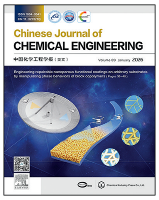
Chinese Journal of Chemical Engineering 89 (2026) 220–229

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE



Full Length Article

Study on pollutant reduction effect and environmental benefits of ultra-low emission retrofit of iron and steel sintering process: A case study of a steel group in Gansu province

Yuhao Zhang [1,2], Peiqiang Zhao [3], Mingli Li [3], Xinglin Zhang [3], Zewei Liu [4], Dahai Yan [5], Chao Chen [5,*], Wei Fang [4,*]

[1] *Lanzhou University, Lanzhou 730000, China*
[2] *Zhengdong Space Industry Co., Ltd., Beijing 100020, China*
[3] *Gansu Academy of Eco-environmental Sciences, Lanzhou 730030, China*
[4] *Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China*
[5] *Research Institute of Solid Waste Management, Chinese Research Academy of Environmental Sciences, Beijing 100012, China*

ARTICLE INFO

Article history:
Received 9 May 2025
Received in revised form
8 August 2025
Accepted 12 August 2025
Available online 4 September 2025

Keywords:
Ultra-low emission
Collaborative governance
Sintering process
Emission reduction effect

ABSTRACT

Iron and steel industry is one of the main sources of air pollution emissions in China. The sintering process is an important link in the blast furnace ironmaking process, but it is also accompanied by a large number of pollutants. Under the background of ultra-low emissions, iron and steel enterprises urgently need to upgrade their existing processes to address the existing process in practical application problems. In this study, a steel group in Gansu Province was taken as an example. By comparing and analyzing the pollutant emission characteristics before and after the ultra-low emission retrofit, the collaborative control effect of the combined process on SO_2, NO_x, particulate matter, and dioxins after the new retrofit was systematically evaluated. The results show that after the retrofit, the concentrations of particulate matter, SO_2 and NO_x have dropped to near-zero levels, and the dioxin removal efficiency has reached 98.87%, with all indicators being better than the national ultra-low emission standards. The study confirms that the optimal combination of multi-pollutant collaborative treatment technologies is the key to achieving efficient emission reduction, among which selective catalytic reduction technology has a particularly significant synergistic removal effect on NO_x and dioxins. This study provides an important technical reference and practical basis for the ultra-low emission retrofit of the steel industry, and has important guiding significance for promoting the green retrofit of the industry. Its ultra-low emission retrofit is of great significance for achieving green and low-carbon development.

1. Introduction

As a resource and energy-intensive industry, the iron and steel industry occupies an important position in China's national economy. The industry not only provides the raw materials, energy, and technical equipment required for the production of the national economic construction, but also supports the production of various types of consumer goods required for daily life, and is an essential pillar of the construction of China's complete industrial system [1–3]. China's steel industry has developed rapidly since the beginning of this century and has now become the world's largest steel producer. Its development level directly reflects the degree of industrialization and economic strength of a country [4–6].

The rapid development of China's infrastructure has driven up the demand for crude steel and pig iron production. In 2023, crude steel output reached 10.2885 million tons and pig iron output was 13.837 million tons (the ten-year production trend is shown in Fig. 1(a)). With the growth of steel demand, the emissions of major air pollutants such as SO_2, NO_x and particulate matter (PM) in production have increased (the emissions in recent years are shown in Fig. 1(b)). Although the improvement of environmental awareness has gradually restricted emissions and alleviated pollution problems, the steel industry remains a high

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* Corresponding authors.
E-mail addresses: chen.chao@craes.org.cn (C. Chen), fangwei@stu.kust.edu.cn (W. Fang).

https://doi.org/10.1016/j.cjche.2025.08.006
1004-9541/

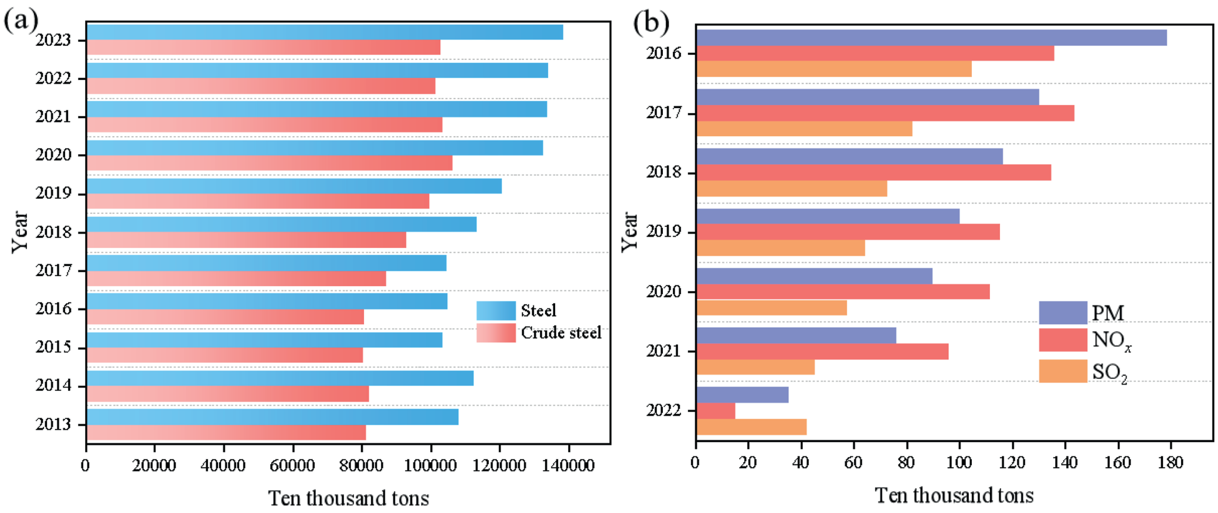

Fig. 1. (a) China's crude steel and pig iron production in the last decade; (b) Emissions of air pollutants from China's steel industry, 2016—2022. Data source: National Bureau of Statistics, Ministry of Ecology and Environment.

energy-consuming and high-pollution sector. It is necessary to promote green and high-quality development through technological transformation and innovation [7,8].

Sintering is an important energy consumer in ironmaking, the second most energy-intensive process after blast furnaces, and its energy consumption accounts for about 10% of total steel production [9]. The sintering process is an important part of steel production, and the gaseous pollutants emitted by this process account for 40% of the total emissions of steel production [10,11]. Sintering flue gas has the characteristics of complex composition, wide temperature range, high oxygen content, and high moisture content [12]. In addition to conventional pollutants, toxic and harmful air pollutants (HAPs) such as mercury and volatile organic compounds (VOCs) are produced in the sintering process, so it is key and difficult to deal with sintering process pollutants. In the face of the dual pressure of high energy consumption and greenhouse gas emissions in iron ore sintering, sustainable energy-saving, and carbon reduction technology has become an urgent need for industry retrofit and upgrading.

