

Chemical constituents in particulate emissions from an integrated iron and steel facility

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Abstract

Particle emissions from four integrated iron and steel plant processes, i.e., coke making, sintering, cold forming, and hot forming, were investigated in this study. Particle compositions of 21 element species, 11 ionic species, elemental carbon (EC), organic carbon (OC) and 16 polyaromatic hydrocarbons (PAHs) were analyzed to create “fingerprints” of the particles emitted from various processes in an integrated iron and steel plant. Results indicated that element compositions (0.11–0.42 g/g), water-soluble ions (0.34–0.52 g/g), elemental carbon (0.008–0.14 g/g), organic carbon (0.02–0.06 g/g) and PAHs (0.52–6.2 mg/g) contributed to the particle mass. In general, sulfur had a higher mass contribution than the other elements, which resulted from the use of coal, flux, heavy oil, and many recycled materials in the iron and steel plant. The particle mass contribution of potassium and chlorine in the sinter plant was higher than in other processes; this may be attributed to the lower boiling point and volatility of potassium. In addition, many recycled materials were fed into the sinter plant, causing a high concentration of potassium and chlorine in the particle phase. Eight PAH compounds were analyzed in the four processes. The carcinogenic compound Benzo(a)pyrene (BaP) was detectable only in the sintering process.

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1. Introduction

The iron and steel industry produces important materials for automotive, construction and consumer product applications. But it is also one of the most energy-intensive industries and produces significant pollution emissions [1–2].

The major operations of the iron and steel industry include coke production, sintering, iron production, iron preparation, steel production, semi-finished product preparation, finished product preparation, heat and electrical supply, and the handling and transport of raw, intermediate, and waste materials. The sinter process, coke making, the heating furnace and the blast furnace are the major air pollution sources.

Over 90% of metallurgical coke production is used in blast furnaces, sintering plants and foundries in the iron and steel

industry [3], where it functions as a reductant. For an integrated iron and steel plant, iron ore is the raw material, and it consists mainly of hematite (Fe_2O_3) and magnetite (Fe_3O_4) or goethite (FeOOH) [4]. The sintering of iron ore is one of the most important processes in an integrated iron and steel plant. The mixture of crushed ores, coke, lime and iron-bearing residues is heated at high temperatures and sintered in a blast furnace.

Coke ovens are the major source of PAH emission in the iron and steel sector; the PAH levels depend on the fuel used [5] and the performance of the combustion control system. In Norway and Canada, coke ovens are one of the major sources of PAH emissions in the industrial sector [6–7]. In addition, PAHs not only are emitted from coke oven particulate, but also have been identified in waste materials from coking processes [8].

Unless in a particulate state, heavy metals may be another important issue for pollution abatement in the iron and steel industry. Most studies have investigated the metal compositions of dust, sludge, and slag of blast furnaces (BF), basic oxygen furnaces (BOF), and electric arc furnaces [9–11]. Few studies

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have focused on metal composition in airborne particulates from iron and steel processes [12]. Machemer analyzed Fe, Mn, Si, and Zn as the major elements from the BOF and BF [4].

There is only one integrated iron and steel plant in Taiwan. But similar processes are used in other countries, including Japan, India, China, and Korea [13]. The iron and steel industry contributed total emissions of 0.89% PM₁₀ (3204 tonnes/year), 5.75% SO_x (23419 tonnes/year), 4.78% NO_x (24692 tonnes/year), 0.15% NMHC (1335 tonnes/year), 1.35% CO (28574 tonnes/year), and 0.01% Pb (0.02 tonnes/year). The iron and steel industry contributed to 8% of Taiwan's GDP (gross domestic product) in 2003 [14]. The yield of coke and steel was 3.9 and 18.8 million tonnes, respectively, in 2003, with 57% of the steel production from integrated plants [13]. The integrated iron and steel plant contributed about 1% of the total steel production in the world [15].

Generally, the source composition profile of the particles does not exactly reflect the ambient particle composition profile. Chemical mass balance (CMB) has been successfully used to identify the source contribution to ambient air pollutants in recent years [16–19]. However, the details of source particle and gas chemical compositions are one of the important components of CMB, with chemical constituents regarded as a “fingerprint.” Therefore, the investigation of source pollution characteristics is necessary to quantify the source contribution to the receptor in the CMB model [18].

According to the Taiwan Emission Data System, sintering, coke making, blast furnaces, and heating processes contribute over 90% of the emissions from the integrated iron and steel plant [20]. Therefore, the objectives of this study were to sample the particles emitted from these processes in an integrated steel plant. Few studies have focused on the detailed compositions of the particle phase. Therefore, the particle samples

were digested with an acid mixture, and then the elemental compositions were determined by ICP-AES and ICP-MS. In addition, PAHs, elemental carbon, organic carbon, and water-soluble ions of particles were measured in this investigation. Particle emission factors and detailed compositions of particles were measured to create “fingerprints” of the particles from various processes in an integrated iron and steel plant.

2. Experimental

Particle samples of all sizes were taken from the sources in an integrated iron and steel plant located in southern Taiwan; sampling was done every four hours to obtain enough particles for analysis. The operation conditions of the four processes carried out in the plant are shown in Table 1.

