



Emission Characteristics and Chemical Compositions of both Filterable and Condensable Fine Particulate from Steel Plants

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ABSTRACT

Steel production is an important source of particulate matter emission. In this study, both filterable and condensable fine particulate (PM_{2.5}) emissions from an electric arc furnace (EAF) and four integrated iron and steel plants were measured. Chemical compositions including water soluble ions and metal elements of these two types of PM_{2.5} were analyzed. The results show that filterable PM_{2.5} concentrations emitted from sintering, coke making, blast furnace, basic oxygen furnace (BOF) and EAF are 1.01, 0.37, 0.16, 0.15 and 0.28 mg/Nm³, respectively. Sintering has the highest filterable PM_{2.5} emission concentrations. Condensable PM_{2.5} concentrations emitted from the above processes are 65.3, 89.7, 3.84, 1.32 and 2.02 mg/Nm³, respectively, which are much higher than filterable PM_{2.5}. K, Fe, Pb and Zn concentrations are high in filterable PM_{2.5} for sintering process, which is attributed to the feedstocks of recycled materials. High sulfur content of the feedstocks results in high concentrations of SO₄²⁻ for all the test plants. In addition to Fe, the emissions of Pb, Zn and Sn are high for EAF, which is due to the complexity of the recycled steel feedstock for EAF. SO₄²⁻ is the highest emission ion for sinter process and coke making. For blast furnace, BOF and EAF, however, Na⁺, K⁺ and Cl⁻ are the predominated ions. For metal elements, concentrations of Na and K are highest for all the plants, which might be caused by their high potential of vaporization.

Keywords: Stationary emission source; Filterable PM_{2.5}; Condensable PM_{2.5}; Chemical composition; Iron and steel plant.

INTRODUCTION

Steel and iron have been vital and major materials for many industries and consumer product applications for a hundred years. Production of iron and steel is an important source of air pollutants including particulate matter (PM). Previous studies identify iron and steel plants as a major contributor of PM and persistent organic pollutants to air in the vicinity of plants (Amodio *et al.*, 2013; Thuong *et al.*, 2014; Xiao *et al.*, 2014). Atmospheric particulates have potentially adverse impacts on human health through inhalation and respiratory deposition. Fine particulate (aerodynamic size less than 2.5 μm, PM_{2.5}) is especially harmful as they can be transported deep into the alveolar region of the lungs and the bloodstream (Pope *et al.*, 2004; Avino *et al.*, 2013; Patterson *et al.*, 2014). Chemical properties of particulate also play an important role affecting human health. It is quite essential to characterize PM_{2.5} and estimate its contributions to the atmosphere from emission sources.

There are two major commercial processes for steel making. The first one is integrated iron and steel making process, which has liquid pig-iron from the blast furnace and scrap steel as the main feed materials. The other is electric arc furnace (EAF) steel making, which uses scrap steel as the main feed material. The main operational units of integrated iron and steel plants include sintering, coke making, blast furnace and basic oxygen furnace (BOF). Sintering and coke making are pretreatment processes for steel making. Fine iron ores and fluxes are agglomerated by combustion for sintering. Coal is converted to coke by driving off impurities to leave almost pure carbon under high temperature in the absence of oxygen. Sinter and coke are introduced into the blast furnace to produce molten iron. The molten iron is combined with scrap steel and small amounts of flux with oxygen in the BOF at high temperatures to produce liquid steel. The EAF reuses existing steel and operates on the basis of an electrical charge providing the heat to melt the scrap steel.

Tsai *et al.* (2007) measured total particulate emissions from four iron and steel plant processes. They analyzed chemical compositions of metal elements and ionic species. Potassium and Cl⁻ in the sinter plant is higher than in other processes (Tsai *et al.*, 2007). The particulate from sintering process collected by Hleis *et al.* (2013) shows high levels

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of K and Cl⁻, followed by Fe, NH₄⁺, Ca, Na and Pb. Blast furnace emits high levels of Fe (Hleis *et al.*, 2013). Until now, no data of direct, fine-particulate measurement from stacks of these steel making units have been reported in the literature.

Particulate matter emissions from stationary sources contain filterable and condensable portions. Filterable PM are particles directly emitted from a stack as a solid or liquid at stack conditions and captured on the filter of a sampling train. Condensable PM means material that is vapor phase at stack conditions, but condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack. PM_{2.5} emission would be underestimated if condensable PM_{2.5} is not included, since condensable PM accounts for a significant portion for PM_{2.5} (Yang *et al.*, 2014). Very few procedures have been established to measure condensable PM emission, impinger method is the most common. Numerous studies have investigated the measurement artifacts and the artifacts have been reduced by optimization of the method (Corio and Sherwell, 2000; Richards *et al.*, 2005). In 2011, the USEPA announced Method 201A and Method 202 to measure filterable and condensable PM, respectively, and the methods were formally used for PM_{2.5} measurement for stationary emission sources.