The ultra-low emission standards currently implemented in China are the world's most stringent pollutant emission standards for the steel industry [13]. Since April 2019, China has fully implemented ultra-low emission transformation in the steel industry, setting strict limits of 10, 35 and 50 $mg\cdot m^{-3}$ respectively for PM, SO_2 and NO_x emissions in the flue gas from sintering machine heads. As early as 2012, the Ministry of Ecology and Environment regulated pollution control in the steel industry through the GB 28662—2012 standard. In contrast, the standards for new and expanded power plants in the United States after 2011 were relatively lenient. The limits for PM, SO_2 and NO_x were 12.3, 136.1 and 95.3 $mg\cdot m^{-3}$ respectively. The European Union has more lenient requirements for new units with a capacity of over 300 MW. The limits for SO_2 and NO_x are both 150 $mg\cdot m^{-3}$, while the limit for particulate matter (10 $mg\cdot m^{-3}$) is on par with that of China [14]. It is evident that the current ultra-low emission limits implemented in China are significantly stricter than those of the current emission standards in the United States and the European Union.

Under the current sustainable development strategy, the industry urgently needs to strengthen emission reduction measures to continuously improve environmental quality [15]. Due to strict pollutant discharge standards, flue gas treatment technology has developed rapidly. According to whether water is added and the status of desulfurization products in the treatment process, flue gas desulfurization (FGD) technology is divided into wet, dry, and semi-dry methods [16,17]. In China, wet and semi-dry methods are mainly used, while in foreign countries, semi-dry and dry methods are the same. Flue gas denitration technology involves activated carbon adsorption, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) [18]. Domestically, SCR is the main method for denitrification, while abroad, hydrogen energy/ammonia fuel denitrification is the primary approach. Electrostatic precipitators and bag dust removal devices have been widely used to remove solid particles, among which electrostatic precipitators are the most widely used because of their high efficiency and low pressure [19]. The removal of dioxins mainly depends on activated carbon adsorption, and SCR also has excellent catalytic degradation effect on dioxins [20]. Ultra-low emissions are mainly achieved by strengthening the existing denitrification, desulfurization and dust removal technologies. At present, the mainstream ultra-low emission technology routes for coal-fired power in China can be classified into three major categories: the technical route centered on the low-low temperature electrostatic precipitator (LLTESP), and the wet electrostatic precipitator (WESP), and the technical route centered on electrostatic bag filter [21].

The types of pollutants discharged from the sintering process of iron and steel are complex, and the traditional single pollutant control technology can not meet the requirements of the current ultra-low emission standards. However, it is worth noting that the current research on the actual operation effect after ultra-low emission retrofit is still insufficient, especially the lack of systematic evaluation cases based on real production data, which restricts the optimization and promotion of collaborative control technology to a certain extent. Therefore, taking a steel group in Gansu as an example, this study studied the emission characteristics of pollutants such as SO_2, NO_x, PM, and dioxins in the steel sintering process before and after the ultra-low emission retrofit through the arrangement of sampling points, field monitoring, and laboratory analysis, and evaluated the collaborative control effect of ultra-low emission retrofit on multiple pollutants. The research results can provide scientific basis and technical support for the steel industry to promote ultra-low emission retrofit and have great significance for improving regional ambient air quality and promoting the green and low-carbon development of the steel industry.

2. Methods

2.1. Overview of the research area and research objects

This study is based on a typical iron and steel enterprise in Gansu, China. The research enterprise is located in Jiayuguan, Gansu, and the specific geographical coordinates are 98°17′14.723″ east longitude and 39°48′24.743″ north latitude. The company is strategically located in Northwest China, close to abundant mineral resources, especially iron ore and coal resources, which provide a solid raw material base for its steel production.

In order to study the collaborative control effect of waste gas treatment facilities before and after the retrofit of ultra-low emission sintering process in the iron and steel industry on pollution indicators such as SO_2, NO_x, PM, CO_2 and dioxins, this study samples of flue gas, desulphurized gypsum, and dust from sintering machine flue gas treatment facilities before and after ultra-low emission retrofit (old production line) and ultra-low emission retrofit (new production line) of iron and steel sintering process were selected for detection.

2.2. Sampling position

When the low chlorine and high chlorine working conditions were studied before the ultra-low emission retrofit of the sintering process, the sampling point was only set at the air inlet of the sintering flue gas environmental protection treatment facility in the low chlorine working condition. The pollutant emission and treatment efficiency were calculated concerning the high chlorine working conditions. Site sampling points are shown in Fig. 2, and specific settings are as follows:

(1) Sintering process before the ultra-low emission retrofit: Before the ultra-low emission retrofit, the sintering flue gas is drawn from the front and back ends of the sintering machine by two fans and is processed by two dust removal devices into a flue, and then processed by wet desulfurization device after discharge. The generation and emission of dioxins and other pollutants under low and high chlorine conditions were studied. Sampling points were set as follows: Under low chlorine conditions, one sampling point (Q1 and Q2) was set before the flue gas entered the two dust removal devices. Under high chlorine conditions, one sampling point is set before the flue gas enters the dust removal device (Q3, Q4), before the desulfurization after dust removal (Q5), and at the chimney general outlet (Q6). One sampling point is provided at the ash outlet (S1, S2) and desulphurized gypsum outlet (S3) of the two dust removal devices.

(2) After the ultra-low emission retrofit of the sintering process: After the ultra-low emission retrofit, the sintering flue gas treatment process is: the flue gas is removed by the electric dust collector and enters the semi-dry desulfurization unit (circulating fluidized bed, CFB), and then enters the SCR device after the bag dust removal, and finally discharged from the chimney. Sampling points are set as follows: flue gas sampling points: before electric dust removal (Q7), before CFB desulfurization (Q8), before SCR denitrification (Q9), after SCR denitrification (Q10-3), and chimney outlet (Q10), a total of 5 points. Dust sampling point: electric dust outlet (S4), bag dust outlet (S5), a total of 2 points.