Coal is used as a raw material in the coke making process. Raw materials for the sintering process include the ash of BF and BOF, returned fine particles from the sintering plant, and blended ore, serpentine, limestone and coke breeze. In the cold forming process, the hot-rolled bands are pickled by acid and then cold-rolled at room temperature to form a thinner coil. Slab (rectangular type) steel is rolled, milled and heated to 1200 °C, then rolled, leveled, and cooled in the hot forming process. Finally, the slab steel is manufactured to form hot-rolled coils.

2.1. Particle sampling

Particle sampling of each process was conducted by U.S. EPA Method 5 [21]. The method selects the proper stack position and then puts the sampling probe into the stack sampling point. Adjusting the suction orifice makes the sampling velocity similar to the flue velocity when it reaches the isokinetic condition. All quartz thimble filters (Advantec, No. 88RH, thickness: 1.6 mm,

Table 1
Baseline information and operating conditions of four processes in the integrated iron and steel plant

Parameters	Coke making	Sintering	Cold forming	Hot forming
Feedstock	Coal: 29.4–192 tonnes/h	Flux: 26–36 tonnes/h; return fine: 139–170 tonnes/h; blended ore: 478.5–585 tonnes/h	Cold-rolled coil: 140–175 tonnes/h	Plate and billet: 164–261 tonnes/h
Fuel	BFG/COG: 19100–62000 N m ³ /h	Coke: 28.2–33.5 tonnes/h; COG: 1200–1320 N m ³ /h	COG: 9267.5–12018 N m ³ /h	COG: 7000 N m ³ /h
Operation temperature (°C)	1230–1260	1050–1150	830–850	1150–1270
Product	Coke: 23.6–150 tonnes/h	Sintering ore: 435–500 tonnes/h	Cold-rolled coil 140–175 tonnes/h	144.2–257.4 tonnes/h
Gas flow rate (N m ³ /min)	2111.56–3477.6	9763.3–16673.8	1141.43–1430.56	1258.97–1724.68
APCD	No	ESP/denitrification	No	No
PM (mg/N m ³)	3.0–4.8	12.9–13.2	0.6–1.2	2.5–226
CO ₂ (%)	17.5–18.7	5.3–7.7	4.9–5.3	5.3–6.7
O ₂ (%)	9.5–10.1	13.5–16.1	11.2–12.3	8.4–12.5
CO (%)	<0.2	<0.2	<0.2	<0.2
THC (ppm)	25.3–59.3	96.8–101.6	228.4–250.6	4.4–5.0
NMHC (ppm)	0.7–22.1	12.6–24	15.2–16.5	4.4–5.0
SO _x (ppm)	15.1–21.6	127–169	54–85	23.4–23.8
NO _x (ppm)	47.4–53.0	23.4–110.5	74–103	67.2–103
H ₂ O (%)	8.8–9.1	6.3–7.5	8.5–9.3	6.7–12.9
PM (mg/N m ³)	3.0–4.8	12.9–13.2	0.6–1.2	2.5–226

APCD is the abbreviated for air pollution control device. ESP is the abbreviated for electrostatic precipitation. BFG and COG is abbreviated for blast furnace gas and coke oven gas, respectively. N m³ is the gas condition at 1 atm and 0 °C.

25 mm × 90 mm, Japan) were baked at 900 °C for 3 h before use in order to ensure low concentrations of organic compounds on the blank filter materials. Each process required three quartz thimble filter samples.

2.2. Determination of elemental constituents in particulate emissions

One-fourth of the particle filter sample was mixed with a 20 ml acid mixture (HNO₃:HClO₄:HF = 5:3:2, v/v) in a Teflon-lined closed vessel and placed in a high-pressure digestion oven at 170 °C for 5 h. The digested acid mixture was analyzed to determine the trace elements. A Perkin-Elmer OPTIMA 3000 ICP-AES was used to determine the Al, Ca, Fe, K, Mg, Na, S, Co and Zn concentrations. Additionally, a SCIEX Elan Model 5000 ICP-MS manufactured by Perkin-Elmer was employed to determine As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, and V concentrations. The blank and duplicate samples were also done in this study.

To validate the digestion method, the NIST Standard Reference Material, SRM 1648, was used. About 0.1 mg of SRM 1648, which approximates the composition of road dust particulates, was used to examine the accuracy and reliability of the digestion method. Al, As, Ba, Co, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sb, Se, V, and Zn were recovered in the acceptable range (recovery: 84–107%); however, the value for Cr recovery was only 47%. A major error in Cr determination was due to the Cr loss incurred through volatilization during sample digestion. Many investigators have reported the volatility effect on Cr(VI) from the digestion and evaporation process. Interference problems due to argon gas, filter media, and/or acid-derived background ions, encountered in low-resolution ICP-MS, introduced additional errors in the Cr determination. Specifically, ⁴⁰Ar¹²C⁺, ³⁸Ar¹⁴N⁺, ³⁵Cl¹⁶OH⁺, and ³⁵Cl¹⁷O⁺ ions inhibit detection of the ⁵²Cr⁺ isotope. Even for relatively minor isotopes, there is interference (e.g., between ⁵³Cr⁺ and ³⁷Cl¹⁶O⁺, and ⁵²Cr⁺ and ⁴⁰Ar¹²C⁺) [22].

