Characteristics of air pollution particulate matters in a Slag Dumping Plant in Taiwan

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Abstract: This paper reports the study of an air quality analysis conducted at an indoor slag dumping plant of a steel factory during hot slag treatment. An air quality analysis of the indoor dumping plant will be carried out prior to improving the operation environment. Samplers used for particulate matters are applied to collect suspended particulates and different analyses are implemented. The item analysis includes total suspended particulates (TSP), PM₁₀, dust amount, and diameter and element of suspended particulates. Sampling results and analysis indicate high concentration level of TSP, PM₁₀, and dustfall during the slag treatment. Due to gravity, dust with larger diameter or heavier weight falls down easier, and therefore sampling site S2 at the center of the slag dumping plant has the most dense slag treatment activities and highest dust concentration. Distribution of suspended particulates indicates most particulate pollutants inside the plant are found to be coarse particles (>10 µm). SEM is used to identify the composition of 17 elements showing diversity of pollutants during hot slag treatment.

Keywords: Slag, slag dumpling plant, MOUDI sampler, SEM.

Introduction

Currently a growing trend is seen in the use of industrial wastes or by-products as supplementary materials in the production of composite cements, due primarily to environmental and economical reasons. The remarkable development of Taiwan's steel industry over the years has spurred exciting economic growth, but it has also produced 2 million tons of steel slag from blast furnace annually. Furnace slag is generated during steelmaking. The major phases (>10 wt.%) of furnace slag are dicalcium silicate (Ca₂SiO₄), tri-calcium silicate (Ca₃-SiO₅), ferrous oxide (FeO), and Ca-Mg-Mn-Zn-ferrite $((Ca,Mg,Mn,Zn)Fe_2O_4)^2$. The main chemical components, which comprise approximately 70-85 wt. % of furnace slag, reported as oxides are CaO, Fe₂O₃, and SiO₂; whereas MgO, MnO, Al₂O₃, P₂O₅, TiO₂, K₂O, Na₂O, and Cr_2O_3 comprise the remainder³⁻⁵.

Furnace ash and slags are the solid wastes from the power plant boilers and other industrial boilers. The slags have a glassy structure and contain porous granular carbon and coke; they have, therefore, adsorption capaci-

ties⁶. As an adsorbent, blast furnace slag (BFS) has been utilized for removal of phosphate, nitrate, lead (Pb), copper (Cu), and nickel (Ni)⁷⁻⁹. However, not much has been reported about its utilization for the treatment of nitrobenzene.

This study conducts an air quality analysis during the hot slag treatment at an indoor slag dumping plant of a steel factory in Taiwan. Item sampling and analysis includes total suspended particulate (TSP), PM_{10} (particulate diameter $<10~\mu m$), dustfall amounts in the air, diameter size of particulates, and element tracing and analysis of particulates. Based on the measurement and analysis mentioned, this study examines the air quality of the indoor slag dumping plant, which is then used as reference for predicting and monitoring future patterns of discharge outlet when counter measures of air pollution are implemented.

Materials and methods

-Sampling-site-of-particulate-pollutants:

The sampling site in this study is in an indoor slag dumping plant of a steel factory in Kaohsiung, Taiwan (shown in Fig. 1) near Kaohsiung Port. Hot slag treatment is being operated at the indoor slag dumping plant and S1, S2, and S3 from the north (upstream), center, to south were selected for sampling of particulate pollutants. This slag dumping plant has the length and width of 288 m and 16 m respectively and sampling was conducted 24 h a day for five consecutive days from July 11 to July 16, 2015.

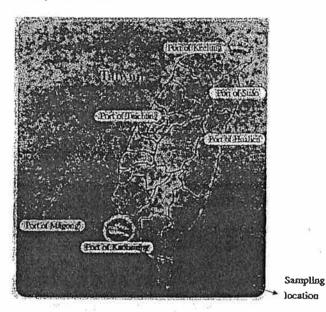


Fig. 1. The Slag Dumping Plant site of this study.

Item sampling and analysis:

Item sampling and analysis in this study includes total suspended particulate (TSP), PM_{10} (diameter < 10 μ m), dustfall amounts, diameter size of suspended particulates, and element tracing and analysis of particulates with field emission scanning electron microscope (SEM).

