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Compositional analysis of dark colored particulates homogeneously emitted with combustion gases (dark plumes) from brick making kilns situated in the area of Khyber Pakhtunkhwa, Pakistan

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ABSTRACT

In Pakistan raw coal and a little quantity of waste plastics are burnt to sustain high temperature inside brick making kilns. The gaseous emissions of the kilns contain a considerable amount of darkish colored particulates. It is currently believed that the plastic burning produces these particulates. Advanced characterization instruments, such as a scanning electron microscope, energy dispersive spectroscopy, X-ray fluorescence, X-ray diffractometer, surface area analyzer using nitrogen gas adsorption isotherms, and thermogravimetric analyzer, were used to find out the chemistry and physics of the particulates. At a magnification of 30,000x, the SEM picture shows masses that are roughly roundish in shape and their size is in between 0.1 to 0.5 microns. The elements detected in these particles are carbon, oxygen, and sulfur (EDS analysis), or in other words, these elements are a typical composition of raw coal. This elemental analysis suggest that fine coal particles come out with usual combustion gases and these emitted particulates are not plastic combustion product. To strengthen this finding, the sample when calcined discarded a significant amount of sulphur oxides species, as determined in the XRF study by noticing a considerable decrease of sulphur content in the calcined particles, suggesting that the particles are actually a coal. The N_2 isotherm graph reveals that the light weight flying coal particles has a very low surface area. Additionally, the XRD and TGA studies supports the conclusion that these dark colored particulate emissions are primarily fine coal particles (cenosphere).

1. Introduction

The brick making industry is in high demand in Pakistan. Making ceramic bricks is a systematic procedure that requires a well-maintained furnaces and trained labor. Khyber Pakhtunkhwa has an extensive history of producing high quality bricks [1-3]. For example, a large number of the buildings in our province are over a century old [4,5]. In Peshawar region, wet clay (90 weight percent), sand (5 weight percent), and coal dust (5 weight percent) are uniformly combined before being moulded into a standard sized bricks [6]. These soft green bricks are burned in trenched furnaces to temperatures ranging from 800 °C to 1100 °C after drying for one to three days in an open atmosphere [7]. Chemically, the structural strength is gained during heating, after which each cooked hard brick is physically removed and is then ready for use in building [8,9]. An average kiln unit can produce between 20,000 and 30,000 bricks per day. This low-tech industry is one of our country's fastest growing business. For example, the demand for quality bricks is increasing as a result of urbanization and infrastructure development projects, and in the near future the global construction industry is likely to exceed many folds [10,11].

Overall, maintaining a temperature of around 900 °C (±100 °C) within the kiln and an appropriate raw material composition (clay, for example) are critical for the manufacturing of quality bricks. This heating process takes place in the furnace trench, where the appropriate temperature (about 900 °C) is gradually achieved [12]. Fuel is usually a homogeneous mixture of waste plastic and coal as shown in Fig. 1 [13,14]. After calculating the cost of the burning, the proportion or weightage of each portion of combustible fuel is determined [14,15]. Here in our province, Fixed Chimney Bulls Trench Kilns (FCBTK) are the most popular furnace for heating the soft dried bricks [15].

Fig. 1. Fuel for the brick kiln, coal (on the left), and used plastics (right side).

Fig. 2 illustrates how the temperature differential or portions in the FCBTK can be divided into three zones. The preheating zone (500°C) comes first, followed by the firing zone (900°C–1100°C), and finally the cooling zone (around 25°C). These temperature zones are not fixed, and the actual firing zone changes over the trench. The dried bricks are correctly placed one above the other inside the U shape circular trench. In summary, in the presence of an initiating flame, a considerable solid fuel layer dispersed at the base of the brick stacks, as well as a small amount of oil poured over the solid fuel bed, help in catching fire. Finally, to maintain a good flame, an additional coal fuel is intermittently fed from the trench ceiling to maintain the necessary temperature for creating quality bricks [16].

