

Chemical and Thermodynamic Processes in Clay Brick Firing Technologies and Associated Atmospheric Emissions Metrics-A Review

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Abstract

Atmospheric emissions arising from brick manufacturing installations are a significant source of atmospheric pollution globally. Brick kiln input and firing variables, chemical reactions and thermodynamic processes occurring within the firing chamber of brick kilns, impact on the outcome of fired bricks, as well as the quantity and nature of pollutants emitted into the atmosphere. A review of these chemical reactions and thermodynamic processes, as well as their atmospheric emissions and associated process metrics, was conducted to evaluate the sensitivity of emission metrics to these reactions and processes occurring at a specific period within the firing chamber. Brick kiln emission concentrations and process metrics exhibit wide ranges of data variability during a firing cycle, implying that they are sensitive to these chemical reactions and thermodynamic processes. Kiln emission control efforts aimed at modifying the combustion and firing process in order to alter the chemical reactions and thermodynamic processes in a way that will result in the release of lower quantity of emissions, are proffered. Kiln technologies were ranked from lowest to highest potential for atmospheric pollution based on available emission metrics as follows: Vertical shaft<Zig-zag<US coal-fired< Clamp< Fixed chimney Bull's trench<Tunnel<Down draft<Bull's trench.

Keywords: Brick kiln technologies; chemistry of clay brick firing; clay brick firing; clay brick review; firing technologies; kiln; pollution from clay brick; thermodynamics of clay bricks

Introduction

Clay bricks are fired in kilns, and they are one of the most widely used forms of building materials in the world [1,2]. The consistent popularity of fired bricks as building material is a result of flexibility in construction and design, cost effectiveness, adaptability in severe conditions and its relatively high plasticity [3-8].

According to the Climate and Clean Air Coalition, annual global brick production is estimated at about 1.5 trillion bricks, with Asia accounting for 89-90% (1.35 trillion) [9,10]. The largest clay brick producing countries in the world are China (54-67%), India (11-16%), Pakistan (3-8%), Bangladesh (1-4%) and Vietnam (~2%) [9-12].

Atmospheric emissions arising from brick manufacturing installations are a significant source of atmospheric pollution worldwide [2,13,14]. Brick kilns have been identified as one of the most significant source of atmospheric pollution, (and have gained international concern in recent years) due to its basic technology application, poor or inefficient combustion processes and the absence of adequate emission control required to capture and mitigate pollutants released to the atmosphere [2,15-22].

The Brick manufacturing industry is also considered to be one of the significant sources of greenhouse gas emissions in various regions of the world [23-25]. Table 1 provides the percentage contribution of brick kilns to total pollutant emissions based on the Greenhouse Gas and Air Pollution Interactions and Synergies (GAINS) Model, operated by the International Institute for Applied Systems Analysis (IIASA). Brick kiln input and firing variables such as chemical composition of clay material, type of fuel utilized, firing temperature, exothermic and endothermic processes, as well as the oxidation or reduction conditions in the firing chamber of the kiln; impact on the outcome of fired bricks, including the quantity and type of pollutants emitted into the atmosphere [18,27-32].

This review therefore evaluates the chemical reactions and thermodynamic processes occurring within the firing chamber of a

brick kiln, as well as the atmospheric emissions and their associated process metrics released from various kiln firing technologies in order to evaluate the sensitivity of the emission metrics to the reactions and processes within the kiln.

Clay brick firing

The clay brick firing process may be classified based on the structure of the firing system adopted-intermittent or continuous; and on the direction of flow of heat and flue gases up-draught, down-draught and

Region	% Contribution of Brick Kilns to Total Emissions				
	BC ¹	OC ²	PM1 ³	SO ²	CO
Africa	0.3	0.1	0.1	0.1	0.1
East Asia and Pacific	8.2	5.1	2.3	6.5	2.3
Latin America and Caribbean	0.5	0.2	0.1	0.1	0.1
North America and Europe	0.2	0.1	0.2	<0.1	0.2
South-West-Central Asia	10.4	4.6	3.7	0.9	3.7
Global	5.5	2.6	1.6	2.9	1.6
NOTE	¹ BC is black carbon				
	² OC is organic carbon				

Table 1: Contribution of brick production to regional and global emissions of air pollutants in 2010-GAINS model [26].

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horizontal or cross-draught [11,28,29,33]. Intermittent or periodic kilns are either fully or partially enclosed structures that employ definite structural patterns in order to permit adequate circulation of heat, which is fed via fire holes in the kiln [28,29]. According to Lopez et al. [34], intermittent kilns generally have low energy efficiencies when compared with continuous kilns, since they require fresh energy for restarting the firing process in every cycle. In intermittent kilns, a steady temperature rise is regulated within the kiln until the firing process is completed and the kiln is de-hacked (unpacked) after cooling down. Intermittent kilns include clamp kilns, scotch kilns, round kilns, annular kilns, zigzag kilns etc., [1,28,33,35].

Continuous kilns, alternatively, are more sophisticated, employing continuous or constant feed of fuel into a structure in which, either green bricks are passed steadily through a stationery firing zone; or a firing system is passed through a stationery pack of green bricks (with the aid of a suction fan or chimney). Continuous kilns include tunnel kilns, vertical shaft brick kilns (VSBKs), Hoffmann kilns, Bull's trench kilns, fixed chimney kilns, high draught kilns etc., [1,35,36].

Merschmeyer, EMEP/EEA, Potgieter and Jansen [33,37,38] classify kilns into three types, based on the direction in which the heat flows, namely, up-draught firing, down-draught firing and horizontal or cross-draught firing.

The up-draught firing system include the clamp kiln and VSBK; the down-draught firing system include the scotch kiln, round kiln, annular kiln and zigzag kiln (arch less); while the horizontal or cross-draught firing system include the Hoffmann kiln, tunnel kiln, fixed chimney Bull's trench Kiln (FCBTK) and Bull's trench Kiln [33,35,36].

Chemistry and thermodynamics of clay brick firing

Rowden, Alfrey and Clark, Mutsago and Diop et al., Velasco et al., Bleininger, Oti and Kinuthia [27,39-44] provide adequate background on the chemical properties of clay material utilized in brickmaking. Clay bricks are formed from either carbonaceous clays and shales, or non-carbonaceous clays, the main chemical constituents being silica, alumina, iron oxide and often lime [27,42].

