Micro-characterization of Dust and Materials of Dust Origin at a Cement Industry located in Bangladesh

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Abstract

Industrial dust generation from material processing is an uninterrupted phenomenon, hence analyzing materials of dust origin with dust particles is important to comprehend the entire scenario of occupational health exposure (OHE). In this study, we investigated the morphological, elemental, and mineralogical characteristics of engendered dust and materials of dust origin in the cement industry (CI) in Bangladesh. The dust samples were accumulated from dust collectors and the internal roadways of the CI to understand the nature of atmospheric dust of the CI. All the materials that could potentially be the sources of the dust of the CI were collected, including clinker, gypsum, limestone, fly ash, slag, and two types of cement products. Scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), x-ray powder diffraction (XRD), and fourier-transform infrared spectroscopy (FTIR) were performed for the characterization. SEM micrographs showed the presence of fine (particles ≤ PM 2.5) and ultra-fine (particles ≤ PM 0.1) particles with diverse morphology in the studied samples. Ca, Si, Al, Mg, Fe, K, Na, Mo, and Ti were found as existing metallic elements in samples through the EDS technique. Several minerals of silicate, oxide, carbonate, and sulfate were detected with major crystalline phases of Portland cement by SEM-EDS, XRD, and FTIR analyses in samples; among which some are well documented as occupational hazards. The trace presence of organic carbon was observed in all FTIR spectra. The most significant outcome of this study is the detection of carcinogenic substances such as crystalline silica (quartz, cristobalite) and asbestoses (anthophyllite, chrysotile, and crocidolite) in samples. For instance, quartz was found in the dust of dust collectors while road dust of the CI showed the existence of both quartz and cristobalite. However, asbestoses were found only in source materials, but they could be released anytime during material handling, thus creating OHE.

Keywords: occupational health exposure, SEM-EDS, XRD, FTIR, crystalline silica, asbestos

1. INTRODUCTION

Cement is vital worldwide as a construction material. During cement production, raw materials (limestone, shale, clay, sand, etc.) are ground and heated into a kiln to form the clinker, clinkers are
then blended with gypsum or other supplementary cementitious materials, and finally reduced to a fine powder to formulate the cement. This entire process generates enormous pollutants in the atmosphere, creating health and environmental hazards. Typical atmospheric emissions of a cement industry (CI) include oxides of nitrogen, sulfur dioxide, oxides of carbon, dust particles, and some trace elements (Allaban and Qudais, 2011). Clinker formation acts as the principal source of gaseous pollutants while dust particles can be generated throughout the cement production process. Quarrying, crushing, and storage of raw materials; clinker production; finish grinding; packaging; and transport of products are reported as possible emission sources of dust generation at CI. (Huang et al., 1996; Zhang et al., 2015).

Exposure to cement dust may result in adverse health effects. Several studies stated skin irritation, wheezing, increased mucus production, asthma, bronchiectasis, pneumoconiosis, chronic obstructive pulmonary disease (COPD), preterm delivery, psychasthenia, endocrine disruption, infertility, and carcinoma of the lungs, stomach, and colon as cement dust-related health issues (Huang et al., 1996; Meo, 2004; Tolinggi et al., 2014; Adeyanju and Okeke, 2019).

The health risks at a dusty occupation is primarily linked with the harmful physical, elemental, and mineralogical features of the dust particles. (Bickis, 1998). For instance, particles having a diameter ≤ 10 μm can deposit in the upper respiratory tract whereas particles with diameter ≤ 2.5 μm can penetrate the lungs and particles with diameter ≤ 0.1 μm can further reach into the alveolar region of the lungs, respectively (Park and Wexler, 2008; Valiulis et al., 2008). Particle shape is also an influencing factor for particle deposition in respiratory system. Thus, determination of particle morphology is vital.

Dust may contain metallic elements that are potentially hazardous to health (Kicińska, 2016). However, metals in particles can mediate toxicity with their existing chemical features.(Oberdörster, 1993; Dick et al., 2003). For example, iron (Fe) is an essential nutrient for human health, but the
breathing of Fe-bearing particles can stimulate reactive oxygen species on the lung surface, which may further lead to scarring of the lung tissue (Knaapen et al., 2004; Mohiuddin et al., 2014). Mineralogical structure often distinguishes the degree of toxicity in dust particles, such as, crystalline silica is categorized as group 1 carcinogen by International Agency for Research on Cancer (IARC) and is significantly harmful than amorphous silica on long term inhalation (Sandberg et al., 2012; Suryadevara, 2016). Hence, understanding the elemental distribution and mineralogical structure of dust particles is crucial.

Dust generated at CI may contain hazardous minerals like crystalline silica, asbestiform, and gypsum with metallic elements (Ca, Al, Fe, Mg, etc.) (Neupane, 2020). Occupational exposure to respirable crystalline silica includes silicosis, tuberculosis, chronic bronchitis, and lung cancer (Merget et al., 2002; Calvert et al., 2003). Chronic asbestos exposure may cause two principal types of lung cancer: cancer of the lung tissue itself and mesothelioma, which is a rare form of cancer found in the thin lining of the lung, chest, abdomen, and heart (Koskinen et al., 2002; Berman and Crump, 2008). Asbestos may also cause a serious progressive, long-term, and non-cancer lung disease called asbestosis (Wyers, 1949). Phlegm and dyspnea, irritation of mucous membranes and upper respiratory tract, cough, sneeze, and runny nose have been reported as a result of long-term exposure to gypsum dust (Neghab, 2015). Dust particles bearing these metallic elements may also cause health impacts. Hence, physical, chemical, and mineralogical characterization of dust particles at CI is essential in regard to evaluate their health impacts on workers.

We selected a CI located in Bangladesh to collect the required samples. Bangladesh has a scarcity of mineral resources and hence is highly dependent on imported raw materials including clinker for cement production. Only two companies among forty-two in Bangladesh have clinker production
facilities at their plants, the rest of them import materials and use grinding technology to produce cement. The selected CI imports the clinker and the other raw materials as well and produces ordinary portland cement (OPC) and portland composite cement (PCC) as two main cement products. OPC is manufactured here by adding 5% gypsum to 95% clinker whereas 3.5% gypsum, 4% limestone, 8.5% slag, and 22% fly ash are added to 62% clinker for PCC.

Bag filters are installed at required points of CI to capture the generated dust. Beyond the control efficiency of the bag filter or due to poor occupational management during material handling, dust may still be released into the atmosphere and even some of them may deposit on the internal roadways of the CI. Therefore, the study collected dust from the bag filters and the roadways to understand the nature of atmospheric dust in the CI. Since the dust generation from material processing is a continuous activity, so to comprehend the total scenario of the OHE in the CI we also analyzed the materials (clinker, gypsum, limestone, slag, fly ash, OPC, and PCC) that could be associated with the dust origin. Consequently, the collection and analysis of generated dust and materials of dust origin in the selected CI located in Bangladesh were carried out focusing on:

1. Observation of existing fine and ultra-fine particles with shape diversity in studied samples
2. Detection of metallic elements in studied samples
3. Identification of existing crystalline phases, organic and inorganic compounds in studied samples

The outcome of the analysis was the basis of determining the potentially harmful metallic elements, minerals, organic and inorganic compounds in the generated dust and materials of dust origin in the CI of Bangladesh that may cause occupational health hazards unless any safety initiatives were taken. The samples were analyzed using SEM-EDS, XRD, and FTIR techniques.