Before the ultra-low emission retrofit of the sintering process (old production line): Under low-chlorine conditions, sampling points were set only before the dust removal devices to focus on the initial emission state of pollutants. Under high-chlorine conditions, sampling was extended to flue gas points before dust removal, before desulfurization, and at the final exhaust stack, along with dust removal ash and desulfurization gypsum sampling points. This approach not only covered the entire gas-phase pollutant control process but also tracked pollutant enrichment in solid waste, enabling a comparison of the impact of different chlorine contents in raw materials on emissions. After the ultra-low emission upgradation of the sintering process (new production line): Following the integrated process of “electrostatic precipitation → semi-dry desulfurization (CFB) → baghouse filtration → SCR denitrification”, sampling points were set at the inlet/

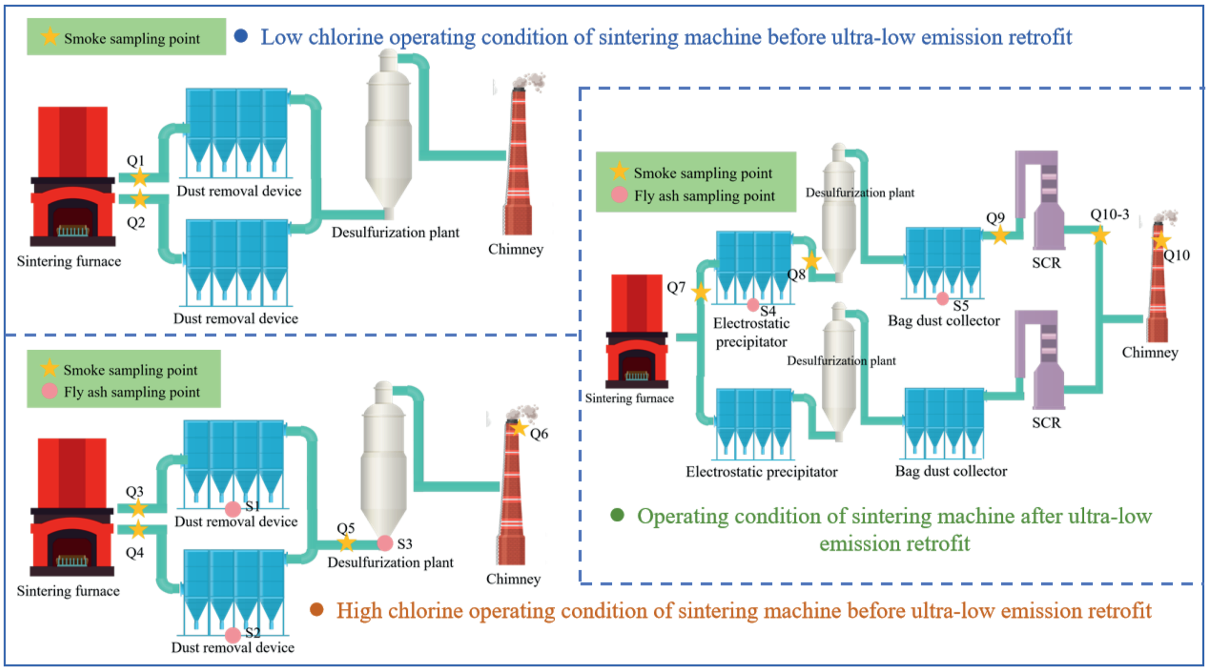

Fig. 2. Sampling point setting diagram of each working condition before and after modification.

outlet of each treatment unit and the final exhaust stack, with additional dust ash sampling points. This design fully reflects pollutant concentration changes across each purification stage after the retrofit while maintaining logical consistency with pre-retrofit sampling for comparative efficacy analysis.

The overall design considers process specificity, operational variability, and data representativeness, providing comprehensive support for analyzing pollutant formation mechanisms and control efficiency.

2.3. Sample collection and analysis

2.3.1. Detection indicators

The detection indexes are tested from five aspects: the operating parameters of the sintering machine, the raw materials of the sintering machine, flue gas, dust removal ash, and desulphurized gypsum. The specific parameters are shown in Table 1 below.

2.3.2. Sampling frequency

Sintering machine raw materials: During the operation of the sintering machine, samples of sintered raw materials are collected at the wide belt before the furnace, and 3 samples are collected at equal intervals within 6 h.

Flue gas: When the first vehicle that has collected raw material samples is discharged, flue gas sampling starts. The sampling time is collected twice within 6 h of each working condition. Each collection time is based on the requirements of relevant sampling standards.

Dust and desulphurized gypsum: During flue gas sampling, 2 samples were collected at the same time for each working condition.

2.3.3. Detection methods

The on-site sampling and testing of flue gas and soot shall be carried out according to the Technical Specification for Monitoring of Fixed Source Exhaust Gas (HJ/T 397—2007). According to national standards (HJ/T 397—2007, GB/T 16157—1996, HJ 973—2018, HJ 870—2017, HJ 1131—2020, HJ 1132—2020, HJ 836—2017, HJ 1331—2023, HJ 657—2013, HJ 777—2015, HJ 77.2—2008, *etc.*)

3. Results and Discussion

3.1. Generation and treatment of major pollutants in sintering industry

The production process of iron and steel enterprises mainly includes raw material field, sintering, pelletizing, iron making, steel making, steel rolling, *etc.*, among which many types of pollutants are discharged in the sintering and coking processes. The sintering flue gas of iron and steel has the typical characteristics of large smoke volume, significant temperature fluctuation, small dust particle size and high concentration, high humidity and oxygen content, and high pollutant concentration. Because the mixture contains a variety of substances, the composition of flue gas produced in the sintering process includes not only dust, SO_2, NO_x, and other conventional pollutants but also heavy metals, VOCs, and other HAPs. The production and sintering processes of the iron and steel industry and the emission nodes of flue gas pollutants are shown in Fig. 3.

3.1.1. NO_x

According to how NO_x is generated, NO_x can be divided into three categories: Thermal NO_x, fuel NO_x, and prompt NO_x. NO_x in the sintering process is mainly fuel NO_x, and 90% of NO_x generated in the sintering process comes from the nitrogen in the fuel, which is fuel type NO_x, and the thermal type and rapid type NO_x are produced in a small amount [22]. During the combustion of coke particles, pulverized coal and other fuels in the sintering bed, nitrogen in the fuel is pyrolyzed and burned, resulting in fuel NO_x entering the flue gas [23].

NO_x in the sintering process mainly comes from the sintering ignition and fuel combustion/high-temperature reaction stages. Emission reduction can be achieved through measures in three aspects: raw material treatment (foundation), process optimization (efficiency improvement), and end-of-pipe treatment (core guarantee). Among them, end-of-pipe treatment is the most crucial means for the steel industry to reduce emissions.