The main mineral constituents of clay are expressed in the form of clay matter ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), feldspathic or micaceous matter ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), quartz (SiO_2), ferric oxide (Fe_2O_3) and Lime (CaO). The clay matter, when heated to a temperature ranging from 450-650°C, is decomposed into its separate constituents, viz. silica, alumina and water. The water constituent in $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, known as "combined water", amounts to about 14% of the weight of the clay matter, and does not form part of the "mechanical water", i.e. the water added into the clay mixture during processing. The mechanical water is steamed off mostly during drying, at temperatures ranging from 20 °C to 150 °C [27,39-41,44-46].

According to Rowden and Vieira et al. [27,45] when a "green brick" or dried brick is heated to extremely high temperatures (>1000°C), it loses weight, a term referred to as "loss-on-ignition". Loss-on-ignition is due to the following:

1. The burning out of carbonaceous matter and combustible sulfur in the clay.
2. The breakdown of carbonates present in the clay to give off carbon dioxide, CO_2 and
3. The release of "combined water" from the clay.

Loss-on-ignition is therefore, an indicator of the amount of

carbonaceous matter and carbonates present in the clay. For instance, a low loss-on-ignition indicates that the amount of carbonaceous matter and carbonates in the clay is low [27,45].

Carbonates found in clay are mostly magnesium, iron and calcium carbonates, which are often regarded as impurities [27,44]. These carbonates decompose on heating to form oxides and CO_2 (shown in Equations 1, 2 and 3).

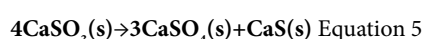
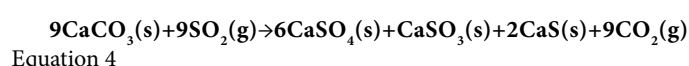


A high percentage of calcium carbonate in the clay material may cause lime flaking in the fired bricks, and/or produce a scum of white calcium sulphate on the exposed surfaces of the fired bricks, especially when a significant amount of SO_2 is released from the fuel during firing [27].

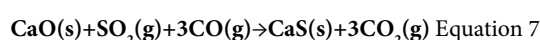
Carbonaceous matter in clay starts to burn out at about 200-350 °C to form hydrocarbons and a more carbonaceous residue [27]. The carbonaceous residue will only be further combusted to emit CO or CO_2 if the following favourable conditions, described by Rowden [27] occur in the kiln:

1. Availability of excess air in the combustion chamber to maintain an oxidising environment in the kiln
2. A high cross sectional area of the clay material being exposed to combustion, as well as adequate spacing employed when packing the bricks; and
3. Uniformity in the rate of combustion, so as to ensure adequate penetration of the clay brick and ignition of the carbon in the core of the bricks.

According to Grim and Johns, Gredmaier [31,32] raw clay materials used in brick firing also contain sulphur and calcium, which are evenly distributed in trace amounts in the unfired bricks. The most likely compound to be formed during brick firing is calcium sulfate (CaSO_4), in a complex reaction proposed by Tourneret et al. [47] as follows:



Equation 6 requires excess oxygen which is only abundant at the brick surface. An insufficient supply of oxygen could change the reaction in Equation 6 to become:



Tourneret et al., Brownell [47,48] opines that the major source of sulfur released during firing is from the oxidation of the pyrite component (FeS_2) in the clay material, as well as the sulfur present in the coal that is mixed with the clay material during brick processing.

In addition, it was established by Brownell [48] that calcium sulfate is one of the most prominent and persistent salts that builds up during the firing process. This is due to the extreme temperatures required for calcium sulfates to dissociate and react with silicates; temperatures which may not be achieved at regular brick kiln temperatures [32,49]. A clear influence of the firing environment on the quantity of water soluble sulfate in bricks made from clay material containing pyrite component was discovered. According to these studies, clays that are

fired in a reducing environment have the potential to retain more sulfates compared to clay fired in an oxidizing environment [50,51].

According to Rowden, Grim and Johns, Gredmaier et al. [27,31,32] it is possible to have both oxidising and reducing conditions occurring within the firing chamber of a kiln. Whilst the excess air in the firing chamber favours oxidation conditions within the firing chamber, the release of a high temperature water vapour (combined water) at a temperature of 450-650 °C inside and around the bricks, may prevent oxygen from entering the core of the bricks. The carbon present in the core of the bricks reacts with the steam being released to produce strongly reducing gases; hydrogen and CO, which at high temperatures may permanently distort the iron in the clay and produce varying degrees of colour.

Gredmaier et al. [31,32] also describe the reaction in which heat is absorbed (endothermic reaction) into the clay material, which may be due to dehydration, destruction of lattice structure and change in crystal phase of the clay material. Alternatively, heat release (exothermic reaction) from the clay material may be due to oxidation or the development of new crystalline phases.

The chemical composition of clay material, the firing temperature, as well as the oxidation or reduction condition in the kiln and/or within the bricks, impact on the colour and physical outcome of fired bricks. Oxidation occurs when an adequate supply of air (oxygen) is circulated within the kiln, impacting a red or dark brown colour to the bricks. Reducing conditions occur when the oxygen supply within the kiln or within the bricks, is limited, impacting an orange, yellow, blue or grey colour to the bricks [27,52-55]. Dark coloured spots of iron oxides have also been observed when a clay material that contains high amounts of iron carbonates is fired in a reducing environment [27].

6 stages in the clay brick firing process have been identified as follows: evaporation, dehydration, oxidation, vitrification, flashing and cooling [7,28]. The temperature range and description for these six stages is provided in Table 2. According to Kornmann, BIA, Merschmeyer [7,28,33] the range of temperature required for firing at each stage is vital to the quality of bricks produced, while the temperature required depends on the type of clay material, the size and “coring” of the fired bricks.

Energy use in the clay brick industry

The types of energy utilized in the clay brick industry are generally one or more of the following: Coal (various types of coal e.g. duff, filter cake, coal fly ash, peas and nuts); Diesel; Heavy fuel oil; Gas; and Electricity. A comparison of the specific energy consumption (SEC) of clay brick industries from various countries was published by Micheal [56] and is reproduced in Table 3. SEC per country ranged from 1.78 MJ/kg (Morocco) to 3.88 MJ/kg (Australia). This wide difference between countries in SEC has been attributed to the difference in clay material used, difference in weather conditions, availability of different energy types, as well as use of different kiln technology per country.

