# Oxygen: An Important Chemical for the Clay Industry

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Clay products are fired to convert a loosely compacted blend of materials to a strong, hard, and stable product. Raw materials undergo both physical and chemical changes during firing, and the final properties that they exhibit (strength, absorption, stability against moisture, thermal expansion, thermal conductivity, and hardness, for example) are all determined by the kind and amount of various phases that are produced in the firing process. However, it is the composition of minerals in the raw materials that determines the path of these reactions.

### Firing: A Four-Stage Process

During a typical firing in a periodic or tunnel kiln (Fig. 1), clay products go through basically four stages: drying, decomposition, oxidation, and full firing. Regardless of whether or not clay products have been thoroughly dried before entering the kiln, they always evolve a large amount of water before they become red hot. The mechanism of this water evolution varies with clay content, and the elimination of water is a most delicate operation. If it occurs too rapidly, the clay product is seriously weakened by the excessive pressure of steam that is produced within the pores of the product.

In the first stage of firing, which occurs at ~250°F (~120°C), the water in the clay (moisture or added water) is removed by heating the clay products very slowly and carefully. Chemically combined water is not removed until the clays are decomposed at a temperature ≥1100°F (~590°C). Unless drying is complete, there is a distinct possibility of cracking. If hot gases contact damp clay products, rapid shrinking occurs and the product surface dries out while moisture remains inside. As the temperature of the product increases, internal water vapor expands and creates a series of irregular cracks through the hard casing.

During the decomposition stage, clay is decomposed, and chemically combined water is released. This stage normally begins at 212°F (100°C) and continues until the product is ~1100°F (~590°C). By the time the product has reached the higher temperature, a large portion of the organic matter and other combustibles have begun to decompose.

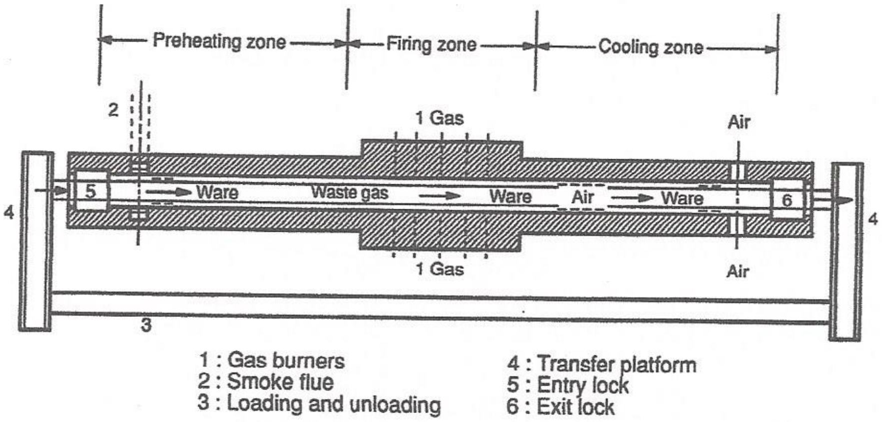

Fig. 1. Operating principle of a gas-fired tunnel kiln.

Oxidation is one of the most important stages of firing. In this stage, the combustible matter is eliminated, and the oxidation of iron and other compounds, which is needed to produce good color, is complete. Here, heating must be controlled to avoid overheating or black coring, and color is often seriously affected if this stage of firing is unduly hurried and if certain parameters are not properly adjusted. The black cores in structural clay products are caused by insufficient oxidation of carbonaceous matter. However, the black color of the cores is not due as much to carbon as it is to the reduced state of iron. The best oxidation range for fired clay is between 1700° and 1900°F (~930° and 1040°C). It is a crucial stage for product quality, and it gives operators the flexibility to increase production and/or vary raw materials blending.

During the full-fire stage, clay products are fully heated to cause sufficient vitrification to form a solid and durable product. The speed at which the temperature rises during this period may be much greater than during other stages, provided the product is not overheated.