Flue gas denitrification technology. Typical denitrification processes include SCR and SNCR, which are widely used in thermal power plants and have relatively mature technology. SCR denitration technology is one of the most commonly used and mature denitration technology at present. This technique works by reacting nitrogen oxides in flue gas with a reducing agent (usually NH_3) in the presence of a catalyst to produce harmless N_2 and H_2O. SCR denitrification technology is mature, denitrification efficiency is high (up to 80%), and it is suitable for flue gas treatment of high-concentration ammonia oxides, with no by-products and no secondary pollution. However, this technology will encounter problems such as catalyst blockage, poisoning, and wear in production, requiring timely replacement and cleaning of catalyst memory [24].

3.1.2. SO_2

The formation of SO_2 in sintering flue gas includes the process of formation, absorption, and re-release. The SO_2 in sintering flue gas mainly comes from iron ore and solid fuels (such as pulverized coal). The sulfur in iron ore usually exists in the form of sulfide (FeS_2, $CuFeS_2$, *etc.*), sulfate ($BaSO_4$, $CaSO_4$, $MgSO_4$, *etc.*), and the sulfur in fuel coal mostly exists in the form of organic sulfur, sulfur,

Table 1
Detection indexes of each parameter.

Category	Argument						
Sintering machine operating parameters	Car loading capacity	Car running speed	Temperature change curve in the car	On-line temperature of flue gas	/	/	/
Sintering machine raw materials	Chlorine content	Volatile matter	Fixed carbon	Cu	Mn	/	/
Smoke	Temperature	Flow rate	Oxygen content	Moisture content	CO	CO_2	SO_2
	NO_x	PM	Total hydrocarbon	Hydrogen chloride	Cu (granular)	Fe (granular)	Mn (granular)
	Cu (gas)	Fe (gas)	Mn (gas)	Dioxin			
Dedusting ash	Dust generation rate	Dioxin	Cl	Cu	Fe	Mn	/
Desulphurized gypsum	Desulfurization gypsum production rate	Moisture content	Dioxin	Cl	Cu	Fe	Mn

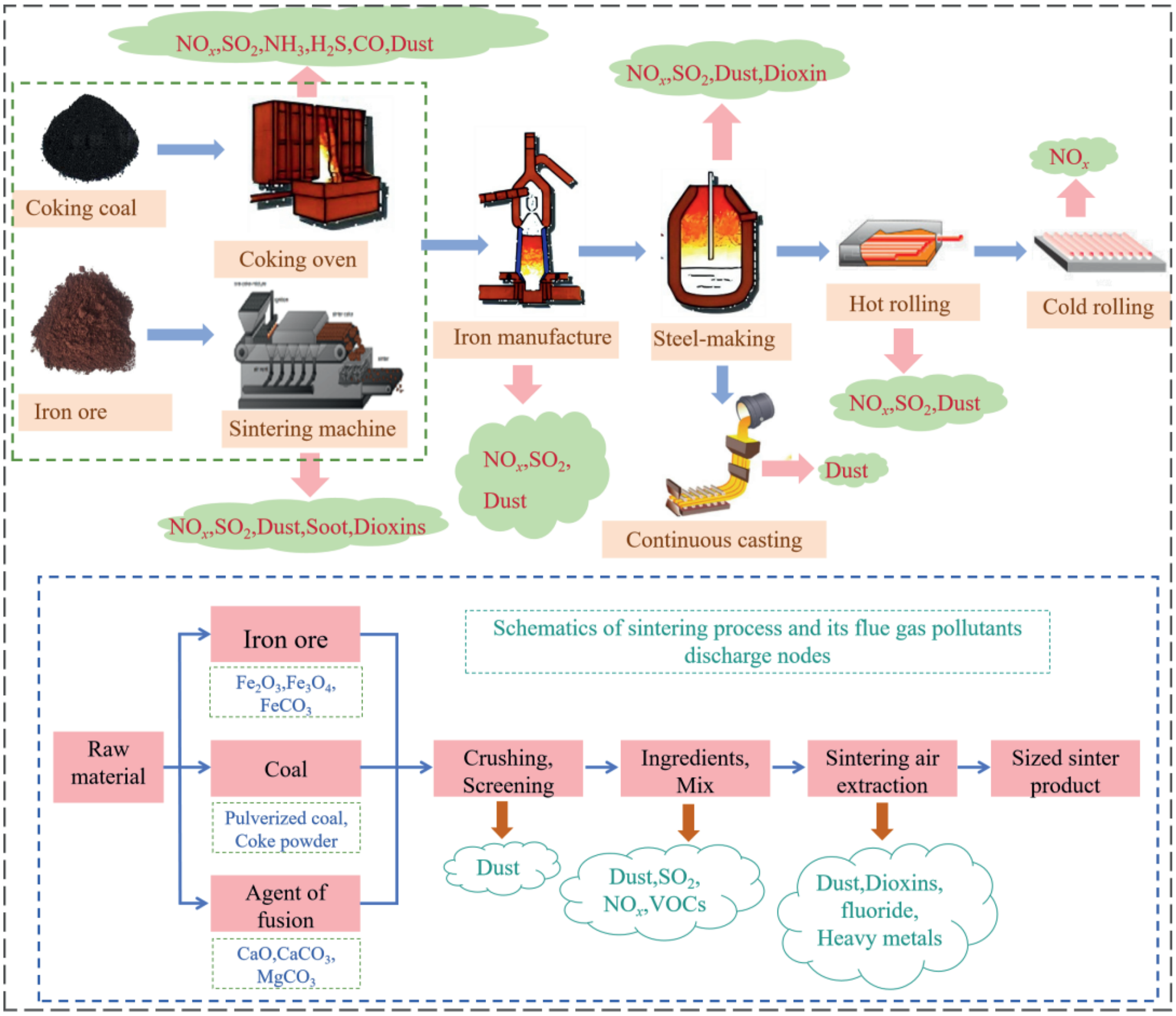

Fig. 3. Production process and sintering process of iron and steel industry and emission nodes of flue gas pollutants.

and organic sulfur decomposition quickly react with O_2 and oxidize to SO_2, and sulfate in the decomposition reaction releases SO_2 [25,26]. Each production of 1 t sinter requires about 35–55 kg of fuel coal, and SO_2 in sintering flue gas mainly comes from iron ore [27]. Sintering is one of the main desulfurization processes in steel production. The desulfurization in sintering process is mainly caused by the high-temperature decomposition and oxidation of S element, and the formation of SO_2 is discharged with the flue gas.