2. METHODS
2.1 Study Location

Khulna is the south-western divisional city of Bangladesh. The selected CI is located in the Labanchara area nearby the renowned Rupsha River of Khulna city (Fig. 1). Labanchara is mainly an industrial zone assembled with different industries such as fish processing industries, Bangladesh Oxygen Company, Khulna Shipyard, Bangladesh Match Factory, and so on.

Fig. 1. Labanchara CI in Khulna City (taken from Google Earth)
2.2 Sample Collection

The study collected bag filtered dust (BFD) and deposited road dust (DRD) to understand the nature of atmospheric dust at the Labanchara CI. The samples of BFD were accumulated from different bag filters located at the CI, and later were mixed. The samples of DRD were collected from three different of spots of the CI also and then got mixed. Materials that could be associated with the origin of generated dust at the Labanchara CI were gathered for the analysis which include clinker, gypsum, limestone, slag, fly ash, OPC, and PCC. So, total nine samples were collected cautiously in some air tight containers from the Labanchara CI and analyzed by SEM-EDS, XRD, and FTIR techniques. SEM-EDS was performed to obtain the microscopic view of particle morphology with the elemental distribution. XRD analysis was accomplished to identify mineral constituents while FTIR analysis was done to determine compounds both in amorphous and crystalline phases here. SEM-EDS also supported the outcome of the XRD and FTIR analyses.

2.2 Scanning Electron Microscopic with Energy Dispersive X-ray Spectroscopic Analysis

Scanning electron microscopic with energy dispersive x-ray spectroscopic (SEM-EDS) analysis was carried out using scanning electron microscope (JEOL JSM 6490 LA), equipped with an energy dispersive X-ray spectrometer (JED 2300 Analysis Station). To achieve the SEM micrographs, samples were mounted on aluminum stubs with double-sided sticky carbon tape. A very thin platinum coat was applied to the sample surface to increase the conductivity. The samples were then introduced into the vacuum chamber and subsequently, digital images were obtained. Three images of each sample were taken at different magnifications by stereo SEM at 30 tilts. Elemental analysis was accomplished of bulk samples by detecting characteristic X-rays generated from samples. The dry silicon drift detector of EDS had an acquisition rate of 2504 cps with a resolution of 20 keV. The detection limit of the detector was around 0.1% wt. The ZAF correction
was applied to EDS data for the semi-quantification of elements. Here, Z, A, and F refers to the atomic power, absorption correction, and fluorescence correction respectively.

2.3 X-ray Diffraction Analysis

In X-ray diffraction (XRD) analysis, the samples were placed into the ground glass depression of a sample holder and positioned onto the X-ray diffractometer (Rigaku Ultima-IV). The X-ray source was a Cu Kα line with a wavelength of 1.54 Å, and the data were collected at Bragg angle 2θ ranging from 10° to 80°. A specific mineral usually generates a characteristic pattern through XRD analysis. RRUFF™ project provides a complete sets of high-quality spectral data including XRD patterns of well-characterized minerals, which can be used as a standard for mineral identification (Lafuente et al., 2015). Currently it contains about 7000 mineral samples representing 3500 mineral species. This study primarily followed the RRUFF database as a standard reference to detect the minerals in samples, by comparing the peak positions at 2θ with corresponding d spacing. In addition, literature studies were followed to confirm a few minerals.

2.4 Fourier-Transform Infrared Spectroscopic Analysis

For fourier-transform infrared spectroscopic (FTIR) analysis, collected ground samples were mixed with an infrared transparent soft salt i.e., potassium bromide (KBr), with a ratio of 20:1. The mixer was then pelletized using hydraulic pressure of 10 tons. KBr based pellets were then analyzed using Shimadzu FTIR-8400s spectrophotometer. The spectral resolution of the spectrometer was 4 cm⁻¹. The infrared (IR) spectra were obtained in the range of 4000–500 cm⁻¹, with an average of 32 scans. The data were collected in attenuated total reflectance (ATR) mode. Identification of minerals and compounds was done accordant with literature studies.

3. RESULTS AND DISCUSSION
3.1 SEM-EDS Analysis

Particles with diverse morphology varying from 0.1 ~ 15µm were observed in SEM micrographs of studied samples (Fig. 2-5) here. EDS analysis simultaneously detected Ca, Si, Al, Mg, Fe, Mo, Ti, K, Na as metallic elements and O, C, S as non-metallic elements, as shown in Table 1.

![SEM micrographs of gypsum and limestone](image)

**Fig. 2 (a-b).** SEM micrographs of gypsum and limestone

Particles with tabular, prismatic, acicular, or massive nature viewed in the micrograph of gypsum (Fig. 2a) indicate the gypsum minerals (CaSO4·2H2O) while silica (SiO2) is observed as clustered form dispersed in between gypsum (Ausset et al., 2000; Shih et al., 2005; Ashrit et al., 2015) Irregular-angular to quasi-spherical shape with rough surface seen in Fig. 2a can be the particles of alumina (Al2O3) and the cubic or rectangular shape might be signifying the molybdenum metal (Mo) (Laha et al., 2005; Yehia et al., 2020). Calcite (CaCO3) and dolomite (CaMg(CO3)2) are the primary minerals of limestone (Zhang and Lv, 2020). Particles of both calcite and dolomite possess layered rhombohedral shape under the microscope, which are abundantly seen in the SEM image of limestone (Fig. 2b) (Yip et al., 2008; Kasha et al., 2015). Small round and angular-shaped
particles might be indicative of silica and alumina respectively, as they may exist as impurities in limestone (Dey et al., 2020). Fine and ultrafine particles are spotted in Fig. 2(a) and Fig. 2(b). The elemental distribution of gypsum and limestone is consistent with these findings (Table 1).

![SEM micrographs of fly ash and slag](image)

**Fig. 3 (a-d).** SEM micrographs of fly ash and slag

The predominant presence of microspheres is found in the SEM images of fly ash (Fig. 3 a-b). Microspheres in fly ash result from the sintering of ash at high combustion temperature, and aluminosilicate glass, mullite, quartz, iron oxides, calcium sulfates, etc. are usually observed as their major
phases (Żyrkowski et al., 2016; Zong et al., 2019). These microspheres may consist of Fe alloys with admixtures of Pb and Ba; or are sometimes composed of entirely of carbon (Kicińska and Bożęcki, 2017). The irregular grains with hollow features primarily indicate mullite-sillimanite minerals (3Al₂O₃.2SiO₂) (Tazaki et al., 1989; Zong et al., 2019). The particle of nearly hexagonal shape viewed in fly ash micrograph (Fig. 3a) might be signifying kaolinite (Al₂Si₂O₅(OH)₄) (Tazaki et al., 1989). K and Ti found in elemental analysis of sampled fly ash, were commonly reported as minor elements of coal fly ash in earlier studies (Martinez-Tarazona and Spears, 1996; Rautray et al., 2009; Tiwari et al., 2014).