Method of item sampling and analysis:

TSP measurement:

This study uses the high-volume air sampler, referred by the "NIEA A102.12A" of Environmental Analysis Lab (the Environmental Protection Agency (EPA), Executive Yuan, Taiwan, 2007) 10 and the filter paper with the filtering rate of $1.1 \sim 1.7~\text{m}^3/\text{min}$ to collect particulate pollutants in 24 h and then weigh them. The collected particle has the diameter size of $< 100~\mu\text{m}$. The measurement steps are : Fold up the longer side of the filter paper and keep the suspended particulates inside the paper; cover

the paper with an appropriate material and examine and weigh it. The high-volume air sampler (type: GPS1 PUF Sampler) used in the study is made by General Metal Work Co.

PM₁₀ measurement:

Manual method is adopted following the rule of "NIEA A208.12C" (EPA, Executive Yuan, Taiwan, 2013)11. Through certain shaped inlet of the air sampler, air is sampled and then classified into one or more groups of different diameter range within PM₁₀. Each range within PM₁₀ is collected by individual paper during the sampling period. From the particle property (sampling efficiency and 50% cutoff diameter) found in the sampling inlet, we identify them as the weight group of PM10. Each filter paper is weighed before and after sampling (after humidity adjustment) and then the net weight (mass) of particle, PM₁₀, is determined. Before and after sampling (after adjusting the moisture content), each filter paper has to be weighed so that the net weight (mass) of PM₁₀ can be measured. The collected total air volume (adjusting to standard state: 25 °C, 1 atm) can be decided by the measured flow rate and sampling timing. The collected total mass of PM₁₀ in diameter range divided by the total air volume equals the PM₁₀ mass concentration in the atmosphere. It results in µg/Nm³ under standard state. The PM_{10} used in the project is type R&PTEOM-1400a, made by Graseby Andersen, USA.

Dustfall measurement:

Gathering method follows the standard listed in "CNS 3916-J2013" (Chinese National Standard, Taiwan, 1976)¹². Dustfall sampler (a bucket) is placed at the minimum distance of 2.44 meters from the ground and maximum distance of 15.2 meters or 1.22 higher than the house surface. Before installation, 200 ~ 1000 mL liquid should be added and the evaporation of liquid is measured. Water, algaecides, or fungicides can be used as liquid according to the need. The lip should be closed till the sampler is moved to the sampling site and installed with a bracket. After collection, the lip should be reclosed and then the sampler shall be removed from the bracket before being sent back to the lab. Filtering steps are introduced to measure dustfall amounts. The dustfall bucket is a columned glass bucket.

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Diameter analysis:

The micro-orifice Uniform Deposit Impactor (MOUDI) sampler of a cascade type, a MSP Model 110 manufactured by MSP in the USA, is used to sample diameter distribution and concentration in this study. Eight-cascade MOUDI is adopted at the air pumping rate of 25 L/ min to collect samples at S2 (the area with the densest operation) and particulates are analyzed in the range from $10-18 \,\mu\text{m}$ to $0.32-0.18 \,\mu\text{m}$. There are two gauge pressures and control valves of flow rate. The top gauge pressure shows the voltages when passing MOUDI and it provides the change of air flow rate after passing the impactor. It is used to check the right index of the sampler's flow. A scale ANDER-202 is used to measure the weight of the filter paper before sampling. After measurement, the filter paper has to be put into a small incubator; it has to be numbered and then put into a sweabox. After sampling, the filter paper has to be put back in the small incubator and immediately into the sweabox for balancing for more than 24 h. The mass of suspended particulates in each diameter range will then be weighed.

Element tracing and analysis:

This study selects S2 as the sampling site and conducts operation and observation under SEM (Scanning

Electron Microscopy) for particulates collected through the MOUDI sampler; at the same time, multi-point analysis is also introduced to trace the elements of collected suspended particulates at each stage. The SEM model used in this study is JEOL-6330.