According to Micheal, Villiers [56,57] the specific energy required to fire a brick can be estimated as a summation of the energy required to dry the bricks and evaporate the mechanical water (estimated to be 0.54 MJ/kg), plus the energy required for chemical reactions in the brick (estimated to be 0.2 MJ/kg). In addition, Heimsoth [58] concluded that a large proportion of the total energy requirement for firing bricks in a tunnel kiln is actually in the form of losses, including wall losses (25%), exhaust losses (30%) and recoverable cooling air (30%). Improved energy efficiency may therefore imply a significant reduction in energy consumption without compromise to the quality or quantity of production; and often, it may result in improved quality and quantity

Stages	Temperature Range (°C)	Description of Reactions during Firing
Evaporation	20-150	Water-smoking or slow heating stage where evaporation of “free or mechanical water” takes place. Mechanical water is the water that is added into the clay mixture during processing. It is essential at this stage to maintain gradual temperature rise so as to prevent cracking of the bricks, since the outer surface of the bricks will contract at a faster rate than inside the bricks, leading to cracking. An endothermic reaction is observed at this stage due to the loss of the mechanical water.
Dehydration	149-650	Burning out and breaking down of the carbonaceous matter and carbonates, as well as the “combined water”, occur during the dehydration stage. The temperature at which the “combined water”, carbonaceous matter and carbonates completely combust depends on the rate of heating. Rapid heating may cause an atmosphere of steam to persist around and within the bricks, resulting in reducing conditions (due to insufficient supply of oxygen within the bricks) that produces discolouration or dark coloured, cored and bloated bricks. An endothermic reaction is observed at this stage due to further release of water and carbonaceous matter.
Oxidation	300-982	Oxidation in the kiln may commence at temperatures as low as 300 °C and may extend as high as over 900 °C, depending on the rate of heating, the quantity of carbon present in the clay, the amount of excess air available in the combustion chamber, the density and area to volume ratio of the clay bricks. In order to produce quality bricks, it is essential that any residue carbonaceous matter be combusted and all iron residues oxidized to its oxides at this stage. This could be achieved by ensuring excess air of 50% or more is circulated within the combustion chamber; holding the temperature at about oxidation 800-900 °C for a few days (3-4 days in some kilns); and keeping the CO ₂ level in the flue gas at 10-12%. An exothermic reaction is observed at this stage, and is due to the oxidation of organic compounds and subsequently, sulfide compounds in the clay material. This exothermic reaction is observed from 300 °C up to 450 °C, and then an endothermic reaction sets in. This is attributed to the loss of water from the crystal structure of the mineral and a change in crystalline phase of the quartz from α to β form. The loss of water is achieved without damage or shrinkage of the of the clay mineral lattice structure.
Vitrification	900-1316	Vitrification usually commences at about 900 °C, when all the carbonaceous matter has been fully oxidized, and extends up to the highest temperature the bricks can withstand without damage. The strength of the fired bricks is developed during vitrification, by sintering of clay particles and melting of the clay mass. The solid particles become coated with liquid which upon cooling solidifies mainly as a glass and binds the particles together. The strength of the fired bricks thus depends on the maximum temperature reached, the duration of the vitrification stage or maximum temperature, as well as amount of fluxes, such as potash, soda, magnesia, lime and ferrous oxide present in the clay. At this stage, a series of exothermic reaction are observed, due to the slow oxidation of sulfur compounds and possibly residual organic material, as well as formation of new crystalline phases.
Flashing	1150-1316	Holding the peak or finishing temperature for a period in order to impact the required colour to the bricks by the addition of “un-combusted fuel” to the kiln.
Cooling	1316-20	This is the decrease of kiln temperature from peak to ambient temperature, lasting a few days (4-5 days or more).

Table 2: Temperature range for various stages of brick firing [27-32,56].

Country	Production (Millions of Tons)	Fuel Consumption (PJ)	SEC (MJ/kg)
Morocco	1.5	3	1.78
Germany	10	19	1.94
Greece	2.16	5	1.96
Ireland	0.95	2	1.97
Italy	17.6	42	2.37
Spain	12.6	30	2.4
France	5.41	14	2.57
U.K.	5	13	2.66
Denmark	0.86	2	2.69
Netherlands	3.1	9	2.76
India	55	120	2.8
Portugal	4.15	12	2.86
Algeria	3	9	3.14
South Africa	11.1	38	3.42
Canada	0.84	3	3.59
Australia	5.73	20	3.88

Table 3: A comparison of SEC by countries [56].

of brick production. A reduction in energy consumption is therefore a significant mechanism for reducing atmospheric emissions and combating global warming, since large proportion of these emissions are released from fuel sources [56].

Emission metrics associated with brick firing technologies

Brick firing technologies

Brick firing has evolved beyond ancient, traditional, basic and common techniques, to more sophisticated, energy efficient technologies [50-61]. RSPCB [35], there are over 3,00,000 continuous and intermittent, formal and informal kilns operating worldwide.

The succeeding sections describe some of the most common firing technologies around the world, which include:

1. Tunnel kiln
2. Hoffman kiln
3. Vertical shaft brick kiln (VSBK)
4. Down-draught kiln (DDK)
5. Fixed chimney Bull's trench kiln (FCBTK)
6. Zig-zag kiln; and
7. Clamp kiln

Less popular types of kiln for brick firing include the Habla kiln, an energy efficient variant to the Zig-zag kiln invented in Germany [62]; the igloo or beehive kiln, which is commonly used in Zimbabwe for firing bricks and other kinds of materials [63,64]; kondagaon kiln [65]; and bhadrawati kiln [65]. Other less common kilns include the scove kiln, which is essentially a typical clamp kiln plastered with mud on the outer walls to reduce heat loss [54]; the scotch kiln; also an improvement on the clamp kiln, in which the base of the kiln, the outer walls and the fire channels are permanently built structures [54]; the marquez kiln, a new type of kiln in Mexico, which consists of two arch-roofed chambers that are connected by a clay channel [66]; shuttle kiln [56,67]; the barrel arch kiln; the suffolk kiln; the stack kiln; the Ideal Kiln; the Belgian kiln [27]; and the dome kiln [64].

Tunnel Kiln

CBA, Kornmann, Daraina et al. [5,7,68] describe a tunnel kiln as a long horizontal tunnel in which green bricks are set on "kiln cars" and are driven continuously through a long stationary firing zone where the bricks and air move in opposite direction and the temperature is regulated at 900-1200 °C. The kiln cars can be moved along the tunnel continuously or at fixed intervals, with air supply and extraction systems provided at several points along the kiln structure [35,36,68].

