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Study on the Removal Efficiency of Heavy Metals in Flue Gas of Small Sintering Machines

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Abstract. Heavy metal pollutants such as Hg, Pb, Cr, and Cd contained in flue gas from the sintering equipment bring about environmental hazards. In this paper, 4 small sintering machines with different control technologies were selected, and the US EPA 29 method was used to analyze the emission concentration of heavy metals from the sintering machines, and the removal efficiency of the different flue gas control technologies on the of heavy metal pollutants was analyzed. The results show that the dry flue gas desulfurization combining baghouse dedusting method has high removal efficiency of heavy metals in flue gas, with mercury removal efficiency of 60.06%, Pb removal efficiency of 92.92%, Cd removal efficiency of 92.20%, Cr removal efficiency of 55.14%. The removal efficiency of heavy metals is obviously higher than that of conventional electrostatic precipitation combining wet desulfurization. This is mainly ascribed to those heavy metals are mainly concentrated in the fine particulate matters of the fly ash. Dust removal technology can effectively coordinate the control of Hg, Cr, Pb and Cd in the flue gas. The semi-dry desulphurization and baghouse dedusting technology can promote the enrichment of Hg and Cr in fly ash. The results of this study can provide theoretical guidance for the control of Hg, Cr, Pb, Cd and other heavy metal pollutants control in sintering equipment, and for flue gas ultra-low emission transformation.

Keywords. Sintering machine, heavy metals, collaboratively control, Hg, Pb, Cr, Cd

1. Introduction

Iron & steel production has the most pollutant emissions in the sintering of iron ore, a process in which iron-making materials that cannot be directly put in a furnace (including iron powder, rich ore fines, roll scale, and blast-furnace dust), mixed with a certain amount of fuel (including coke powder and anthracite) and flux (including limestone and dolomite), are heated up to 1,300-1,500°C to make the powder sintered to blocks, which, after undergoing a range of processes including crushing, screening, and cooling, will become finished sinter available for blast furnace iron-making [1]. Much flue gas is generated during sintering, which contributes roughly 40%-60% of total gaseous pollutant emissions in iron & steel production [2-5].

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Sintering requires large quantities of fuel and ores, which contain certain amounts of heavy metals such as mercury (Hg), plumbum (Pb), chromium (Cr), and cadmium (Cd), in addition to a certain amount of sulfur content. In addition to conventional pollutants like sulfur dioxide (SO_2), nitric oxides (NO_X), and particulate matters which are among the high-temperature flue gases emitted by the head of sintering machines, heavy metal emissions such as mercury, plumbum, chromium, and cadmium are sparking increasing attention [6-7]. Reportedly, the mercury content in iron ore is generally 0.01-0.05mg/kg [8]. As shown by relevant studies, each tonne of produced crude steel means around 40mg of mercury emissions, above 80% of which go into the air in the form of gaseous zero-valent mercury along with sintering flue gas, with the remaining 20% existing in the form of gaseous divalent mercury and mercury particulates [9-11].

As pollution control facilities can help to remove heavy metal pollutants to some extent, studies have been carried out in both China and elsewhere with respect to mercury emissions from flue gas of sintering machines. However, there have been few studies carrying out such heavy metal pollutants as plumbum, chromium, and cadmium, all of which feature difficulties in biodegradation, great harm, and prolonged cycles, among others. As such, delving into the characteristics of heavy metal pollutants (Hg, Pb, Cd, and Cr) emitted by sintering machines can be of great realistic significance to controlling heavy metal pollution in the air, and thus to minimize harms to the ecological environment and human health. Small-sized sintering machines are widely distributed and many of them have yet to complete upgrading towards ultra-low emissions (ULE). Considering this, this study evaluating the efficiency of pollution control facilities on removing heavy metal pollutants may provide a basis for selecting ULE control measures.

2. Experimental Method and Instruments

2.1. Study Object

Four sintering machines less than 180m^2 were selected and the technologies used to control their flue gas pollution is shown in table 1. Their NOx emission concentration was below 300mg/m^3 and no denitration facilities were installed. To control flue gas pollutants, the technology of electrostatic dedusting in combination with wet limestone-gypsum flue gas desulfurization (FGD) was used.

Table 1. Technical measures for flue gas pollution control.

No.	Dedusting technology	Desulfurization technology	Deep purification technology
1	Electrostatic dedusting	Wet limestone-gypsum FGD	-
2	Electrostatic dedusting	Wet magnesium hydroxide FGD	-
3		Semi-dry FGD	Bag dedusting
4	Electrostatic dedusting	Wet limestone-gypsum FGD	-

2.2. Sampling Method and Instrument for Flue Gas

Each sampling point was set after dedusting and after desulfurization. At each sampling point, parallel samples were collected three times before they were averaged. For this study, the EPA Method 29 (M29 method) [12-14] was used for sampling and analyzing the heavy metal emission concentrations of sintering machines. The M29 method, issued by the US Environmental Protection Agency (EPA), is the standard method for testing metal content in flue gas from stationary sources. The method includes analysis and testing of the total amount of heavy metals such as Hg, Cr, Pb, and Cd. The sampling system for the M29 method is shown in figure 1.

