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13—The Use of Controlled Atmospheres

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ABSTRACT

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Water vapour-gas atmospheres are convenient to produce in a furnace and the oxidizing and reducing power of the atmosphere can be easily regulated. These atmospheres have been used for the firing of iron-containing ceramics such as porcelain and blue bricks. In particular the results of laboratory and works experiments on the bluing of bricks are referred to. Blue bricks can be cooled after firing by introducing small proportions of reducing material into the furnace as a dilute aqueous solution or emulsion. The heat used in evaporating the water can be used for the controlled fast cooling of the fired bricks.

L'emploi des atmosphères contrôlées

Des atmosphères de gaz-vapeur d'eau sont aisément produites dans un four et le pouvoir d'oxydation et de réduction de l'atmosphère peut facilement être réglé. De telles atmosphères ont été utilisées pour la cuisson de céramiques contenant du fer telles que la porcelaine et les briques bleues. Les résultats d'expériences faites au laboratoire et en usine sur des briques bleues sont en particulier indiqués. Les briques bleues peuvent être refroidies après cuisson par introduction de petites proportions de substance réductrice dans le four sous la forme de solution ou d'émulsion aqueuse diluée. La chaleur utilisée dans l'évaporation de l'eau peut être employée pour le refroidissement rapide contrôlé des briques cuites.

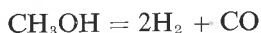
Anwendung kontrollierter Atmosphären

Wasserdampf-Atmosphären lassen sich in einem Ofen leicht einstellen, ebenso die Oxydations- oder Reduktionswirkung dieser Atmosphäre. Diese Atmosphären wurden verwendet, um eisenhaltige Keramik wie Porzellan und Klinkersteine zu brennen. Im besonderen werden die Untersuchungsergebnisse von Laboratorien und Betrieben über Klinkersteine (durch Blaudämpfen hergestellt) besprochen. Klinkerstein können nach dem Brand gekühlt werden, indem man kleine Mengen von reduzierenden Stoffen in den Ofen gibt in Form einer verdünnten wässrigen Lösung oder Emulsion. Die Wärme, die zum Verdampfen des Wassers benötigt wird, kann benutzt werden, um die schnelle Kühlung der blaugedämpften Steine zu kontrollieren.

1. INTRODUCTION

An earlier publication¹ has explained the advantages of using water-vapour/gas atmospheres in the reduction of copper-containing lead glazes. These atmospheres were obtained by pouring into

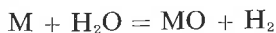
the furnace an aqueous solution of methanol at the temperature of reduction. At high temperatures the methanol is decomposed according to the equation:



As the composition of this atmosphere is determined by the water-gas reaction,



it is possible from the equilibrium constant of this reaction to calculate for various temperatures the concentration of methanol solution required in order to produce an atmosphere with a given $p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ ratio. This ratio determines whether an equilibrium of the type



is shifted to the right or to the left at high temperatures. The reaction of a water-vapour/gas atmosphere therefore depends largely on the value of the ratio just mentioned.

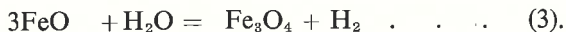
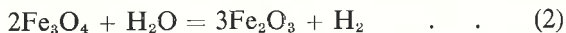
As atmospheres containing water vapour can be conveniently produced, and the oxidizing or reducing power can be regulated fairly easily by adjusting the value of the $p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ ratio, this method has been experimented with in the firing of iron-oxide-containing ceramics, such as porcelain² and bricks.

2. CALCULATIONS CONCERNING IRON-OXIDE-CONTAINING CERAMICS

Most deposits of clay and china-clay contain iron compounds in greater or smaller proportion, which may give the fired material a more or less distinct colouring. With porcelain artware and tableware a good white colour is essential and as the china clay contains iron, special measures must be adopted in order to achieve the desired result. Firing is so controlled that the iron oxides in the body are reduced to ferrosilicates, the colour of which is near-white, with only a faint tinge of blue. In this way the iron compounds are reduced to the first stage of oxidation, FeO.

Blue bricks are produced from iron-containing clay through a reducing firing, which converts the red Fe_2O_3 into the dark Fe_3O_4 or FeO.

When blue bricks are fired, it is presumably unnecessary to reduce the iron oxides to the extent of converting them into FeO; a reaction corresponding to complete conversion of the red Fe_2O_3 into the almost black Fe_3O_4 seems sufficient. The following reactions are therefore of interest to the ceramist.