2.3. Determination of PAHs in particulate emissions

2.3.1. Chemicals

The 16 USEPA PAH standards (purity of >99%) including Naphthalene (NaP), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IND), Dibenzo(a,h)anthracene (DBA), and Benzo(g,h,i)pyrene (BghiP) were purchased from Supelco Inc. (USA). In general, the higher the molecular weight of PAHs, the more serious the carcinogenic risk they pose [23]. They are classified by the numbers of aromatic rings as follows: 2-ring including NaP; 3-ring including AcPy, Acp, Flu, PA and Ant; 4-ring including FL, Pyr, BaA and CHR; 5-ring including BbF, BkF, and BaP; and 6-ring including IND, DBA, and BghiP. Dichloromethane, hexane, silica gel (0.063–0.200 mm, activated at 150 °C for 18 h prior to use), anhydrous sodium

sulfate (baked at 400 °C for 4 h prior to use) and other reagents were pesticide analysis grade and/or residue analysis grade and purchased from E. Merck, Germany.

2.3.2. Sample extraction and cleanup

Samples one-fourth of the thimble quartz filter size were extracted using the Soxhlet extraction procedure in an all-glass Soxhlet system combined with an electro-thermal heating plate. The samples were extracted for 24 h with 200 mL of mixed solvent (hexane:dichloromethane = 50:50, by volume) in a 250-mL flat-bottom flask. The extract was concentrated on a rotary evaporator (EYELA, Japan) equipped with a water bath held at 35 °C, and the solution volume was reduced to 1–2 mL. In the cleanup process, the residual solution was introduced into a silica column (1 cm i.d. and 25 cm length), and the column was eluted with 50 mL of mixed solvent (hexane:dichloromethane = 50:50, by volume) after elution of 10 mL of hexane. About 2 cm height of anhydrous sodium sulfate was packed at the fore-end of the cleanup column for the purpose of excluding water. Only the part of the elution using the mixed solvent, the effluent containing the PAHs, was collected and concentrated again as above, then quantified to 2 mL (adding mixed solvent). The final solution (2 mL) was analyzed with the PAH gas chromatography (GC) method.

2.3.3. Gas chromatography mass spectrometry

The GC apparatus consisted of a Hewlett-Packard GC 6890 equipped with a mass (5973 N) and split/splitless injector. An HP-5MS capillary column (5% phenyl methyl siloxane, 30 m, i.d. 0.32 mm, and film thickness 0.25 μm) was used. To analyze the PAHs, the injector program was set to 280 °C at the pulsed splitless mode (12 psi for 1 min). The oven temperature program was 60 °C for 1 min, 35 °C min⁻¹ to 170 °C, 8 °C min⁻¹ to 210 °C, and 4 °C min⁻¹ to 300 °C, which was held for 15 min. The carrier gas (99.9995% nitrogen) flow rate was held at 1.5 mL min⁻¹. The detector temperature was 300 °C, and the total gas flow rate was 30 mL min⁻¹ (makeup plus column). The mixed stock solution was used to make five concentrations of mixed standard solution, which were required to establish calibration curves for PAH measurement. The injection volume was 1 μL for all samples. The PAH spike was added to the blank sampling thimbles prior to extraction for recovery analyses. The average recoveries of the PAHs based on QA/QC were 74% (naphthalene) to 98% (benzo(k)fluoranthene).

2.4. Determination of ionic constituents in particulate emissions

A sample, one-quarter of the thimble quartz filter, was put into an 80 ml vial. The filter was first wet in 2 ml of HPLC grade methanol and then mechanically extracted for 30 min with 18 ml distilled deionized water. After extraction, all of the extracts were filtered by a 0.4 μm filter, and then the concentrations of the major water-soluble particle species (anion species: SO₄²⁻, NO₃⁻, NO₂⁻, Cl⁻, F⁻ and Br⁻; cation species: Na⁺, NH₄⁺, Ca²⁺, Mg²⁺) were determined using a Dionex model 120 ion chromatograph [24–25].

The anions were analyzed with an AG12A guard column and an AS12 analytical column. The eluent for anion analysis was 2.7 mmol/L Na_2CO_3 and 0.3 mmol/L NaHCO_3 . The cations were analyzed with a CG12A guard column and a CS12A analytical column. The eluent was 20 mmol/L $\text{CH}_4\text{O}_3\text{S}$. Samples were injected manually with a 100 μL loop. The variation of cation and anion charge balance was less than 15%.

2.5. Determination of organic and elemental carbon in particulate emissions

Particle samples that were intended for carbon analysis were collected on quartz-fiber thimble filters that had previously been heated in air at 900 °C for 3 h to lower their carbon blank level. The particle thimble sample was stored below 4 °C until analysis. Total carbon (TC) and elemental carbon (EC) were measured with a C/H/N elemental analyzer (Carlo Erba EA 1110). The procedure performed in this study to determine particle carbon content is similar to the method described by Cachier et al. [26]. Samples one-eighth of each thimble filter were heated in advance in a 340 °C oven for 100 min to expel the organic carbon (OC) content, then fed into the elemental analyzer to obtain the elemental carbon content. Another one-eighth sample was fed directly into the elemental analyzer without pre-treatment to obtain the TC concentration. In general, the use of this method to measure the EC fraction could result in overestimation. This is a very controversial issue, and the use of thermo-optical techniques is highly recommended by other studies [27–29].