Results and discussion

Concentration analysis of TSP:

Fig. 2 indicates the slag practice operation during sample detection at the indoor slag dumping plant and the operation is conducted continuously on a 24 h run. Accordingly, the concentration level of the sampled TSP, no matter when we collected it, remained high. What deserves attention is that in the afternoon (12:00-16:00) on July 13, a blast accident occurred and caused suspended particulates to fly and scatter around on the site and an abnormally high concentration was shown. For instance, the concentration level monitored at S1, S2, and S3 increased to 20878 $\mu g/m^3$, 26072 $\mu g/m^3$ and 30610 μg/m³ respectively, only within four hours. After continuous detection for five days, the concentration level of TSP at S1, S2, and S3 reached 110613 µg/m³, 100047 μg/m³, and 89564 μg/m³, indicating that when there is no preventive equipment of air pollution to be used for

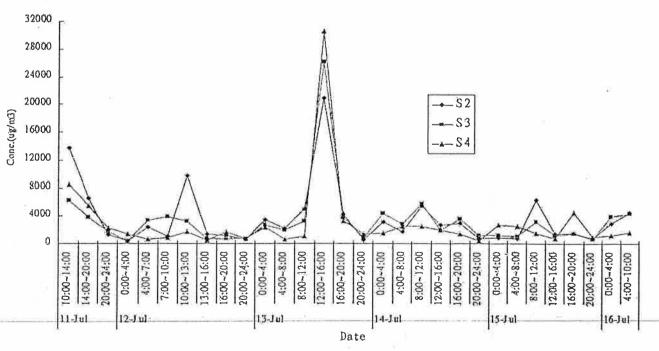


Fig. 2. TSP concentration results at three sampling sites.

hot slag splashing operation, it is easy to see dust flying in the air and causing air pollution. In addition to flying suspended particulates, careless slag processing can also cause accidents, likely posing great risk to occupational safety. When a blast occurs, hot slag may initiate air explosion to cause injury or burns to operators on the site.

Moreover, although Fig. 2 also shows the all-day high concentration level of the sampled TSP, yet in contrast, concentration level from 8:00 pm to 12:00 pm is relatively low, because fewer operations are normally carried out in this time slot. In addition, three selected sampling sites, S1, S2, and S3, were found to have similar accumulated concentration level after continuous operation for five days because the operation area at the slag plant is large and the TSP generated flies away, resulting in high concentration and even distribution.

Concentration analysis of suspended particulate, PM₁₀:

 PM_{10} refers to suspended particulates with the diameter less than 10 μ m, so Fig. 3 shows the comparison of sampled concentration levels of PM_{10} and TSP. Due to the relatively low concentration level of PM_{10} , we assume that the suspended particulates generated, in majority, have the diameter larger than 10 μ m. Furthermore,

as indicated in Fig. 3, we detected the increase of PM₁₀ concentration level caused by blast during the period from 12:00 to 16:00 on July 13; the concentration pattern is identical to that of TSP. From the highest to the lowest were samples at S3, 2517 μ g/m³, S2, 1890 μ g/m³, and S1, 1024 μ g/m³. After the five-day continuous monitoring, the concentration levels of PM₁₀ at S1, S2, and S3 are 13873 μ g/m³, 17670 μ g/m³, and 13627 μ g/m³. If we calculate on the PM₁₀ concentration percentage to that of TSP at S1, S2, and S3, they are 12.5% (13873/110613 = 0.125), 17.7% (4349/100047 = 0.177), and 13.7% (13627/99761 = 0.137) respectively.

Moreover, if we look at the concentration change in different operation time periods, PM₁₀ and TSP have the identical pattern. It is mainly due to the shorter processing and operating time at nights. When it is operated longer at daytime, the PM₁₀ concentration tends to be higher accordingly.

Concentration analysis of dustfall:

Fig. 4 shows the sampling results of five-day collection of dustfalls: the concentration levels of dustfalls at S1, S2, and S3 are 266.34 (gram/square meter/5 days), 339.35 (gram/square meter/5 days), and 199.11 (gram/square meter/5 days), and 199.11 (gram/square meter/5 days).

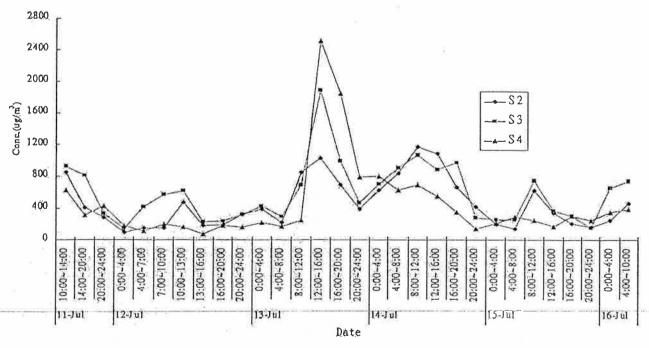


Fig. 3. PM₁₀ concentration results at three sampling sites.