The XC 572 heavy metal sampler by Apex Instrument was used for sampling flue gas. The sampling process was isokinetic sampling, with a sampling time of about 1 hour and a sampling air flow of about $1m^3$. To prevent devaporation in flue gas, which may affect analysis result, the temperature of the sampling tube remained 120°C. Particulated heavy metals were captured by quartz fiber filter paper and gaseous heavy metals were absorbed by HNO_3/H_2O_2 solution and $KMnO_4/H_2SO_4$ solution.

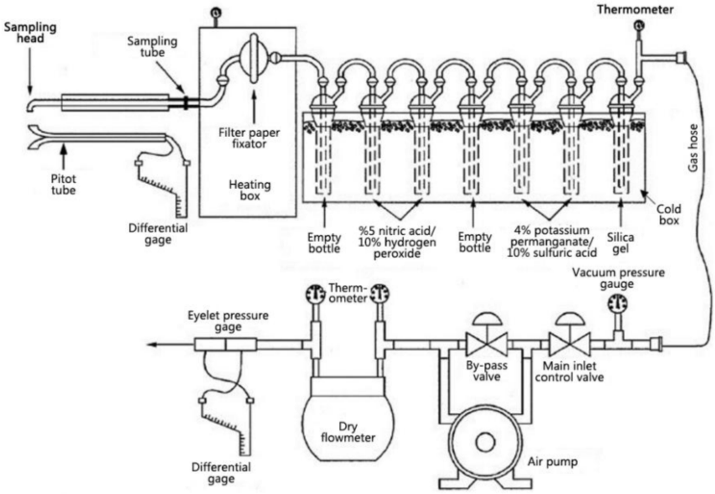

Figure 1. M29 sampling system.

2.3. Analysis Method for Heavy Metals

The USEPA Method 29 was used to collect samples. In analyzing particulated heavy metals, the method as set forth in the ASTM D6414 standard of the US was followed. Specifically, the samples collected to filter membranes were recovered and digested, before the content of heavy metals of these samples were measured using Atomic Absorption Spectrometry (AAS) or ICP-AES [14-15]. The ingredients of other heavy metals in the liquid samples including effluents were analyzed using AAS and ICP-OES.

3. Result and Analysis

3.1. Emission Characteristics of Heavy Metal Pollutants before and after Flue Gas Control

The USEPA Method 29 was used to collect samples of heavy metal pollutants in flue gas, and after analysis and testing by ICP-OES, the concentrations of heavy metal pollutants (Hg, Cr, Pb, and Cd) in flue gas before and after flue gas control were obtained, as shown in table 2.

Table 2. Emission concentrations of heavy metals from sintering machine.

No.	Flue gas testing point	Heavy metal concentration in flue gas μg/m^3			
		Hg	Pb	Cd	Cr
1	Before dedusting	18.69	348.56	1.50	17.52
	After desulfurization	8.34	56.43	0.43	14.34
2	Before dedusting	26.35	402.64	3.01	41.79
	After desulfurization	11.24	73.23	1.54	32.13
3	Before desulfurization	27.79	186.54	2.05	36.49
	After dedusting	11.10	13.20	0.16	16.37
4	Before dedusting	69.90	130.44	2.22	72.10
	After desulfurization	41.69	22.00	1.04	53.28

As shown in table 2, before control facilities in flue gas, ρ(Hg) was 18.69-60.90 μg/m^3, averaging 35.68 μg/m^3; ρ(Cr) was 17.52-70.10 μg/m^3, averaging 41.98 μg/m^3; ρ(Pb) was 130.44-402.64μg/m^3, averaging 267.05 μg/m^3; and ρ(Cd) was 1.50~3.01μg/m^3, averaging 2.20 μg/m^3. In descending order, the original emission concentrations of the four heavy metal pollutants were successively ρ(Pb)>ρ(Cr) >ρ(Hg) >ρ(Cd). As noted in the EU Industrial Emissions Directive [16], in the flue gas of sintering machines, the original emission concentration of Pb averages about 3 mg /Nm^3 and that of Hg averages about 15-82 μg /Nm^3. The analysis result of this paper shows that, the original emission concentration of Pb in the flue gas of sintering machines is lower than the concentration stipulated in 2010/75/EU, while the original emission concentration of Hg is relatively close to the concentration stipulated in 2010/75/EU.

