Physicochemical properties of particulate matter (PM$_{2.5}$) from the steel industry in Indonesia

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Abstract. Particulate matter (PM) as one of the pollutants in the atmosphere needs to be studied. PM has physical and chemical characteristics and is called physicochemical properties. These properties vary depending on the source of the PM. PM samplers are used for air sampling to characterize some fine particles (PM$_{2.5}$). The PM$_{2.5}$ samples have collected from four sampling sites in the steel industry in Cilegon, Indonesia. The sampling sites are the main gate, the hot strip mill, the billet post, and the hot blast plant. The sampling period was four months. The physicochemical properties analysed are morphology, elements content, heavy metals, and particle size. The instruments used to analyse were Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and Particle Size Analyzer (PSA). The morphology of PM$_{2.5}$ detected varied, but the elements and the most elements found were F and C particles. The metals concentration was below the Indonesia Regulation. While the average particle size analysed was below 2,500 nm. The physicochemical properties of PM$_{2.5}$ are affected by the type of production process in the industry.

1. Introduction
World Health Organization (WHO) states that particulate matter (PM) is one of the most air pollutants, apart from gases such as ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and metals such as lead [1]. PM is an indicator of air pollution that enters into the air by various activities, both natural and human activities [2]. PM can be travelled for a long distance in the atmosphere and survived for a long time (chronic) or a short time (acute), so it can cause various diseases to lead reduction in human life significantly.

The size of particles is directly related to their potential for causing health problems. Small particles of concern include inhalable coarse particles with a diameter of 2.5 to 10 µm and fine particles with a diameter of fewer than 2.5 µm [2]. Fine particles (PM$_{2.5}$) have a more increased risk to health due to after inhalation can invade into your lungs and even reach the bloodstream.

Particulate matter is an air pollutant that is quite a lot produced from iron and steel industry or metal smelting process. Particulate matters (PM) have classified into rough sizes (10-2.5 µm) and fine sizes (<2.5 µm), each referred to as PM$_{10:2.5}$ and PM$_{2.5}$. Generally, PM$_{2.5}$ can stay in the atmosphere for the long term (days or weeks) and can fly at very long distances (10 - 1000 km). PM$_{2.5}$ is emitted directly into the atmosphere or can also form from the results of chemical reactions between other particles. Then produce toxic effects regarding their chemical and physical properties. The process of
condensing nitrogen and sulfur oxides in the atmosphere produces nitrates and sulfates. These substances form secondary particles that dominate the composition of fine particles. Other sources of fine particles are fly ash from power plants and particulates from the combustion of hydrocarbon fuels or vehicle exhaust emissions [3].

The composition of particulate matter is organic or inorganic components. The organics are usually polycyclic aromatic hydrocarbons, dioxins, benzene, and 1-3-butenes. Whereas, the inorganics are carbon, chloride, nitrate, sulfates, and metals [4]. The chemical composition of PM$_{2.5}$ varies, depending on the emission source, the specific atmospheric chemistry, and the weather conditions.

The use of automatic instruments in air monitoring has been carried out in several developed countries while developing countries such as Indonesia still use manual monitoring instruments. Therefore, the objective of this research is to identify the physicochemical properties of PM$_{2.5}$ in the steel industry in Cilegon, Indonesia, using an automatic particulate matter sampler.

2. Materials and methods

2.1. Particulate matter samples
PM$_{2.5}$ was sampling based on SNI 7119.15: 2016 using Low Volume PM samplers [ART Plus, Korea]. The four sampling locations pointed out in figure 1. In details, each site is as follows: Site 1 is area of main gate, Site 2 is area of hot strip mill, Site 3 is area of billet post, and Site 4 is area of hot blast furnace. Each site has different production activities from each other. In order, A is Cold Rolling Mill Factory, B is Wire Rod Mill Factory, C is Hot Strip Mill Factory, D is Coke Oven Plant Blast Furnace Area, E and F are Slab Steel Factory, and G is Direct Reduction Factory.

![Figure 1. Sampling sites in the steel industry in Cilegon, Indonesia [5].](image)

2.2. Measurement
The filter paper of PM$_{2.5}$ is characterizing using instrumentations. The characterization of morphology and elemental composition are measured using a Scanning Electron Microscope [SEM, JOEL JSM-6510 LA] in Faculty of Math and Science, Bandung Institute of Technology. The heavy metals content measured by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Shimadzu 5100) in Centre for Chemical and Packaging and the particle size distribution measured by Particle Size Analyzer (PSA Malvern Zetasizer Nano ZS) with dynamic light scattering system in National Nuclear Energy Agency.
3. Results and discussion

3.1. Particle concentration

The condition of PM2.5 in the steel industry, Cilegon, in the study can be seen in figure 2. The measured PM2.5 concentration varies greatly for each location for 120 days. The concentration of PM2.5 are 4.18 – 91.97 µg/m³ at Site 1, 8.36 – 92.05 µg/m³ at Site 2, 4.18 – 125.42 µg/m³ at Site 3, and 8.37 – 91.97 µg/m³ at Site 4. It showed that the particle concentration was influenced by types of industrial activities and the number of emission sources. The types of activities and sources of air pollution at each site have been described in section 2.1.