According to whether water is added and the status of desulfurization products in the treatment process, desulfurization technology can be divided into wet, dry and semi-dry desulfurization technology [28]. The wet desulfurization technologies commonly used in China's iron and steel industry include limestone-gypsum and ammonia desulfurization. Dry desulfurization refers to the desulfurization process carried out in a dry state. The dry desulfurization technology commonly used in iron and steel industry is activated carbon (coke) adsorption technology. Semi-dry desulfurization has the characteristics of both dry and wet desulfurization. The semi-dry desulfurization technology has high desulfurization efficiency, no waste water and little corrosion, but the desulfurization products are difficult to treat. The commonly used semi-dry desulfurization techniques include CFB, spray drying absorber desulfurization and dense coherent tower method.

3.1.3. PM

Steel emissions in the production process of a large amount of dust, iron, and steel enterprises, according to the source of PM, can be divided into two categories. One is produced by chemical reactions such as combustion in the production process, and the other is produced during material handling and transportation. The production of PM mainly produced by the sintering process is mainly generated in the process of loading and unloading, screening, mixing, and transportation of raw materials, and the ruptures due to the removal of crystal water from the mixture in the drying zone and the combustion of coke dust in the combustion zone [29,30]. Dust removal technology is the main approach for the terminal treatment of PM, mainly including gravity dust removal (suitable for particles above 20 μm, efficiency 40% to 60%), cyclone dust removal (resistant to high temperatures and corrosion, efficiency <80%), electrostatic dust removal (high efficiency, large flue gas volume processing, efficiency 99%), and bag dust removal (highly efficient removal of submicron particles, efficiency 99.99%).

3.1.4. *Dioxin*

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively known as PCDD/Fs, are a class of persistent polluting chlorinated volatile organic compounds with teratogenic, carcinogenic and mutagenic properties [31]. The iron ore sintering process is considered to be the main industrial source of PCDD/Fs [12]. Iron and steel production is one of the major dioxin emission industries in the world. There are two main ways of dioxin production in the sintering process: de novo synthesis and precursor synthesis [5,32,33]. The formation of dioxins requires the presence of chlorine source, carbon source, copper, iron and other catalysts in the sintered raw materials, sufficient oxygen and appropriate reaction temperature. In the process of iron ore sintering, both copper and iron are catalysts to promote dioxin synthesis and precursor synthesis, in which copper has the main catalytic activity [34]. In the sintering process, the concentration of PCDFs in the homologous distribution is 10 times that of PCDDs. End-treatment dioxin control mainly includes gas phase dioxins and particle phase dioxins, dust removal technology is mainly for particle phase dioxins, at 200 °C, dioxins are mainly adsorbed on the PM in solid form, most of the particle phase dioxins can be removed by dust removal technology, but the gas phase dioxins removal is not ideal.

3.2. *Comparison of pollutant emission concentration before and after ultra-low emission retrofit*

3.2.1. *Flue gas sampling*

(1) Dioxin

Through the analysis of dioxin emission data from each sampling point, it can be seen that there are significant differences in the removal effect of dioxin in different processes (Fig. 4(a)). Toxicity equivalence quantity (TEQ) is an international standard indicator used to assess the comprehensive toxicity of dioxin-like pollutants. In the old production line, the dioxin concentration reached 0.505–0.640 ng toxicity equivalence ng·kg^{-1} under high chlorine conditions (Q3/Q4), which was significantly higher than that under low chlorine conditions, confirming that chlorine content was the key factor promoting dioxin formation. After the retrofit, the new production line shows obvious technical advantages: the initial concentration (Q7) is 24.8% lower than the old line, and after the combined process of “semi-dry desulfurization + bag dust removal + SCR denitration,” the final emission concentration (Q10-3) is reduced to 0.011 ng·kg^{-1}, far better than the national standard of 0.1 ng ·m^{-3}. Among them, the

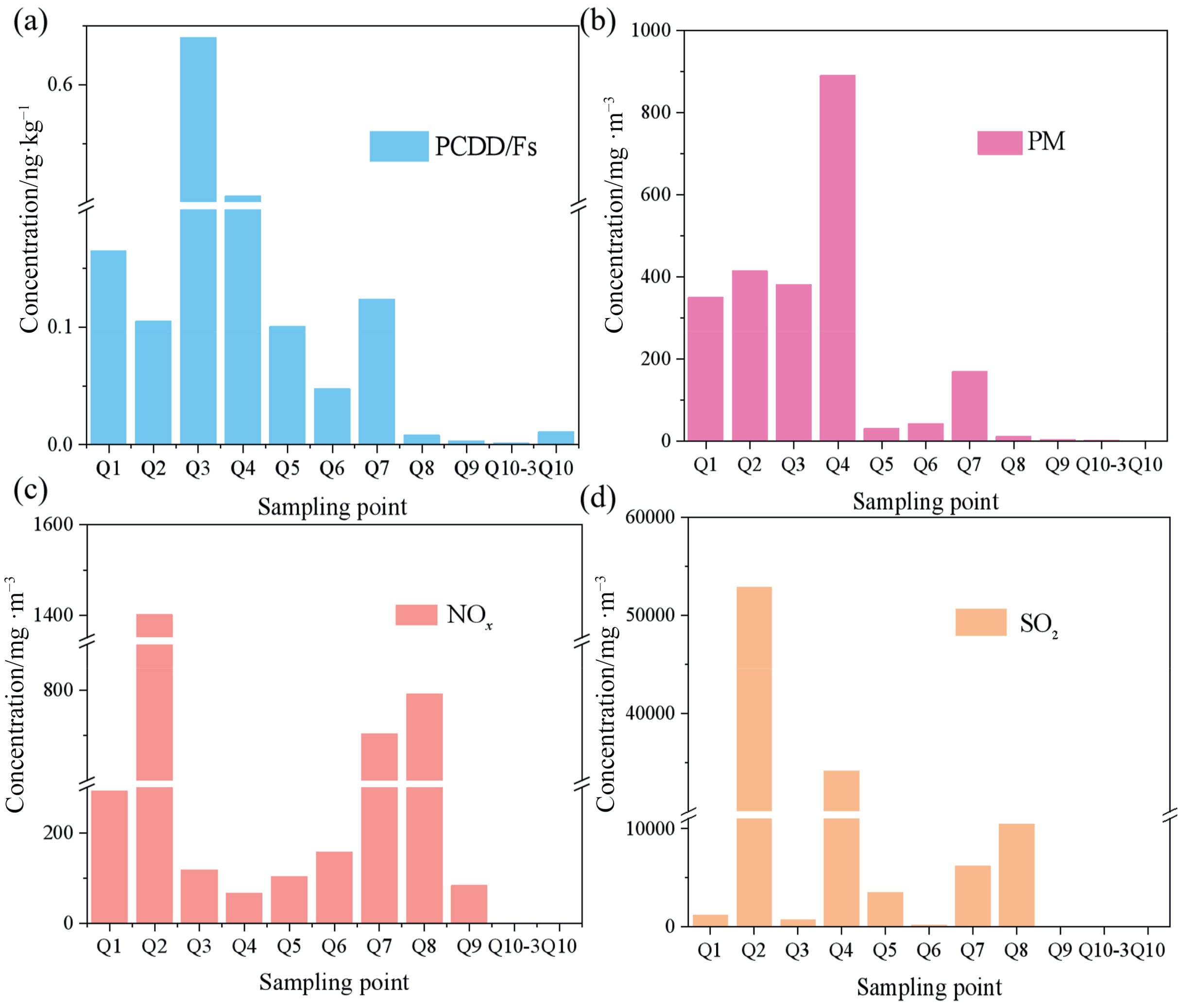

Fig. 4. Pollutant emission concentrations at each sampling point: (a) PCDD/Fs, (b) PM, (c) NO$_x$, (d) SO$_2$.

