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Exposure characterization and risk assessment of ultrafine particles from the blast furnace process in a steelmaking plant

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Abstract

Objectives: This study aimed to clarify the exposure characteristics and risks of ultrafine particles from the blast furnace process and to provide a reasonable control strategy for protecting the health of workers.

Methods: The blast furnace location of a steelmaking plant was selected as a typical investigation site. A membrane-based sampling system was used to collect ultrafine particles to analyze their morphology and elemental compositions. A real-time system was used to monitor the total number concentration (NC), total respirable mass concentration (MC), surface area concentration (SAC), and size distribution by number. The risk level of ultrafine particles was analyzed using the Stoffenmanager-Nano model.

Results: The total NC, total MC, and SAC increased significantly relative to background concentrations after slag releasing started and decreased gradually after the activity stopped. The three highest total concentrations during slag releasing were 3-10 times higher than those of the background or non-activity period. The ultrafine particles were mainly gathered at 10.4 or 40 nm, and presented as lump-like agglomerates. The metal elements (Al and Pt) in the ultrafine particles originated from slag and iron ore. The risk level of the ultrafine particles was high, indicating the existing control measures were insufficient.

Conclusions: The blast furnace workers are at high risk due to exposure to high levels of ultrafine particles associated with working activity and with a bimodal size distribution. The existing control strategies, including engineering control, management control, and personal protection equipment need to be improved.

KEYWORDS

exposure control, occupational exposure, risk assessment, ultrafine particles

Xiangjing Gao and Xingfan Zhou contributed equally to this work.

1 | INTRODUCTION

The steelmaking industry contributes significantly to the world's industrial economy, with a total estimated worth of $900 billion per year.[1] Materials used in almost everything today either come from steel or are manufactured using steel equipment.[1] In developing countries, there is an increasing demand for steel production for industrialization. China has become the largest steel producer in the world.[2,3] With the increasing use of steel production, its negative impact on the air quality during manufacturing processes is becoming prominent.[4-6] The amount of dust released from steelmaking industries accounts for 27% of China's dust emissions, which are estimated at 2-5 million tons per year.[7,8] Melting, blast furnaces, and other hot processes are known to be significant contributors to dust emission in steelmaking plants.[9] Ultrafine particles account for more than 50% of the dust released as a result of these hot processes.[10]

Exposure to ultrafine particles or their aggregates (fine particles) may result in adverse health problems for humans, such as acute respiratory illness, chronic coughing, and a reduction in lung function.[11,12] Ultrafine particles produced by steelmaking have attracted public attention. There have been many studies on the exposure to these ultrafine particles. For example, the concentration of volatile organic compounds released into the atmosphere from the integrated steelmaking industry has been analyzed.[13] Typical hazardous air pollutants, size-segregated particulate matter (TSP/PM_{10}/$PM_{2.5}$), gaseous pollutants (SO_2, NO_x, CO), and heavy metals (Pb, Cd, Hg, As, Cr, Ni, etc) from the steelmaking industry in China exhibited characteristic temporal and spatial variations or trends.[14] The composition of the various size fractions of cast house dust, blast furnace and the chemical composition and source apportionment of particles in the atmosphere near steelmaking industrial areas in China was investigated.[15,16] Previous studies investigated the chemical characterization of particles emission from steelmaking plant, and reported that the blast furnace and sinter were big contributors to PM_{10}, the size of particles was mainly below 1.0 μm, the main elements were Fe and Ca content in blast furnace dust.[17,18]

The above studies revealed the compositions and concentrations of ultrafine particles in the atmosphere released from manufacturing processes in the steelmaking industry. As the steel manufacturing workers often work close to the particle releasing source, their occupational exposure to complex mixtures of particles is one major problem of public concern worldwide. Until now, there have been few studies on the occupational exposure characteristics of ultrafine particles in steelmaking plants. Marcias et al reported the composition of metallic elements and size distribution of ultrafine particles in a steelmaking factory.[19] Järvelä et al described the mass concentration (MC), number concentration (NC), and size distribution of fine and ultrafine particles in the production chain of ferrochromium and stainless-steel during sintering, ferrochromium smelting, stainless steel melting, and hot and cold rolling operations.[20] While these studies did describe the metallic compositions and concentrations of ultrafine particles in steelmaking factory, they nevertheless failed to provide a comprehensive characterization of ultrafine particles released from the blast furnace process in the steelmaking factory. A detailed characterization of the particle nature and temporal variations in particle concentrations or size distribution, which covers one full period of working activity, is lacking. Temporal variations in size distribution should be taken into account as it might be affected by the agglomeration of primary particles.[21] The particle nature, which can provide information on the chemical compositions associated with the potential health risk of workers, should be assessed using qualitative or quantitative approaches.