3. Results and discussion

Table 1 shows the operation conditions, which included the feed rate, temperature, product, gas flow rate, and air pollution control devices for the four processes – i.e., coke making, sintering, hot forming, and cold forming – selected to investigate iron and steel plant emission characteristics in this study. The mixing and crushing coking coals are charged into the coke oven. Dry distillation in the oven produces hot coke and crude coke oven gas (COG.). Blast furnace gas (BFG) and COG are used as the fuel in the coke-making process. In general, the content of the COG includes CO (21%), CO_2 (21%), H_2 (3.2%) and N_2 (55%).

3.1. General characteristics of emissions

Table 1 shows the water vapor content, particle, SO_x , NO_x , NMHC (non-methane hydrocarbon), THC (total hydrocarbon), CO_2 , CO, and O_2 concentrations of the four processes. Results indicate that the hot forming process produced a wider particle concentration than the other processes. This is attributed to the bloom via the descaling, scarfing, rolling and cutting process that forms billets and readily emits particles. In the cold forming process, THC concentration is higher than in the other processes. This is caused by the oil addition; the oil is volatilized by heating, and THC is produced by the incomplete combustion of COG. In addition, the sintering process provides a higher SO_x concentration than the other processes, which might be contributed by the

BF and BOF recycle ash and ore, especially the BOF de-sulfur ash.

3.2. Chemical constituents of particulate emissions

3.2.1. Elemental composition of the particles

Table 2 shows the elemental compositions of particles for the four processes. Results indicate that sulfur, iron, and sodium are the major elements in the coke making process. The contribution of K and Pb is higher in the sintering process than in the other processes, especially the K contribution, which is about 15% of the particle mass in the sintering process. High lead content (2%) is also found in the sintering process. Furthermore, S, Fe, Na, K and Ni contribute 0.15, 0.13, 0.03, 0.025, and 0.021 g/g, respectively, to the particles in the cold forming process. In hot forming, S, Fe, Na and Ca are the major particle elements.

According to the elemental composition of blast furnace particles in Machemer's investigation [4], the BF particle iron content was significantly higher than in the other processes in this study. Al, Ca, K, Mg and S contents of the four process particles were higher than that of the BF particle. In addition, the zinc content (1.9–9.4 mg/g) in particles of the four processes was higher than that of the BF particle [4].

The BF, BOF, desulfur, BF fly, and fly ashes from the sinter plant electric precipitation, and the recovery of BF de-zinc slurry and BOF dewatering slurry were recycled to the sinter plant. In addition, the return fines from the sintering plant, blended ore, serpentine, limestone and coke breeze were also recycled and mixed to make sinter. The amount of these materials was about 1500 tonnes/day. Therefore, a large amount of recycled material, which may contain chloride and potassium compounds, is used in sinter plants. The recycled materials are also the reason for the high lead and zinc emissions in particles of the sintering process; correct disposal of these particles is essential.

The chloride compounds may be attributed to materials like polyvinyl chloride contained in the iron and steel scrap. Hydrochloric acid pickling is used in the Tandem Cold Mill (TCM) process; the acid tank slurry is recycled into the sinter plant and may cause chloride emissions during the sintering process.

Potassium was more easily volatilized than other metal elements except mercury in this study. Therefore, potassium compounds volatilized in the sintering process and then condensed into particles. In addition, there were many raw materials containing K_2O , i.e., BF slag and slurry. Furthermore, KCl is used as a kind of flux in the sinter plant; therefore, it may cause the K and Cl content in the particle phase.

Some of the Ca^{2+} , K^+ , and Na^+ concentrations measured by ionic chromatography were higher than ICP data in particulate constituents, which may be attributed to the pretreated procedures, analysis method and matrix interference.

3.2.2. Organic and black carbon and ionic compound concentration

Table 3 shows the iron compounds and organic and elemental carbon concentrations in the particles. Results indicate that the

Table 2
Elemental concentrations in particulate emissions from various processes in steel plant