semi-dry desulfurization process has the most significant removal effect, and the SCR denitration process contributes to a better removal rate. In contrast, the end emission concentration (Q6) of the old production line is still 0.0475 $\mathrm{ng \cdot kg^{-1}}$ through dust removal and desulfurization treatment.

(2) PM

Through the analysis of the particle concentration data of each sampling point, the dust removal effect of different process links and the performance comparison before and after the retrofit can be clearly reflected (Fig. 4(b)). The concentration of PM at the sampling point (Q1—Q4) at the front end of the old production line fluctuated between 349.67 and 889.73 $\mathrm{mg \cdot m^{-3}}$, among which the concentration at Q4 point reached the highest 889.73 $\mathrm{mg \cdot m^{-3}}$, which may correspond to high load conditions. After dust removal treatment (Q5 points), the concentration is significantly reduced to 29.84 $\mathrm{mg \cdot m^{-3}}$, showing the good performance of the electric dust removal equipment. After the retrofit, the initial concentration of the new production line (Q7 point 168.68 $\mathrm{mg \cdot m^{-3}}$) is lower than that of the old line. After the combined process of "electric dust removal + semi-dry desulfurization + bag dust removal + SCR", the concentration of PM is reduced in a stepped way: After electric dust removal (Q8 points), it is reduced to 10.46 $\mathrm{mg \cdot m^{-3}}$, after cloth bag dust removal (Q9 points), it is further reduced to 3.07 $\mathrm{mg \cdot m^{-3}}$, and finally after SCR treatment (Q10-3 points), it reaches an ultra-low emission level of nearly zero. In particular, it may indicate that the system can achieve near-zero emissions of PM under optimal operating conditions.

(3) NO_x

Through the analysis of NO_x concentration data at each sampling point, it can be seen that there are significant differences in the denitrification effect before and after the retrofit (Fig. 4(c)). Before the retrofit (in the old production line), the concentration of NO_x in Q1 and Q2 under low chlorine conditions was significantly different, indicating that the distribution of nitrogen oxides in the flue gas at different positions was uneven, especially the very high concentration of NO_x in Q2 (1400.67 $\mathrm{mg \cdot m^{-3}}$), which may be due to the high content of nitrogen oxides in the flue gas at the rear end of the sintering machine. The concentration of NO_x in Q3 and Q4 under high chlorine conditions is low, indicating that the nitrogen oxide generation is relatively low under high chlorine conditions. After the wet desulfurization unit (Q6), the concentration of NO_x slightly increased (156.73 $\mathrm{mg \cdot m^{-3}}$), which may be due to the error of the monitoring point data. After the retrofit, the concentration of nitrogen oxides was significantly reduced, especially after the SCR denitrification device (Q10 point) was nearly zero emission, and the concentration of NO_x was reduced by 83.57 $\mathrm{mg \cdot m^{-3}}$. The final discharge outlet (Q10) is fully compliant with ultra-low emission standards.

(4) SO_2

According to the data from the detection point (Fig. 4(d)), it can be seen that under the low chlorine condition, the concentration difference between Q1 and Q2 is large, indicating that the distribution of pollutants in the flue gas at different locations is uneven, especially the concentration of Q2 is extremely high. After sintering, the overwet zone slowly disappears, and not only loses the adsorption effect, but also loses the absorption effect. SO_2 adsorbed in the form of sulfate in the overwet zone before sintering and S in the material layer are also released in large quantities, so the concentration of SO_2 reaches a peak [35].

The characteristics of SO_2 concentration distribution in the sintering process are due to the complex process of SO_2 precipitation, reabsorption, and reprecipitation. Under high chlorine conditions, the concentration difference between Q3 and Q4 is large, which again indicates the uneven distribution of pollutants in flue gas. After the dust removal device (Q5), the pollutant concentration was significantly reduced but still high (3500.3 $\mathrm{mg \cdot m^{-3}}$). After the wet desulfurization unit (Q6), the pollutant concentration is further reduced to 163.6 $\mathrm{mg \cdot m^{-3}}$, indicating that the wet desulfurization has a significant removal effect on pollutants, but the final emission concentration is still high, but it still does not reach the ultra-low emission standard. After the retrofit (new production line), the concentration of Q7 and Q8 is higher, indicating that the removal effect of the electric dust removal device is limited. After semi-dry desulfurization and bag dust removal (Q9), the pollutant concentration was significantly reduced to 0.15 $\mathrm{mg \cdot m^{-3}}$, indicating that semi-dry desulfurization and bag dust removal had a very significant effect on pollutant removal and were the main removal devices for SO_2 removal. It shows that the SCR denitrification device further removes residual pollutants and achieves ultra-low emission.

3.2.2. *Dust removal ash and desulphurized gypsum*

Sintering machine head electric dust dust is the sintering machine head electric dust collector captured dust, sintered ash contains a certain amount of iron, has the value of recovery, but at the same time contains high alkali metal, and contains lead, zinc, copper and other valuable metals (Table 2) [36,37].

Through the analysis of pollutant detection data at each sampling point (Fig. 5), it was found that the content of chlorine, dioxins, and heavy metals (Cu, Fe, Mn) in electric dust (S1/S2) was significantly higher, with chlorine content exceeding 127000 $\mathrm{mg \cdot kg^{-1}}$ and dioxin concentration as high as 908.5 $\mathrm{ng \cdot kg^{-1}}$. The results indicate that the high chlorine content in the raw material may be the key catalyst for synthesizing dioxins in the sintering process, especially in the presence of Cu/Fe. In contrast, the concentration of pollutants in desulphurized gypsum (S3) and dust ash (S5) is significantly reduced. The dioxin concentrations of S3 and S5 confirmed that desulfurization and bag dust removal had synergistic removal effects on chlorine, dioxin, and heavy metals. During the sintering process of iron ore powder, due to the accumulation of potassium and sodium in the raw ore in the sintering system, the alkali metal content in the electric dust removal ash of the sintering machine head is high. The comprehensive recovery and utilization of the electric dust removal ash of the sintering head can not only solve the problems of grate clogging or bellows caking caused by a high content of alkali metal but also realize the efficient recovery and utilization of potassium, lead, and silver and other elements in the sintering ash.