In addition to in-stack sampling method, various types of dilution systems for PM_{2.5} measurement have been developed (e.g., Kong *et al.*, 2013; Lee *et al.*, 2013). Filterable and condensable PM_{2.5} can be collected on the same filter and the chemical compositions can be analyzed with this filter. However, a few parameters could affect the measurement accuracy of the dilution sampling system and standardized specification is still developing. Until standards or guidelines for dilution methods are established, USEPA Method 201A and 202 are the standard methods for PM_{2.5} measurement of stationary sources. Moreover, the extremely large, bulky sampling equipment used, with limited space for sampling plates, make it difficult to measure PM_{2.5} emissions. Today and in the foreseeable future, in-stack filter/impinger method is still the most practical way to collect PM_{2.5} samples from stationary sources. Since

condensable PM_{2.5} is seldom measured, very few reports for condensable PM_{2.5} emission characteristics have been published in the literature. In this study, filterable and condensable PM_{2.5} emissions from integrated iron and steel plants and EAF are measured. This is the first paper to report both filterable and condensable PM_{2.5} emissions and to characterize their chemical emissions. The results could improve the knowledge of compositions of the particulate and further used for control strategy.

EXPERIMENTAL SECTION

Test Stacks

PM_{2.5} emissions from four integrated iron and steel plants and EAF located in Taiwan were measured in this study. Basic information about these plants is listed in Table 1. Sintering process agglomerates iron ore fine material with other fine materials at high temperature to create a sinter product that can be used in the blast furnace. In sintering, constituent materials fuse to make a single porous mass with little change in the chemical properties of the ingredients. The purpose of sinter is to be used in converting iron into steel. Coal is converted to coke by driving off impurities to leave almost pure carbon. The coking process consists of heating coking coal to around 1000–1100°C in the absence of oxygen to drive off the volatile compounds (pyrolysis). This process results in the hard, porous coke. The coking process takes place over long periods of time between 12–36 hrs in the coke ovens. Once pushed out of the vessel the hot coke is then quenched with either water or air to cool it before storage, or is transferred directly to the blast furnace for use in iron making. A blast furnace is fed with the iron ore, coke and small quantities of fluxes (minerals, such as limestone, which are used to collect impurities). Air which is heated to about 1200°C is blown into the furnace through nozzles in the lower section. The air causes the coke to burn, producing carbon monoxide which reacts with the iron ore, as well as heat to melt the iron. Finally, the tap hole at the bottom of the furnace is opened and molten iron and slag are drained off. In the BOF, the iron is combined with varying amounts of steel scrap and small amounts of

Table 1. Basic information of the test plants in this study.

Plant	Sintering	Coke making	Blast furnace	BOF	EAF
Feedstock (t/h)	Flux (468)	Coal (159)	Liquid steel (166), coke (110)	Waste steel (15.7), liquid steel (581)	Waste steel (144), Charcoal (2.1)
Product (t/h)	Sintering ore (439.7)	Coke (119)	Liquid steel (266)	Liquid steel (583)	Steel (132)
Fuel	Coke (13.71 t/h), Coking oven gas (889 Nm ³ /h)	Coke oven gas (55 k Nm ³ /h)	Hot-blast stove of mixed gas (113 km ³ /h)	Natural gas (105 Nm ³ /h), Coke oven gas (2335 Nm ³ /h)	Natural gas (430 Nm ³ /h)
Air pollution control device	ESP, denitrification, de-dioxin	No	Bag house	Bag house	CO convertor, bag house
Stack temp. (°C)	161	178	57.5	57.8	70.5
Water content (%)	18.6	9.99	1.66	2.26	1.67
O ₂ (%)	12.2	6.1	20.7	20.6	20.0
CO ₂ (%)	9.9	20.6	< 0.2	< 0.2	0.60
CO (%)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
N ₂ (%)	77.9	73.3	79.3	79.4	79.4

flux. A lance is introduced into the vessel and blows 99% pure oxygen causing a temperature rise to 1700°C. The scrap melts, impurities are oxidized, and the carbon content is reduced by 90%, resulting in liquid steel.

The EAF reuses existing steel, avoiding the need for raw materials and their processing. The EAF operates on the basis of an electrical charge between two electrodes providing the heat for the process. Power is supplied through electrodes placed in the furnace, which produce an arc of electricity through the scrap steel, which in turn raises the temperature to 1600°C, melting the scrap. Any impurities may be removed through the use of fluxes and draining off slag through the tap hole.