According to Maithel et al. [69] the length of a tunnel kiln varies from 60 to 150 metres, with three distinct zone identified in the operating kiln, namely: *the preheating zone* (where preheating and final drying occur); *the firing zone* (where the fuel, usually pulverized or granulated coal, is fed and combustion occurs); and *the cooling zone* (where inflow of cold air is used to cool the bricks at the exit end of the kiln). Tunnel kilns are low in labour demand but require high electricity and capital costs. They are capable of receiving 60,000-2,00,000 bricks per day; and the bricks require 3-5 days for drying and firing to be completed [36]. According to CBA, Maithel et al. [5,36] tunnel kilns are capable of firing a variety of bricks; producing bricks that meet specific demands in terms of size, shapes and colour. Its advantage lies in its ability to establish control over the firing process; its ease of mechanization (thereby reducing the labour requirement); and large production volume. A modification to the tunnel kiln is the roller kiln, described by Kornmann [7], which can fire bricks at a short duration of 3-8 hours.

Hoffman Kiln

The Hoffman kiln, a semi-mechanized kiln, was invented by Friedrich Hoffman in Germany in 1858 [11,70]. It is similar to the transverse arch kiln (TVA) and was initially used for firing roofing tiles [68,71]. The Hoffmann or barrel arch kiln has a number of open-wall circular ring chambers through which bricks and fuel are stacked for firing in a continuous process [72,73].

The fire in a Hoffmann kiln passes through stacked bricks inside a rectangular or elliptical shaped annular circuit. The movement of the fire in the firing zone-where fuel is fed to the kiln-is induced by draught from a chimney that is connected to the central flue duct [36,71]. The fired bricks are removed from the cooling zone or chamber when the firing and cooling process is complete. Simultaneously, another load of bricks is fed to the fire chamber at the pre-heating zone to ensure a continuous firing process [4,70,72,73].

According to Neaverson and Plamer [70], Hoffmann kilns are seldom operated in India since the early 20th century and have been replaced by the large, wall chambered TVAs and the tunnel kilns. Another variation of the Hoffmann kiln is the hybrid Hoffmann kiln, which was developed in China and is still extensively used in China and South Asia [74]. According to Baum, Lopez et al. [11,34], an estimated 90% of the total bricks produced in China are fired using modifications of Hoffman Kilns.

Vertical Shaft Brick Kiln

The vertical shaft brick kiln (VSBK) was invented in China in 1958 as a modification to the traditional updraft intermittent kiln, operating on the principles of effective consumption of the heat produced by the combustion of the fuel [36]. A VSBK consists of a long, rectangular, vertical shaft through which green bricks and pulverized coal or fuel are lowered from top to bottom in batches [36,75]. According to Maithel et al., Giovanetti and Volsteedt [36,76], the kiln works in the form of a "counter-current heat exchanger", since heat exchange occurs between

the continuous flowing updraft air and the intermittently downwards moving bricks. There are 3 distinct sections in an operating VSBK: *the preheating zone*-this is the top section of the shaft where the incoming green bricks are preheated by the upward moving flue gases; *the firing zone*-this is located in the mid-section of the shaft where fuel combustion occurs; and *the cooling zone*-located in the lower section of the shaft where the fired bricks are cooled down by the cold ambient in-coming air entering the shaft.

The bricks pass through pre-heating, firing and cooling zones before reaching the bottom of the shaft where they are de-hacked [36,68,77]. Thermal efficiency in the kiln is enhanced with the aid of insulating materials such as fly ash, clay, rice husk and even glass wool [78]. In the modern VSBKs, typical in South Africa, Vietnam and Malawi, the use of internal or body fuel is supplemented by a small quantity of external fuel [76,78-80].

Chimneys are also fitted into the kiln and the lid is shut tight during operation in order to minimize fugitive emissions. As a result, VSBKs are relatively high in energy efficiency, low in operating costs, and they are suitable for firing bricks of high quality and specifications [36,76-78].

Down-Draught Kiln

The down draught kiln (DDK) is an intermittent kiln with a permanently built structure which includes a rectangular firing chamber and a barrel-vaulted roof that is connected to a chimney through an underground flue duct [4,68,81,82]. Fireboxes are used to supply hot gases from the bottom of the chamber to the roof of the kiln where they are drawn downwards by the chimney draft through the green bricks and out through the chimney stack [4,81]. Continuous feeding of fuel (e.g. by coal, gas or oil, firewood, twigs and branches) helps ensure there is a uniform heat distribution in the kiln until the target temperature is attained. This target temperature is maintained for a specific period until the fire subsides, thereby ensuring better thermal performance and lesser heat loss [4,81,82]. The kiln cools down in 2-3 days and the fired bricks are de-hacked in readiness for the next batch [4,81,82]. Other kilns with similar configuration to the down-draught kiln are the up-draught and cross-draught kilns, differing in the direction of the heat flow.

Fixed Chimney Bull's Trench Kiln

Maithel et al., Maithel et al. [36,83] describe the fixed chimney bull's trench kiln (FCBTK) as a continuous, cross-draught, ring-shaped or annular, moving-fire kiln that is fixed with a permanent chimney structure that provides natural draught to the kiln. In the FCBTK, the bricks are stacked in the firing zone, a ring space formed between the inner and outer walls of the kiln, while the moving fire passes through the green bricks [83,36].

The FCBTK utilizes an immovable chimney, an improvement over the Bull's trench kiln (BTK) and the movable chimney Bull's trench kiln (MCBTK), which employs a moving metallic chimney. The sidewalls in the FCBTK are permanent, constructed above the ground, while the roof is temporary, formed from a covering of ash or brick dust, which serves as a seal over the green bricks [54,83]. According to Maithel et al. [36], the bricks are stacked in a column and blade arrangement, with the unloading end of the kiln kept open for inflow of cold air, while the brick-loading end of the kiln is sealed with various kinds of materials, including plastic, paper, cloth or iron.

Three distinct zones are identified in the FCBTK, namely, the cooling, combustion and pre-heating zone. In the *cooling zone*, air

enters the kiln from the unloading end of the kiln, exchanges heat with fired bricks, resulting in the heating of air and the cooling of the fired bricks. In the *combustion zone* (the fuel feeding and firing zone), hot gases are released from combustion of coal, firewood, or agriculture residue (which is fed from the kiln feedholes on the roof). Finally, the *brick pre-heating zone* utilizes heat from fugitive flue gases to dry green bricks [36,75,83]. According to CDM [75], FCBTK has the capacity to produce consistent colour and high quality fired bricks.