Concentration (mg/g)	Coke making	Sintering	Cold forming	Hot forming	MDL ^a (mg/g)
Al	2.8370 ± 0.0995 ^b	4.2761 ± 2.4121	8.7778 ± 3.2238	5.2900 ± 5.3599	0.02421
Ca	6.7926 ± 1.0266	15.8186 ± 4.6889	32.2222 ± 6.8883	13.5919 ± 8.9493	0.05098
Fe	17.6574 ± 7.2020	54.5726 ± 0.3225	130.7222 ± 4.5520	52.8329 ± 0.1314	0.04861
K	9.8056 ± 2.5142	157.2067 ± 6.2398	25.0556 ± 5.2342	8.0994 ± 5.1486	0.03754
Mg	0.9556 ± 0.4871	1.3873 ± 0.4957	3.8889 ± 0.7300	1.6107 ± 0.6072	0.00372
Na	11.7148 ± 5.3059	31.5101 ± 0.2962	33.3333 ± 2.3845	40.7018 ± 4.5513	0.02784
S	51.9426 ± 23.0883	42.1204 ± 0.5281	146.9444 ± 20.3318	60.0358 ± 22.3788	0.01037
As	0.1252 ± 0.1264	0.0750 ± 0.0125	0.3702 ± 0.0978	0.2032 ± 0.0944	0.00096
Ba	1.4174 ± 0.2904	0.0751 ± 0.0425	1.6031 ± 0.1832	0.1601 ± 0.1266	0.00015
Cd	0.0966 ± 0.0262	1.3359 ± 0.0885	1.1779 ± 0.0714	0.0727 ± 0.0396	0.00001
Co	0.0006 ± 0.0005	0.0071 ± 0.0021	0.2401 ± 0.0167	0.0350 ± 0.0175	0.00012
Cr	ND ^c	0.2106 ± 0.1252	0.5226 ± 0.1719	0.1819 ± 0.1805	0.00484
Cu	0.1188 ± 0.0351	1.1535 ± 0.2525	0.6200 ± 0.3064	7.9531 ± 4.8316	0.00042
Mn	0.1299 ± 0.0787	0.4828 ± 0.0073	4.3517 ± 0.0821	0.6847 ± 0.1004	0.00091
Ni	0.2247 ± 0.2365	0.6311 ± 0.0151	20.9803 ± 0.3035	0.7688 ± 0.3587	0.00583
Pb	0.2915 ± 0.0318	22.8822 ± 0.0990	0.8136 ± 0.0903	1.4519 ± 0.0802	0.00082
Sb	0.0039 ± 0.00004	0.0025 ± 0.0013	0.0029 ± 0.0014	0.5106 ± 0.5019	0.00004
Se	0.0677 ± 0.0052	0.3984 ± 0.0204	0.1565 ± 0.0105	ND	0.00463
Sr	0.0317 ± 0.0191	0.0558 ± 0.0307	0.0048 ± 0.0036	0.0240 ± 0.0120	0.00029
V	ND	ND	ND	0.0201 ± 0.0089	0.00205
Zn	1.8920 ± 0.5755	4.6306 ± 1.6814	9.4265 ± 1.0019	5.6844 ± 0.1488	0.00573

^aMDL: Method detection limit; Al, Ca, Fe, K, Mg, Na, and S were measured by ICP-AES and Co, Zn, Pb, Cu, Sr, As, Cr, Ba, Mn, Ni, Se, Cd, Sb, and V were measured by ICP-MS.

^bMean value ± standard deviation.

^cND: not detectable.

^dEach processor took 3 samples and each sample took 3 duplicate analyses. ^eCr value is a reference data that is due to the recovery is poor.

sulfate concentration is higher than in other iron compounds, with concentrations ranging from 0.12 to 0.35 g/g. In the coke making process, the concentrations of NH₄⁺, Cl⁻, Na⁺, K⁺, and Ca²⁺ were 0.036, 0.024, 0.016, 0.016, and 0.014 g/g, respectively. In addition, the concentrations of K⁺ and Cl⁻ were higher than that of S (0.20 and 0.17 g/g, respectively), in the sintering process. Moreover, the concentration of SO₄²⁻, NH₄⁺, and Ca²⁺ was higher than that of other ions in the cold forming process. In the hot forming process, the Ca²⁺ and Na⁺ concentrations were higher than the others.

Sulfate content in the particles was higher than 10% in all four processes. This may be due to the sulfur content in the raw materials, which oxidizes to form SO₂. Further, SO₂ is adsorbed or deposited on particles and then forms sulfate. In another pathway, SO₂ may be catalyzed (e.g., Fe, Ni, etc.) to form sulfate in the particle phase. There is a substantial sulfate contribution to the particle mass.

Elemental carbon ranged from 0.009 to 0.14 g/g and organic carbon from 0.016 to 0.064 g/g. Results indicate that the total carbon content ranged from 0.040 to 0.17 g/g. The low carbon

Table 3
Elemental carbon, organic carbon and ionic compound concentrations in the four processes

Concentration (mg/g)	Coke making	Sintering	Cold forming	Hot forming	MDL ^a (ng/g)
F ⁻	1.524 ± 0.076 ^b	3.178 ± 0.029	0.520 ± 0.010	4.862 ± 0.105	277.344
Cl ⁻	24.476 ± 0.353	173.713 ± 2.160	0.529 ± 0.061	5.589 ± 0.284	575.0
NO ₂ ⁻	ND ^c	0.133 ± 0.003	0.135 ± 0.005	0.036 ± 0.002	809.375
Br ⁻	ND	4.612 ± 0.014	ND	ND	276.562
NO ₃ ⁻	9.781 ± 0.173	0.870 ± 0.033	0.745 ± 0.026	4.401 ± 0.131	375.781
SO ₄ ²⁻	224.738 ± 1.879	121.623 ± 0.690	302.463 ± 2.482	348.914 ± 1.295	444.531
Na ⁺	16.245 ± 1.519	8.830 ± 2.834	1.688 ± 0.038	31.767 ± 1.779	157.031
NH ₄ ⁺	35.865 ± 1.118	3.812 ± 0.064	26.855 ± 0.179	6.176 ± 0.493	302.344
K ⁺	16.386 ± 0.666	198.809 ± 11.642	2.872 ± 0.027	8.761 ± 0.367	125.0
Mg ²⁺	0.645 ± 0.126	0.407 ± 0.005	1.329 ± 0.016	7.525 ± 0.028	14.062
Ca ²⁺	14.039 ± 1.241	9.684 ± 0.160	10.413 ± 0.132	46.739 ± 3.003	199.219
EC	137.466 ± 71.217	8.653 ± 1.202	89.146 ± 52.414	23.967 ± 11.732	456.348
OC	31.835 ± 21.600	56.496 ± 18.283	63.898 ± 54.558	16.505 ± 4.260	687.653

^aMDL: Method detection limit.