Table 2
Concentrations ($\mathrm{mg \cdot kg^{-1}}$) of elements in dust removal ash and desulphurized gypsum sampling points.

Type of element	S1	S2	S3	S4	S5
K	170183.00	173893.00	5355.03	176336.00	1099.88
Mg	5640.30	5735.40	1890.00	7415.10	2720.40
Na	16468.00	16777.00	3946.73	15027.50	641.77
Si	17747.30	18150.10	21739.90	21992.60	12515.80
Pb	106661.00	87123.50	329.50	61179.50	535.50
Zn	3631.50	3340.50	16.50	1015.00	20.00
Cl	127818.00	131660.00	4202.50	33030.00	10223.50
Cu	1145.23	947.99	8.16	720.57	6.39
Fe	228000.00	252000.00	2140.00	306500.00	2170.00
Mn	7170.00	7450.00	65.15	5570.00	164.00

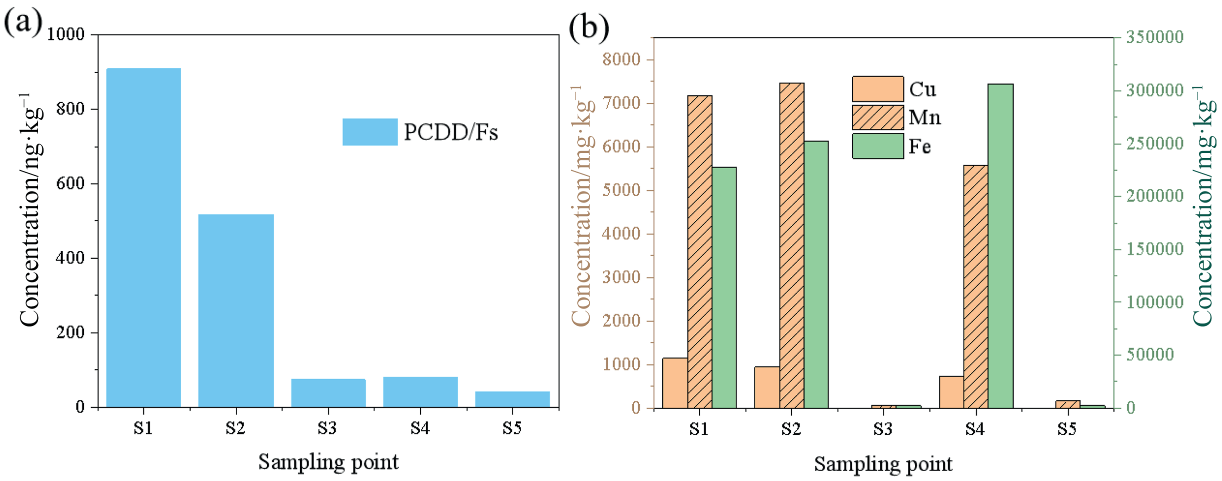

Fig. 5. (a) PCDD/Fs concentrations in dust removal ash and desulphurized gypsum sampling points; (b) Fe, Mn, Cu concentrations in dust removal ash and desulphurized gypsum sampling points.

3.3. Analysis of emission reduction effect

This data system shows the removal effect of various pollutants in different process links and the overall emission reduction performance after the ultra-low emission retrofit of iron and steel sintering process. By analyzing the emission reduction rates of SO_2, NO_x, PM, dioxins, and gaseous/granular heavy metals (Mn, Cu, Fe), as shown in Fig. 6, the following key conclusions can be drawn:

The conventional pollutant control effect is excellent, SO_2 and NO_x: although the electric dust removal process has a negative efficiency (SO_2: −69%, NO_x: −12.4%), complete purification is achieved through subsequent processes. Semi-dry desulfurization has the characteristics of dry and wet desulfurization. The increase in SO_2 and NO_x concentrations at the outlet of the electrostatic precipitator is the result of the combined effect of measurement deviation and change in gas state. Some of the potential reasons may be: high dust at the inlet interferes with the measurement, resulting in the underestimation of the concentration; the dust at the outlet is reduced, and the dry basis concentration increases due to moisture or volume changes. A small amount of adsorbed pollutants desorb and are released. Semi-dry desulfurization means that the desulfurizer is dissolved in water or sprayed into the flue in the form of slurry, and the flue gas is washed for desulfurization. The moisture in the absorption liquid absorbs the heat of the flue gas and evaporates, so the desulfurization product is in a dry powder state. Semi-dry desulfurization technology has the characteristics of high desulfurization efficiency, no waste water, and low corrosion, and the removal rate of SO_2 by semi-dry desulfurization reaches 100%. SCR selective nitrogen removal process and activated carbon adsorption process are the main nitrogen removal technologies in China's iron and steel industry. SCR nitration usually uses NH_3, urea, or hydrocarbons as reducing agents. Under the action of the catalyst, the reducing agent selectively reduces nitrogen oxides to N_2 and H_2O. The removal rate of NO_x by SCR denitrification is as high as 98.3%, and the final emission concentration is close to zero, which proves the core role of the desulfurization and denitrification system.

PM: The electric dust collector has high dust removal efficiency, can handle a large amount of flue gas, can handle medium and high temperature flue gas, the electric dust removal as the primary component contributes 93.8% of the removal rate, combined with the subsequent bag dust collector process to achieve 99.16% of the total removal rate, the emission concentration is reduced to 1.41 mg·m^{-3}, significantly better than the ultra-low emission standard (10 mg·m^{-3}). It is recommended to continuously optimize the operating parameters of the bag dust collector and strengthen the maintenance of SCR catalyst to maintain the long-term stable operation of the system. The removal rate of dioxins by electric dust removal reached 93.43%, and the total removal rate was 98.87% after subsequent desulfurization SCR process. The end residual concentration (0.0014 ng·kg^{-1}) was acceptable, but could be further reduced by adding activated carbon injection.