Electric static precipitators (ESP) are installed in sintering plants, and bag house is used for blast furnaces BOF and EAF to control particulate emission. Exhaust gas properties of the test plants are also listed in Table 1. Stack temperatures are 161, 178, 57.5, 57.8 and 70.5°C for sintering, coke making, blast furnace, BOF and EAF, respectively. Coke-making plant has the highest stack temperature.

Sampling

Both filterable and condensable PM_{2.5} emissions were measured in this study. USEPA Method 201A (Determination of PM₁₀ and PM_{2.5} emissions from stationary sources) was performed for filterable PM_{2.5} measurements. Condensable PM_{2.5} was collected by USEPA Method 202 (Dry impinger method for determining condensable particulate emissions from stationary sources) set up downstream of Method 201A (USEPA, 2010) sampling equipment.

An APEX XC-5000 Automated Isokinetic Sampling Console sampling system which meets USEPA methods 201A and 202 requirements was used in this study. The main equipment for Method 201A includes front nozzle, PM_{2.5} cyclone, filter holder, pitot tube and stainless steel (with glass liner) sampling tube, vacuum pump and computer control console. The sampling rate for this study was controlled to within ± 20% isokinetically. Particulates with diameter less than 2.5 µm are sucked through the cyclone and are primarily collected on a 47 mm filter. The cyclone sampling-head temperature was maintained within ± 10°C of the stack temperature to ensure proper sizing and prevent condensation on the walls of the cyclones. Method 202 equipment includes a condenser, water dropout impinger, modified Greenburg Smith impinger and condensable PM filter. Condensable PM_{2.5} is mainly collected in the water dropout impinger and the (backup) modified Greenburg Smith impinger. A condensable PM_{2.5} filter placed between the second and the third impingers is used to improve the collection efficiency. Condensable PM_{2.5} is collected by condenser, dry impingers, pipelines and a backup Teflon filter after filterable PM is removed by a 47 mm filter. Leakage check is conducted before each sampling. To collect sufficient samples, the sampling volume was at least more than 2 m³. A detailed description of sampling method and materials can be found in Yang *et al.* (2014).

Sample Analysis

PM_{2.5}

A Pallflex 47 mm quartz filter is used for filterable PM collection. The filter is conditioned under a temperature of 20–23°C and a relative humidity of 30–40% for 24 hrs before and after sampling. After conditioning, the filter is weighed by the gravimetric technique (Sartorius balance, model Cubis 6.6S-DF). Condensable PM_{2.5} is collected in the water dropout impinger, the modified Greenburg Smith impinger and the condensable PM filter of the sampling train. The impinger contents are purged with Ultra-High Purity compressed nitrogen immediately after sample collection to remove dissolved sulfur dioxide gases from the impinger. The condensable PM train is purged at a minimum of 14 L/min for at least 1 hr. Purified water and organic solvents (n-hexane and acetone) were used to rinse the whole sampling pipeline, condenser, water dropout impinger, modified Greenburg Smith impinger and condensable PM filter, respectively. The aqueous (water soluble) and organic (organic solvent soluble) fractions were dried and weighed in the laboratory. Condensable PM_{2.5} is the summation of the two fractions. Field blanks (e.g., organic solvents and water field blanks) were measured for each sampling. Detailed procedures can be referred to in the USEPA Method 202.

Chemical Analysis

In addition to PM_{2.5} mass concentration, ion and metal concentrations were measured in this study. One-fourth of the PM_{2.5} filter sample was extracted with distilled deionized water in an ultrasonicator (Branson, model 5210) for 120 mins. The extracted samples were filtered by a 0.4 µm filter and then analyzed for ions (Na⁺, NH₄⁺, K⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻) by ion chromatography (IC, Dionex, model DX-120). The eluent was 1.8 mM Na₂CO₃/1.7 mM NaHCO₃ for anion and 20 mM methane sulfonic acid for cation analysis, respectively. Anion standards from High-Purity Standards (1033506 and 1034819) and cation standard from AccuStandard (210125090) were used to make calibration lines of the measured species. The R² of the calibrations are all higher than 0.995. Blank and duplicate tests were conducted for quality control. After weighing, the dried water-rinsed and organic solvent-rinsed condensable PM samples were rinsed to vials and dilute to 50 mL by distilled deionized water. A 25 mL sample was extracted following the above procedure and analyzed for the same ion species. Another 25 mL sample was used for metal analysis.

Another one-fourth of the PM_{2.5} filter sample was digested with acid mixture (HNO₃:Cl = 1:3) on a hot plate for 1 hr. The digested sample was analyzed for metal elements (Al, Ca, Fe, Mg, Mn, K, Na, Cu, Cd, Ni, Pb, Zn, As, Ba, Sb, Se, Sn) by inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Scientific, model iCAP 6000 Series). For condensable PM_{2.5}, the remaining 25 mL sample from ion analysis was digested by the same procedure for the filter sample and then analyzed for the same metal elements. Calibration lines were made by the standard from Merck (1.09492.0100). Blank and duplicate tests were conducted for quality control. Calibration verification was also performed during sample analysis. A new calibration

line should be made when the bias is higher than $\pm 10\%$.