In addition, the risk level of workers exposed to ultrafine particles from the blast furnace process in the steelmaking industry has been rarely reported. The control banding (CB) tools, which offer simplified guidance for managing the risks without toxicological and/or detailed exposure information, are applicable methods and have been used for risk assessments of different ultrafine particles in various work environments.[22] Comparative studies between different CB tools showed the Stoffenmanager-Nano model had a comprehensive advantage.[23]

In order to bridge the above research gaps, it is necessary to investigate the exposure characteristics and risks of ultrafine particles in the steel-making industry, and provide a basis for developing a reasonable control strategy to reduce the health risks for workers exposed to ultrafine particles in the steelmaking industry. This study aimed to understand the exposure characteristics of ultrafine particles from the blast furnace process and the risks associated with the exposure, and to recommend reasonable control measures to reduce the health risks for workers. The following four aspects were investigated in this study: (i) the particle nature (morphology and elemental compositions); (ii) the temporal variations in total concentrations of particles (namely, total NC, total respirable MC, personal NC, and surface area concentration [SAC]) and size distributions by number; (iii) the risk levels of workers exposed to ultrafine particles; and (iv) the control measures to be improved for reducing the health risks of workers.

2 | MATERIALS AND METHODS

2.1 | Description of workplace

A blast furnace position in a steelmaking plant in an industrial region of Ningbo City in Zhejiang province of east China was selected for field investigation. In this plant, the major production process is described as follows: (i) coking: coal is coked through a coke oven; (ii) blast furnace: solid raw materials such as iron ore, coke, and flux agents are fed into a blast furnace in batches by a top charging device based on the specified batch ratio. The iron ore is gradually reduced and melted into iron and slag during the process of falling. Liquid iron and slag are gathered in a furnace belly, and periodically released from the iron and slag mouth; (iii) converter: the liquid iron from the blast furnace and scrap steel is heated in an oven; and (iv) steel rolling: the molten steel is transported to a turntable through steel drums, and is then divided into several strands through a molten steel distributor and injected into casting molds. Finally, solidified shells are formed after cooling and solidifying. Among these processes, the blast furnace, which comprises a continuous melting process and periodical slag releasing operations, is a potential source for the release of ultrafine particles.

2.2 | Monitoring and sampling systems

The real-time system was used to monitor the total NC, personal NC, total respirable MC, SAC, and size distribution by number. The total NC was determined using a P-TRAK ultrafine particle counter (Model 8525; TSI, Shoreview, MN, USA). It is a portable condensation particle counter (CPC) for measuring the NC of ultrafine particles.[24] The personal NC was measured using a Diffusion Size Classifier Miniature (DiSCmini), which can measure the number and average size of nanoparticles (<approximately 0.7 μm) in air. The total respirable MC was tested using a real-time aerosol monitor (DustTrak 8533; TSI), which can measure particles ranging from 100 to 1000 nm. The alveolar deposition mode of SAC was determined using a surface area monitor (Aero TrakTM 9000; TSI). A suite of aerosol instruments covering the size range from 10.4 nm to 10 μm is used to capture the particle size distribution and NC, including the scanning mobility particle sizer (SMPS, Model 3034; TSI) and optical particle sizer (OPS, Model 3330; TSI).

A membrane-based sampling system was used to collect ultrafine particles to analyze their morphology and elemental compositions. Ultrafine particles were collected using a cascade impactor (Nano-MOUDI, 125A; MSP, Shoreview, MN, USA). The impactor comprised 13 stages, corresponding to the cutting size of 10 000, 5600, 3200, 1800, 1000, 560, 320, 180, 100, 56, 32, 18, and 10 nm, respectively. The morphology of ultrafine particles collected at the 13th stage was analyzed using a scanning electron microscopy (SEM, S4800; Hitachi, Tokyo, Japan), while elemental compositions were qualitatively analyzed using an energy-dispersive X-ray spectroscopy (EDX, S4800; Hitachi). The capture velocity of local exhaust ventilation (LEV) used to evaluate the effectiveness of LEV was measured by hot-wire anemometer (9515; TSI).