^bMean value ± standard deviation.

^cND: not detectable.

^dEach processor took 3 samples and each sample took 3 duplicate analyses.

Table 4
PAHs concentrations in the four processes

PAHs (mg/g)	Coke making	Sintering	Cold forming	Hot forming	MDL (ng/g)
Acenaphthylene (AcPy)	0.93 ± 0.40 ^a	0.37 ± 0.31	3.15 ± 2.63	1.28 ± 1.41	351.65
Fluorene (Flu)	0.13 ± 0.003	0.01 ± 0.02	ND	0.06 ± 0.07	334.07
Phenanthrene (PA)	0.20 ± 0.05	0.03 ± 0.03	1.12 ± 0.83	0.12 ± 0.12	325.27
Pyrene (Pyr)	0.018 ± 0.008	ND ^b	0.474 ± 0.052	0.058 ± 0.014	536.26
Chrysene (CHR)	0.085 ± 0.021	0.016 ± 0.001	0.334 ± 0.103	0.004 ± 0.002	439.56
Benzo(b)fluoranthene (BbF)	0.111 ± 0.058	0.023 ± 0.012	0.442 ± 0.223	ND	1010.99
Benzo(k)fluoranthene (BkF)	0.312 ± 0.291	0.031 ± 0.018	0.658 ± 0.275	0.127 ± 0.156	1230.77
Benzo(a)pyrene (BaP)	ND	0.041 ± 0.018	ND	ND	1134.07
Total PAHs	1.78 ± 0.90	0.51 ± 0.34	6.18 ± 3.07	1.64 ± 1.67	–

^aMean value ± standard deviation.

^bND: not detectable.

^cNaphthalene (NaP), Acenaphthene (Acp), Anthracene (Ant), Fluoranthene (FL), Benzo(a)anthracene (BaA), Indeno(1,2,3-cd)pyrene (IND), Dibenzo(a,h)anthracene (DBA), and Benzo(g,h,i)pyrene (BghiP) were not detected in these samples. But their method detection limit (MDL) is 378.02, 509.89, 298.9, 465.93, 536.26, 1054.95, 1028.57, and 1116.48 ng/g, respectively. ^dEach processor took 3 samples and each sample took 3 duplicate analyses.

content was due to the high temperature (>850 °C) manufacturing processes and the carbon burnoff. The coke making and cold forming processes revealed high carbon content, which was caused by the reduction reaction of coke formation and low thermal temperature treatment for the cold forming process.

3.2.3. PAHs concentration

Sixteen PAHs were analyzed in this study. Eight species, i.e., Naphthalene, Acenaphthene, Anthracene, Fluoranthene, Benzo(a)anthracene, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene, and Benzo(g,h,i)pyrene, were not detected in these particle samples. Table 4 shows the PAH concentrations. The sequence of PAH content in the particle phase was as follows for the four processes: cold forming (6.2 mg/g) > coke making (1.8 mg/g) > hot forming (1.6 mg/g) > sintering (0.5 mg/g). This may be due to the oil added into the cold-rolled process and the lower operating temperature, which enhances PAH formation. BaP was not detectable in the coke-making particles in this study, but 1.4–5.8 mg/g was detected in coke plant particles that were measured by Bjørseth et al. [30].

The major PAH species were AcPy, and BkF in the coke making process. In the sintering process, the concentration of AcPy was higher than those of the others. The concentration sequence of the top three PAH species was AcPy > PA > BkF in the cold forming process. In the hot forming process, the sequence of the top three PAH was similar, but the concentrations were lower than in the cold forming process.

Fig. 1 shows the ring distribution of the PAHs. The percentage of the mass contribution of the 16 PAHs was 3-ring (88–69%) > 5-ring (3–13%) > 4-ring (8–24%) in this study. In general, two- and three-ring PAHs were the dominant form of the PAHs measured in coke manufacturing [5,31]. In addition, eight PAHs were detectable, including four species (AcPy, Flu, PA and Pyr) that are non-carcinogenic and non-mutagenic, and four species (CHR, BbF, BkF and BaP) that are potential or provable carcinogens and/or mutagens. Mass contribution of the four potential carcinogenic and mutagenic species is cold forming (1.4 mg/g) > coke making (0.51 mg/g) > hot forming

(0.13 mg/g) > sintering (0.11 mg/g). In addition, BaP is a higher potential carcinogen compound than the other PAHs studied and is detectable in the sintering process (0.041 mg/g).