Zig-zag Kiln

The zig-zag kiln is a modification and improvement over the FCBTK. The heat in a zig-zag kiln follows a zig-zag pattern, rather than the straight path in the FCBTK [36,54]. The zig-zag kiln design results in higher heat transfer rates between the bricks and air due to increased turbulence and velocity achieved through frequent change in direction of flue gases [2,36]. Consequently, improved combustion is achieved due to increased mixing of air and fuel in the combustion zone. Also, a smaller footprint can be designed for the kiln due to increased combustion and longer volatilization time in the combustion zone [2,36,84]. A high or induced draught zig-zag kiln is an improved zig-zag kiln fitted with a fan in order to stimulate the draught required for the air flow [36,84].

Three distinct zones are identified in the Zig-zag kiln, which are similar to the FCBTK: *the cooling zone*, where the cold air exchanges heat with the fired bricks, resulting in the heating of air and the cooling of the fired bricks; *the combustion zone*, where hot gases are released from the combustion of the fuel (coal), usually fed from the feedholes; and *the brick pre-heating zone*, where pre-heating of the green bricks is made possible by flue gases [36,84]. The kiln does not have a permanent roof structure; hence stacked bricks are covered with a layer of ash brick dust. This acts as a temporary roof and also seals the kiln from leakages, thereby minimizing heat loss [36,84]. The Zig-zag kiln is also known as the high draught kiln (HDK) developed by the Central Building Research Institute (CBRI) in India [35,36,75].

Clamp Kiln

Clamps are primitive or traditional kilns, lacking a permanent structure and invented by the Egyptians around 4000 BC [11,35]. According to CCAC, Baum, RSPCB, Maithel et al., Lordan, Wienerberger, Smith, Guttikunda et al. [9,11,35,36,85-88], the clamp kiln is one of the most commonly used brick firing technique in developing countries, including India (25-40%) and South Africa (68-85%). The bricks in a clamp kiln are packed in a pyramid-shaped configuration with layers of combustible material such as wood, cinder, coal or coke at the floor or bottom of the kiln (common practice in South Africa), and after each layer of bricks (common practice in Asia). Few layers of previously fired bricks are arranged to serve as a funnel or conduit to accommodate the base combustible matter. A layer or two of previously fired bricks are also packed on top of the 'green' bricks to serve as insulation [4,5,35,18,89].

According to RSPCB [35], clamp kilns are labour intensive and are often operated in clusters. They burn fuel inefficiently and are highly polluting. On the positive side, they are simple to build, thereby affording operators the ease of locating close to a clay source, in order to minimize cost of transportation and production logistics.

When the bottom layer of the kiln packed with fuel is ignited, it sets the bricks on fire one layer at a time until the whole kiln is ablaze. The temperature inside the kiln rises gradually, kindling the fuel packed on top of each layer (for informal clamps) or fuel mixed into the clay (for

South African industrial scale clamps) at about 800 °C and peaking at a maximum of 1200-01400 °C [4,5,35,84,89,90].

Pollutants associated with clay brick firing

Akinshipe and Kornelius, USEPA, Maithel et al., Bellprat, Skinder et al., EIP, Skinder et al., Imran et al., [18,29,36,66,91-94] identify pollutant emissions from clay brick firing to include the following:

1. Particulate matter (PM) or total suspended particulates (TSP)
2. Particles which pass through a size-selective inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter (PM₁₀)
3. Particles which pass through a size-selective inlet with a 50% efficiency cut-off at 2.5 µm aerodynamic diameter (PM_{2.5})
4. Particles which pass through a size-selective inlet with a 50% efficiency cut-off at 1 µm aerodynamic diameter (PM₁)
5. Sulfur dioxide (SO₂)
6. Sulfur trioxide (SO₃); Nitrogen oxides (NO_x), (including nitrogen dioxide (NO₂) and nitrogen monoxide (NO))
7. Carbon monoxide (CO)
8. Carbon dioxide (CO₂)
9. Metals (including Copper (Cu), Chromium (Cr), Lead (Pb), Nickel (Ni), Zinc (Zn), Cadmium (Cd), Iron (Fe), Manganese (Mn))
10. Fluorides and
11. Organic compounds (including methane, ethane, volatile organic compounds (VOCs), persistent organic compounds (POPs) and some hazardous air pollutants such as hydrogen chloride (HCl) and hydrogen cyanide (HCN).

Brickmaking activities include mining, crushing and blending, grinding and screening, souring, ageing, drying, packing, firing, unpacking and packaging. Extensive literature on these activities have been published by Kornmann, Akinshipe and Kornelius, USEPA, Merschmeyer [7,18,29,33]. Typical pollutants associated with these activities are summarized in Table 4.

Effects of clay brick firing and atmospheric pollution

The most abundant and destructive pollutants in brick production

sites have been identified as SO₂, NO_x, CO, ozone (O₃), hydrogen fluoride and heavy metals, as well as suspended PM [91,96,97]. Various studies have measured the ground level concentration of atmospheric pollutants from brick kilns [2,93,98-101]. The concentrations were, in most of the cases, high, and result in exceedance of local and international guidelines or permissible limits. The concentration declines as the distance from the kiln increases.

The negative effects of pollution from brick kilns include health challenges to humans and animals, degeneration of land cover, loss of land, damage to agriculture, reduced visibility, depletion of soil nutrients and the ozone layer, increased soil erosion, damage to buildings, contamination or acidification of surface and ground water systems, as well as consequential social and economic effects [2,20,22,28,93,100-109].

Health effects and symptoms associated with atmospheric emissions from brick production are mostly respiratory, pulmonary and cardiovascular infections. These include contraction or spasm of the airways and bronchi (commonly referred to as asthma attacks), inflammation of the mucous membranes (bronchitis), increased secretions in lung and heart tissues, impairment of the lung function, increase in blood and throat pressure, headache, fatigue, dizziness and chest pain, as well as irritation of the eyes and nose [23,91,100,102,104,105,110-114]. It has also been reported that adults and children engaging in brick making activities are at a higher risk of being exposed to smoke, dust and organic pollutants, especially when wood or coal are utilized as fuel. These fuels also release dust-bound polycyclic aromatic hydrocarbons (PAHs) which have been identified as high risk carcinogens. Brick workers may be exposed to PAHs via dermal contact, inhalation, as well as ingestion [115].

The effects of brick kiln emissions on soil characteristics and vegetation have also been investigated. Studies show increase in soil acidity, as well as increase in concentration of heavy metals, nitrate and sulfate near brick kilns (100 to 150 metres downwind of the kiln), which consequently results in reduced soil quality [101,108].