2.3 | Sampling and testing strategies

The sampling process was performed in August 2019. The testing day was sunny and the outdoor temperature was 29-32 °C. The air velocity of outdoor was low (0.41 ± 0.04 m/s). The sampling protocol of ultrafine particles based on the "Nanomaterial Exposure Assessment Technique (NEAT 2.0)"[25] and the "Determination of dust in the air of workplaces—part 6: Total number concentration of ultrafine and fine particles",[26] was as follows: (i) field investigation: to investigate the processing technique, number of workers, work tasks, the frequencies and durations of operations, and the exposure control devices, (ii) concentration screening: the CPC was conducted to identify the potential source of particle emission; (iii) background measurements: the sampling location was on the semi-open platform of the blast furnace, 45 m away from the ultrafine particles source of release, as shown in Figure 1A(a). The sampling date was the same date as the area sampling, and the sampling duration covered 1 hour before working activity started, during which no incidental particle sources were present in the workshop; (iv) area sampling based on activity: the sampling locations were selected based on the information gathered and the walk-through survey, while also considering several other factors, such as the air movement and currents, and the work tasks and whether they could allow for the placement of large instruments without normal work activities being affected. In this study, both blast furnace and slag releasing were substantial sources of ultrafine particles. However, the temperature of the blast furnace was too high to place the testing instruments close to it. Hence, the slag releasing was selected as the sampling location. The sampling location was selected far away from vents and places where the air may swirl, which was 4 m away from the observation window of the slag ditch and was downwind, as shown in Figure 1A(b). Instruments were performed 1.3 m above the floor and close to the operating position. Area sampling covering one complete work cycle was performed during and after slag releasing under the stable production status; and (v) personal sampling: the operating worker at the blast furnace position was selected as the subject. The sampler was placed near the snout, approximately 30 cm away from the breathing zone.

The capture velocity sampling based on an occupational health standard in China[27] (namely, Regulation on Technical Specifications for Capture Velocity for LEV Facilities, AQ/T4274-2016) was tested three times while the LEV was working, and the average value was used. The location was

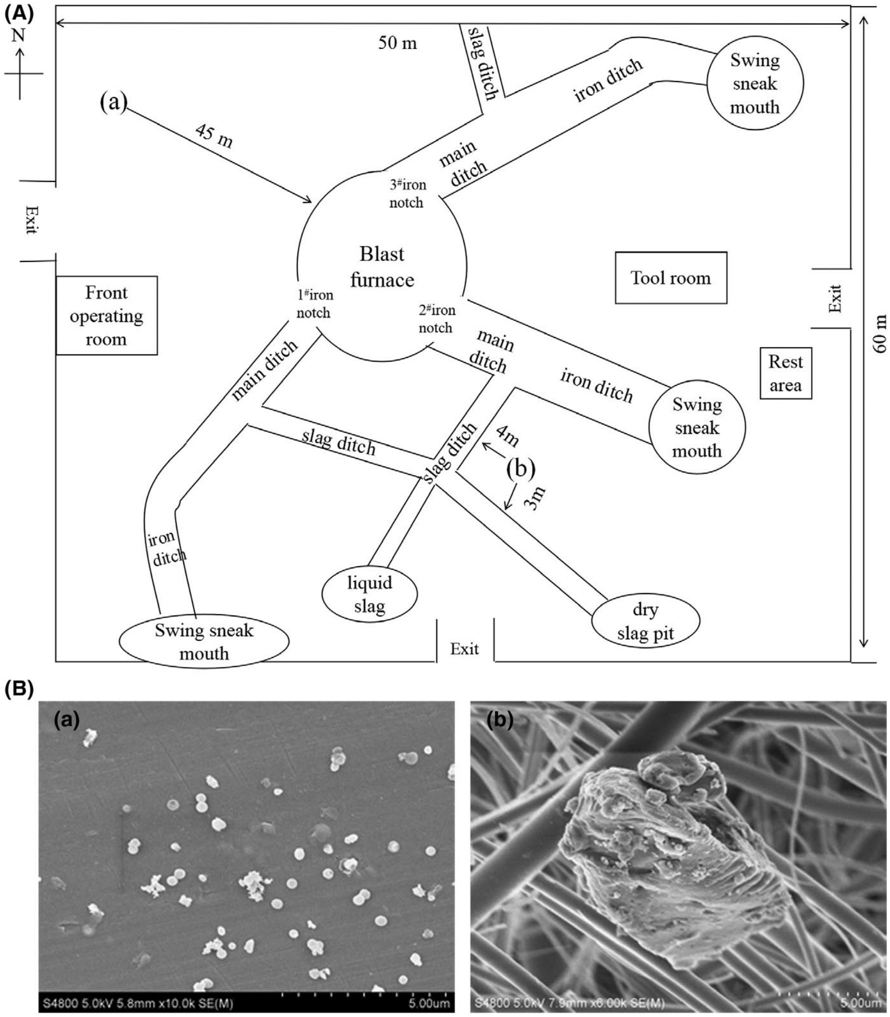

FIGURE 1 Sample sites and morphology of ultrafine particles. (A) Sampling locations of background (a) and slag releasing (b); (B) Scanning electron micrographs of particles from the background and slag releasing location. (a) irregular spherical particles from the background; (b) lump-like agglomerates of ultrafine particles from the slag releasing location

selected at the farthest particle source of release from the exhaust hood, and the direction indicator on the instrument was windward.