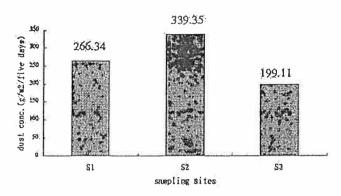


Fig. 4. Dustfall amounts at three sampling sites.

square meter/5 days). Because slag dumpling process was conducted during the dustfall sampling period, not only suspended particulates but also dusts are accumulated in great amounts. In particular, S2 has the closet distance to the slag processing area where more dusts with larger particulate size are found due to gravity. S1 and S3 also have considerable amount of dustfalls, but less than that of S2. In terms of pollution, these three sampling sites are regarded as highly polluted and we can attribute the air pollution inside the plant to dusts coming along with slag processing, particularly the large amount of dustfalls sampled at S2 after a blast occurred.

Diameter analysis of suspended particulate:

This study shows the diameter distribution of suspended particulates sampled at S2 site, indicating the major diameter distribution falls between $3.2 \sim 18 \, \mu m$, largely in the diameter range of coarse particle between $10 \sim 18 \, \mu m$. Another peak lies in fine particles of $0.32 \sim 0.56 \, \mu m$. From the distribution diagram, we notice that particulate pollutants at the slag dumping plant mainly are coarse particles that are proved by the previous TSP and dustfall analysis 13 : at S2, dustfalls with large particulates have the high concentration (reaching 266.34 (g/square meters/5 days)) and PM₁₀ concentration only accounts for 17.7% (17670/100047 = 0.177) of the TSP concentration. This phenomenon shows that air quality in the slag dumping plant is indeed influenced by the operation.

Trace and analysis of TSP:

The main elements of TSP sampled at S2 is shown in Table 1; the structure of suspended particulates with the diameter between $10 \sim 18~\mu m$ and $5.6 \sim 10~\mu m$ is observed by SEM as shown in Figs. 5 and 6. In S2, 17 elements are traced. From Table 1, suspended particulate in general has different diameters and element composition. In the case of Al and Si, the smaller the diameter,

| | | Table 1. 1 | Element trace an | id analysis of su | spended particul | ate at S2 samplin | g silc | |
|---------|------------------------------------|------------|------------------|-------------------|------------------|-------------------|---------------------|-------------|
| Element | The range of particulate size (μm) | | | | | | | |
| | 18 ~ 10 | 10-5.6 | 5.6 - 3.2 | 3.2-1.8 | 1.8-1.0 | 1.0-0.56 | 0.56-0.32 | 0.32 ~ 0.18 |
| Al | 1.29 | 3.98 | | 1.54 | 3.85 | 4.39 | 5.52 | -5.40 |
| Si | 13.66 | 15.03 | 33.47 | 17.69 | 20.93 | 50.02 | 54.65 | 58.03 |
| P | 2.20 | | | | | | | |
| K | 2.53 | 7.79 | 6.53 | 2.76 | 3.35 | 6.44 | 8.06 | 6.62 |
| Ca | 44.62 | | 4.48 | 49.71 | 33.69 | 6.28 | 2.86 | 2.90 |
| Mn | 2.45 | 4.37 | | 1.74 | 1.62 | | | |
| Fe | 33.25 | 26.82 | | 8.43 | 7.29 | 1.64 | | |
| Mg | | 5.42 | | | 1.18 | | | |
| S | | 1.24 | | 1.77 | 3.86 | 2.87 | 0.99 | |
| Cl | | 5.95 | | 8.51 | 13.50 | 3.09 | 0.95 | |
| Zn | | 1.95 | 8.08 | 2.81 | 2.07 | 3.72 | 5.58 | 4.26 |
| Rb | | 23.68 | 29.16 | | | | | |
| Ba | | 3.77 | 13.74 | 5.04 | 3.65 | 10.22 | 10.70 | 11.19 |
| In | | | 4.54 | | | | | |
| Na | | | | | 5.01 | 11.33 | 9.91 | 9.47 |
| Cr | 6. O 100 1 N | | | | | | THE PERSON NAMED IN | 2.13 |
| Со | | | | | | | 0.78 | |
| (%) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