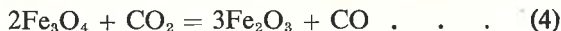
The equilibrium constant $K = p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ of these reactions can be calculated for various temperatures, for example from the standard free energy of formation of the substance of the reactions in question, thus:

$$-\Delta G^\circ = 4.57 \times T \times \log_{10} K.$$

From these data the values of $p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ can be calculated which at a given temperature favour the formation of a given oxidation stage of the iron, with particular reference to the production of blue bricks.

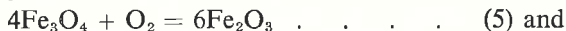
The bluing of bricks is normally done by introducing excess fuel into the furnace at the firing-temperature ($900^\circ - 1,000^\circ\text{C}$).³ The furnace is then closed, and not re-opened until the temperature has fallen to about 300°C ., for not until cooling has proceeded this far can the possibility of re-oxidation of the lower oxides of iron in the surface of the fired bricks be ruled out. Because of the specific conditions for cooling, blue bricks are usually fired in intermittent kilns.

Since the iron in the clay from which blue bricks are made is present mainly as Fe_2O_3 , and since the firing temperature is fairly low—below $1,000^\circ\text{C}$.—one can safely assume that reaction (2) is concerned, and so the reduction of ferric oxide with CO need not be considered:



The relationship between the equilibrium constants of the reactions (2) and (4) and the equilibrium constant of reaction (1) makes it necessary merely to control either the ratio $p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ or $p_{\text{CO}}/p_{\text{CO}}$ in order to judge whether Fe_2O_3 will be reduced or not.

The equilibrium constant of reaction (2) is found by calculation from the equations



By subtracting Equation (6) from Equation (5), and by dividing the result by 2, one gets Equation (2). And from the alteration in the standard free energy in reactions (5) and (6), ΔG° for reaction (2) can be calculated by subtraction and division by 2.

One finds that within the temperature range of 400° to $1,000^\circ\text{C}$. ΔG° of reaction (2) increases from about 16.5 kcal to about 27.0 kcal. The equilibrium constant K_2 is calculated on the basis of these figures from

$$-\Delta G^\circ = 4.57 \times T \times \log_{10} K_2.$$

Within this temperature range one gets

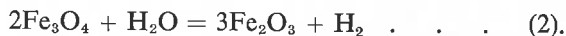
$$3 \times 10^{-6} < K_2 = p_{H_2}/p_{H_2O} < 3 \times 10^{-5},$$

which means that, with all values of p_{H_2}/p_{H_2O} above 3×10^{-5} , there is a tendency towards the complete conversion of Fe_2O_3 to Fe_3O_4 .

It should be noted that the activity of the iron oxides has been estimated as unity, since one assumes them to be present in the solid state.

Consequently it seems possible to fire blue bricks even with a very small proportion of hydrogen in the kiln atmosphere.

If the atmosphere contains mainly water vapour, together with a comparatively small proportion of H_2 , the partial pressure of hydrogen necessary for blue firing of bricks is obtained from $p_{H_2}/p_{H_2O} = K_2 \sim 3 \times 10^{-5}$, which corresponds to the equilibrium constant for the reaction



The magnitude of the partial pressure of hydrogen will be in the range $3 \times 10^{-5} \times 760 \sim 3 \times 10^{-2}$ mm Hg, equivalent to 0.003 vol. % H_2 .

So only a very slight excess of fuel is necessary for the bluing of bricks. For reasons of economy, amongst other things, this slight excess of fuel can be suitably obtained by introducing into the furnace a very dilute solution of alcohol or some other soluble organic substance, or a weak emulsion of oil, just before bluing begins, for the products of cracking will contain the necessary hydrogen. Whatever is used, the amount of solution or emulsion must contain enough organic substance for the desired degree of reduction to be attained.

3. LABORATORY EXPERIMENTS

Firing-experiments have been performed to illustrate how clay products can be reduced in this way. The kiln concerned was electric, the heating-elements being Kanthal wire situated at the sides, bottom and roof (Fig. 1). The furnace was also gas-tight, and had a useful capacity of about 15 litres.

The kiln door had three openings: through the top opening the thermocouple was inserted; the bottom opening was kept open, to act as an outlet from the interior of the furnace; through the middle opening was inserted a copper tube with an outside diameter of 8 mm. A length of about 500 mm remained outside the furnace.