Ground granulated blast-furnace slag (GGBFS) is used in the CI due to its high cementitious properties. The presence of Ca, Si, Al, Mg, O as major elements in EDS data implies the sampled slag is a blast furnace slag (Grubeša et al., 2016). Glassy or crystalline phases of gehlenite, akermanite, merwinitc, rankinite (Ca₃Si₂O₇), and wollastonite (CaSiO₃) are to be generally present in GGBFS (Snellings et al., 2012; Tripathy et al., 2020). Akermanite, rankinite, and wollastonite can be spotted by the structure with elongated, plate-like, and stick shapes respectively while gehlenite with irregular shapes, in slag micrograph (Fig. 3a) (Sofilić et al., 2013; Wilczyńska-Michalik et al., 2015). Fig. 3(b) and Fig. 3(d) are showing particles with diameter ranging from 10 to 0.1 µm. The elemental distribution of fly ash and slag has shown similar findings (Table 1). However, molybdenum found in the sample of slag is considered as the most valuable element that can exist in slag (Parada et al., 2009).

Alite (Ca₃SiO₅), belite (Ca₂SiO₄), aluminate (Ca₃Al₂O₆), and ferrite (Ca₄Al₂Fe₂O₁₀) are the typical mineral phases of portland cement. The small roundish particles seen in microscopic images of clinker, PCC, and OPC (Fig. 4 a-c) are the belite minerals while euhedral to anhedral-shaped particles usually bigger than belite are the alite minerals (Kolovos et al., 2005; Stutzman...
et al., 2016). The elongated or prismatic particles indicate ferrite phases whereas aluminates are seen as fine to lath-like crystals consisting of a matrix between ferrite crystals (Stutzman et al., 2016). Periclase and alkali sulfates (arcanite, thenardite, etc.) might appear in the dark zone like the voids (Stutzman et al., 2016). Free lime might be seen as bright small round shapes or sometimes as clustered form (Stutzman et al., 2016). Asbestos is the fibrous silicate mineral and particles with acicular shape seen in OPC might be indicating asbestos. SEM images of PCC basically presents particles with different morphology originated form the supplementary materials (slag, fly ash, limestone) in addition to clinker and gypsum.

![SEM images of Clinker and OPC with various phases](image-url)
Fig. 4 (a-c). SEM micrographs of clinker, OPC, and PCC

Apparently, the BFD micrograph (Fig. 5a) exhibited irregularly fume-shaped particles. The particles of BFD might be very fine, to be detected with their actual morphology in microscales. EDS analysis found Ca, Si, Al, Fe, Mg, Mo, K, O, and C as existed elements in BFD. Particles with irregular and rounded shapes observed in the DRD micrograph (Fig. 5b) might be indicating soil-derived minerals and quartz. Kaolinite is seen as the nearly hexagonal shape ranges more than 15 microns in Fig. 5b. EDS data showed the abundance of Si, Al, and O elements in DRD. The presence of a significant amount of Na may indicate clayey minerals such as albite, beidellite, etc.
**Fig. 5 (a-b).** SEM micrographs of BFD and DRD

**Table 1.** Semi-quantitative Elemental Analysis of Samples by SEM-EDS technique

<table>
<thead>
<tr>
<th>Name of the Samples</th>
<th>Atomic weight percentage of different elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Clinker</td>
<td>16.20</td>
</tr>
<tr>
<td>Gypsum</td>
<td>7.32</td>
</tr>
<tr>
<td>fly ash</td>
<td>-</td>
</tr>
<tr>
<td>Slag</td>
<td>10.35</td>
</tr>
<tr>
<td>Limestone</td>
<td>12.39</td>
</tr>
<tr>
<td>OPC</td>
<td>17.11</td>
</tr>
<tr>
<td>PCC</td>
<td>38.61</td>
</tr>
<tr>
<td>BFD</td>
<td>10.00</td>
</tr>
</tbody>
</table>
XRD Analysis

XRD is one of the highly applied techniques to determine the mineralogical composition in materials. The minerals detected in studied samples by XRD analysis are presented in Table 2 with their corresponding diffraction peaks (2θ values) and d-spacings. Fig. 6 and Fig. 7 exhibit the XRD diffractograms of all collected samples.

Fig. 6. XRD diffractograms of studied samples

The silicate minerals are the primary concern because of their relative abundance and significance (Kumar and Rajkumar, 2014). Quartz, mullite-sillimanite, rankinite, wollastonite,
albite, beidellite, kaolinite, microcline, anthophyllite, and serpentine minerals were found as existing silicate minerals here along with Portland cement-based calcium silicate phases (alite, belite, aluminate, and ferrite). Alite, belite, aluminate, and ferrite were detected in OPC, PCC, clinker, and BFD (Jadhav and Debnath, 2011; Sedaghat et al., 2014). Anthophyllite is an amphibole mineral from the inosilicate group, contains the chemical formula: □Mg2Mg5Si8O22(OH)2 (□ is for a vacancy, a point defect in the crystal structure), might also be present in four of them (Lafuente et al., 2015). Serpentine is the group of hydrous magnesium-rich phyllosilicate minerals, and a diffraction peak at 12.18° at 2θ in the XRD pattern of OPC indicates the existence of serpentine minerals (Lafuente et al., 2015). Chrysotile, antigorite, and lizardite are three of the primary serpentine minerals and their composition approximates Mg3Si2O5(OH)4.

The most common form of crystalline silica, quartz was detected in samples of PCC, gypsum, fly ash, limestone, BFD, and DRD (Lafuente et al., 2015; Neupane et al., 2020). Cristobalite is another polymorph of crystalline silica that is formed at very high temperatures, found to be present in DRD (Yusan et al., 2012; Lafuente et al., 2015). Experimental evidence shows cristobalite and quartz as more cytotoxic than other polymorphic forms of crystalline silica (Meldrum and Howden, 2002). The XRD diffractogram of fly ash revealed the abundance of mullite-sillimanite minerals (Jozić et al., 2010; Lafuente et al., 2015). Both sillimanite and mullite have similar d-spacings but their compositions are different; sillimanite is Al2O3·SiO2 while mullite is 1.6 - 1.9 Al2O3·SiO2 (Tazaki et al., 1989). The respiratory hazard of mullite or sillimanite is little known, although one study cited chronic bronchitis, silico-tuberculosis, and pneumoconiosis as occupational exposure of mullite (Artamonova et al., 2000). In addition, Brown et al. (2011) stated mullite as a potential respiratory hazard in their study.
Typical GGBFS minerals i.e., akermanite, gehlenite, rankinite, merwinite, and wollastonite usually produce major diffraction peaks between 20°– 40° at 2θ range during XRD analysis (Kasina et al., 2014; Lafuente et al., 2015). The presence of a broad hump in the range of 20°– 40° at 2θ with only two discrete maxima indicates the glassy nature of sampled slag. The distinct peak at 30.5° at 2θ in slag XRD pattern might be attributed to akermanite or rankinite, or wollastonite crystals. Albite (NaAlSi₃O₈) and microcline (KAlSi₃O₈) are Na-rich plagioclase feldspar and K-rich alkali feldspar respectively and belong to the tectosilicate mineral group. The obvious presence of albite was found in DRD with a trace amount of microcline (Feng et al., 2012; Lafuente et al., 2015). Two clayey minerals from the phyllosilicate group i.e., beidellite and kaolinite were also detected in DRD (Lafuente et al., 2015; Neupane et al., 2020). Beidellite contains chemical formula as (Na,Ca)₀.₃Al₂(Si,Al)₄O₁₀(OH)₂·nH₂O.