RESULTS AND DISCUSSION

PM_{2.5} Concentrations

Filterable $PM_{2.5}$ concentrations emitted from sintering, coke making, blast furnace, BOF and EAF are 1.01, 0.37, 0.16, 0.15 and 0.28 mg/Nm^3 , respectively (Fig. 1). Sintering has the highest filterable $PM_{2.5}$ emission concentrations, followed by coke making, although an electric static precipitator was installed to remove particulate emission for sintering. The manufacturing process would result in much higher $PM_{2.5}$ concentrations for sintering process. The trend of filterable $PM_{2.5}$ emission concentration is the same as that of total PM emissions from the integrated iron and steel facility measured by Tsai *et al.* (2007). Condensable $PM_{2.5}$ concentrations for this study are shown in Fig. 1. Condensable $PM_{2.5}$ concentrations emitted from sintering, coke making, blast furnace, BOF and EAF are 65.3, 89.7, 3.84, 1.32 and 2.02 mg/Nm^3 , respectively. Coke making has the highest condensable $PM_{2.5}$ emission concentrations. Formation of condensable PM might depend on control devices, exhaust temperature and other source-specific conditions. Stack temperature is significantly important among these factors (Yang *et al.*, 2014). Coke making has the highest stack temperature (178°C), resulting in high emission of condensable PM.

Fig. 2 shows the percentages of filterable and condensable portion in $PM_{2.5}$ for the test plants. Real primary $PM_{2.5}$ contribution to the atmosphere is the summation of both filterable and condensable $PM_{2.5}$. The percentages of condensable $PM_{2.5}$ are 98.5%, 99.6%, 96.0%, 89.8% and 87.8% for sintering, coke making, blast furnace, BOF and EAF, respectively. Condensable $PM_{2.5}$ concentrations, which are significant, are much higher than filterable $PM_{2.5}$. Given

the significance of $PM_{2.5}$ to public health implications, condensable $PM_{2.5}$ measurements should not be ignored.

In this study, condensable $PM_{2.5}$ was collected by condenser, dry impinger and backup filter following USEPA Method 202. The sampling media was rinsed by water and organic solvents (acetone and hexane) sequentially. Condensable $PM_{2.5}$ thus consists of aqueous fraction (water rinse) and organic fraction (solvent rinse). The partitions of aqueous and organic fraction of condensable $PM_{2.5}$ for the test plants are shown in Fig. 3. The aqueous fraction accounts for 95.4%, 52.0%, 69.9%, 63.6% and 58.4% for sintering, coke making, blast furnace, BOF and EAF, respectively. Aqueous fraction dominates in condensable $PM_{2.5}$, which agrees with previous studies (Corio and Sherwell, 2000; Richards *et al.*, 2005; Yang *et al.*, 2014).

Chemical Emissions of Filterable $PM_{2.5}$

Concentrations of chemical species in the filterable and condensable $PM_{2.5}$ are listed in Table 2. Concentrations of K (156 $\mu g/m^3$), Fe (150 $\mu g/m^3$), Pb (63.1 $\mu g/m^3$) and Zn (8.13 $\mu g/m^3$) are the most common elements in the sintering process. Since iron ore is the major feedstock, high Fe emission in sinter process is predictable and reasonable. In addition to iron ore, recycled materials, including blast furnace fly ash, BOF, and sinter plant and blast furnace de-zinc slurry are added as feedstock. The recycled materials contain K, Pb and Zn, causing high concentrations of these elements. The results of the measured ions are similar with metal element. K^+ concentration (45.3 $\mu g/m^3$) is high for sinter plant. SO_4^{2-} (72.6 $\mu g/m^3$) is the highest emission ion for sinter process and other plants. The raw materials contain a significant amount of sulfur, which reacts with oxygen to form sulfur dioxide (SO_2). SO_2 could further be transformed to SO_4^{2-} . High emission of Cl^- (11.8 $\mu g/m^3$) is due to the addition of KCl as flux in the sinter process. The