According to the Organization for Economic Co-operation and Development, OECD (1981) and National Acid Precipitation Assessment Program, NAPAP (1990), visible damage to sensitive plant species may become noticeable when they are exposed to heavy metals concentrations of 1 850 µg/m³ for 1 hour or concentrations of 500 µg/m³ for 8 hours or concentrations of 40 µg/m³ for the entire maturing

Pollutants	Mining	Crushing	Milling	Drying 1	Hauling2	Firing
Total PM	√	√	√	- or ü	√	√
PM ₁₀	√	√	√	- or ü	√	√
PM _{2.5}	√	√	√	- or ü	√	√
SO ₂	4	-	-	- or ü	√	√
SO ₃	-	-	-	- or ü	-	√
NO _x (NO ₂ and NO)	-	-	-	- or ü	√	√
CO	-	-	-	- or ü	-	√
CO ₂	-	-	-	- or ü	-	√
Metals	-	-	-	- or ü	-	√
Fluorides	-	-	-	- or ü	-	√
TOCs ⁵	-	-	-	- or ü	√	√
NOTE	Drying is either sun-drying “-” or process drying “ü” [4,18,29]					
	Hauling emissions include vehicle entrained emissions from roads, as well as vehicle exhaust emissions					
	Size of the tick indicates the anticipated extent of the emissions					
	indicate that emissions are insignificant					
	TOCs include methane, ethane, volatile organic compounds (VOCs), persistent organic compounds (POPs) and some hazardous air pollutants (HAPs)					

Table 4: Summary of emissions from brickmaking processes [4,18,66,94,95].

season. Visible foliar injury to mango, apricot and plum trees have been investigated and associated with increased hydrogen fluoride concentrations in ambient air near brick kilns in Southeast Asia [97].

Soil contamination around brick making facilities may also lead to distortion of plant biomass, alteration of plant structure as well as change in species diversity [106,104,108,116].

Finally, contamination of water resources as a result of pollutant dispersion around brick clusters in India has also been investigated, indicating an increase in total solids, calcium and total hardness, as well as a reduction in dissolved oxygen in all water resources assessed [117].

All studies and investigations mentioned above have either identified a direct association of emissions with brick kilns, or were conducted in a region with high brick kiln activities relative to other industrial activities. For instance, the charts in Figure 1 show brick kilns as the highest and second highest source of PM_{10} and TSP respectively, in the Kathmandu valley, Nepal [16,118].

Brick kiln emissions and process metrics

Brick kiln emission concentrations and process metrics exhibit a wide range of data variability during a firing cycle, suggesting that they are sensitive to these chemical reactions and thermodynamic processes occurring within the kiln at a particular period. Brick kiln emission control efforts should therefore be aimed at modifying the combustion and firing process in order to alter the chemical reactions and thermodynamic processes in a way that will result in the release of lower quantity of emissions. This should be done in collaboration with measures aimed at capturing and mitigating the release of emissions into the atmosphere.

Effective measures for modifying the combustion and firing process in order to reduce the quantity of emissions from a kiln are proffered. These include

1. Measures targeted at reducing the energy input in order to minimize release of atmospheric emissions without compromising the firing process or quality of bricks fired.
2. Measures aimed at regulating the complex oxidation and reduction reactions occurring in the firing chamber of the kiln. This involves promoting or favouring reducing conditions in the firing chamber of the kiln in order to minimize atmospheric emissions, while ensuring the retention of $CaSO_4$ and FeS_2 in the clay material and in the internal fuel mixed into the clay during processing.
3. Measures aimed at regulating the complex thermodynamic processes in the firing chamber of the kiln. This involves regulating the firing chamber temperature at certain levels for a specific duration in order to regulate the exothermic and endothermic complexes in the kiln, which in turn controls the chemical processes and the release of pollutants associated with those processes. NO_x emissions, for instance, are only given off at certain higher temperatures; while significant $CaSO_4$ retained within the clay brick material can only be dissociated to give off SO_2 at extreme temperatures (i.e. above $1200^\circ C$). Hence, maintaining peak temperatures below $1200^\circ C$ reduces the potential for SO_2 emissions.

Several literature sources have published results on emissions and process metrics from various types of brick firing technologies. These literatures provides results of monitoring campaigns conducted on various kiln firing technologies around the world using established scientific methodologies. Firing process metrics from various kiln

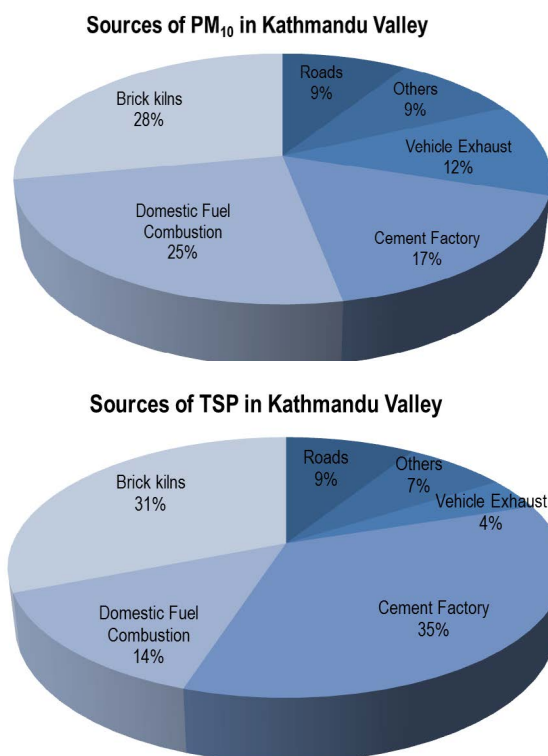


Figure 1: Sources of PM_{10} and TSP in Kathmandu valley, Nepal [16,118].