The study found the existence of dolomite and three main polymorphs of calcium carbonates i.e., vaterite, aragonite, calcite, as carbonate minerals in samples. Calcite is the most stable polymorph of calcium carbonate found as governing mineral in the sampled limestone (Jadhav and Debnath, 2011; Lafuente et al., 2015). The samples of OPC, PCC, clinker, and BFD also indicated the existence of calcite. Aragonite is preferred phase of calcium carbonates at high pressures and low temperatures and was detected only in BFD (Lafuente et al., 2015). The high pressure of the bag-filter might cause the alteration of calcite into aragonite. The presence of the vaterite was observed in DRD (Lafuente et al., 2015). Dolomite is composed of calcium magnesium carbonate and was noticed in limestone (Stutzman et al., 2016). A case study by Mishra et al. (2004) stated that prolonged exposure to dust in mines of limestone and dolomite might have caused tuberculosis in several workers.
The occurrence of gypsum mineral was evidently identified in the sample of gypsum (Jadhav and Debnath, 2011; Stutzman et al., 2016). Mineral of gypsum was also found in OPC, PCC, clinker, and BFD. Arcanite (K₂SO₄) is a sulfate mineral, usually known as alkali when exists in cementitious materials. The presence of arcanite was noticed in PCC, fly ash, and BFD (Lafuente et al., 2015; Stutzman et al., 2016).

Corundum (Al₂O₃), periclase (MgO), hematite (Fe₂O₃), brookite (TiO₂), and molybdite (MoO₃) were the found as oxide minerals in samples. The crystalline form of aluminum oxide, known as corundum, was observed in gypsum, limestone, BFD, and DRD (Lafuente et al., 2015). The samples of OPC, PCC, clinker, and BFD showed the presence of both periclase and hematite (Behera and Sarkar, 2016; Cvetković et al., 2018). Periclase and hematite were also detected in slag and fly ash respectively. Wüstite (FeO) is another mineral form of iron oxide like hematite and might exist in slag (Shao et al., 2015). Inhalation of respirable calcite can irritate eyes, skins, lungs, and its higher exposure may cause pulmonary edema (Manisalidis et al., 2020). Breathing of alumina dust can generate local inflammation in the respiratory tract which may lead to occupational asthma and fibrosis (Haleatek et al., 2005). Inhaling magnesia and iron oxides fume can cause metal fume fever flu-like illness with symptoms of cough, fever, chills, malaise, and myalgias (Drinker et al., 1927; Mueller and Seger, 1985). Chronic exposure to iron oxides fume might instigate fibrotic pulmonary changes (Jones and Warner, 1972).

Brookite is the orthorhombic variant of titanium dioxide, and the characteristic peaks of brookite were observed in the XRD pattern of fly ash (Lafuente et al., 2015). XRD diffractogram of BFD showed the presence of molybdite, a natural mineral form of molybdenum trioxide (Alemán-Vázquez et al., 2005; Lafuente et al., 2015). In addition, the study found the occurrence of molybdenum metal in gypsum (Lafuente et al., 2015; Pandharkar et al., 2018). Molybdenum
trioxide is classified as possible carcinogen (Group 2B) while high concentrations of molybdenum metal may irritate the upper respiratory tract and cause a gout-like syndrome in the human body (Koval'skii et al., 1961; Barceloux and Barceloux, 1999). In addition, several studies reported that nanoparticles of titania accumulate in the lungs, alimentary tract, liver, heart, spleen, kidneys, and cardiac muscle after inhalation or oral exposure (Wójcik et al., 2020).