### Role of Oxygen with Clay Products

A kiln is not simply a heat-generating machine; it can also be considered a chemical and physical reaction vessel. But heat is not all that is required from a tunnel or periodic kiln to change raw materials into useful ceramic products. A major element of the environment—the gaseous atmosphere—directs these physical and chemical processes.

The common gases in the kiln are oxygen, nitrogen, carbon dioxide, carbon monoxide, steam, sulfur dioxide, and sulfur trioxide. For the most part, the nature of the raw materials determines the kind and quantity of these gases. Oxygen and nitrogen are derived from the air. The combustion of such hydrocarbon fuels as coal, oil, propane, producer gas, and natural gas produces carbon dioxide and steam under complete combustion and carbon monoxide and hydrogen if combustion is not complete. Sulfur compounds evolve from impure fuels. The chemical reactions in clay products are controlled by controlling the proportion of oxygen and carbon monoxide present to react with the iron (Fe), manganese (Mn), vanadium (V), and carbon (C) in clay products.

Carbon is a naturally occurring element in some ceramic products. Occasionally, it is also added as an organic binder, internal lubricant, and porosity control filler; in any case, it needs to be burned out at the proper stage in the firing process. The solid, elemental carbon is changed by oxidation into a gas that can escape through the open pores in the body.

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*Member, American Ceramic Society.

The valence states of iron control the color of all clay products, from whiteware bodies to red building bricks; the valence nature of manganese and vanadium determines the reactivity of these elements to form soluble or insoluble compounds. In an oxidation process, an electron is lost, and, as shown below, ferrous ion becomes ferric.

$$\underset{\text{Ferrous ion}}{Fe^0} \xrightarrow[2e^-]{} Fe^{2+} \xrightarrow[e^-]{} \underset{\text{Ferric ion}}{Fe^{3+}}$$

When these electrons are gained by an element, the process is called reduction.

$$2e^- + O^0 \longrightarrow O^{2-}$$

Thus, oxygen is reduced in this chemical process. Stated differently, oxidation is accomplished by a reduction process. Here, there is no dependence of these chemical processes on oxygen, but oxygen is the main oxidizing agent.

When oxygen is added through combustion air, oxygen is used in burning a hydrocarbon fuel, as follows:

$$\underset{\text{Natural gas}}{CH_4} + \underset{\text{Oxygen}}{2O_2} \longrightarrow \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{2H_2O}$$

Clearly, oxygen in the kiln atmosphere during the firing of clay products comes either from air in excess of that required for the combustion of the fuel or from injecting pure oxygen into the kiln atmosphere. This excess oxygen is important for the oxidation processes that occur in clay products. Some of these reactions follow.

$$2C + O_2 \longrightarrow 2CO$$
$$2CO + O_2 \longrightarrow 2CO_2$$
$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$
$$V_2O_3 + O_2 \longrightarrow V_2O_5$$
$$4MnO + O_2 \longrightarrow 2Mn_2O_3$$
$$2FeS + O_2 \longrightarrow 2FeO + 2SO_2$$
$$2SO_2 + O_2 \longrightarrow 2SO_3$$

Excess air or excess oxygen keeps iron oxide (FeO) in the ferric state ($Fe_2O_3$) during the firing process. This is red iron oxide, and its shade of red varies from orange to purple, depending on the temperature to which it is exposed. This form of iron oxide gives a cream white color to whitewares, a buff color to fired clay bodies, and a red color to building bricks. The amount of ferric oxide that can be dissolved in mullite increases with temperature. Whenever iron occurs in excess of these amounts, the body will be pink to red under oxidizing conditions.