2.4 | Methodology for risk assessment

The Stoffenmanager-Nano (http://nano.stoffenmanager.nl/), which follows a stepwise binary decision tree and provides three risk levels,[28] was developed by the Organization for Applied Scientific Research based in the Netherlands. The tool will calculate the exposure score and hazard score, respectively, and then divide them to four exposure levels (1-4) and five hazard levels (A-E). Among exposure levels, first is the lowest exposure and fourth is the highest exposure. Among hazard levels, A is the lowest hazard and E is the highest hazard. Finally, the results from the hazard and exposure levels are combined in a risk matrix containing three risk levels, of which 1 is a high risk, 2 is medium risk, and 3 is low risk. Table 1 shows the hazard and the exposure input data for the Stoffenmanager-Nano.

2.5 | Statistical analysis

One-way analysis of variance, followed by the Dunnett's T3 multiple comparison methods, was used to analyze the differences in the total NC, total respirable MC, and SAC between the sampling location and background. Pearson correlation was applied to analyze the relationships among different exposure metrics (total NC, total respirable MC, and SAC). The total NC, total respirable MC, and SAC were corrected using background concentrations to obtain the concentration ratios (CRs) (sampling location vs background), which reflected the degree of ultrafine particles released from the source.

3 | RESULTS

3.1 | Mean concentrations and mode sizes of particles

The mean concentrations and mode sizes of particles at the slag releasing location and background are listed in Table 2. The mean total NC, SAC, and total respirable

TABLE 1 Hazard data and exposure scenario data of ultrafine particles generated from the blast furnace

CB tool	Materials information requested	Ultrafine particles
Stoffenmanager-Nano	Source domain	Release of primary particles during actual synthesis
	Do you know the exact concentration of the nano component in the product?	No
	Concentration	Main component (10%-50%)
	Does the product contain fibers/fiber like particles?	No
	Inhalation hazard	Carcinogenic and mutagenic
	Task characterization	Chemical vapor condensation
	Duration task	0.5-2 h/d
	Frequency task	4-5 d/wk
	Is the task being carried out in the breathing zone of an employee (distance head-product <1 m)	Yes
	Is the working room being cleaned daily?	No
	Are inspections and maintenance of machines/ancillary equipment being done at least monthly to ensure good condition and proper functioning and performance?	Yes
	Volume of the working room	100-1000 m^3
	Ventilation of the working room	Mechanical and (or) natural ventilation
	Local control measures	Containment of the source with local exhaust ventilation
	Is the employee situated in a cabin	No
	Is personal protective equipment applied?	Filter mask P2

Abbreviation: CB, control banding.

TABLE 2 Mean concentrations and mode size of ultrafine particles at different sampling sites

	Background (n = 60)		Slag releasing (n = 50)		Personal sampling during working activity period (n = 60)	Personal sampling during non-activity period (n = 50)
Metrics	Mean ± SD	CR	Mean ± SD	CR		
Total NC (10^4 pt/cm^3)	2.11 ± 0.67	1.00	6.05 ± 1.82	2.87	95.39 ± 68.70	2.21 ± 0.60
Total respirable MC (mg/m^3)	0.09 ± 0.01	1.00	0.20 ± 0.02	2.22	—	—
SAC ($\mu m^2/cm^3$)	301.98 ± 18.79	1.00	1628.07 ± 740.11	5.39	—	—
Mode size (nm)	58.28 ± 13.87	—	26.08 ± 10.88	—	28.48 ± 4.53	86.50 ± 9.40

Abbreviations: CR, concentration ratio; MC, mass concentration; NC, number concentration; SAC, surface area concentration; SD, standard deviation.