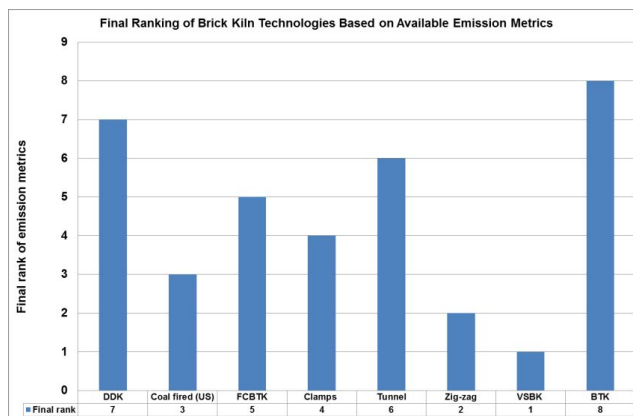


Figure 2: Final ranking of brick kiln technologies based on available emission metrics-VSBK and the Zig-zag kilns have the lowest potential for atmospheric pollution, while BTK and the DDK have the highest potential for atmospheric pollution.

technologies are provided in Table 5. A summary of measured suspended PM, CO_2 , PM_{10} , SO_2 , NO_x , Hydrocarbon and CO emissions for various brick firing technologies are presented in Table 6.

Ranking of brick kiln technologies based on available emissions metrics

An evaluation of emission metrics presented in Section 3.4 was conducted for various firing technologies (including BTK, DDK, Tunnel, VSBK, zig-zag, FCBTK, clamp and US coal-fired kilns) [128]. The various technologies were then ranked in order of their potential

Flue gas metrics	Unit	Kiln Technology		
		BTK/MCBTK	FCBTK	Zigzag
Exit temperature	°C	100-200	80-120	75-100
Exit velocity	m/s	7-May	10-Aug	15-Dec
Exit flow rate	m ³ /hour	5500-7000	7000-9000	10000-12000

Table 5: Flue gas metrics for various brick firing technologies [35].

Measured suspended PM emissions							
Source	Clamp	VSBK	Tunnel	MCBTK	FCBTK	Zigzag	Hoffmann
[35]	-	-	-	602-1721 mg/Nm ³	219-558 mg/Nm ³	354-853 mg/Nm ³	-
Maithel et al. [36]	-	0.11 g/kg	0.31 g/kg	-	0.86 g/kg	0.26 g/kg	-
Maithel et al. [69]	-	-	41 mg/Nm ³	-	-	-	-
Maithel et al. [71]	-	-	-	-	-	-	260 mg/Nm ³
Maithel et al. [78]	-	107 mg/Nm ³	-	-	-	-	-
Maithel et al. [83]	-	-	-	-	570 mg/Nm ³	-	-
Maithel et al. [84]	-	-	-	-	-	96 mg/Nm ³	-
Russel and Vogel [119]	-	-	-	-	-	-	60-70 mg/Nm ³
Baum [11]	-	70 mg/Nm ³	-	1021 mg/Nm ³	380 mg/Nm ³	-	-
Sarraf et al. [120]	-	-	-	-	1000 ⁺ mg/Nm ³	500-1000 mg/Nm ³	<100 mg/Nm ³
Maithel et al. [121]	-	170 mg/Nm ³	-	-	350 mg/Nm ³	550 mg/Nm ³	-
Manandhar and Dangol [122]	-	101 mg/Nm ³	-	840 mg/Nm ³	125-238 mg/Nm ³	116 mg/Nm ³	-
Manandhar and Dangol [122]	-	-	-	-	0.86 g/kg	-	-
Klimont [26]	-	0.18 g/kg	0.3 g/kg	-	0.85 g/kg	0.195 g/kg	-
Lopez et al. [34]	1.91 g/brick	-	-	8.06 g/brick	1.71 g/brick	-	-
Measured CO ₂ emissions							
	Clamp	VSBK	Tunnel	MCBTK	FCBTK	Zigzag	DDK
RSPCB [35]	-	-	-	3.3 %	2.7 %	3 %	-
Maithel et al. [69]	-	-	166.3 g/kg	-	131 g/kg	-	-
Maithel et al. [78]	-	70.5 g/kg	-	-	-	-	-
Müller [123]	-	41 g/kg	-	-	186 g/kg	-	-
Maithel et al. [81]	-	-	-	-	-	-	282.4 g/kg
Maithel et al., Hoque et al. [36,124]	-	70 g/kg	166 g/kg	-	115 g/kg	103 g/kg	282 g/kg
Maithel et al. [83]	-	-	-	-	131 g/kg	-	-
Manandhar and Dangol [122]	-	-	-	-	115 g/kg	-	-
Maithel et al. [84]	-	-	-	-	-	105 g/kg	-
Baum, Lopez et al. [11,34]	77-171 tons/100,000 bricks	26-38 tons /100,000 bricks	42-96 tons /100,000 bricks	46-67 tons /100,000 bricks	42-58 tons /100,000 bricks	-	-
Manandhar and Dangol [122]	471 g/brick	166 g/brick	-	249 g/brick	182-232 g/brick	182 g/brick	-
Measured PM ₁₀ emissions							
	Clamp	VSBK	Tunnel	Hoffmann	FCBTK	Zigzag	DDK
Maithel et al. [69]	-	-	0.24 g/kg	-	1.18 g/kg	-	-
Maithel et al. [74]	-	-	-	0.29 g/kg	-	-	-
Maithel et al. [78]	-	0.15 g/kg	-	-	-	-	-
Müller [123]	-	0.15 g/kg	-	-	1.14 g/kg	-	-
Maithel et al. [81]	-	-	-	-	-	-	1.56 g/kg
Maithel et al. [83]	-	-	-	-	1.18 g/kg	-	-
Maithel et al. [84]	-	-	-	-	-	0.24 g/kg	-
Burger and Breitenbach, Akinshipe [18,125]	6.59 g/brick	-	-	-	-	-	-
Burger and Breitenbach, Akinshipe [18,125]	2.32 g/kg	-	-	-	-	-	-
Baum [126]	-	0.1g/kg	0.26 g/kg	-	1.18 g/kg	0.21 g/kg	1.55 g/kg
Measured SO ₂ emissions							
	Clamp	VSBK	Tunnel	MCBTK	FCBTK	Zigzag/HDK	-
RSPCB [35]	-	-	-	0.26 mg/Nm ³	0.29 mg/Nm ³	1.12 mg/Nm ³	-
(using reverse modelling) Akinshipe [18]	0.73 g/kg	-	-	-	-	-	-
(using sulphur balance) Akinshipe [18]	0.84 g/kg	-	-	-	-	-	-
Müller [123]	-	0.02 g/kg	-	-	0.38 g/kg	-	-
Maithel et al. [36]	-	0.54 g/kg	0.72 g/kg	-	0.66 g/kg	0.32 g/kg	-