Table 2. Mineralogical Analysis of Studied Samples by XRD

<table>
<thead>
<tr>
<th>Assigned minerals</th>
<th>Name of the samples</th>
<th>Major peaks at 2θ (°)</th>
<th>d-spacings (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alite</td>
<td>OPC, PCC, clinker, BFD</td>
<td>29.32, 29.33, 29.36, 29.37, 30.00, 30.01, 30.03, 51.61, 51.65, 51.67, 51.69</td>
<td>3.043, 3.042, 3.039, 3.037, 2.976, 2.975, 2.974, 2.972, 1.769, 1.768, 1.767, 1.767</td>
</tr>
<tr>
<td>belite</td>
<td>OPC, PCC, clinker, BFD</td>
<td>32.47, 32.51, 32.55, 34.28, 34.31, 34.33, 41.18, 41.25, 41.26, 41.27</td>
<td>2.754, 2.751, 2.748, 2.613, 2.611, 2.609, 2.190, 2.186, 2.185, 2.185</td>
</tr>
<tr>
<td>aluminate</td>
<td>OPC, PCC, clinker, BFD</td>
<td>33.13, 33.17, 33.20, 33.22, 47.15; 47.28</td>
<td>2.702, 2.699, 2.696, 2.695, 1.926, 1.921</td>
</tr>
<tr>
<td>ferrite</td>
<td>OPC, PCC, clinker, BFD</td>
<td>12.18, 32.10, 32.14, 32.18, 32.21, 33.79, 33.82, 33.84, 33.88</td>
<td>7.264, 2.785, 2.782, 2.779, 2.776, 2.651, 2.648, 2.647, 2.643</td>
</tr>
<tr>
<td>cristobalite</td>
<td>DRD</td>
<td>22.047, 36.018</td>
<td>4.028, 2.491</td>
</tr>
<tr>
<td>mullite-sillimanite</td>
<td>fly ash</td>
<td>16.41, 26.21, 26.60, 30.88, 33.18, 35.15, 40.80, 42.47, 60.56, 64.51</td>
<td>5.396, 3.397, 3.347, 2.892, 2.697, 2.551, 2.209, 2.126, 1.527, 1.443</td>
</tr>
<tr>
<td>rankinite/wollastonite</td>
<td>slag</td>
<td>30.5</td>
<td>2.927</td>
</tr>
<tr>
<td>albite</td>
<td>DRD</td>
<td>13.67, 13.87, 22.04, 27.90, 27.98</td>
<td>6.468, 6.468, 4.028, 3.194, 3.185</td>
</tr>
<tr>
<td>kaolinite</td>
<td>DRD</td>
<td>12.56, 17.8, 40.32, 45.45, 50.16</td>
<td>7.036, 4.971, 2.234, 1.993, 1.816</td>
</tr>
<tr>
<td>Assigned minerals</td>
<td>Name of the samples</td>
<td>Major peaks at 2θ (°)</td>
<td>d-spacings (Å)</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------</td>
<td>-----------------------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>beidellite</td>
<td>DRD</td>
<td>18.84, 26.84, 29.90</td>
<td>4.706, 3.318, 2.985</td>
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<tr>
<td>microcline</td>
<td>DRD</td>
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<td>serpentine minerals</td>
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<td>anthophyllite</td>
<td>OPC, PCC, clinker, BFD</td>
<td>29.32, 29.33, 29.36, 29.37, 22.93, 22.88, 22.88</td>
<td>3.876, 3.884, 3.882, 3.043, 3.042, 3.039, 3.037</td>
</tr>
<tr>
<td>calcite</td>
<td>OPC, PCC, clinker, limestone, BFD</td>
<td>23.04, 29.32, 29.33, 29.36, 29.37, 29.39, 29.90, 47.51, 48.47, 48.50</td>
<td>3.856, 3.043, 3.042, 3.039, 3.037, 3.035, 1.927, 1.876, 1.875</td>
</tr>
<tr>
<td>aragonite</td>
<td>BFD</td>
<td>26.60, 27.15, 33.13, 45.77</td>
<td>3.348, 3.282, 2.702, 1.980</td>
</tr>
<tr>
<td>vaterite</td>
<td>DRD</td>
<td>20.87, 25.23, 27.49, 43.25</td>
<td>4.251, 3.527, 3.242, 2.090</td>
</tr>
<tr>
<td>dolomite</td>
<td>limestone</td>
<td>30.93, 41.12, 44.91</td>
<td>2.887, 2.192, 2.016</td>
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<tr>
<td>brookite</td>
<td>fly ash</td>
<td>25.94, 30.88, 36.50</td>
<td>3.432, 2.89, 2.45</td>
</tr>
<tr>
<td>periclase</td>
<td>OPC, PCC, clinker, limestone, BFD</td>
<td>43.12, 43.14, 43.16, 43.16, 62.15, 62.21, 62.30, 62.33</td>
<td>2.096, 2.095, 2.094, 2.094, 1.491, 1.493, 1.489, 1.488</td>
</tr>
<tr>
<td>hematite</td>
<td>OPC, PCC, clinker, fly ash, BFD</td>
<td>33.13, 33.17, 33.18, 33.20, 49.37, 49.72, 49.86, 49.94, 49.99</td>
<td>2.702, 2.699, 2.696, 2.695, 1.844, 1.832, 1.827, 1.824, 1.823</td>
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<tr>
<td>wüstite</td>
<td>slag</td>
<td>42.7</td>
<td>2.115</td>
</tr>
<tr>
<td>alumina</td>
<td>fly ash, gypsum, limestone, BFD, DRD</td>
<td>25.49, 35.15, 35.34, 43.12, 43.14, 43.16, 43.25, 57.33, 57.47, 57.48, 57.56</td>
<td>3.491, 2.551, 2.537, 2.095, 2.094, 2.092, 1.604, 1.602, 1.602, 1.600</td>
</tr>
<tr>
<td>arcanite</td>
<td>PCC, fly ash, BFD</td>
<td>30.92, 30.88, 31.00</td>
<td>2.889, 2.892, 2.883</td>
</tr>
<tr>
<td>molybdite</td>
<td>BFD</td>
<td>27.15</td>
<td>3.28</td>
</tr>
<tr>
<td>Assigned minerals</td>
<td>Name of the samples</td>
<td>Major peaks at 2θ (°)</td>
<td>d-spacings (Å)</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------</td>
<td>----------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>molybdenum</td>
<td>gypsum</td>
<td>40.59, 58.10</td>
<td>2.220, 58.103</td>
</tr>
</tbody>
</table>

### 3.2 FTIR analysis

FTIR is a universal analytical tool used to evaluate a wide range of materials, especially to detect unknown materials. The study found the existence of several minerals, compounds with amorphous or glassy nature, and organic carbon through FTIR analysis. The vibrational frequencies in the IR spectra of studied samples and their tentative assignment to the corresponding minerals and compounds are presented in Table 3. Fig. 8 and Fig. 9 are presenting IR spectra of studied samples.

IR spectra of OPC and clinker, showing medium intense broad peaks at 927 and 931 cm⁻¹ respectively, might be occurred from asymmetric stretching vibrations of Si-O-Si in SiO₄ tetrahedra of alite (Ghosh and Handoo, 1980; Fernández-Carrasco et al., 2012). Another medium intense peak with sharp nature at 522 cm⁻¹, viewed in both OPC and clinker, can be produced from out-of-plane bending vibrations of Si-O in SiO₄ tetrahedra of alite or belite (Ghosh and Handoo, 1980; Fernández-Carrasco et al., 2012). The other two vibrational peaks seen at 457 and 460 cm⁻¹ in OPC and clinker respectively, might be resulted from the in-plane Si-O bending in SiO₄ tetrahedra of alite (Ghosh and Handoo, 1980; Fernández-Carrasco et al., 2012). These two vibrational peaks (522 and 460 cm⁻¹) can also be resulted from the bending of Al-O bonds within AlO₆ octahedral groups present in aluminate (Ghosh and Handoo, 1980; Fernández-Carrasco et al., 2012).
Fig. 7. IR spectra of studied samples

The pure phases of alite and belite usually generate vibrations in the range of 1000-800 cm\(^{-1}\) due to the stretching of Si-O-Si in their SiO\(_4\) tetrahedra (Ghosh and Handoo, 1980; Fernández-Carrasco et al., 2012). Although, the presence of impurities (MgO, Na\(_2\)O, Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\)) triggers a change in the crystalline structure of the silicate phases which may cause modifications in the IR spectra (Fernández-Carrasco et al., 2012). IR spectrum of PCC showing the main band near 1080 cm\(^{-1}\) with strong and broad nature, might be originated from the vibrations of calcium silicate phases i.e., alite, belite. The vibrational peak at 1080 cm\(^{-1}\) may also indicate the presence of quartz, sulphates, and amorphous silica in PCC (Ojima, 2003; Fernández-Carrasco et al., 2012). Two sharp vibrational peaks at 779 and 462 cm\(^{-1}\) in the PCC spectrum can result from stretching of AlO\(_4\) tetrahedra and bending of AlO\(_6\) octahedra in aluminates, respectively while another one at
688 cm\(^{-1}\) might be derived from OH liberation modes of anthophyllite (Fernández-Carrasco et al., 2012; Della Ventura et al., 2018). These three peaks (779, 688, 462 cm\(^{-1}\)) can be occurred from stretching and bending vibrations of Si-O in SiO\(_4\) tetrahedra of quartz as well (Ojima, 2003; Kumar and Rajkumar, 2014). However, the sharp and single peak at 779 cm\(^{-1}\), has also been reported as characteristic peak for crocidolite (Della Ventura et al., 2018; Neupane et al., 2020).