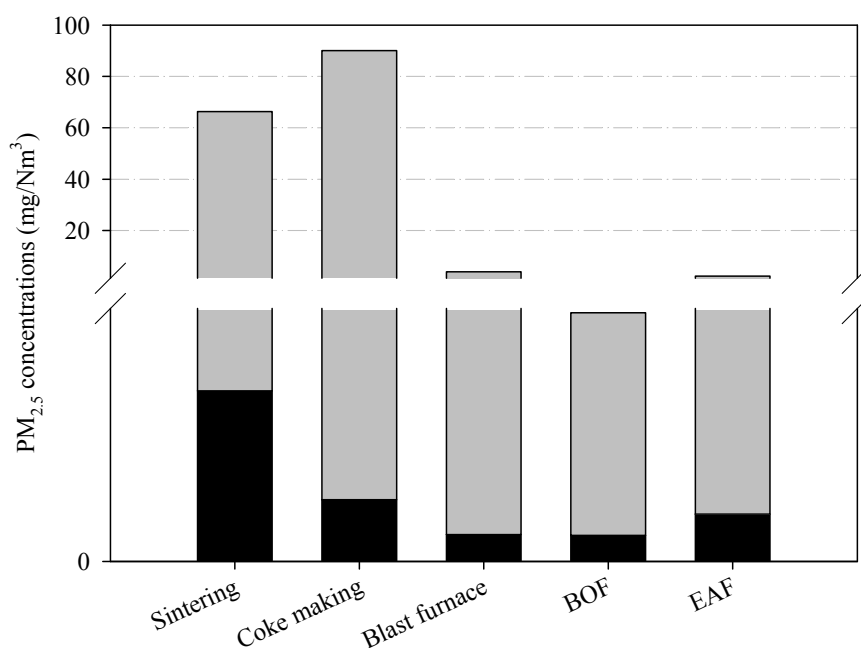


Fig. 1. $PM_{2.5}$ concentrations for the plants.

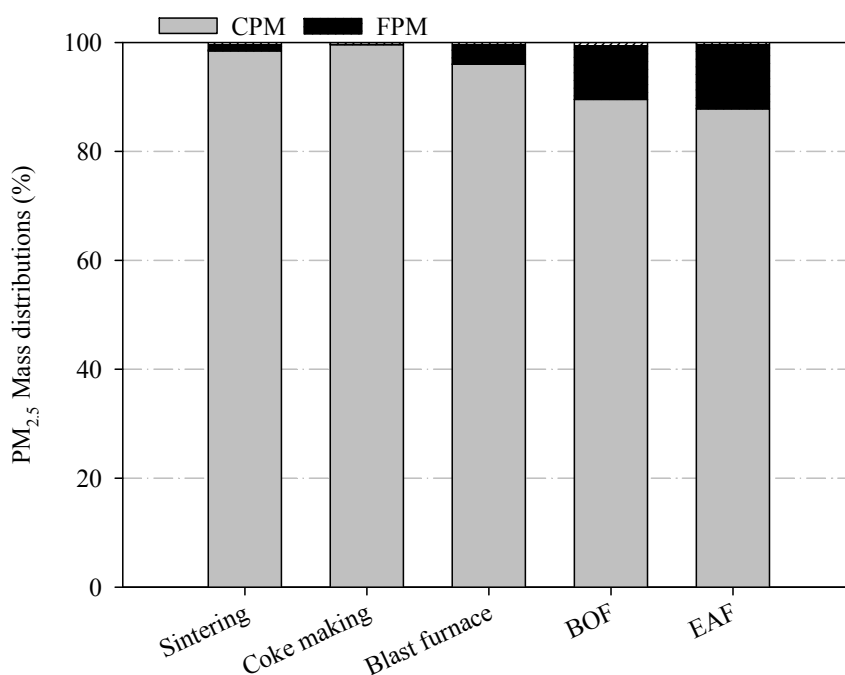


Fig. 2. Partitions of filterable and condensable PM_{2.5} for the plants.