The external end of the tube was bent upwards, and to it a funnel was fitted, above which was a funnel acting as a reservoir for the solution or emulsion that was to be introduced into the kiln. The entire length of the copper tube outside the furnace could be heated by means of a special Bunsen burner (see Fig. 1).

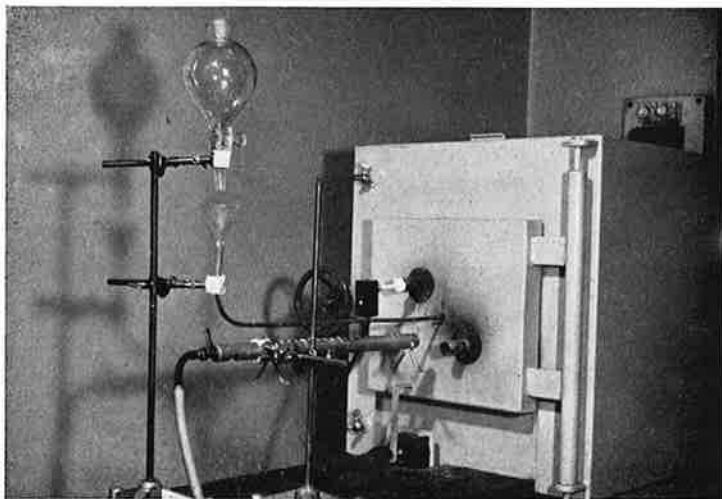


FIG. 1.—Furnace with funnel reservoir and copper tube

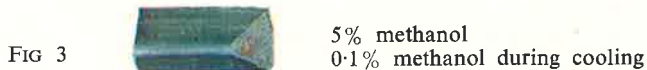
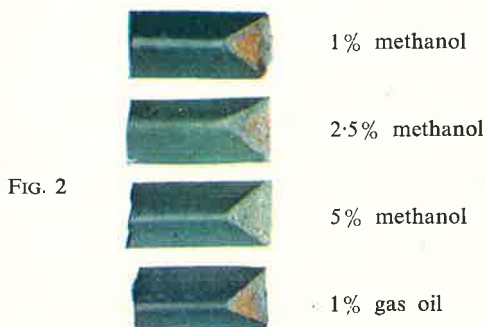
When the solution or emulsion was passing through the copper tube it was almost completely vaporized before reaching the interior of the kiln. Before each experiment, the copper tube had been blown through with vapour when red-hot.

The test pieces were cylinders of red-firing clay (50 mm long \times 30 mm diam). Twelve were placed for each firing experiment in various positions in the kiln room, and fitted in open chamotte capsules.

During the experiments the kiln, containing the test-pieces, was heated to a temperature of 980°C.; when this temperature had been reached, solution from the separate funnel was added at the rate of 2 l/h. The temperature had to be maintained for the first half-hour during which the solution was being added; after that, the electricity to the furnace was turned off, but solution from the separate funnel continued to be introduced into the furnace through the red-hot copper tube. When the temperature in the kiln had fallen to 300°C.—about 2 h after the current had been switched off—the kiln door was opened, and the test specimens were taken out for examination.

3.1 Reduction with Methanol or Oil

According to calculations, blue specimens should be obtained when solutions with a methanol content as low as 0.1% are used, but owing to the fairly high proportion of iron oxide in the clay a solution containing less than 1% methanol was not used. In fact aqueous solutions of 1, 2.5, and 5% methanol, respectively, were tested, and also an emulsion of 1% gas oil in water (weight %) (Fig. 2). It is obvious that, during cooling, p_{H_2}/p_{H_2O} is constantly above 3×10^{-5} , and so the value necessary for the bluing of the specimens is obtained.



During the experiment in which gas-oil emulsion was introduced into the furnace, samples were taken from the vapour-gas mixtures at 980°, 800° and 500° C. respectively, and analysed.⁴

Table 1 shows the results and the content of the products resulting from cracking. Apart from them, the atmosphere essentially contains water vapour only.

After firing, test-pieces were bluish grey. When sawed through, those pieces fired with a 5% solution of methanol were bluish grey all through, whereas those fired with a more dilute solution of methanol or a 1% oil emulsion had a greyish brown core, obviously less reduced than the surface (Fig. 2). This is probably because the amount of reducing agent in the kiln atmosphere had not been enough to completely convert the ferric oxide in the specimens.