IR spectrum of BFD exhibiting vibrational peak at 997 cm\(^{-1}\), might be attributing the asymmetric stretching of Si-O-Si of belite (Ghosh and Handoo, 1980; Fernández-Carrasco et al., 2012). Orthorhombic crystal unit of molybdenum trioxide may also produce band at 997 cm\(^{-1}\) due to unresolved stretching vibrations of Mo=O (Seguin et al., 1995; Ding et al., 2006). Another peak at 869 cm\(^{-1}\) in the BFD spectrum, can occur from the Al-O stretching in AlO\(_4\) tetrahedra of aluminate, or from symmetric Si-O-Si stretching in SiO\(_4\) tetrahedra of alite (Ghosh and Handoo, 1980; Fernández-Carrasco et al., 2012). However, stretching of the oxygen atoms in a Mo-O-Mo entity of molybdenum trioxide may generate vibrations near 869 cm\(^{-1}\) (Seguin et al., 1995). A broad natured peak seen at 470 cm\(^{-1}\) in the BFD spectrum is characteristic for hydrated amorphous silica (Fröhlich, 1989; Bertaux et al., 1998). A shoulder peak at 1107 cm\(^{-1}\) in clinker, and more distinctive peaks at 1111 cm\(^{-1}\) in OPC and 1109 cm\(^{-1}\) in BFD, might be indicating the presence of sulphates, hematite, and anthophyllite (Li et al., 2011; Fernández-Carrasco et al., 2012). However, FTIR analysis could not find any significant frequencies for ferrite in samples of OPC, PCC, clinker, and BFD which is consistent with the earlier study (Hughes et al., 1995).

A broad and strong peak at 3441 cm\(^{-1}\) in the OPC spectrum might be originated from stretching vibrations of the Si-OH bond (Soheilmoghaddam et al., 2014; Jiang et al., 2017). PCC, clinker,
BFD showing spectra at 3435, 3450, and 3454 cm$^{-1}$ respectively can be derived from OH stretching vibrations in molybdenum trioxide (Seguin et al., 1995). Chrysotile consists of octahedral sheets of magnesium hydroxide (brucite) covalently bonded to tetrahedral sheets of silicon oxide (tridymite), with a regular layered structure (Falini et al., 2004). The characteristic peak of chrysotile resulting from external Mg–OH stretching in octahedral sheets of brucite, can be observed at 3699 cm$^{-1}$ in the IR spectrum of OPC (Falini et al., 2004).

A vibrational peak near 800 cm$^{-1}$ occurred from Si-O-Si symmetrical stretching is mostly used as an analytical peak of crystalline silica (Ojima, 2003; Hart et al., 2018). Quartz, cristobalite, and tridymite are the main three polymorphs of crystalline silica. Vibrational peaks at 464 and 1089 cm$^{-1}$ in the IR spectrum of fly ash might have resulted from bending and asymmetric stretching of Si-O respectively, indicating the presence of quartz, cristobalite, and amorphous silica (Ojima, 2003; Correcher et al., 2009; Neupane et al., 2020). A small and single peak at 790 cm$^{-1}$ in the fly ash spectrum might have occurred from the presence of crystalline silica i.e., cristobalite or tridymite (Correcher et al., 2009). Asymmetric stretching of S-O in arcanite and asymmetric stretching of (Si, Al)-O-Si in mullite may also generate vibrations near 1089 cm$^{-1}$ (Ojima, 2003; Zhang et al., 2012). A sharp medium intense peak at 551 cm$^{-1}$ might have occurred from Al-O stretching of mullite or Si-O bending of cristobalite (Ojima, 2003). However, a vibrational peak near 551 cm$^{-1}$ resulting from Fe-O stretching is also typical for hematite (Li et al., 2019). A very weak peak observed near 850 cm$^{-1}$ in the fly ash spectrum might be generated from the stretching of Ti-O-Ti in the titania polymorph (Kralevich and Koenig, 1998). Another sharp medium intense peak at 1631 cm$^{-1}$ might have resulted from O-H bending vibrations and characteristics for both mullite and titania polymorph (Ojima, 2003; Zhang et al., 2017). A strong peak with broad nature at 3454 cm$^{-1}$ might be generated from OH stretching vibrations, suggesting the presence of silicate
material (Escribano et al., 2017). IR spectrum of fly ash shows a weak peak at 3695 cm\(^{-1}\) which may imply the presence of hydroxyl group in kaolinite or alumina (Ojima, 2003; Kumar and Rajkumar, 2014). Also, the peak at 3691 cm\(^{-1}\) in the PCC spectrum might have originated from kaolinite of fly ash.

Vibrational peaks at 601 and 669 cm\(^{-1}\) in the gypsum spectrum can be assigned to S-O bending and 1126 cm\(^{-1}\) to asymmetric S-O-S stretching (Fernández-Carrasco et al., 2012). Another peak at 466 cm\(^{-1}\) might have occurred from bending modes of Si-O of quartz (Ojima, 2003). IR spectrum of gypsum exhibiting two sharp peaks at 1622 and 1685 cm\(^{-1}\) can be produced from O-H bending vibrations (Fernández-Carrasco et al., 2012). The other two strong broad peaks at 3404 and 3545 cm\(^{-1}\) might be attributed to the stretching of the OH group. A very weak peak centered at 3770 cm\(^{-1}\) might be indicating a free active hydroxyl group that characterizes alumina in gypsum (Escribano et al., 2017). Accordingly, IR spectra of OPC, PCC, clinker, fly ash, slag, limestone, BFD, DRD demonstrated peaks at 3776, 3770, 3774, 3772, 3776, 3772, 3774, 3770 cm\(^{-1}\) respectively might be resulted from hydroxyl groups of alumina.

A broad and strong vibrational peak at 997 cm\(^{-1}\) in the IR spectrum of slag might have generated from asymmetric stretching of Si(Al)-O of glass gehlenite (Taylor, 1990). The glass akermanite may also produce a vibrational peak near 997 cm\(^{-1}\) due to the stretching of Si-O-Si (Dowty, 1987). However, crystalline phases of rankinite and belite generate characteristic vibrational peaks near 997 cm\(^{-1}\) due to the asymmetric stretching of Si-O-Si (Fernández-Carrasco et al., 2012; Wang et al., 2018). A shoulder peak at 881 cm\(^{-1}\) in the slag spectrum might have occurred from the presence of an appreciable amount of SiO\(^{4-}\) groups in the glass network of gehlenite or from the oscillation of oxygen atoms between Si and Mg in akermanite (Sharma et al., 1983; Dowty, 1987). IR spectrum of slag showing a weak peak at 673 cm\(^{-1}\) might be attributed to Si-O-Si symmetric
stretches of wollastonite or Al-O-Al symmetric stretching of gehlenite (Taylor, 1990; Ding et al., 2014). A medium intense peak at 474 cm\(^{-1}\) resulting from bending of Si-O can be originated from crystalline phases of both wollastonite and akermanite (Kimata, 1980; Ding et al., 2014).