MC at the slag releasing were $6.05 \pm 1.82 \times 10^4$ pt/cm^3, 1628.07 ± 740.11 $\mu m^2/cm^3$, and 0.20 ± 0.02 mg/m^3, respectively, which were significantly higher than those of the background particles ($P < .01$). The mean total NC of personal sampling during the working activity period was 95.39 ± 68.70 pt/cm^3, which was much higher than the slag releasing measured with P-TRAK. The mode sizes of the slag releasing and background were 26.08 ± 10.88 and 58.28 ± 13.87 nm, respectively. The mode size of personal sampling was 28.48 ± 4.53 nm during the working activity period, which was similar to that of slag releasing (26.08 ± 10.88 nm). The mode size of personal sampling during the non-activity period (86.50 ± 9.40 nm) was larger than the background (58.28 ± 13.87 nm).

3.2 | Morphology and elemental composition of ultrafine particles

Figure 1B(b) shows that the shape of the particles from the slag releasing was lump-like agglomerates under the scanning electron microscopy, and Figure 1B(a) illustrates that the background particles were irregularly spherical.

Table 3 lists the elemental compositions of raw materials and the particles sampled. The main components in iron ore were Fe, Al, and Pt, the dominant metal elements in coke were Na and Ca, and those in slag were Al and Pt. This suggested that the metal elements (Al and Pt) in ultrafine particles from the slag releasing process came from slag and iron ore. The most abundant elements of background particles were C, O, and Si, which were different from the particles collected from the slag releasing location.

3.3 | Temporal variations in the total particle concentrations and size distributions by number

The temporal variations in total particle concentrations and size distributions by number are shown in Figure 2. The total NC, total respirable MC, and SAC during the working activity period were significantly higher than those during the background or non-activity periods (Figure 2A,C). The highest total NC of the working activity period reached 9.5×10^4 pt/cm^3, approximately three times higher than that of the background or non-activity period. The highest SAC of the working activity period was approximately 2700 μm^2/cm^3, which was about 10 times higher than that of the background or non-activity period. The total respirable MC of the working activity period reached 0.52 mg/cm^3, approximately four times higher than that of the non-activity period. The total NC and SAC increased immediately after slag releasing started around 10:52 AM and decreased gradually to the background level after the operation stopped. The total respirable MC varied with activities, but was delayed for 15 minutes. The enterprise was close to the sea and the blast furnace was installed in a big semi-open platform with a roof, the total NC, SAC, and total respirable MC fluctuated even during the non-activity period. Figure 2B shows that personal NC varied with working activities. The highest personal NC reached a peak of 3×10^6 pt/cm^3 at 10:52 AM after starting the activity, which was more than 10 times higher than the non-activity period and about 100 times higher than the total NC.

Figure 2D,E,F show a typical particle size distribution (dN/dLogDp, pt/cm^3) as a function of time as measured by SMPS and OPS over a combined range of particle diameters, namely 10.4-96.5 nm for SMPS with the Nano differential mobility analyzer (DMA), 103.7-469.8 nm for SMPS with Long DMA, 0.3-10 μm for OPS. The highest number of particles released from slag releasing appeared at 10.4 and 40 nm (Figure 2D), which reached up to 3×10^6 pt/cm^3. The highest number of particles in the range of 103.7-469.8 nm and >374 nm was about 8×10^5 and 2×10^4 pt/cm^3, respectively (Figure 2E,F). Large particles were usually present in lower concentrations than ultrafine particles, as illustrated in Figure 2.

3.4 | Relationships among the total NC, SAC, and total respirable MC

Figure 2A shows that the variations in the total NC and SAC with the activities were quite similar. Table 2 shows that the order of CR value at the location of slag releasing was: CR_{SAC} (5.39) > $CR_{total\ NC}$ (2.87) > CR_{MC} (2.22). The results of correlations show that the order of the correlation coefficients between the total NC, SAC, and respirable MC was $R_{total\ NC\ and\ SAC}$ (r = .681) > $R_{SAC\ and\ total\ respirable\ MC}$ (0.456) > $R_{total\ NC\ and\ total\ respirable\ MC}$ (0.424).

3.5 | The risk level of exposed workers and the control measures to be improved

Table 4 shows the results of the risk assessment obtained from the Stoffenmanager-Nano model. The hazard level,

TABLE 3 Elemental compositions of raw materials and ultrafine particles

Sources	Constituent elements (% by mass)
Raw materials	
Iron ore	Fe (65.02), Al (6.53), Pt (5.56), Si (3.53), P (0.56), Ca (0.75)
Coke	C (68.19), O(16.5), Na (2.89), Al (2.23), S (2.56), Si (2.46), Ca (2.73), Fe (1.53)
Slag	O (60.05), Al (7.52), Si (11.14), Pt (4.39), Ca (3.75), Na (1.47), Fe (0.78)
Ultrafine particles from the 13th stage of the cascade impactor	
Background particles	C (36.03), O (43.31), Si (17.46), Ca (1.46), Al (0.44), Zr (0.82), Ti (0.49)
Particles from slag releasing	Al (42.51), O (17.98), Si (24.72), Pt (10.71), Na (3.30), Fe (0.78)

Note: A typical particle was qualitatively analyzed by the energy-dispersive X-ray spectroscopy based on the instruction for operation.