The permissible daily limit of PM2.5 based on the Republic of Indonesia regulation No. 41 - 1999 is 65 µg/m³ and World Health Organization (WHO) regulation is 25 µg/m³. In this case, the concentration of PM2.5 meets the requirements of the standard, but some exceed the threshold.

![Figure 2. The PM2.5 concentration from four locations in the steel industry in Cilegon, Indonesia, as well as Indonesia Government Regulation and WHO Regulation.](image)

The concentration of particles can be affected by the sampling location. The highest PM2.5 concentrations from each location were 125.42 µg/m³ at Site 3, 92.05 µg/m³ at Site 2, 91.97 µg/m³ at Site 4, and 91.97 µg/m³ at Site 1. A difference in the daily concentration of PM2.5 can be influenced by daily process activities. For comparison, the steel industry in China has a particle emission of 50 µg/m³ for PM2.5 [6].

Site 3 produces the highest PM2.5 concentrations because it is located in billet post area and affected by the process activities from the Direct Reduction Factory and Slab Steel Factory. It is due to the source of the pollution that comes from emissions that were produced by those plants. Moreover, there is also transportation activities for factory supporting goods, which produced dust from the traffic that could be one source of pollution. In a previous study, the same steel industry produced the highest PM2.5 concentrations, namely 141.96 µg/m³ at area of billet post [5]. Based on previous and this study, the PM2.5 concentrations were obtained more by reduction process and slab steel process than other activities in the steel industry.

Furthermore, that identifies the second highest PM2.5 concentration is Site 2, which is close to the production activity in the hot strip mill area. Then, Site 1 and Site 4 have the same level of PM2.5, respectively. Site 1 is located in the main gate of the steel industry, where there is no activity of production process. The pollution in site 1 generated from transportation activity. For air pollution at site 4 is formed from the activity of the coke oven or blast furnace. The blast furnace can produce dust in a short time, so it has the most significant contribution in generating dust emission [7]. Some references have been clearly stated that most particulate matter in the atmosphere has formed by the
complex reaction of sulphur dioxide and nitrogen oxides, which are pollutants emitted from power plants, industries, and vehicles exhaust [8–10].

3.2. Particle morphology from SEM images
Different particle concentrations can be studied further by knowing the particle morphology. Morphology types of PM$_{2.5}$ can figure out as regular mineral particles, irregular mineral particles, soot particles, and fly ash [11]. The morphology of PM$_{2.5}$ can be shown as SEM images in figure 3.

![SEM images of PM$_{2.5}$ particles](image)

Figure 3. Image of SEM (10,000 X) at four sites in the steel industry in Cilegon, Indonesia.

Site 1 was produced particles in soot aggregates and fly ash coated with ultrafine particles (figure 3a and figure 3b). Particles on Site 2 were dominated soot aggregates, elongated and irregular minerals, and fewer fly ashes (figure 3c and figure 3d). Whereas on Site 3, lots of spherical particles
associated with the fiber filter and other particles formed soot aggregates (figure 3e and figure f). The spherical particles with greasy surfaces were fly ashes. And the particles on Site 4 were soot aggregates and elongated mineral (figure 3g and figure 3h).

The results showed that the morphology of particles varies depending on the emission sources. It can be attained from figure 3a to 3h, that almost site or production area in the steel industry produced numerous spherical particles or fly ashes and in the main gate area has fly ash coated with ultrafine particles. Specifically, at Site 2 (Hot Strip Mill Area) and Site 4 (Hot Blast Plant Area), SEM images show more elongated minerals or irregular mineral particles than other sites. It is because the area has the most significant contribution to producing dust emissions in the steel industry. These are almost similar to particles morphology in a city within steel industrial area in China was spherical, irregular morphologies, massive, columnar, and layered [12].

From the result of this study and other references, the morphology of particles can indicate the source of air pollution. So, the information about the morphology is necessary for improving air pollution monitoring efforts. It can reduce the harmful effects of particles and finally improve the air quality in the atmosphere [12,13].

3.3. Elements mapping and compositions

The elements mapping of PM$_{2.5}$ shown in figure 4. The elemental detected in PM$_{2.5}$ from the steel industry in Indonesia are Al, C, Cl, F, Fe, K, Mg, Na, O, S, and Si. The distribution of each element is different in each location and time of sampling. The emission from different process activities will produce different elemental. A case study from an iron and steel smelting industry in Nigeria also stated that the concentration of elements within industry was higher than outside industry and detected 28 species of element for PM$_{2.5}$ [14].