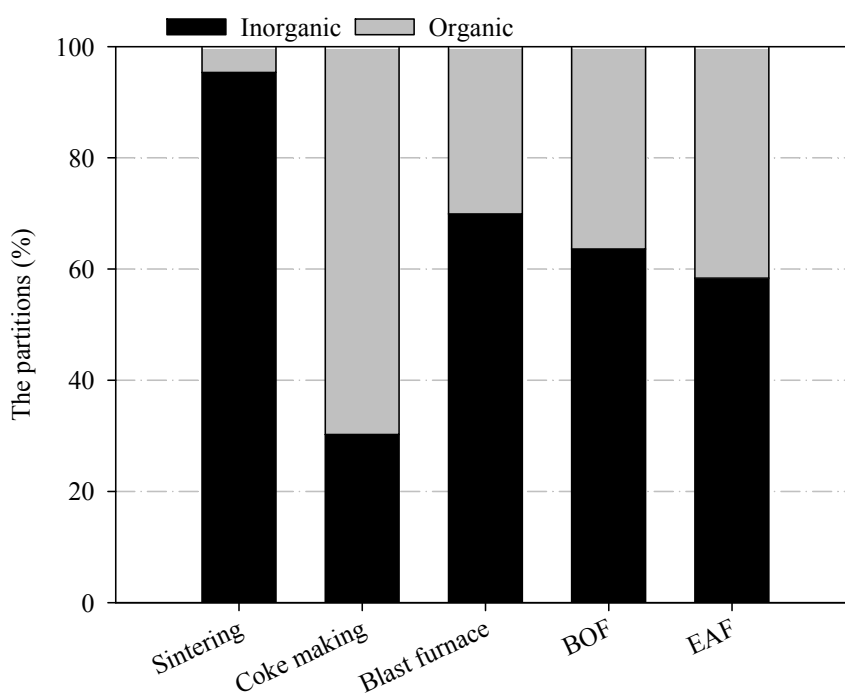


Fig. 3. The partitions of aqueous and organic fraction of condensable PM_{2.5}.

results are similar with total particulate matter emissions from sinter plant investigated by Tsai *et al.* (2007).

The coking coals are carbonized under high temperature (1100°C) for 16–18 hrs in an oxygen deficient oven to concentrate the carbon. Dry distillation in the oven produces the hot coke. The concentration of NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻ are 46.0, 27.1, 27.7 and 44.0 μg/m³, respectively (Table 2). The coking coals comprise mainly carbon and other minor elements like H, O, N, S, etc. Since the raw

material for coke making contains fewer metal elements, ion emissions are higher than metal elements. Sintered ore, coke, crushed ore and lime are fed into the blast furnace at high temperature. Air is blown into the furnace and the chemical reaction takes place inside. The major end product is molten iron which is then transferred to BOF with oxygen flow to make steel. Flux of burnt lime is added to remove impurities and protect the furnace lining. Since the major feedstocks of blast furnace and BOF are from sintering and

Table 2. Concentrations of chemical species in the filterable and condensable PM_{2.5} (μg/Nm³).

Species	Sintering		Coke making		Blast furnace		BOF		EAF
	FPM ^a	CPM ^b	FPM	CPM	FPM	CPM	FPM	CPM	FPM
Al	8.01	8.93	0.950	18.7	1.51	9.63	0.520	0.55	0.310
Ca	2.80	8.72	1.97	9.87	1.85	15.1	0.670	8.43	0.680
Fe	150	33.2	3.14	14.8	13.1	2.58	4.19	1.24	27.9
Mg	2.76	16.8	N.D.	18.6	N.D.	3.21	N.D.	1.56	0.440
Mn	0.970	1.56	0.080	1.27	0.040	0.150	0.140	0.050	2.31
K	156	23.0	1.38	122	4.40	52.8	1.66	19.6	5.71
Na	1.22	87.8	3.71	174	0.520	68.4	1.21	34.7	5.69
Cu	0.920	5.64	0.310	3.39	N.D.	0.360	0.200	0.270	0.540
Cd	2.24	0.008	N.D.	0.020	N.D.	N.D.	N.D.	N.D.	0.170
Ni	N.D.	1.92	1.02	2.48	0.340	0.560	0.220	0.130	0.550
Pb	63.1	0.123	0.070	0.460	N.D.	0.040	0.180	0.030	9.54
Zn	8.13	8.92	N.D.	26.9	0.540	2.11	0.960	1.08	75.8
As	N.D.	N.D.	N.D.	0.120	N.D.	0.010	N.D.	0.020	N.D.
Ba	N.D.	0.036	0.100	0.460	N.D.	0.070	N.D.	0.020	0.030
Sb	N.D.	N.D.	N.D.	0.160	N.D.	0.010	N.D.	0.050	0.120
Se	N.D.	0.060	0.210	0.280	N.D.	N.D.	N.D.	0.010	N.D.
Sn	N.D.	0.052	N.D.	0.240	0.370	0.060	0.200	0.090	5.33
Na ⁺	6.84	15.2	5.73	362	1.94	301	2.05	137	4.00
NH ₄ ⁺	0.830	321	46.0	851	9.29	8.39	7.15	5.46	7.06
K ⁺	45.3	8.62	5.26	662	1.96	182	2.27	70.8	3.54
Ca ²⁺	9.45	15.3	2.7	100	1.00	11.6	1.26	4.75	1.28
Cl ⁻	11.8	161	27.1	927	10.1	216	12.0	100	14.8
NO ₃ ⁻	1.84	0.820	27.7	175	9.87	39.0	11.9	23.5	12.9
SO ₄ ²⁻	72.6	580	44.0	2551	9.26	19.7	10.8	33.3	11.8

^aFPM: filterable PM_{2.5}; ^bCPM: condensable PM_{2.5}.

coke making, the major metal elements and ions are similar with the two processes. The EAF heats charged material by electric arcs. The feedstock is primarily recycled steel for the test EAF. In addition to Fe (27.9 μg/m³), the emissions of Pb (9.54 μg/m³), Zn (75.8 μg/m³) and Sn (5.33 μg/m³) are high (Table 2). This is due to the complexity of the recycled steel feedstock.