An analysis of table 2 reveals that after control facilities, ρ(Hg) was 8.34-41.69 μg/m^3, averaging 18.09 μg/m^3; ρ(Cr) was 14.34-53.28μg/m^3, averaging 29.03 μg/m^3; ρ(Pb) was 13.20-73.23 μg/m^3, averaging 41.22 μg/m^3; And ρ(Cd) was 0.16-1.54 μg/m^3, averaging 0.79 μg/m^3.

3.2. Efficiency of Wet Desulphurization in Controlling Heavy Metal Pollutants in Flue Gas

Figure 2 shows the efficiency of three wet flue gas pollution control facilities in controlling heavy metal pollutants in flue gas (Hg, Cr, Pb, and Cd). It is found that the removal efficiency of electrostatic dedusting in combination with wet desulphurization is 40.36 %-57.34 % for Hg, 81.81 %-83.81 % for Pb, 48.84 %-71.33 % for Cd, and 18.15 %-26.10 % for Cr.

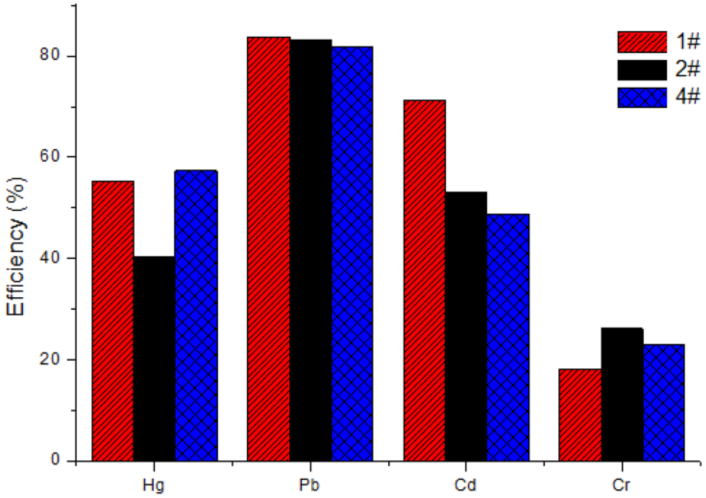

Figure 2. Removal efficiency of the heavy metals of the wet flue gas cleaning system.

Relevant studies have indicated that, Hg in flue gas exists primarily in the form of particulated Hg and gaseous Hg. It is difficult to remove gaseous zero-valent Hg through wet spraying. Electrostatic dedusting can remove much of particulated Hg. Therefore, wet desulphurization in combination with electrostatic dedusting can remove much of particulated Hg and some absorbable divalent Hg. As the flue gas of sintering machines has high levels of chlorine element, Cr can easily react with chlorine and others to form water-soluble compounds. The removal efficiency for Cr is low, because Cr exists mainly in the form of chlorides and sulfates and is highly volatile in flue gas, and some of Cr gathers on fine particulate matters. In the condition of high-temperature flue gas, chlorine element can easily react with Pb to form water-soluble Pb^{2+}, which can be easily absorbed through wet desulfurization. An overwhelming majority of Pb exists in flue gas in the form of particulates and can be easily removed through electrostatic dedusting. Therefore, the removal efficiency for Pb is high. The Cd in flue gas exists mainly in the form of chlorides, sulfates, and elementary substance Cd, which can be easily adsorbed or congealed on the surface of fly ash particles to form particulated Cd, which can be easily removed through dedusting units.

As for wet desulfurization and dedusting, the removal efficiency for Pb is the highest, followed by for Cd, Hg, and Cr. In the flue gas of sintering machines, Pb and Cd exist mainly in the form of compounds and it is easy to be adsorbed or congealed on particles and therefore to be removed by dedusting units. Some Hg and Cr in the flue gas of sintering machines exists in the form of elementary substance and has low vapour pressure. Some of Hg and Cr exist in the form of gas and the removal efficiency for them through spraying is not obvious. Therefore, the removal efficiency for them is low.

3.3. Efficiency of Dry Desulphurization and Dedusting in Controlling Heavy Metal Pollutants in Flue Gas

Figure 3 shows the efficiency of the dry flue gas purification system in controlling heavy metals in the flue gas of the head of sintering machines. It is found that the removal efficiency of dry desulfurization in combination with bag dedusting is 60.06% for Hg, 92.92% for Pb, 92.20% for Cd, and 55.14% for Cr.