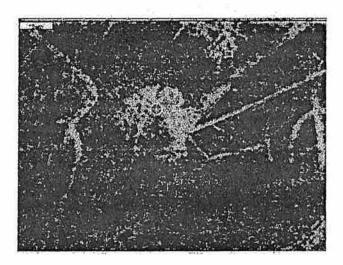


Fig. 5. Structure of suspended particulates of 10 – 18 μm sampled at S2 sampling site.

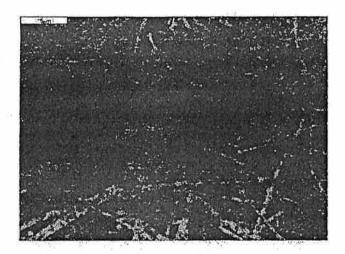


Fig. 6. Structure of suspended particulates of 5.6 ~ 10 μm sampled at S2 sampling site.

the higher composition of the elements; thus, Al and Si comprises the highest level when the diameter size falls in the range of fine particle between $0.32 - 0.18 \, \mu m$. Slag is mainly composed of Si and Ca. As seen in Table 1, Si accounts for 58.3% in the range of $0.32 - 0.18 \, \mu m$. That is to say, if the slag belongs to the type of fine particle, then its main element is Si. In terms of Ca, the high composition level is found in fine particles of $3.2 - 1.8 \, \mu m$ and coarse particles of $18 - 10 \, \mu m$, indicating high dustfall concentration in the slag dumping plant where besides Si, Ca accounts for the majority. The same holds true in the case of Fe. Table 1 shows the second highest composition of Fe, next to Ca, in coarse particles of $18 - 10 \, \mu m$

μm, accounting for 33.25%. It, therefore, is assumed that the abnormally high concentration levels of particulates (in particular, TSP and dustfalls) during operation inside the plant and the main elements are Ca, Fe, and Si. Among them, Ca and Fe have larger molecular weight, so to them we attribute the highly concentrated particulate pollutants 14. On the other hand, Table 1 proves that coarse particles with diameters between 18 ~ 10 µm comprise 91.35% of Si, Ca, and Fe. Rb accounts for 23.68% and 29.16% of the coarse particles of 10~5.6 μm and 5.6-3.2 µm respectively as illustrated in Table 1, indicating that slag is also composed of Rb. K is shown with an even diameter distribution. S and Cl have the identical distribution range found in fine particles of 10 ~ 5.6 µm as well as $3.2-0.32~\mu m$. Ba and Zn are found in coarse particles of $5.6 \sim 3.2 \, \mu m$ and their composition is also found in the range of 10~0.18 μm whereas Na is detected only in fine particles of 1.8 - 0.18 µm and P is traced in coarse particles of 18-10 µm, accounting for 2.20%. Mn is found in the range of $18 \sim 5.6 \mu m$ and $3.2 \sim 1.0 \mu m$ with low composition level. The element In, rarely found in nature, accounts for 4.54% in the range of 5.6~3.2 μm; Cr comprises of 2.13% in the range of 0.32~0.18 μm. In addition, radioactive trace element Co in fine particles of 0.56 ~ 0.32 µm are found, but it only accounts for 0.78%.

Conclusion

Operation at the slag dumping plant contributes to air pollution with TSP and the problem elevates when blasts occur, causing the concentration level of TSP to become abnormally high. The PM₁₀ concentration levels in that of the TSP sampled at S1, S2, and S3 are 2.5%, 17.7%, and 13.7% respectively, indicating low composition of PM₁₀ in TSP. S2 is located in the center of the slag dumpling plant and the sampler is able to collect flying particulate pollutants of the type of suspended particulate; thus, PM₁₀ concentration level at S2 is similar to those at S1 and S3. The coarse particles with diameters between 18~10 μm make up 91.35% of Si, Ca, and Fe. The diameter analysis above shows that slag composes of elements with large diameter size and Ca and Fe have heavier molecular weight and higher density. Furthermore, 17 elements are detected at S2, indicating serious air pollution in the slag dumping plant.

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