3.3. Emission factors of chemical constituents

Table 5 lists the emission factors of particle compositions of the four processes. The emission factor is the rate of species emission divided by the rate of production during the sampling period. Particle composition emission factors could be used to estimate emissions from similar iron and steel processes where there are no emission inventory data. Ca, Fe, K, Na, and S are the major trace elements in the coke making process. Furthermore, sulfate, ammonium, and calcium ions were the major ionic compounds in the particles. In the coke making process, the concentration of EC was about eight times that of OC. For PAHs, the AcPy was the predominant particle compound in this study. In the sintering plant, K, Fe, S, Na and Pb were the major trace compounds. Furthermore, the emission factors of chloride ions, sulfate, potassium ions, and calcium ions were

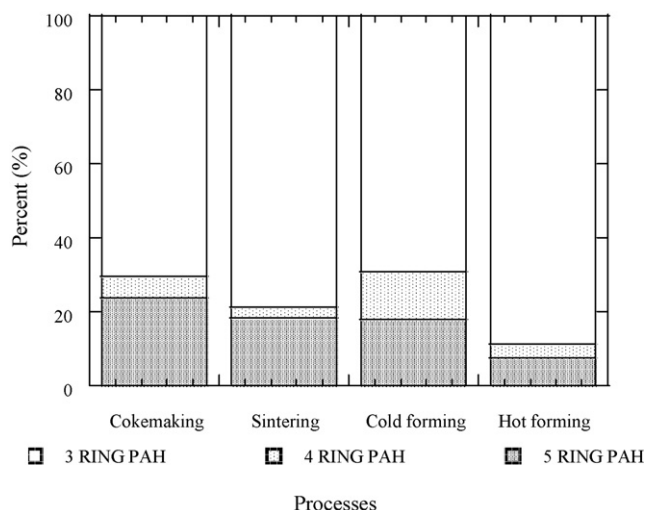


Fig. 1. Distribution of various classes of PAHs.

Table 5
Emission factors (g/tonne-product) of particle compositions of the four processes

Particle Composition	Coke making (g/tonne-coke)	Sintering plant (g/tonne-sintering ore)	Cold forming (g/tonne-steel)	Hot forming (g/tonne-steel)
Al	0.05521 ± 0.05782 ^a	0.10158 ± 0.16163	0.06082 ± 0.05783	0.07299 ± 0.08987
Ca	0.13995 ± 0.15350	0.35953 ± 0.51700	0.22325 ± 0.23457	0.34095 ± 0.45288
Fe	0.26654 ± 0.21034	1.17701 ± 1.46839	0.90572 ± 1.12358	2.43623 ± 3.36777
K	0.16265 ± 0.14520	3.41812 ± 4.36694	0.17360 ± 0.21235	0.20904 ± 0.27835
Mg	0.01346 ± 0.00952	0.03186 ± 0.04696	0.02694 ± 0.02865	0.05483 ± 0.07453
Na	0.17164 ± 0.12946	0.68145 ± 0.85706	0.23095 ± 0.26459	1.72882 ± 2.38032
S	1.22039 ± 1.46505	0.90737 ± 1.12800	1.01812 ± 1.35690	2.05165 ± 2.78987
As	0.00115 ± 0.00005	0.00157 ± 0.00179	0.00256 ± 0.00265	0.01236 ± 0.01728
Ba	0.02423 ± 0.02238	0.00179 ± 0.00284	0.01111 ± 0.01235	0.00334 ± 0.00436
Cd	0.00159 ± 0.00140	0.02850 ± 0.03441	0.00816 ± 0.00965	0.00208 ± 0.00280
Co	ND ^b	0.00015 ± 0.00015	0.00166 ± 0.00188	0.00105 ± 0.00142
Cr	ND	0.00503 ± 0.00808	0.00362 ± 0.00549	0.01656 ± 0.02341
Cu	0.00192 ± 0.00167	0.02393 ± 0.02634	0.00430 ± 0.00457	0.21239 ± 0.28364
Mn	0.00171 ± 0.00106	0.01045 ± 0.01318	0.03015 ± 0.02754	0.03471 ± 0.04819
Ni	0.00196 ± 0.00009	0.01357 ± 0.01676	0.14536 ± 0.09459	0.02398 ± 0.03240
Pb	0.00526 ± 0.00514	0.49366 ± 0.61639	0.00564 ± 0.00756	0.06428 ± 0.08869
Sb	0.00007 ± 0.00008	0.00006 ± 0.00009	0.00002 ± 0.00004	0.00754 ± 0.00939
Se	0.00135 ± 0.00144	0.00852 ± 0.01037	0.00108 ± 0.00147	ND
Sr	0.00079 ± 0.00099	0.00132 ± 0.00209	0.00003 ± 0.00005	0.00072 ± 0.00098
V	ND	ND	ND	0.00121 ± 0.00169
Zn	0.03049 ± 0.02629	0.09352 ± 0.09299	0.06531 ± 0.07564	0.26640 ± 0.36854
F ⁻	0.02720 ± 0.02628	0.07230 ± 0.04510	0.00360 ± 0.00007	0.35723 ± 0.50241
Cl ⁻	0.16994 ± 0.09553	3.86320 ± 1.96746	0.00367 ± 0.00042	0.23744 ± 0.32693
NO ₂ ⁻	ND	0.00214 ± 0.00303	0.00093 ± 0.00004	0.00326 ± 0.00461
Br ⁻	ND	0.09198 ± 0.00728	ND	ND
NO ₃ ⁻	0.08236 ± 0.01016	0.01954 ± 0.01098	0.00516 ± 0.00018	0.07321 ± 0.09283
SO ₄ ²⁻	4.62113 ± 5.06009	2.55539 ± 0.53739	2.09564 ± 0.01720	16.06585 ± 22.20740
Na ⁺	0.10775 ± 0.07318	0.20361 ± 0.14076	0.01170 ± 0.00026	0.20536 ± 0.20259
NH ₄ ⁺	0.92149 ± 1.16449	0.10178 ± 0.13887	0.18606 ± 0.00124	0.20253 ± 0.27466
K ⁺	0.11164 ± 0.06808	4.22821 ± 1.16573	0.01990 ± 0.00019	0.10172 ± 0.12111
Mg ²⁺	0.01143 ± 0.01096	0.01101 ± 0.01557	0.00921 ± 0.00011	0.68495 ± 0.96866
Ca ²⁺	0.26795 ± 0.27589	0.23008 ± 0.19250	0.07215 ± 0.00092	3.76434 ± 5.30755
EC	2.97638 ± 3.38563	0.16058 ± 0.08120	0.61765 ± 0.36315	0.82107 ± 1.11668
OC	0.35885 ± 0.14307	1.27023 ± 0.71754	0.44272 ± 0.37801	0.79847 ± 1.10619
Acenaphthylene	0.01372 ± 0.01053	0.00911 ± 0.00953	0.02185 ± 0.02346	0.01301 ± 0.01772
Fluorene	0.00250 ± 0.00256	0.00014 ± 0.00019	ND	0.00041 ± 0.00054
Phenanthrene	0.00423 ± 0.00481	0.00066 ± 0.00080	0.00774 ± 0.00835	0.00160 ± 0.00221
Pyrene	0.00120 ± 0.00136	ND	0.00329 ± 0.00436	0.00525 ± 0.00743
Chrysene	0.00088 ± 0.00103	0.00035 ± 0.00011	0.00232 ± 0.00236	0.00040 ± 0.00056
Benzo(b)fluoranthene	0.00115 ± 0.00186	0.00062 ± 0.00088	0.00306 ± 0.00436	ND
Benzo(k)fluoranthene	0.00308 ± 0.00057	0.00074 ± 0.00063	0.00456 ± 0.00539	0.00078 ± 0.00104
Benzo(a)pyrene	ND	0.00133 ± 0.00186	ND	ND
total PAHs	0.02676	0.01295	0.04284	0.02145