The elemental composition of PM$_{2.5}$ for this study has summarized in table 1. The result showed that PM$_{2.5}$ has high proportions of elements F and C in all sampling locations. It’s related to the analysis from the study before that the primary particles of fine fraction (PM$_{2.5}$) are F-rich and C-rich particles, which mostly related to the type of factory pollution. Fluorine-rich particles can be emitted from industries that produce fluorine-based chemicals or from burning coal. And, carbon-rich particles came from vehicular activities [15].

| Table 1. Elemental composition of PM$_{2.5}$ (% mass) at four sites in the steel industry in Cilegon, Indonesia. |
|-----------|-----------|-----------|-----------|-----------|
| Element   | Site 1    | Site 2    | Site 3    | Site 4    |
|           | Sept. (fig.4a) | Oct. (fig.4b) | August (fig.4c) | Oct. (fig.4d) | July (fig.4e) | Oct. (fig.4f) | July (fig.4g) | August (fig.4h) |
| Al        | -         | -         | -         | 0.34      | -         | -         | -         | -         |
| C         | 37.50     | 43.25     | 41.75     | 43.82     | 46.08     | 39.45     | 42.65     | 43.35     |
| Cl        | 0.13      | 0.11      | 0.23      | -         | 0.27      | 0.08      | 1.04      | 0.99      |
| F         | 51.97     | 43.28     | 46.13     | 35.09     | 37.14     | 48.36     | 45.12     | 40.33     |
| Fe        | 0.32      | 0.3       | 0.27      | 1.52      | 1.46      | 1.37      | -         | 2.41      |
| K         | 0.30      | 0.58      | 0.42      | 0.79      | 0.43      | 0.38      | -         | 0.37      |
| Mg        | -         | -         | -         | 0.23      | -         | -         | -         | -         |
| Na        | 0.24      | 0.4       | 0.34      | 0.84      | 0.43      | 0.12      | 0.52      | 0.35      |
| O         | 7.41      | 9.92      | 8.79      | 14.05     | 11.5      | 8.08      | 8.59      | 10.52     |
| S         | -         | -         | -         | 0.87      | 0.72      | -         | -         | -         |
| Si        | 2.13      | 2.16      | 2.07      | 2.45      | 1.97      | 2.17      | 2.09      | 1.69      |
Figure 4. Elements mapping of PM$_{2.5}$ at four sites in the steel industry in Cilegon, Indonesia. (Note: the colour in the map indicates the element).
3.4. Heavy metals content
The heavy metals content of PM$_{2.5}$ from this study has summarized in table 2. Metals measured by ICP-OES were Cd, Fe, Mn, Pb, and Zn. All of the metals have detected with varying concentrations at each site. From all the heavy metals monitored, only Pb has regulated in Indonesia, namely the Republic of Indonesia regulation No. 41-1999. The permissible limit of Pb in Total Suspended Particles according to the regulation is 2 μg/m$^3$. The result of Pb in this study still below the allowed limit if compare with the national regulation and international standard. Besides that, Cd, Fe, Mn, and Zn also meet the standard.

| Heavy Metal (µg/m$^3$) | Site 1  | Site 2  | Site 3  | Site 4  | RI Government Regulation | International Regulation |
|------------------------|--------|--------|--------|--------|--------------------------|--------------------------|
| Cd                     | 0.002  | 0.003  | 0.003  | 0.003  | -                        | 0.005$^a$                |
| Fe                     | 0.289  | 0.432  | 0.745  | 1.030  | -                        | 7$^b$                    |
| Mn                     | 0.094  | 0.090  | 0.121  | 0.142  | -                        | 0.15$^a$                 |
| Pb                     | 0.221  | 0.070  | 0.061  | 0.379  | 2 (daily)                | 0.5$^a$                  |
| Zn                     | 0.076  | 0.114  | 0.148  | 0.338  | -                        | 5$^b$                    |

$^a$WHO [16]  
$^b$U.S. National Ambient Air in Industrial [17]

3.5. Particle size distribution
Fine particles from this study have varied sizes, but all the particles are below 2.5 μm or 2,500 nm. Particle size differs from site to site. It can be seen in table 3 that the PM$_{2.5}$ at Site 3 and Site 4 have a larger size distribution than other sites. This means that the billet post activity and the hot blast plant activity produce particles with a larger size than the main gate activity and the hot strip mill activity.

| Sampling location | Particle size (nm) |
|-------------------|--------------------|
| Site 1            | 173.00 – 459.17    |
| Site 2            | 61.55 – 505.90     |
| Site 3            | 280.50 – 768.80    |
| Site 4            | 558.80 – 579.50    |

4. Conclusions
The study result of physicochemical characteristics of PM$_{2.5}$ from the steel industry in Indonesia has concluded, the concentration PM$_{2.5}$ has been ranging between 4.18 – 125.42 µg/m$^3$. The morphology of particles can figure out as regular mineral particles, irregular mineral particles, soot particles, and fly ash. The elements detected are Al, C, Cl, F, Fe, K, Mg, Na, O, S, and Si, but dominated by F-rich and C-rich particles. The measured metals such as Cd, Fe, Mn, Pb, and Zn have varied concentrations and still below the regulation, especially for Pb. The average particle size varies between 61.55 – 768.8 nm, and all of the particles are below 2,500 nm. Overall air quality in the Cilegon steel industry is still within the regulation limits.

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