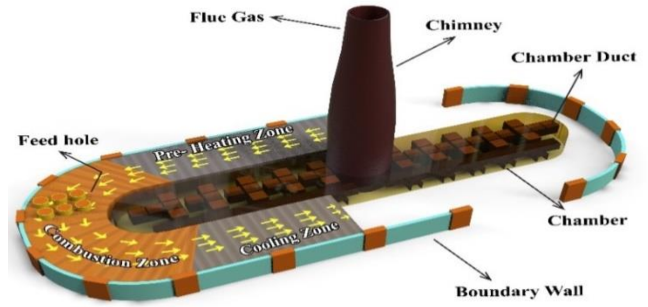

Fig. 2. An illustration of the fixed chimney bull's trench kiln's (FCBTK) layout, showing how the main trench is connected to tubular chambers.

The usage of huge furnaces is not a new phenomenon. Since 6000 BC, people have been using the advantages of controlled heating to create a variety of useful materials. A minimum required temperature must be maintained for a specific period of time in order to make structurally stronger ceramic products. In general, all different designs of the kiln are somewhat similar, that is soft bricks can be heated in a zigzag, tunnel, Haffman, and vertical shaft brick making kilns [17]. No matter what, low-quality fuel produces combustion gases with a complex composition that lead to black smoke stacks (Fig. 3). SOx, NOx, CO_2, CO, hydrocarbons, free carbon, and other hydrocarbon particles are the typical emissions of the coal combustions reactions [18,19]. These black clouds are hazardous to both animals and plants. Furthermore, these dark colored clouds get with the wind before settling or dispersing in areas with low pollutant concentrations. Currently, according to an environmental protection agency (EPA), winter smog is because of the emissions of the brick making furnaces [20].

Fig. 3. Emissions of gases and particles from a brick kiln.

In brief, the government and civil society are both concerned about the current rate of environmental contamination [21]. On the other side, thousands of middle-class families are employed in the bricks making industry. On social media, there have been a few unfortunate instances where government employees sprayed the furnace with water to put out the fire. The main accusation leveled against the furnace owners is that the plastic is burned in order to heat the kiln. Few business owners have ceased using waste polymers since they believe it to be the main cause of the dark emissions, but tragically, they are still having problems with the dark colored emissions.

Moreover, we are fully aware of the financial constraints faced by the majority of brick-making businesses and understand the impossibility of a large-scale technological replacement of the current furnace technology. Altering the purity of the fuel and installing efficient furnaces is a road map that requires effective execution plans and government support. The objective of our research was to determine the chemical composition of the released blackish particulates, which are currently assumed to be the result of burning plastics.

2. Methodology

2.1 Sample collection

Coal is the fuel used in the brick making business, and because it is not always of the same quality, the exhaust gas composition differs from industry to industry. The kiln chimney, which is usually 23 meters tall, maintains the air flowrate inside the kiln to ensure proper burning of the coal fuel. A number of scaffolds were carefully arranged to collect samples from the top end of the chimney (Fig. 4). Sample collection was one of the main tasks of the conducted study. Despite the fact that the gaseous emissions contain a range of gases, the blackish look of the smoke is particularly unattractive. Analysis of the physicochemical composition of these fine particles is the main objective of the present work. At the highest end of the chimney, the temperature of the gases from combustion byproducts, including particles, was approximately at 80 °C, and for this reason these particles were collected on a lab grade filter paper, which was placed in the path of the exhaust gas, because the filter paper ignition temperature is above 120 °C, making it safe to operate at the range of 80 °C.

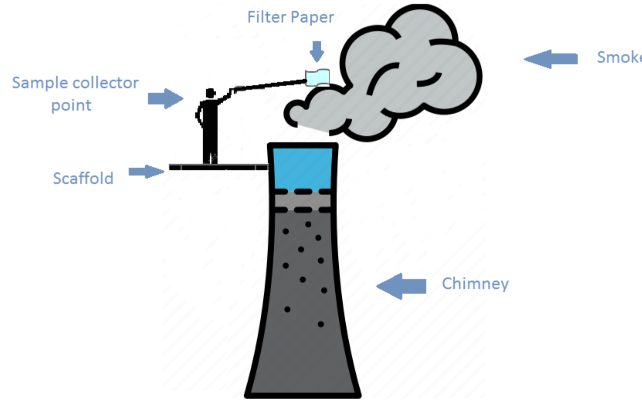

Fig. 4. Collecting samples from the exhaust.