### Controlling Product Quality

Oxygen is needed to burn carbon out of the ceramic products and completely oxidize the products of combustion to the relatively inert gas carbon dioxide. When firing clay products containing carbon, the carbon must be removed while the body is still porous. This means that an oxidizing atmosphere (excess $O_2$) must be maintained in the preheating stage (1200° to 1800°F (~650° to 980°C)). Manganese is sometimes added to ceramic bodies, and, under oxidizing conditions, its trivalent form is stable. Where manganese staining becomes a problem, it is best to keep manganese in an oxidized form.

Oxidizing conditions are essential to remove sulfur, which occurs in some ceramic products in the form of iron sulfides (pyrites and pyrrhotites). Since there is a strong tendency for sulfur trioxide ($SO_3$) molecules to be absorbed into the internal surface of silicate bodies, it is desirable to sweep sulfurous gases out of the kiln at the time of their evolution. Vanadium trioxide readily oxidizes in the presence of oxygen to vanadium pentoxide, which is an inert chemical in the presence of silica and alumina.

When there is an insufficient amount of oxygen, a hydrocarbon fuel will produce carbon monoxide. As shown below, this gas acts as a reducing agent for iron, vanadium, and manganese. This is undesirable because iron in the ferrous state (FeO) is black and can act as a flux in aluminosilicate products. Also, in whiteware, a blue-white color is obtained in carbon monoxide atmospheres. Finally, carbon monoxide in the kiln atmosphere reduces vanadium to a more reactive form, and it is undesirable to maintain manganese oxide in a ceramic body because of its greater solubility in acidic solution.

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$
$$V_2O_5 + 2CO \longrightarrow V_2O_3 + 2CO_2$$
$$Mn_2O_3 + CO \longrightarrow 2MnO + CO_2$$

### Increasing the Oxidation Rate

Chemical and physical reactions in the kiln depend on oxygen concentration and reaction temperature. Thus, when either kiln temperature or oxygen concentration is increased, the oxidation rate increases. Steam and carbon dioxide are the products of combustion of hydrocarbon fuels, and ceramic raw materials evolve steam and carbon dioxide in great quantities. The effect of this is to dilute the oxygen content in the environment around the ware. Since it is desirable to maintain the oxidizing atmosphere, it is necessary to either increase the air flow to sweep steam and carbon dioxide away from the bodies or to introduce pure oxygen.

Any attempts to increase production rates will require more firing and more oxygen input. In addition, large quantities of air are needed to maintain the proper concentration of oxygen in the atmosphere when more fuel is burned. Every five volumes of air has one volume of oxygen and four volumes of the inert gas nitrogen. Thus, for one volume of oxygen, five volumes of air must be introduced.

This large quantity of air has to be heated as it travels through the different zones of a kiln. The only way this air transfers heat to the clay product is through convection and conduction. Large turbulence is required to optimize the use of air, and, even then, additional means are required to capture the heat leaving the kiln through the exhaust. In the past, many users have employed this approach and incurred large capital costs to capture costs to capture heat leaving the kiln. Thus, adding pure oxygen accomplishes two key objectives that are important to the user: combustion efficiency is improved, and the rate of oxidation is increased.

### Improving Combustion Efficiency

The difference between injecting pure oxygen and using air to supply oxygen is the absence of nitrogen. For the stoichiometric combustion of 1 ft³ (~0.03 m³) of natural gas and 10 ft³ (~0.3 m³) of air, the combustion equation is

$$CH_4 + 8N_2 + 2O_2 \longrightarrow 8N_2 + CO_2 + 2H_2O$$

One cubic foot (~0.03 m³) of natural gas burns to release about 1000 BTU of energy. This energy is used to heat 11 volumes of reaction products, and the result is a flame with a temperature of 3400°F (~1870°C). If, instead of air, pure oxygen is used, the nitrogen is eliminated. The same amount of energy is released, but now the volume of combustion products is smaller and the result is a smaller, hotter, more intense flame with a temperature of ~5000°F (2760°C). Thus, any attempt to reduce the nitrogen content in a combustion product will have the following two results:

(a) The flame temperature will increase for the same amount of energy released. There is more available heat; as the heat transfers from the radiating flame to the furnace, it varies with the fourth power of temperature. Turbulence in the kiln atmosphere is not needed to transfer heat to the clay body.