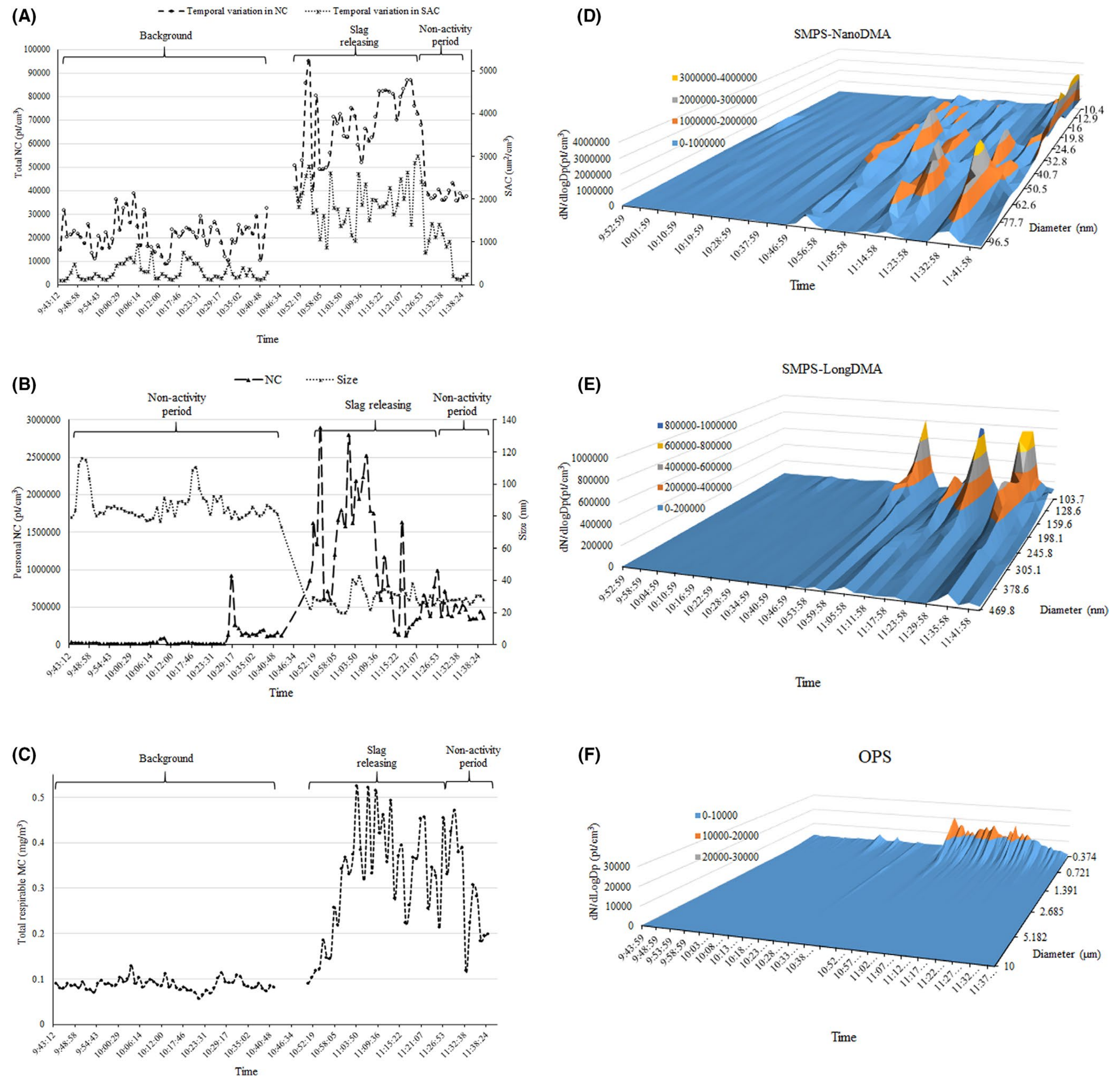

FIGURE 2 Temporal variations in total particle concentrations and size distributions by number. (A) Temporal variations in total number concentration (NC) and surface area concentration (SAC) at background and operation locations. (B) Temporal variations in personal NC and its size during the working and non-activity periods. (C) Temporal variations in total respirable mass concentration (MC) at the background and operation location. (D) Real-time particle size spectrum of scanning mobility particle sizer (SMPS) with Nano differential mobility analyzer (DMA); (E) Real-time particle size spectrum of SMPS with Long DMA; (F) Real-time particle size spectrum of optical particle sizer (OPS). Most of the particles were smaller than 100 nm, and the highest number reached 3×10^6 pt/cm^3 at 10.4 and 40 nm