Emission of Chemical Species in the Condensable PM_{2.5}

Concentrations of chemical species in condensable PM_{2.5} for the test plants are also listed in Table 2. Concentrations of ions in condensable PM_{2.5} are higher than those of metal elements for all the test plants. SO₄²⁻ is the highest emission ion for sinter process and coke making. For blast furnace, BOF and EAF; however, Na⁺, K⁺ and Cl⁻ are the predominating ions. The measurement method of condensable PM_{2.5} has been criticized since it was first promulgated in 1991. Positive bias might exist in the measured data due to the conversion of dissolved SO₂ to SO₄²⁻ in the sampling procedure. Studies using the former Method 202 show that SO₄²⁻ is the major form of condensable PM (Corio and Sherwell, 2000; Farber and Sloat, 2005). Numerous improvements have been made to reduce the positive bias by the more recent USEPA Method 202 published in 2011. Since SO₄²⁻ concentrations are not as high as the previous studies, the bias seems reduced by the later revised method.

For metal elements, concentrations of Na and K are highest for all the plants. Na concentrations in condensable

PM_{2.5} are 87.8, 174, 68.4, 34.7 and 43.9 μg/m³ and K concentrations are 23.0, 122, 52.8, 19.6 and 34.8 μg/m³ for sintering, coke making, blast furnace, BOF and EAF, respectively. The two elements account for 56.3%, 75.2%, 78.2%, 80.1% and 77.3% of the analyzed metals for sintering, coke making, blast furnace, BOF and EAF, respectively. The high percentages of these two elements might be caused by their high vaporization potential. Tsukada *et al.* (2008) found that some metals exist in condensable phase with high concentration. According to thermodynamic equilibrium calculations, the metals can exist in gas form and be collected by Method 202.

Comparison between Filterable and Condensable PM_{2.5}

Partitions of the analyzed chemical species for filterable and condensable PM_{2.5} are listed in Table 3. Percentages of ions are 84.8%, 93.5%, 83.4%, 84.7% and 84.5% for sintering, coke making, blast furnace, BOF and EAF, respectively. Ions are dominant in condensable PM_{2.5} for all the test plants. During sampling using methods 201A and 202, gas-phase precursors in the stack penetrate the filter and form condensable PM_{2.5} upon cooling (e.g., SO₃ combines with water to form H₂SO₄ and NH₃ reacts with HCl to form NH₄Cl), which results in the predominance of ions in condensable PM_{2.5}.

The same for particulate, the real contribution of the chemical elements to the atmosphere is the summation of both filterable and condensable portions. Chemical element emissions of the two portions are shown in Table 4. The

Table 3. Percentages of Chemical species of filterable and condensable PM_{2.5} (%).

Species	Sintering		Coke making		Blast furnace		BOF		EAF
	FPM ^a	CPM ^b	FPM	CPM	FPM	CPM	FPM	CPM	FPM
Al	1.47	0.69	0.55	0.31	2.28	1.03	0.90	0.12	0.16
Ca	0.51	0.67	1.15	0.16	2.80	1.62	1.16	1.90	0.36
Fe	27.5	2.55	1.83	0.25	19.82	0.28	7.28	0.28	14.6
Mg	0.51	1.29	0.00	0.31	0.00	0.34	0.00	0.35	0.23
Mn	0.18	0.12	0.05	0.02	0.06	0.02	0.24	0.01	1.21
K	28.6	1.77	0.80	2.03	6.66	5.66	2.88	4.43	3.00
Na	0.22	6.76	2.16	2.89	0.79	7.33	2.10	7.84	2.99
Cu	0.17	0.43	0.18	0.06	0.00	0.04	0.35	0.06	0.28
Cd	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09
Ni	0.00	0.15	0.59	0.04	0.51	0.06	0.38	0.03	0.29
Pb	11.6	0.01	0.04	0.01	0.00	0.00	0.31	0.01	5.01
Zn	1.49	0.69	0.00	0.45	0.82	0.23	1.67	0.24	39.8
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.06	0.01	0.00	0.01	0.00	0.00	0.02
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06
Se	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.00	0.00	0.00	0.00	0.56	0.01	0.35	0.02	2.80
Na ⁺	1.26	1.17	3.34	6.01	2.94	32.3	3.56	31.0	2.10
NH ₄ ⁺	0.15	24.7	26.8	14.1	14.1	0.90	12.4	1.23	3.71
K ⁺	8.31	0.66	3.07	11.0	2.97	19.5	3.94	16.0	1.86
Ca ²⁺	1.73	1.18	1.57	1.66	1.51	1.24	2.19	1.07	0.67
Cl ⁻	2.17	12.4	15.8	15.4	15.3	23.2	20.8	22.6	7.77
NO ₃ ⁻	0.34	0.06	16.16	2.91	14.93	4.18	20.67	5.31	6.77
SO ₄ ²⁻	13.3	44.7	25.67	42.36	14.01	2.11	18.76	7.52	6.19

^aFPM: filterable PM_{2.5}; ^bCPM: condensable PM_{2.5}.

measured metal and ion emissions increase significantly for all the test plants in comparison with filterable PM_{2.5} only (Table 2) while the condensable PM_{2.5} is included. The increase is considerable.