(b) The volume of combustion products will decrease, leading to less dilution of oxygen in the kiln atmosphere, a higher oxygen concentration in the kiln, and faster oxidation reactions. This provides flexibility for increased production (see Fig. 2).

Burner efficiency also increases with a decrease in nitrogen. Replacing air completely with oxygen is not recommended because it requires new burners. Also, the refractory lining of the kilns has to be checked for higher temperature compatibility. However, the combustion air line can be enriched with oxygen to increase the oxygen concentration from 21% to 24% in air. This increases the amount of energy available for the same amount of fuel and enables the user to cut back on the input of combustion air. It also results in less dilution of the kiln atmosphere.

### Injection Techniques for Improving Productivity

Lancing oxygen into the area where oxidation reactions take place allows the user to significantly cut back on air and enhances the oxidation reaction rate. The

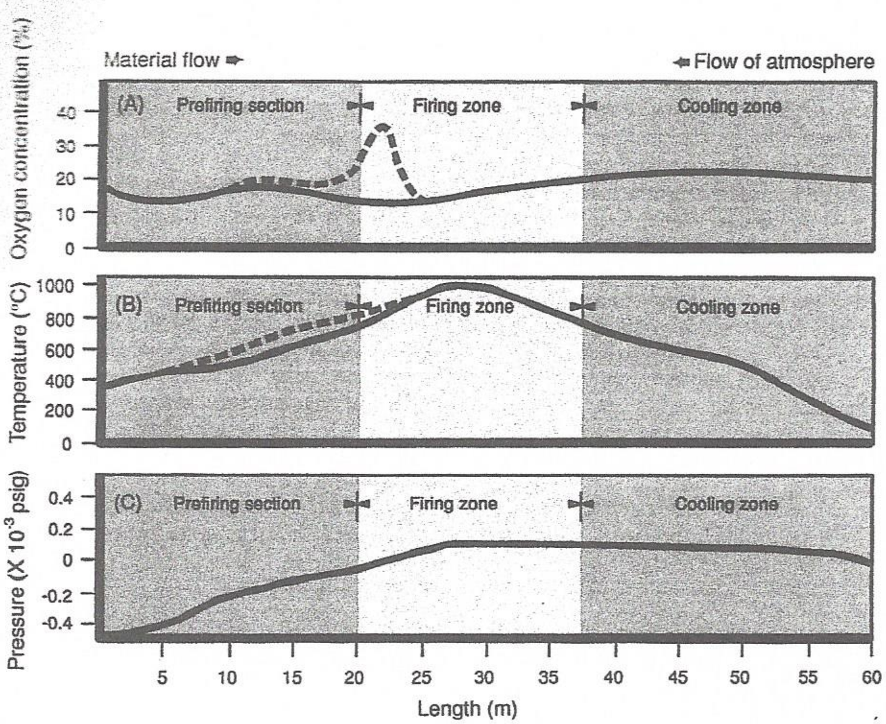

Fig. 2. Variations in (A) oxygen concentration, (B) temperature, and (C) pressure in a tunnel kiln. The dotted lines indicate profiles with oxygen injection, and the solid lines indicate normal kiln profiles (without oxygen injection).

overall effect of oxygen lancing is the flexibility to increase production because less retention time is necessary to complete oxidation reactions.

Because direct-fired tunnel kilns cannot be seen as closed furnaces, a special method for oxygen has to be used to avoid oxygen losses. To save fuel, the oxygen content in the combustion air stream is increased 3% to 4% higher than that of air (21%), and the burners are adjusted to an appropriate air-to-gas ratio to maintain the process temperature.