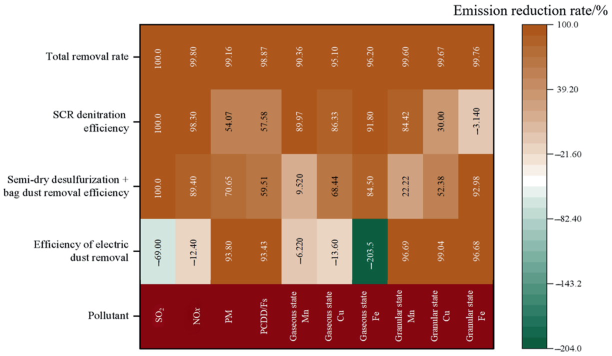

Fig. 6. Pollutant emission reduction rates of each process after upgradation.

Differential removal characteristics of heavy metals, gaseous heavy metals: electric dust removal is basically ineffective on gaseous metals (Mn −6.22%, Cu −13.6%, Fe −203.5%), but SCR showed excellent removal effects (Mn 89.97%, Cu 86.33%, Fe 91.8%), which may be related to catalytic oxidation. Granular heavy metals: the removal rate of particulate metals by electric dust removal is more than 96%, and the terminal removal rate of particulate copper is the highest (99.67%), indicating that the whole process has the best trapping effect. Process chain coordination and problem points, negative efficiency links: the negative efficiency of electric dust removal on SO_2, NO_x, and gaseous heavy metals reflects that it is only suitable for PM control, and the process connection needs to be optimized.

Some researchers have carried out ultra-low emission renovations on the technical routes of coal-fired power plants. The post-renovation process technology route is: SNCR denitrification + electrostatic precipitator renovation + single-

Table 3
Pollutant emission reduction before and after renovation.

	Before upgradation	After upgradation
Standard dry flow rate/$m^3 \cdot h^{-1}$	1.557×10^6	9.255×10^5
NO_x/$kg \cdot m^{-3}$	2.138×10^6	0.000
SO_2/$kg \cdot m^{-3}$	2.231×10^6	0.000
PM/$kg \cdot m^{-3}$	5.761×10^5	0.000
(PCDD/Fs)/$g \cdot m^{-3}$	6.479×10^{-1}	8.918×10^{-2}

tower integrated ultra-low emission renovation, adopting the SNCR + wet process. After the renovation, all pollutants meet the emission requirements [38]. Although the wet desulfurization process adopted features a fast reaction speed and strong operational stability, it has problems such as severe equipment corrosion, high operating costs, and potential secondary pollution. Semi-dry desulfurization has a moderate investment, strikes a balance between efficiency and cost, and is more water-efficient compared to wet desulfurization, while also having a higher efficiency than dry desulfurization. In terms of denitrification, SCR denitrification technology is currently the most widely used and mature denitrification process. It is suitable for relatively low temperatures (usually 200–400 °C) and has a high denitrification efficiency. Therefore, considering the geographical environment of Gansu and meeting the requirements of ultra-low emissions, the technical route of “semi-dry desulfurization + bag filter + SCR” of this process has better advantages.

3.4. Environmental impact of pollutant emission reduction

According to the flue gas emissions at Q6 before the retrofit and Q10 after the retrofit, the comparative data of annual emissions of each pollutant were roughly estimated to explore the impact of emission reduction on the environment. The specific pollutant emission reduction is shown in Table 3.

After the implementation of the ultra-low emission retrofit project, the environmental benefits have been significantly improved. Through the combination of “semi-dry desulfurization + bag dust removal + SCR denitrification” process, pollutant emissions were greatly reduced: sulfur dioxide and nitrogen oxides were completely eliminated, and the annual emission reduction reached 2231500 kg and 2137800 kg respectively; The annual emission of PM was reduced by 576100 kg, a reduction of 100%; dioxin emissions were also reduced by 86%, with annual emissions falling from 0.648 g TEQ to 0.089 g TEQ.

These emissions reductions translate directly into significant environmental improvements: these improvements are directly reflected in the overall improvement of regional environmental quality: the reduction of nitrogen oxides and sulfur dioxide significantly reduces the frequency of acid rain, the reduction of PM effectively reduces the concentration of fine particles and their precursors in the atmosphere, and near-surface ozone pollution is alleviated. At the broader ecological level, the implementation of the project effectively mitigated the environmental impact on the surrounding sensitive ecosystem, reduced the risk of water and soil pollution, and improved the regional environmental capacity. Overall, the project not only greatly improves the environmental quality of the region, but also provides a demonstration for promoting the green retrofit of industry, whose environmental benefits will continue to emerge and contribute to sustainable development.

4. Conclusions

This study takes a steel group in Gansu Province as a case study, conducting a comparative analysis of pollutant emission characteristics and treatment effectiveness before and after ultra-low emission retrofits. The main conclusions are as follows; the ultra-low emission retrofit realizes the collaborative and efficient control of multiple pollutants. Through the application of the combination process of “semi-dry desulfurization + bag dust removal + SCR denitrification”, the emission concentration of pollutants such as SO_2, NO_x, PM and dioxins has been significantly reduced, among which the concentration of PM, SO_2 and NO_x has achieved nearly zero emission, and the removal rate of dioxins has reached 98.87%, fully meeting the requirements of the national ultra-low emission standard. The optimal combination of multi-pollutant collaborative treatment technology is the key. The synergistic effect of semi-dry desulfurization, SCR denitrification and high-efficiency dust removal technology not only improves the removal efficiency of pollutants, but also reduces the risk of secondary pollution. Therefore, SCR technology has a significant synergistic removal effect on NO_x and dioxins. This study confirmed the significant environmental benefits of ultra-low emission retrofit. However, in future follow-up research, attention should still be paid to operational cost issues such as the consumption of SCR catalysts and additional process energy consumption after the retrofit, as well as technical challenges such as catalyst poisoning. Future research still needs to further integrate pollutant control with carbon reduction targets, develop a “dynamic carbon footprint assessment model for end-of-pipe treatment technologies” driven by real-time monitoring data, reveal the carbon cost-benefit balance mechanism of unit processes such as SCR/desulfurization throughout the entire steel production process, and promote the formation of a technology optimization system that achieves synergy in pollution reduction and carbon emission reduction.

CRediT Authorship Contribution Statement

Yuhao Zhang: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. Peiqiang Zhao: Supervision, Methodology, Conceptualization. Mingli Li: Writing – review & editing. Xinglin Zhang: Methodology, Investigation, Conceptualization. Zewei Liu: Project administration, Methodology, Conceptualization. Dahai Yan: Writing – review & editing, Methodology. Chao Chen: Writing – review & editing. Wei Fang: Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the Key Research and Development Program of Gansu Province (22YF7FA070), the National Natural Science Foundation of China (22406076, 22466026), and the Basic Research Project of Yunnan Province (202301BE070001-017, 202401CF070139, 202401AS070085).

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