exposure level, and risk level were D, 3, and 1, respectively, all of which belong to a high level. The capture velocity of LEV for dust removal at the blast furnace was 0.5 m/s, which was lower than the limit value (1.2 m/s) in an occupational health standard in China[27] (namely, AQ/T4274-2016).

The current control measures taken in the workplace were listed in Table 4, including engineering controls, occupational health management, and PPE. Based on the high-risk level, the following control measures need to be improved: (i) due to the insufficient capture velocity, the exhaust speed of LEV for dust removal at the blast furnace needs to be increased, including the redesign of the hood for total enclosure; (ii) the preventative maintenance schedule for ensuring the effectiveness of engineering control measures should be established; (iii) sensitive indicators for ultrafine particles need to be developed in occupational health examination; and

TABLE 4 Risk level of blast furnace workers exposed to ultrafine particles and control measures to be improved

CB tool	Hazard band	Exposure band	Risk level	Existing control measures	Additional control measures to be improved
Stoffenmanager Nano	D	3	High	1. Engineering controls: the blast furnace was equipped with a LEV, the slag ditch was covered with bricks and cement and had only one observation window. The capture velocity of LEV for dust removal at the blast furnace was insufficient. 2. Occupational health management system: regular occupational health training, reduced exposure time, and occupational health examinations for workers. The preventative maintenance schedule and sensitive indicators for ultrafine particles were missing. 3. PPE: use of NIOSH-certified N95 filtering facepiece respirators (3M Co.; 8110, 9210, Saint Paul, MN, USA).	1. Engineering controls: the exhaust speed of LEV for dust removal at the blast furnace needs to be increased, including the redesign of hood for total enclosure. 2. Occupational health management system: The preventative maintenance schedule for ensuring the effectiveness of engineering control measures should be established; Sensitive indicators for ultrafine particles need to be developed in occupational health examination. 3. PPE: regular inspection should be conducted to ensure workers are properly wearing the PPE.

Abbreviations: CB, control banding; LEV, local exhaust ventilation; PPE, personal protective equipment.

(iv) regular inspection should be conducted to ensure workers are properly wearing the PPE.

4 | DISCUSSION

Ultrafine particles from the blast furnace process were collected, and their exposure characteristics and risks were investigated in this study. To our knowledge, this is the first study conducted on detailed exposure characterization and risks for ultrafine particles from the blast furnace in the steelmaking industry using multiple metrics (eg total NC, total respirable MC, SAC, personal NC, size distribution, morphology, elemental composition, and risk level).

The SEM images illustrated the particle shape and the state of aggregation. Particles from both the background and blast furnace were irregular agglomerates; however, the two kinds of shapes were different. Simultaneously, the dominant mental elements of the particles at the slag releasing location were Al and Pt, which were similar with the main components in iron ore and slag, but were different from those of background particles or coke. The similarity in the characteristic elements (Al and Pt) of slag, iron ore, suggested the metal elements in ultrafine particles from slag releasing were more likely to come from slag and iron ore. The differences in the shapes and characteristic elements of particles at the slag releasing and background indicated the different particle sources. These findings suggested that steelmaking workers were exposed to these specific ultrafine particles generated from the slag releasing activity.

The total NC, SAC, and total respirable MC released from the slag releasing location were significantly higher than those from the background or during the non-activity period (Figure 2), which indicated that the slag releasing operation was able to generate high levels of ultrafine particles. As Figure 2 shows, the temporal variations of total NC, SAC, and personal NC exhibited an activity-related characteristic. This finding was supported by our previous study, which demonstrated the exposure characteristics of nanoparticles at an automobile manufacturing facility.[29] These results indicated that the working activity had a significant effect on the temporal variations in particle concentrations.[24] In addition, our previous field studies approved that the particle concentrations were significantly influenced by the sampling distance from sources, air velocity, background particles, and engineering control measures.[29-31] In this study, the personal NC was significantly higher than the total NC (Table 2), the reason might be that the personal NC was measured closer to the particle source. High wind velocity could enhance air exchange in the workshop, which was one of the main mechanisms for particle removal.[32] In this study, insufficient capture velocity of LEV might lead to high exposure levels of particles. The improved local exhaust ventilation could increase the efficiency of nanoparticle clearance.[29] Background particles appear to influence measurements because they are easily transported via airflow,[25] hence, background particles were selected as the control particles in this study to minimize their influence.