When the objective is to save fuel and increase production, oxygen is also injected through special lances. Depending on the tunnel kiln design, oxygen lances with properly sized orifices are installed. The ideal temperature zone for the higher oxygen concentration must be determined by successively moving lances toward the higher temperature zones of the tunnel kiln. All lances must be connected to a manifold to monitor the total flow of oxygen.

## Actual Industry Situations

As shown in Table I, adding oxygen to ceramic kilns can produce significant improvements in product quality, fuel consumption, and production efficiencies. Clay manufacturers increase production by (1) reducing kiln-related rejects and increasing product recovery rates, (2) pushing more product through the kiln at the same or a lower product recovery rate, or (3) both. When more product is pushed through the kiln, more heat is required to maintain the desired kiln temperature profile, and more oxygen is required for timely completion of the oxidation of clay wares before the vitrification stage begins. When burners have the capacity to add more heat, oxygen lancing is recommended. When burners are not capable of providing the desired amount of heat, oxygen enrichment, coupled with oxygen lancing, produces successful results.

Customers A, B, D, H, I, J, K, and L (structural brick, pavers, wall tile, floor tile, dinnerware, whiteware, frit, and ceramic color manufacturers) in Table I had a keen interest in production increases and/or quality improvements. Even with the additional blower capacity to increase the excess air rate through the burner, quality was a serious problem at higher production rates. As demonstrated earlier, increasing the excess air rate through the burner required heating additional nitrogen, which, in turn, required more fuel. The burner efficiency was adversely affected, and it was difficult to attain the desired temperature.

In addition, more air in the preheat section of the kiln meant reduced oxygen concentrations. This was due to the nitrogen dilution effect and made it even harder to oxidize clay products. Furthermore, the additional air also increased the dependence on convective- and conductive-type heat transfer to raise the product temperature, requiring a high turbulence in the kiln environment. Consequently, much wasted energy was delivered to the exhaust. When oxygen lances were installed in the preheat zones and preheat and full-fire burners were adjusted to stoichiometric air/gas settings, the total nitrogen into the kiln was reduced, considerably lessening the dilution effect. Also, there was higher elemental oxygen concentration, faster diffusion of oxygen into clay bodies, and increased oxidation rates. Oxidation reactions were also completed in a shorter time.

In addition, complete oxidation was

Table I. Effects of Adding Industrial Oxygen on Product Quality, Fuel Consumption, and Production Efficiency of Ceramic Kilns

| | Without oxygen | | | | With oxygen | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Manufacturer | Cars/d | lb/d | ×10$^6$ BTU/d | BTU/lb | Oxygen amount (scf/lb)* | Cars/d | lb/d | MM BTU/d | BTU/lb |
| | | | | Brick manufacturers | | | | | |
| A | 14.4 | 52 800 | 150 | 2841 | 0.27 | 18 | 66 000 | 110 | 1667 |
| B | 20 | 239 040 | 420 | 1757 | 0.27 | 20 | 239 040 | 380 | 1590 |
| C | 16 | 97 920 | 320 | 3268 | 0.41 | 16 | 97 920 | 270 | 2757 |
| E | 2.7 | 172 800 | 260 | 1505 | 0.16 | 2.7 | 172 800 | 220 | 1273 |
| F | 19 | 374 400 | 510 | 1362 | 0.13 | 20 | 394 105 | 450 | 1142 |
| G | 21 | 420 000 | 302 | 719 | 0.06 | 21 | 420 000 | 268 | 638 |
| | | | | Paver, tile, dinnerware, and color manufacturers | | | | | |
| D | 36 | 40 000 | 114 | 2850 | 0.64 | 42 | 46 667 | 99 | 2121 |
| H | 6 | 150 000 | 305 | 2033 | 0.40 | 9 | 225 000 | 265 | 1178 |
| I | 14 | 58 000 | 68 | 1172 | 0.23 | 15 | 60 970 | 57 | 935 |
| J | 12 | 48 031 | 125 | 2602 | 1.08 | 13 | 52 033 | 125 | 2402 |
| K | 8 | 3 744 | 40 | 10684 | 2.79 | 12 | 5 616 | 40 | 7127 |
| L | 22.15 | 4 657 | | | 2.58 | 26.2 | 5 502 | | |