A previous study (EPRI, 2008) investigated the accuracy of the inclusion of some components in condensable PM_{2.5}. There is no formal definition of condensable PM_{2.5} and its component. Condensable PM_{2.5} is defined operationally by USEPA Method 202 as the material collected. It is suggested that speciation of certain condensable components can be done for more accurate estimation of their influences on the atmosphere if necessary (EPRI, 2008). Although a lot of analytical artifacts have been eliminated or reduced, condensable PM_{2.5} collected by dry impingers cannot accurately represent particulate contributions to the atmosphere. Dilution techniques are thought to more closely replicate the process of condensation upon mixing of stack gases with ambient air. However, dilution sampling is quite bulky and expensive to operate so that no data for iron and steel industries is reported. The data measured in this study provide deeper understanding of both filterable and condensable PM_{2.5} emissions from iron and steel industries and the data can be used for further estimations of their contributions to the atmosphere.

CONCLUSIONS

PM_{2.5} samples emitted from four integrated iron and steel plants and an EAF were collected. Both filterable and

condensable PM_{2.5} concentrations were measured. Chemical characteristics of water soluble ions and metal elements for these samples were investigated. Sintering has the highest filterable PM_{2.5} emission concentrations, followed by coke making, even though an electric static precipitator was installed on the stacks to remove particulate emission produced by sintering. Coke making has the highest condensable PM_{2.5} emission concentrations. The percentages of condensable PM_{2.5} are 98.5%, 99.6%, 96.0%, 89.8% and 87.8% for sintering, coke making, blast furnace, BOF and EAF, respectively. Condensable PM_{2.5} concentrations are much higher than filterable PM_{2.5}. Concentrations of K (156 µg/m³), Fe (150 µg/m³), Pb (63.1 µg/m³) and Zn (8.13 µg/m³) are the highest elements in filterable PM_{2.5} of sintering process. SO₄²⁻ is the highest emission ion for sinter process and other plants. The coking coals comprise mainly carbon and other minor elements like H, O, N, S and etc. Since the raw material for the coke-making process contains fewer metal elements, ion emissions are higher than metal elements. The feedstock of EAF is mainly recycled steel, resulting in high emissions of Fe, Pb, Zn and Sn. Most measured chemical species are mainly distributed in condensable PM_{2.5}. Contributions of primary PM_{2.5} and the chemical species include filterable and condensable fractions. This study provides a deeper understanding of both filterable and condensable PM_{2.5} emissions from iron and steel industries. The measured data can be used to estimate their contributions to the atmosphere.

Table 4. Chemical emissions of PM_{2.5} (summation of filterable and condensable PM_{2.5}) (µg/Nm³).

Species	Sintering	Coke making	Blast furnace	BOF	EAF
Al	16.9	19.7	11.1	1.07	4.93
Ca	11.5	11.8	16.9	9.10	13.3
Fe	183	17.9	15.7	5.43	28.5
Mg	19.5	18.6	3.21	1.56	2.63
Mn	2.53	1.35	0.190	0.190	2.39
K	179	123	57.2	21.3	40.5
Na	89.1	178	68.9	35.9	49.6
Cu	6.56	3.70	0.360	0.470	0.650
Cd	2.25	0.020	N.D.	N.D.	0.170
Ni	1.92	3.50	0.900	0.350	0.710
Pb	63.2	0.530	0.040	0.210	9.57
Zn	17.0	26.9	2.65	2.04	78.4
As	N.D.	0.120	0.010	0.020	0.020
Ba	0.036	0.560	0.070	0.020	0.080
Sb	N.D.	0.160	0.010	0.050	0.130
Se	0.060	0.490	N.D.	0.010	N.D.
Sn	0.052	0.240	0.430	0.290	5.37
Na ⁺	22.0	368	303	139	206
NH ₄ ⁺	322	897	17.7	12.6	18.5
K ⁺	53.9	667	184	73.1	113
Ca ²⁺	24.8	103	12.6	6.01	8.00
Cl ⁻	172	954	226	112	128
NO ₃ ⁻	2.66	203	48.9	35.4	43.3
SO ₄ ²⁻	653	2595	29.0	44.1	93.8

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