ferrite). The end of the brick nearest the furnace bag-wall shows traces of vitrification and the characteristic greenish cast (Zone 5). Here the iron compounds have possibly recombined from the melt to form pyroxene minerals, such as diopside, as reported by Klaarenbeek(2).

Apart from the absence of the reduced central core, the bricks fired in the reducing atmosphere show the same colour zones as those fired under "neutral" conditions, although the zones occur at correspondingly greater depths from the surfaces. Also, the hottest ends of the specimens show a greater development of greenish colour, although fired at a slightly lower temperature; that is, the glass-forming reactions take place at lower temperatures with increasingly reducing atmospheres.

The brown efflorescent stain that developed on the "neutral" and reduced specimens possibly consists of hydrous iron sulphates formed by reaction between sulphates in solution and reduced but uncombined iron, or from sulphuric acid attack upon the iron-bearing compounds or glasses. The writer is unable to recall an instance where such staining occurred on high-lime brick that showed indications of fusion on the surfaces, although the usual white efflorescences were frequently present. Possibly the iron compounds formed through fusion processes are the most stable.

CONCLUSIONS

The colours of high-lime buff brick are both temperature and atmosphere dependent:

(1) fired in an oxidizing atmosphere, below vitrification temperature, the brick are red (or pink) owing to free iron in the oxidized condition;

(2) fired under reducing conditions, below the solid-state reaction temperatures, the brick are grey to greyish-buff owing to the dark colours of the reduced iron;

(3) fired in a reducing atmosphere, above the solid state reaction temperature but below the vitrification temperature, the brick are buff; and

(4) fired in a reducing atmosphere, above the vitrification temperature, the brick are buff, turning green with increasing vitrification - the vitrification temperature itself is lowered with increasing degree of reduction.

A clear buff colour of the most permanent nature should be obtained in a mildly reducing atmosphere at a temperature where the brick surfaces are just at the point of incipient fusion. Since this temperature is atmosphere-dependent, both must be controlled.

Further, the suitable firing range would be very narrow, since the rate of fusion, once begun, is very rapid. Thus, the point of temperature measurement should be within the brick setting itself, and the most effective means would probably be by optical or radiation pyrometer, provided there is no significant luminosity from combustion.

Similarly, samples of atmosphere for analysis should be from within the setting, where the composition of the gases is affected by CO_2 liberated from the carbonate components of the raw material. Standard Orsat analysis fails to define the conditions sufficiently closely, and an analyzer of the % O_2 - % combustibles type would probably be more effective.

Finally, to obtain maximum uniformity over both faces and headers of the brick, it would appear desirable to flat-set them, or use coarse placing sand between the faces. This would apply particularly to smooth-faced or fine-textured types; heavily textured types might allow sufficient natural penetration of the kiln atmosphere between the faces.

REFERENCES

1. Richard West, "Coloration of Brick Manufactured from Limey Clays", J. Can. Cer. Soc., 31, 94-99 (1962).
2. F. W. Klaarenbeck, "Development of Yellow Colors in Calcareous Brick", Trans. Br. Cer. Soc., 60 (10) 738-72 (1961).