*Standard cubic feet per pound (70°F, 1 atm).

feasible prior to vitrification of clay, even in hard-to-reach areas. There was no need to depend on turbulence to transfer heat because the burners effectively radiated heat. In the cases of customers H and K, production rates increased as much as 50% without sacrificing product quality and strength. In other cases, the quality of the product was improved from good to excellent.

In most cases, kiln exhaust rates were reduced more than 20%. Since radiative heat transfer greatly improved the effectiveness of the burners, there was no need to depend on air to preheat the incoming product. The reduced exhaust was at a higher temperature, which, in turn, caused higher heat transfer to the incoming cold product. In addition, even at higher production rates, the temperature profile for the kiln was close to the desired profile.

In the case of customer I, a dinnerware and chinaware manufacturer, the burners had to be rich in fuel to maintain the desired zone temperature. Since kiln atmosphere greatly affects the quality of ware, the glaze was becoming dull; some of the colors were faint, and the redip rates had been increased. When the oxygen lances were installed in the preheat zone and the oxygen-enrichment system was implemented in full-fire zones, the burner efficiency was greatly improved. The kiln atmosphere became oxidizing, and there was hardly any turbulence in the kiln. Zone instrumentation controllers, even at former maximum production rates, were also well within controllable range. Because of a reduction in the rate at which organic matter was driven out of the ware in the preheat section, the following results occurred: the glaze was brighter, the redip rate was reduced >50%, the product quality was found to be excellent, the product color was uniform throughout the car, and the net savings in reject rates alone were significant.

In the case of customer L, oxygen lancing resulted in a stronger product and improved color and texture. When the production rates were increased to more than 15%, the product quality was also improved. When the substandard material was added to the raw material, the fired product showed the same or better quality as standard color without oxygen.

### Fuel Savings: Another Plus

In most cases, the energy consumption per unit weight of product improved greatly and burner efficiency increased significantly with oxygen addition. Depending on kiln configuration and raw material (for example, the addition of ash or sawdust), the energy requirements differed greatly.

In the cases of customers C, E, F, and G, where the prime objective was fuel savings, the oxygen enrichment technique was implemented. Adjusting burners to stoichiometric air/gas ratios and reducing nitrogen concentration enhanced radiative-type heat transfers, which, in turn, led to less fuel consumption but uniform temperature throughout the car. Hard-to-reach areas were uniformly heated, the red color of clay product was deep, the quality of the product was excellent, and the mechanical properties were the same or better.

Similar results are possible with any clay product where tunnel kilns are employed. In most cases, a return on the economics investment arrives within only a few months.

### Benefits from Using Oxygen

It is obvious that oxygen is a valuable chemical for the clay industry. It can be used in many facets of the industry, including structural brick, frit, ceramic colors, tile, pavers, dinnerware, whiteware, chinaware, electrical fittings, and sanitary ware.

The benefits from using elemental oxygen for fired clay processes are numerous. By injecting oxygen into tunnel kilns, the production of clay products can increase by as much as 50%, while the number of rejects is drastically reduced. Clay products from tunnel kilns that have been enriched with industrial oxygen display greater product uniformity also. Using an oxygen-enriched atmosphere, face and common brick and tile can obtain a deep red color. The firing power of a kiln increases when the combustion air is enriched with oxygen, which improves burner efficiency and lowers the specific fuel consumption. Oxygen injection also significantly reduces temperature differences across the top and bottom of a car and also reduces waste gas. Finally, the use of oxygen is simple and safe to operate; the oxygen system can be safely incorporated into the firing process after just a few hours of operator training. All of these benefits support the importance of oxygen as a processing tool in the clay industry. ■