2.2 Sample characterization

The scanning electron microscope (SEM) analyzer, model number JSM5910, JEOL Japan, was used to generate magnified images of the samples. The instrument can sustain ultra-high vacuum inside the sample holder chamber. Furthermore, because the sample is nonconductive or is insulator, thus it was first bounded with conductive carbon tape before being placed inside the sample holding chamber. A fast-moving electron beam was produced with a voltage of 30 kV. The secondary electrons of the sample produced the morphology images. An integrated, externally mounted energy dispersive X-ray (EDX) analyzer detected elements of the samples.

The silicon and aluminum elements of the sample particles were determined using the X-ray fluorescence spectroscopy (XRF) technique. The sample was crushed and sized into proper size pellets for the analysis. Binder is often used to keep the pellet intact, however in this experiment, the binder was avoided to reduce the possibility of presence of the unexpected metals. The Bruker S2 PUMA series equipment was used for the analysis.

The sample crystallinity and non-crystallinity were assessed using an X-ray diffractometer. The copper anode generated X-rays with monochromatic radiation of approximately 1.5 Å for getting the diffraction data. The analytical equipment is of Japanese made, model number JDX-3532. The detecting arm of the instrument varied with an angle ranging between 0 to 130 degrees. For the diffraction peaks, a sizable quantity of the sample was firmly inserted within the sample holder by following standard methodology.

The expose surface area of the sample was measured in Quanta chrome, using autosorb-IQ software. Before the analysis the sample was dried at about 105 °C in a thermal chamber. The chamber was connected to vacuum pump to extracts the adsorb moisture from the sample. About a full day was spent on the degassing procedure. After the sample mass measurement, nitrogen gas was adsorbed on the sample surface to determine the surface area per unit mass at a temperature of -195 °C. Ignoring the capillary condensation factor, the sample surface area was determined using the standard BET equation.

The particle sample was also subjected to a weight loss analysis while being heated continuously under controlled conditions in an inert atmosphere of nitrogen gas. The instrument used was a standard thermogravimetric analyzer of the Pyris diamond series manufactured by Perkin Elmer, United States. The gathered particles were put in a ceramic vessel and heated at a ramp rate of 5 °C/min from ambient temperature to 1000 °C. The data compared the amount of volatile and inorganic ash in the sample particles.

3. Results and Discussion

High magnification scanning electron microscopy (SEM) technique was used to determine the surface texture of the sample particles. These images were magnified to 500, 1000, 5000, and 30,000 times of the original size. As can be seen in Fig. 5, the topology primarily exhibits the roundish or bulgy entities on the external side of the surface. The outer margins or edges of the roundish objects glow because of the electron charging, as can be seen at magnifications of 500x, 1000x, and 5000x, indicating the presence of a substantial quantity of organic or nonmetallic material composition. These very fine smaller sized round bodies are illustrated in a zoomed image as shown in Fig. 5(d). The diameters of these tiny spherical masses are between 0.1 to 0.5 µm.

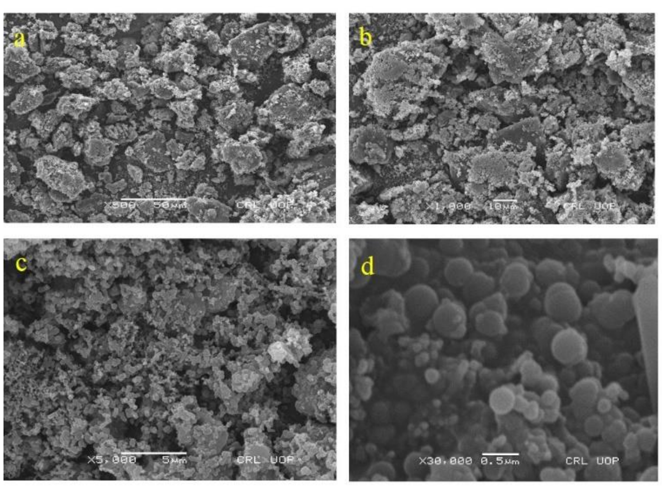

Fig. 5. SEM micrograph of the airborne particles at 500x, 1000x, 5000x, and 30000x magnifications (d).