Epidemiological evidence of wollastonite demonstrated a nonspecific increase in bronchitis and reduced lung function (Maxim and McConnell, 2005). A broad and strong intense peak at 3446 cm\(^{-1}\) occurring from OH stretching might be an indicator of amorphous silica (Ojima, 2003).

Two strong vibrational peaks at 925 and 881 cm\(^{-1}\) in the DRD spectrum might have resulted from the OH liberation mode associated with octahedral Al-OH groups in beidellite structure (Farmer, 1974; Kloprogge and Frost, 1999). The peak centered at 520 cm\(^{-1}\) might be presenting the coupling between the O-Si-O deformation and the Na-O stretching due to albite in DRD (Dowty, 1987; Zhang et al., 2019). The vibrational peak at 1101 cm\(^{-1}\) might have derived from asymmetric stretching of Si-O-Si of albite or cristobalite while at 459 cm\(^{-1}\) due to Si-O bending of quartz (Mollah et al., 1992; Ojima, 2003). The peaks at 881 and 1431 cm\(^{-1}\) may occur from vibrations of carbonate bonds that existed in vaterite (Neupane et al., 2020). A weak vibrational peak at 3691 cm\(^{-1}\) in the DRD spectrum may indicate the presence of the O-H group of kaolinite (Ojima, 2003; Kumar and Rajkumar, 2014).

Vibrational peaks at 1427, 875, and 709 cm\(^{-1}\) in the IR spectrum of limestone can be assigned to the asymmetric stretching, out-of-plane bending, and in-plane bending mode of CO\(_3^{2-}\) respectively (Hsiao et al., 2019). The vibrational peaks at 1427 cm\(^{-1}\) and 875 cm\(^{-1}\) are characteristic for both calcite and dolomite, although the small sharp peak at 709 cm\(^{-1}\) distinguishes calcite from dolomite (Reig et al., 2002; Hsiao et al., 2019). The weak peak appearing at 1801 cm\(^{-1}\) in the limestone spectrum is also an indication of the presence of CO\(_3^{2-}\) (Nagabhushana et al., 2008; Hsiao et al., 2019). Accordingly, the vibrational peaks with broad nature appearing at 1438 cm\(^{-1}\) in OPC, 1409...
cm\(^{-1}\) in PCC, and 1433 cm\(^{-1}\) in clinker might be attributed to the asymmetric stretching of CO\(_3^{2-}\) of calcite. However, a medium intense peak at 1477 cm\(^{-1}\) in the BFD spectrum, might have arisen from asymmetric stretching of CO\(_3^{2-}\) of aragonite (Toffolo et al., 2019).

Two weak peaks at 1373 and 1423 cm\(^{-1}\) in the slag spectrum might be corresponding to the asymmetric stretching vibration of O-C-O bonds indicating a slight degree of carbonation that has already taken place in the raw material (Gao et al., 2014). Another weak vibrational peak at 1379 cm\(^{-1}\) detected in the fly ash spectrum might also be attributed to CO\(_3^{2-}\) probably due to some carbonation during the sample preparation (Rafeet et al., 2019). In addition, the limestone spectrum shows vibrational peaks at 1111 and 474 cm\(^{-1}\) which might have resulted from quartz.

The very weak peak at 3697 cm\(^{-1}\) might be generated from hydroxyl groups of Mg(OH)\(_2\) (Wang et al., 2016; Jing et al., 2019). Vibrational frequencies between 2850-2950 are ascribed to the stretching mode of C-H bonds, found in all samples. IR spectra at 2935, 2927, 2926, 2924 cm\(^{-1}\) and 2868, 2864, 2862, 2860, 2858, 2854, 1705 cm\(^{-1}\) are attributed to asymmetric and symmetric stretching of C–H respectively (Kumar and Rajkumar, 2014).

Table 3. Vibrational frequencies of studied samples and their tentative assignments