Burger and Breitenbach, Akinshipe [18,125]	0.34 g/kg	-	-	-	-	-	-
USEPA [29]	-	-	0.6 g/kg	-	-	-	-
Manandhar and Dangol [122]	-	-	-	-	0.66 g/kg	-	-
Manandhar and Dangol [122]	-	36	-	-	170-228 mg/Nm ³	145 mg/Nm ³	-
Measured NO_x emissions							
	Clamp	MCBTK	FCBTK	Zigzag	-	-	-
RSPCB [35]	-	0.08 mg/Nm ³	0.11 mg/Nm ³	0.2 mg/Nm ³	-	-	-
Burger et al (2008), Akinshipe (2013)	0.31 g/brick	-	-	-	-	-	-
Burger et al (2008), Akinshipe (2013)	0.11 g/kg	-	-	-	-	-	-
Measured Hydrocarbons emissions							
	Clamp	MCBTK	FCBTK	Zigzag	-	-	-
RSPCB [35]	-	275 mg/Nm ³	216 mg/Nm ³	227 mg/Nm ³	-	-	-
Measured PM_{2.5} emissions							
	VSBK	Tunnel	FCBTK	Zigzag	DDK	-	-
Maithel et al. [36]	0.09 g/kg	0.18 g/kg	0.18 g/kg	0.13 g/kg	0.97 g/kg	-	-
Maithel et al. [36]	-	-	-	-	331 mg/Nm ³	-	-
Baum [126]	0.09 g/kg	0.18 g/kg	0.18 g/kg	0.09 g/kg	0.95 g/kg	-	-
Manandhar and Dangol [122]	-	-	0.18 g/kg	-	-	-	-
Measured CO emissions							
	VSBK	Tunnel	MCBTK	FCBTK	Zigzag	DDK	-
RSPCB [35]	-	-	0.33 %	0.3 %	0.3 %	-	-
Maithel et al. [36]	1.84 g/kg	2.45 g/kg	-	2.25 g/kg	1.47 g/kg	5.78 g/kg	-
Maithel et al. [69]	-	3.31 g/kg	-	2 g/kg	-	-	-
Maithel et al. [78]	1.8 g/kg	-	-	-	-	-	-
Maithel et al. [81]	-	-	-	-	-	5.78 g/kg	-
Maithel et al. [83]	-	-	-	2 g/kg	-	-	-
Maithel et al. [84]	-	-	-	-	1.6 g/kg	-	-
Manandhar and Dangol [122]	-	-	-	2.25 g/kg	-	-	-
Le and Oanh [127]	-	-	-	2.3 mg/Nm ³	-	-	-

Table 6: Measured suspended PM, CO₂, PM₁₀, SO₂, NO_x, Hydrocarbon and CO emissions for various brick firing technologies (obtained from literature).

for atmospheric emissions (Table 7). The technology with the highest potential for atmospheric emissions, BTK, was assigned a ranking of 8, while the DDK was assigned a ranking of 7. Tunnel kilns ranked in position 6, while position 5, 4, 3, 2 and 1 were assigned to FCBTK, Clamps, US coal-fired kilns, Zig-zag kilns and VSBKs respectively. It can be concluded based on available emission metrics, that the VSBK and the Zig-zag kilns have the lowest potential for atmospheric pollution; while the BTK and the DDK have the highest potential for atmospheric pollution.

Conclusion

Chemical reactions and thermodynamic processes occurring in the firing chamber of brick kilns have been qualitatively linked to the amount and type of pollutant emissions released at different period during the firing cycle. These reactions and processes include release of 'mechanical water' and 'combined water'; combustion of internal and external fuel; oxidation of carbonates in the clay material; oxidation conditions; and destruction or development of lattice structure and change in crystal phase of the clay material. Brick kiln emission concentrations and process metrics exhibit wide ranges of data variability during a firing cycle, implying that they are sensitive to these chemical reactions and thermodynamic processes. Brick kiln emission control efforts should therefore be aimed at modifying the combustion and firing process in order to alter the chemical reactions and thermodynamic processes in a way that will result in the release of lower quantity of emissions. These effective measures may include measures targeted at reducing the energy input in order to minimize release of atmospheric emissions; measures aimed at regulating the complex oxidation and reduction

Kiln Types	SO ₂	CO	NO _x	PM/PM ₁₀	CO ₂	Final Score	Final rank
DDK		6 ⁺		7 ^s	5 ^{##}	6 ⁺	7 ^s
Coal fired (US)	3 ^{***}	1 ⁺	2 ^{**}	6 ⁺		2.8 ^{**}	3 ^{***}
FCBTK	4 [#]	4 [#]		5 ^{##}	3 ^{***}	4 [#]	5 ^{##}
Clamps			1 ⁺	4 [#]	6 ⁺	3.8 [#]	4 [#]
Tunnel	5 ^{##}	5 ^{##}		3 ^{***}	4 [#]	4.4 [#]	6 ⁺
Zig-zag	1 ⁺	2 ^{**}		2 ^{**}	2 ^{**}	1.9 ^{**}	2 ^{**}
VSBK	2 ^{**}	3 ^{***}		1 ⁺	1 ⁺	1.6 ^{**}	1 ⁺
BTK				8 ⁻		8 ⁻	8 ⁻
Highest emissions Lowest emissions							
8 ⁻	7 ^s	6 ⁺	5 ^{##}	4 [#]	3 ^{***}	2 ^{**}	1 ⁺

Table 7: Ranking of various firing technologies based on available emission metrics.

reactions occurring in the firing chamber of the kiln; and measures aimed at regulating the complex thermodynamic processes in the firing chamber of the kiln. Kiln technologies were ranked from lowest to highest potential for atmospheric pollution based on available emission metrics as follows: Vertical shaft brick kiln<Zig-zag kiln<US coal-fired kiln<Clamp kiln<Fixed chimney Bull's trench kiln<Tunnel kiln<Down draft kiln<Bull's trench kiln.

Ambient air quality around a brick kiln facility is most likely to be affected by air pollution due to the localised effect of the emission on the immediate environment as a result of the lower height of release and the limited buoyancy of the relatively cool emissions (i.e. compared to other industrial processes). It is therefore expedient to identify the area around brick kiln operations which may potentially be affected by the release of these emissions. Consequently, in order to minimize

the effect of toxic emissions from brick making facilities (including health challenges to humans and animals, degeneration of land cover, loss of land, damage to agriculture, reduced visibility, depletion of soil nutrients, increased soil erosion, damage to buildings, contamination or acidification of surface and ground water systems); an impact or buffer zone (an area where residential occupation, agricultural and other activities should be restricted or minimized) may be delineated around brick kiln installations based on findings of site-specific air quality impact assessment studies.

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