Particle size distributions showed that the highest NC of particles released from the slag releasing location appeared at 10.4 and 40 nm. The bimodal size distribution of particles from the slag releasing activity differed from the unimodal distribution of background particles. This finding was in agreement with our previous study that reported the bimodal size distribution of airborne alumina nanoparticles associated with separation and packaging processes in a pilot factory.[31] The total NC of particles less than 100 nm was approximately 10 times higher than that of particles above 100 nm. The results of personal sampling showed that the size of the particles decreased from 100 to 30 nm as the working activity started. These results provided direct evidence that workers were exposed to high levels of ultrafine particles during the slag releasing process.

In this study, the order of CR value at the location of slag releasing was: CR_{SAC} (5.39) > $CR_{total\ NC}$ (2.87) > CR_{MC} (2.22); the order of the correlation coefficients between the total NC, SAC, and respirable MC was $R_{total\ NC\ and\ SAC}$ (r = .681) > $R_{SAC\ and\ total\ respirable\ MC}$ (0.456) > $R_{total\ NC\ and\ total\ respirable\ MC}$ (0.424). These results were supported by our previous study[29-31,33] that examined the relationships among the NC, SAC, and MC of different nanoparticles in workplaces, and found that the total NC and SAC had a positive correlation (0.558-0.673), which were greater than the $R_{SAC\ and\ MC}$ or $R_{NC\ and\ MC}$.

The CB tool of Stoffenmanager-Nano can be used to effectively assess the risk of nanoparticles in the workplace.[23,34] In this study, the Stoffenmanager-Nano model shows that the blast furnace workers exposed to high levels of ultrafine particles were at high risk level, suggesting that the existing exposure control measures were insufficient. According to the National Institute for Occupational Safety and Health regulation,[35] the most desirable alternative for mitigating risks is to employ the following additional measures: (i) the exhaust speed of LEV for dust removal at the blast furnace needs to be increased, including the redesign of the hood for total enclosure; (ii) the preventative maintenance schedule for ensuring the effectiveness of engineering control measures should be established; sensitive indicators for ultrafine particles need to be developed in occupational health examination; and (iii) regular inspection should be conducted to ensure workers are properly wearing the PPE.

Although the workers were at high risk, no significant adverse effects on the respiratory system have been reported among these workers. We analyzed the routine occupational health examination data of 585 blast furnace workers with average 5 years of exposure, and no abnormal opacity was found in chest X-ray graphs (data is not shown in the results). The most possible reason might be the insensitivity of existing occupational health examination indicators to ultrafine particles. Therefore, sensitive indicators should be developed for worker health surveillance.

Based on the above findings, conclusions can be drawn as follows: (i) the blast furnace workers was exposed to high levels of ultrafine particles with Al and Pt as the dominant metal elements; (ii) the temporal variations in particle exposed concentrations exhibited an activity-related characteristic and a bimodal size distribution; (iii) the blast furnace workers exposed to the ultrafine particles were at high-risk level; (iv) the existing control strategies in this steelmaking plant, including engineering control, management control, and personal protection equipment need to be improved. More field investigations are needed to improve the exposure control strategies for the steelmaking industry.

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DISCLOSURE

Approval of the research protocol: N/A. *Informed consent:* N/A. *Registry and the Registration no. of the study/trial:* N/A. *Animal studies:* N/A.

CONFLICTS OF INTEREST

The authors declare that they have no competing interests.

AUTHORS' CONTRIBUTIONS

Xiangjing Gao contributed to conceptualization, data curation, investigation, funding acquisition, supervision, and writing original draft. Xingfan Zhou contributed to investigation, data curation, methodology, funding acquisition, and formal analysis. Hua Zou contributed to investigation and funding acquisition. Qunli Wang contributed to formal analysis and supervision. Zanrong Zhou contributed to formal analysis. Rui Chen contributed to methodology. Weiming Yuan contributed to supervision. Yuqing Luan contributed to supervision. Quanchang Jian contributed to data curation. Meibian Zhang contributed to conceptualization, funding acquisition, review, and editing.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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