^aMean value ± standard deviation.

^bND: not detectable.

^cEmission factor was measured by the pollutant emission per unit product (g-pollutant/tonne-product).

3.86, 2.55, 4.23, and 0.23 g/tonne, respectively. Organic carbon (1.27 g/tonne) was higher than elemental carbon (0.16 g/tonne). AcPy was higher than the other PAHs, but the BaP emission factor was 0.00133 g/tonne and found only in the sintering process.

S, Fe, Na and Ca are the major elements of particles in the cold forming process. For ionic compounds, sulfate (2.10 g/tonne) and ammonium (0.19 g/tonne) were the major species. In addition, EC was slightly higher than OC. For PAHs, the AcPy was also higher than the other PAHs.

In hot forming, the emissions of Fe, Na, S, Cu, and Zn contributed 2.44, 1.73, 2.05, 0.21, and 0.27 g/tonne, respectively. Moreover, the ionic compounds of SO₄²⁻, Ca²⁺, and Mg²⁺ were 16.07, 3.76, and 0.68 g/tonne, respectively. Furthermore, the EC was also slightly higher than OC. For PAH compounds, the sequence of emission factors was AcPy > Pyr > PA > BkF > Flu ≈ Chr.

Twenty-one PAHs were investigated from four steel and iron plants that use coal as fuel; results indicated about 0.015 g/tonne-product in the particle phase [5]. The top three PAH species

were Nap > AcPy > Acp [5]. In our investigation, AcPy was the major PAH compound of the four processes. The 21 PAH emission factors were a little lower than our study in the cold forming (0.04283 g/tonne-steel), hot forming (0.02145 g/tonne-steel), and coke-making processes (0.02676 g/tonne-coke) but higher than the sintering process (0.01295 g/tonne-sintering ore).

In general, S, Fe, and Na are major elemental constituents of the particulate emission in the four processes studied. In addition, Pb was measurable in the sintering process. Sulfate was the dominant water-soluble ion in the particles. AcPy is the major PAH in this study.

4. Conclusions

Integrated iron and steel industrial facilities are intense air pollution sources of the industrial sector. In this study, coke making, sintering, cold forming, and hot forming processes were selected from an integrated iron and steel plant to investigate the chemical compositions of particulates. Sulfur and sulfate proved to be the highest in the particle phase of the four processes. Potassium and chlorine ions in the sintering process were higher than in the other processes, which may be due to the recycled material and flux content. About 2% lead was found in particle of the sintering process; it is higher than other processes, and its correct disposal is necessary. High carbon content was found in the coke making and cold forming processes as a result of the high PAH content of the two processes. AcPy (3 ring) was the predominant PAH species. In addition, BaP was found only in the sintering plant. This study provides the detailed particle compositions and establishes baseline information on emissions from integrated iron and steel facilities. Detailed particle composition can be used as a “fingerprint” to identify the pollution source contribution from the atmospheric particle samples and establish some control measures for pollution reduction.

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