<table>
<thead>
<tr>
<th>Minerals, Compounds, and Groups</th>
<th>Name of the Samples</th>
<th>Frequency (cm(^{-1}))</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>alite</td>
<td>OPC, PCC, clinker, BFD</td>
<td>1080, 931, 927, 869, 522, 460, 457</td>
<td>stretching of Si–O–Si, out of plane and in-plane bending of Si–O</td>
</tr>
<tr>
<td>belite</td>
<td>PCC, slag, BFD</td>
<td>1080, 997, 869, 522</td>
<td>stretching of Si–O–Si, out of plane bending of Si–O</td>
</tr>
<tr>
<td>aluminate</td>
<td>OPC, PCC, clinker, BFD</td>
<td>869, 779, 522, 462, 460</td>
<td>Al-O stretching in AlO(_4) tetrahedra, Al-O bending in AlO(_6) octahedra</td>
</tr>
<tr>
<td>quartz</td>
<td>PCC, gypsum, limestone, fly ash, DRD</td>
<td>1111, 1089, 1080, 790, 474, 466, 464, 462, 459</td>
<td>stretching of Si–O–Si, bending of Si–O</td>
</tr>
<tr>
<td>cristobalite</td>
<td>fly ash, DRD</td>
<td>1101,1089, 790, 520, 551, 464</td>
<td>stretching of Si–O–Si, bending of Si–O</td>
</tr>
<tr>
<td>Minerals, Compounds, and Groups</td>
<td>Name of the Samples</td>
<td>Frequency (cm⁻¹)</td>
<td>Tentative Assignment</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------------</td>
<td>------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>amorphous silica</td>
<td>PCC, fly ash</td>
<td>3446, 1089, 1080, 464, 1089, 1080, 464</td>
<td>OH stretching, stretching of Si–O–Si, bending of Si–O</td>
</tr>
<tr>
<td>opal</td>
<td>BFD, slag, DRD</td>
<td>3446, 3427, 470</td>
<td>OH stretching, bending of Si–O</td>
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<td>mullite</td>
<td>fly ash</td>
<td>1631, 1089, 551, 464</td>
<td>OH bending, stretching of Si–O–Si, Al-O stretching in AlO₆ octahedra, bending of Si–O</td>
</tr>
<tr>
<td>glass gehlenite</td>
<td>slag</td>
<td>997, 881</td>
<td>stretching of Si(Al)-O, stretching of Si–O–Si</td>
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<tr>
<td>gehlenite</td>
<td>slag</td>
<td>673</td>
<td>stretching of Al-O-Al</td>
</tr>
<tr>
<td>glass akermanite</td>
<td>slag</td>
<td>881, 474</td>
<td>stretching of Si-O-Si</td>
</tr>
<tr>
<td>glass akermanite</td>
<td>slag</td>
<td>997</td>
<td>oscillation of oxygen atoms between Si and Mg, bending of Si–O</td>
</tr>
<tr>
<td>rankinite</td>
<td>slag</td>
<td>997</td>
<td>stretching of Si-O-Si</td>
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<tr>
<td>wollastonite</td>
<td>slag</td>
<td>673, 474</td>
<td>stretching of Si-O-Si, bending of Si–O</td>
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<tr>
<td>albite</td>
<td>DRD</td>
<td>1101, 520</td>
<td>stretching of Si-O-Si, coupling between O-Si-O deformation and Na-O stretching</td>
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<td>kaolinite</td>
<td>PCC, clinker, DRD</td>
<td>3695, 3691</td>
<td>OH stretching</td>
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<tr>
<td>beidellite</td>
<td>DRD</td>
<td>881, 925</td>
<td>OH liberation mode associated with Al-OH octahedra (Al-OH-AL)</td>
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<tr>
<td>chrysotile</td>
<td>OPC</td>
<td>3699</td>
<td>external Mg–OH stretching in octahedral sheets of brucite</td>
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<tr>
<td>anthophyllite</td>
<td>OPC, PCC, clinker</td>
<td>1111, 1109, 1107, 1080, 688, 460, 457</td>
<td>stretching of Si-O-Si, OH liberation mode, bending of Si–O</td>
</tr>
<tr>
<td>crocidolite</td>
<td>PCC</td>
<td>779</td>
<td>silicate chain vibration</td>
</tr>
<tr>
<td>calcite</td>
<td>limestone, OPC, PCC, clinker</td>
<td>1438, 1433, 1427, 1409, 875, 709, 1801</td>
<td>stretching of CO₃²⁻, in plane and out-of-plane bending of CO₃²⁻, combinational mode of C–O of calcite and vaterite</td>
</tr>
<tr>
<td>vaterite</td>
<td>DRD</td>
<td>1431, 881</td>
<td>stretching of CO₃²⁻, out-of-plane bending of CO₃²⁻</td>
</tr>
<tr>
<td>aragonite</td>
<td>BFD</td>
<td>1477</td>
<td>stretching of CO₃²⁻, out-of-plane bending of CO₃²⁻</td>
</tr>
<tr>
<td>dolomite</td>
<td>limestone</td>
<td>1427, 875</td>
<td>stretching of CO₃²⁻, out-of-plane bending of CO₃²⁻</td>
</tr>
<tr>
<td>magnesium hydroxide</td>
<td>limestone</td>
<td>3697</td>
<td>stretching of OH occurred from magnesium octahedral</td>
</tr>
<tr>
<td>aluminum oxides</td>
<td>OPC, PCC, clinker, gypsum</td>
<td>3770, 3772, 3774, 3776, 3695</td>
<td>OH stretching</td>
</tr>
<tr>
<td>Minerals, Compounds, and Groups</td>
<td>Name of the Samples</td>
<td>Frequency (cm⁻¹)</td>
<td>Tentative Assignment</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------</td>
<td>-----------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>titanium oxide</td>
<td>fly ash</td>
<td>1631, 850</td>
<td>OH bending, stretching of Ti-O-Ti</td>
</tr>
<tr>
<td>hematite</td>
<td>OPC, clinker,</td>
<td>1111, 1109, 1107, 551</td>
<td>bending and stretching of Fe-O</td>
</tr>
<tr>
<td>molybdenum trioxide</td>
<td>PCC, clinker, BFD</td>
<td>3435, 3450, 3454, 997, 869</td>
<td>OH stretching, unresolved stretching vibrations of Mo=O, stretching of the oxygen atoms in a Mo-O-Mo entity</td>
</tr>
<tr>
<td>gypsum</td>
<td>OPC, PCC, gypsum, clinker, BFD</td>
<td>3545, 3404, 1685, 1622, 1126, 1111, 1109, 1107, 1080, 669, 601</td>
<td>stretching and bending of OH, stretching and bending of SO₄²⁻</td>
</tr>
<tr>
<td>arcanite</td>
<td>OPC, PCC, fly ash, BFD</td>
<td>1111, 1109, 1107, 1080, 1089</td>
<td>stretching of SO₄²⁻</td>
</tr>
<tr>
<td>molecular water</td>
<td>OPC, PCC, clinker, BFD</td>
<td>3454, 3450, 3444, 3441, 1633, 1631, 1629, 1625, 1624, 1620</td>
<td>stretching and bending of OH</td>
</tr>
<tr>
<td>organic carbons</td>
<td>OPC, PCC, clinker, gypsum, limestone, slag, fly ash, BFD, DRD</td>
<td>2935, 2927, 2926, 2924, 2868, 2864, 2862, 2860, 2858, 2854, 1705</td>
<td>stretching of C–H,</td>
</tr>
</tbody>
</table>

4. CONCLUSION

- SEM micrograph of BFD exhibited roundish and irregularly fume-shaped particles whereas DRD showed particles with irregular, hexagonal, and roundish shapes. Other studied samples also demonstrated diverse particle morphology, such as tabular, prismatic, rectangular, angular, irregular, spherical, quasi-spherical, acicular, platy, rhombohedral, hexagonal, elongated, and roundish; among which microparticles with acicular or fibrous shapes are perilous for health as they can travel further in the lung airway.
Samples of DRD and BFD showed particles ranging from 0.1 µm to nearly 15 µm through SEM analysis. Fine and ultra-fine particles were evidently seen here in micrographic views of the rest of the samples.

EDS analysis detected Ca, Si, Al, Mg, Fe, Mo, Ti, K, Na as metallic elements and O, C, S as non-metallic elements in studied samples, distributed with different percentages.

The presence of silicate minerals (quartz, cristobalite, mullite-sillimanite, kaolinite, beidellite, akermanite, gehlenite, rankinite, wollastonite, albite, anthophyllite, chrysotile, crocidolite); carbonate minerals (calcite, aragonite, vaterite, dolomite); sulfates minerals (gypsum, arcanite); oxides minerals (alumina, hematite, wüstite, periclase, brookite, molybdite); and molybdenum were found in studied samples along with Portland cement-based minerals, by SEM-EDS, XRD, and FTIR techniques. Breathing some of these minerals may cause health hazards unless any safety measures are taken.

The occurrence of organic carbon and a few silicate compounds such as amorphous silica, glass gehlenite, glass akermanite, opal was viewed in the IR spectra of different samples.

The occupational health hazard of carcinogens like crystalline silica (quartz, cristobalite) is well recognized. Quartz was found in BFD and DRD showed the existence of both quartz and cristobalite. A potential carcinogen, molybdenum trioxide was also detected in the sample of BFD.

Another carcinogen: asbestoses (anthophyllite, chrysotile, crocidolite) were found in the samples of OPC, PCC, and clinker, but not in the BFD and DRD. But workers could be exposed anytime to asbestoses during material handling, or even at the construction site, where the cement products would be used.
Therefore, this study recommends Government of Bangladesh to implementing strict laws for occupational health safety in CIs regarding the potential toxicity of generated dust.

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**REFERENCES**


Oxide/Hydroxide Structures by Electrodeposition from Magnesium Nitrate Melts.


and Biomarkers in Rats. *International journal of occupational medicine and environmental health* 18: 59-70.


Parada, F., Parra, R., Watanabe, T., Hino, M., Palacios, J. and Sánchez, M. In (Ed.)(Eds.) Proc. VIII Int. Conf. on ‘Molten slags, fluxes and salts’, Santiago, Chile, 2009.