Table 1
Water-vapour/Gas Atmosphere (Composition, vol. %)

	Temperature		
	980°C.	800°C.	500°C.
Carbon dioxide	0.6	0.3	0.3
Heavy hydrocarbons	0.0	0.1	0.02
Oxygen	0.0	0.0	0.0
Carbon monoxide	0.3	0.3	0.1
Hydrogen	0.5	0.4	0.03
Methane	0.3	0.2	0.06

Another experiment was then carried out with a 5% solution of methanol during the $\frac{1}{2}$ h when the temperature was kept at 980°, but with only a solution of 0.1% methanol during the entire cooling-period—a solution which, during cracking, could generally be expected to provide an atmosphere the composition of which is close to the equilibrium composition of reaction (2).

The core and the surface of the fired pieces were found to be an even, bluish grey (see Fig. 3).

3.2 Results

The results suggest that bricks can be blued as follows: when the maximum temperature is reached (about 1,000°C.) and the openings in the kiln have been closed, the fires are extinguished by being slowly sprinkled with water. The damper between the kiln to the chimney must be kept open. The water gas formed from the excess fuel ($C + H_2O \rightarrow CO + H_2$) acts as reducing agent on the setting. When, owing to cooling, water gas has ceased to form, the setting is sprinkled with water to which has been added a small amount of reducing agent (0.1–5% of the water) and the resulting atmosphere protects the blue bricks.

This procedure is not only economical in fuel, but also so shortens the time taken for the kiln to cool that the risk of the bricks re-oxidizing is eliminated, for the water vapour formed will provide positive pressure in the furnace and so keep the oxygen out of the furnace. Instead of the not unusual cooling-period of approximately 3 weeks, the rate of cooling may be expected to be as fast as the rate of heating, which means that the cooling-period is presumably reduced to 1/10 of the normal time.

3.3 Strength of Blue Bricks

The strength of the blue bricks was tested, to see whether the method of cooling had impaired this property. From a red brick

20 test-pieces ($10 \times 20 \times 70$ mm) bars were cut; 10 were fired blue, in the way described, with the furnace atmosphere formed from a 2% solution of methanol. The other 10 pieces were fired according to the same schedule, but with an air atmosphere. The average bending strength of the blued test pieces was $\bar{\rho} = 115$ kg/cm², while that of the other test bars was $\rho = 82$ kg/cm² (Table 2).

Table 2

	Test bar No.	Bending-strength (kg/cm ²)	
		ρ	$\bar{\rho}$
OXIDIZED BARS	1	84	82
	2	85	
	3	86	
	4	—	
	5	74	
	6	86	
	7	97	
	8	86	
	9	70	
	10	71	
BLUE FIRED BARS	1	113	115
	2	104	
	3	110	
	4	106	
	5	103	
	6	112	
	7	136	
	8	132	
	9	—	
	10	—	

4. WORKS EXPERIMENTS

In a further experiment, tiles were fired blue in an industrial kiln—a coal-fired down-draught having a capacity of about 35 m³ (kindly supplied by Frederiksholms Kalk- og Teglværker, Holte). The furnace held about 6,000 tiles of ordinary red-firing clay, and was heated to about 980°C. in about 36 h.

When the kiln temperature had been kept at 980°C. for about $\frac{1}{2}$ h, the flue and the firemouths were closed with sand seals. The damper between the flue and the chimney was closed, but an outlet to atmosphere below the furnace was kept open.

About 25 litres of water was then poured into each combustion chamber, and a vigorous steaming was observed at the outlet from the furnace. After a few minutes, a 5% solution of methanol was introduced at three places in the top of the kiln at about 5 l/min.

When the temperature had fallen to about 650°C., the rate was lowered to 1 l/min; when the temperature had dropped to 500°C., the rate was restored to 5 l/min. Altogether about 5 m³ of solution was added.

After about 36 h the kiln was opened, and the colour of the bricks was bluish grey. Moreover, both the bricks and the inside of the furnace were free from soot and graphite but the bricks that had been immediately under the point at which solution was injected were cracked, obviously due to uneven distribution of the solution within the furnace. This feature can no doubt be remedied.

5. CONCLUSIONS

As with the reduction of Cu-containing glazes, it is economical to be able to reduce with very dilute solutions of alcohol or with oil emulsion, which not only conserves that part of the reducing agent uniting by combustion with the oxygen in the setting just before the beginning of reduction, but also that part used owing to the entrance of air through leaks is saved.

This method also enables the reducing atmosphere to be easily controlled and a given ratio of the partial pressure of hydrogen to that of water vapour can be maintained during firing.

Finally the heat used to evaporate the aqueous phase can also be used to accelerate the cooling of the fired product.

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