The sample was subsequently tested in a same instrument with distinctive energy dispersive X-rays (EDX) to identify the elemental composition. The data collected suggests that carbon, oxygen, and sulfur are present in higher concentrations as compared to other elements. Untreated coal fuels usually contain significant amounts of sulfur. In addition, the presence of sulphur element in plastic materials is quite unlikely. This analysis proposes that the sample tested are actually coal particles that were not burned in the furnace and thus emitted along with the combusted gases. The finding is important since experts from Environmental Protection Agency of Pakistan think that the burning of discarded rubber or plastic produces particles, which give the stack emissions a blackish appearance.

Table 1

EDX examination of the gathered particle

Elemental composition	Wt. %	Atoms %
Carbon	66	78
Oxygen	14	13
Sodium	0.26	0.15
Magnesium	0.12	0.06
Aluminum	1.14	0.61
Silicon	1.91	0.97
Sulphur	10.3	4.6
Chlorine	0.25	0.11
Potassium	0.53	0.18
Calcium	1.53	0.56
Titanium	0.26	0.08
iron	2.11	0.56
Zinc	0.69	0.05
Total	100	100

These preliminary findings also indicates that unburned airborne coal particles of various sizes are extremely light in weight and were released into the atmosphere via the chimney. The XRF method of analysis was also employed to support the previously stated claim. In XRF, relatively low energy photons of carbon and oxygen cannot be detected as a normal spectrum. The atoms with atomic masses larger than sodium are the only ones that can be observed in a typical XRF instrument. The principal elements of the dark-colored sample are SiO_2, Fe_2O_3, and SO_3. However, in the presence of a significant amount of sulphur, the signal of aluminum photon emissions is too weak for the observation. The amount of SO_3 decreases to around 7.5 % from 28 % after heating the sample to a temperature of 600 °C. This compositional information (Table 2) demonstrates that the particulates are, in fact, tiny coal particles. This finding adds evidence to the concept that fine coal particles contribute significantly to dark emissions from the kiln chimneys.

Table 2

XRF analysis of the calcined sample, which was created by heating the vent sample to 600 °C, and the dark-colored particles, which were retrieved from the chimney's exhaust.

Sample		Sample when calcinated at a temperature of 600 °C	
Chemical Composition	Oxide (by weight)	Chemical Composition	Oxide units (by weight)
SiO_2	29.06	SiO_2	41.01
SO_3	28.04	Al_2O_3	22.96
Fe_2O_3	23.98	Fe_2O_3	14.69
CaO	9.05	CaO	7.78
K_2O	3.27	SO_3	7.57
ZnO	2.72	K_2O	2.77
TiO_2	2.42	TiO_2	1.77
PbO	0.12	ZnO	1
Sum	100 %	sum	100 %

The phase study of the sample using an ordinary goniometer revealed an amorphous structure. The literature suggests that the coal polymeric hydrocarbons are scattered randomly or other words is amorphous. Surprisingly, the same sample did not exhibit the crystallographic peaks when heated to a high temperature (600 °C) in order to completely eliminate the hydrocarbon component. The presence of the structural iron element was most likely the primary cause of the absence of crystalline peaks in the silicon and aluminum solid ash structure. The amorphous form of the material following the calcination is demonstrated in Fig. 6.

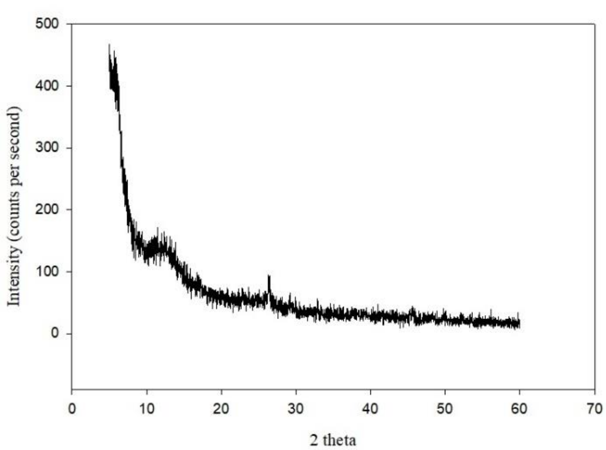

Fig. 6. Calcined particle sample's XRD image.

The sample was simply heated to a temperature of 105 °C in order to degas it from any surface adsorbed compounds for the study of surface areas. This removal of adsorbed species (mainly moisture) was under the vacuum. Because the sample is chemically a hydrocarbon, there is always a chance that heating for a lengthy period of time (24 h) could alter the surface morphology to some value. In any case, the standard BET equation does not appropriately characterize the extremely small surface areas. However, if we assume that the nitrogen gas that is being absorbed forms a monolayer, the surface area determined using the BET equation is about 3.5 m^2g^{-1}. Additionally, it appears that the surface contains relatively few holes or nonporous because the release of attached nitrogen gas (desorption behavior, Fig.7) produced almost the same data pattern.

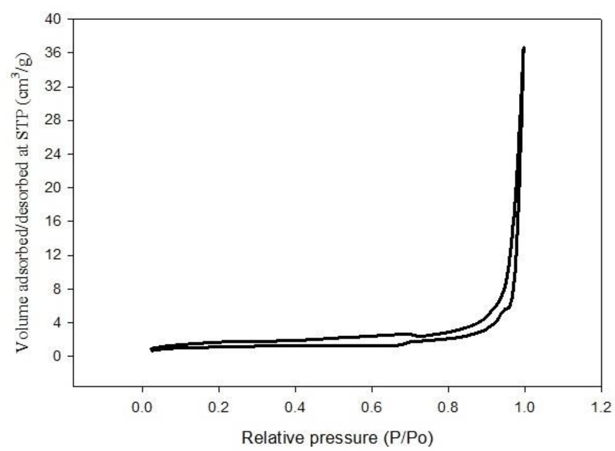

Fig. 7. Nitrogen adsorption at a temperature of -195 °C (isothermal curve).

Fig. 8 depicts a mass loss analysis with increasing temperature. The stained data points are characteristic of a coal pyrolysis. Mass loss zones can be split into three distinct phases or zones. These are, water evaporation, or the elimination of moisture, occurs in the zone where there is a small mass loss of around 5 %, which is between 100 °C and 200 °C. The actual hydrocarbon loss is at a temperature rise of 650 °C. The smaller hydrocarbon chains are eliminated first, followed by relatively larger polymeric chains, which are taken away by the inert nitrogen flowing over the sample. In general, a mass loss of 60 % appears in a steeper curve range.

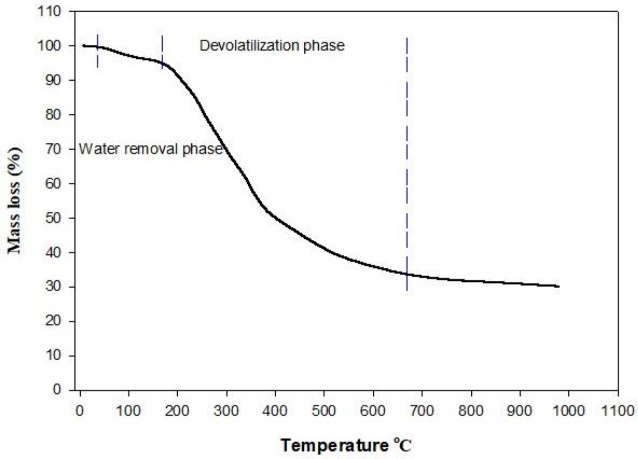

Fig. 8. TGA analysis of the collected particulates

4. Conclusion

Thousands of underprivileged Pakistanis are employed in the brick making industry. Currently, brick kilns are considered to be the prime reason for the smog formation. Massive amounts of black particles are released into the air when low quality (unprocessed) coal is burned. The environmental officials have an opinion that the burning of the discarded plastics produces the dark colored emissions. In addition to cutting expenses, using waste biomass expands the fire flames, which are critical for the strength of the top stacked bricks arranged inside the kiln trench. To determine the chemistry of the dark brown particles, we used a wide range of sophisticated analytical tools. In the SEM images, the dark particles appear to be round. The presence of carbon, oxygen, and sulphur was detected using EDS, while silicon, aluminium, and iron were determined using the XRF instrument. Coal deposit contains these elements. Our data show that coal accounts for the majority of fine particles released from chimneys, disproving the popular theory that black emissions from brick kiln chimneys are generated by the use of discarded plastic as fuel.

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