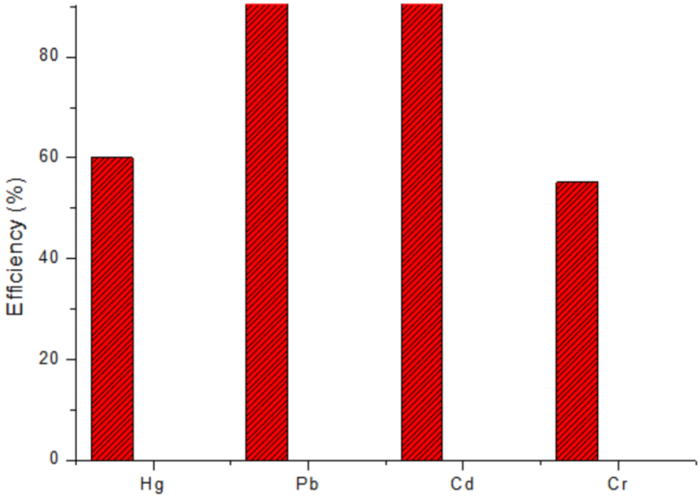

Figure 3. Removal efficiency of the heavy metals of the dry flue gas cleaning system.

The efficiency on removing heavy metals of dry flue gas desulfurization and dedusting is significant. Through comparison with figure 2, it is found that the removal efficiency of electrostatic dedusting in combination with wet desulphurization for Cr is only 18.15 %-26.10 %; while the removal efficiency of dry flue gas desulfurization in combination with bag dedusting for Cr is up to 55.14 %, and the removal efficiency for Hg, Pb, and Cd is also increased.

This is mainly because, heavy metals primarily gather in fine particulate matters in fly ash, dry desulfuration makes large quantities of fly ash and desulfurizer fully exposed to flue gas, and some gaseous Cr and other heavy metals are adsorbed on particles before being removed through subsequent bag dedusting. Meanwhile, the particles on the surface of the bag increases adsorbing time, which makes it easier for heavy metals in flue gas to be adsorbed on particles, transforming gaseous heavy metals into particulated ones, which are collected through bag dedusting. In this way, these heavy metal pollutants are removed [17-18].

Dedusting technology can effectively control Hg, Cr, Pb, and Cd in flue gas. Semi-dry desulfurization in combination with bag dedusting can significantly improve the removal efficiency for Hg and Cr gathering on fly ash.

3.4. Analysis of Heavy Metals in Solid Samples

The wet desulphurization gypsum and dry desulphurization dedusting ash were respectively sampled. The desulphurization gypsum was collected from dewatering belt conveyor or gypsum stockpile; bag dedusting ash samples were taken from desulphurization ash bin. There were 3 samplings, with a time interval of 30min between two samplings. After reduction, 1kg of samples was collected and sealed up for keeping. The ASTM D6414 method of the US was followed for analyzing solid samples.

Table 3 shows the analysis result of heavy metals in solid samples. Pb has the highest content of 3.00 mg/kg. As shown in figure 3, dry desulfurization in combination with bag dedusting can significantly enable Pb to gather; dry desulfurization in combination with bag dedusting can effectively enable Cd to gather; Cd content in the ash of bag dedusting unit is higher than in desulphurization gypsum. The mechanism behind the gathering of Hg, Pb, Cr, and Cd during desulfurization and dedusting of flue gas in small-sized sintering machines remains to be further studied.

Table 3. Heavy metal contents in by-products of sintering machine.

Pollution control technology	**By-product**	**Hg (mg/kg)**	**Pb (mg/kg)**	**Cd (mg/kg)**	**Cr (mg/kg)**
Electrostatic dedusting+Wet desulphurization	Desulphurization gypsum	0.54	0.01	0.001	0.002
Dry desulfurization+Bag dedusting	Bag dedusting ash	0.16	3.00	0.02	0.01
Electrostatic dedusting+Wet desulphurization	By-product from slag desulfurization	0.12	0.38	0.003	0.51

4. Conclusions

Flue gas pollutants of sintering machines are mainly emitted through their head. By analyzing the emission characteristics of heavy metal pollutants of sintering machines, this paper studies the efficiency of different flue gas control facilities in removing heavy metal pollutants, with the following conclusions reached:

According to the result of testing on the emission concentration of heavy metals in the head of 4 sintering machines, Pb has the highest concentration, and Cd has the lowest. In descending order, the original emission concentrations of the four heavy metal pollutants were successively ρ(Pb)>ρ(Cr) >ρ(Hg) >ρ(Cd).

In the flue gas of sintering machines, Pb and Cd exist mainly in the form of compounds and it is easy to be adsorbed or congealed on particles and therefore to be removed by dedusting units. Some Hg and Cr in the flue gas of sintering machines exists in the form of elementary substance and has low vapour pressure. Some of them exists in the form of gas and the removal efficiency for them through spraying is not obvious. Therefore, the removal efficiency for them is low.

Dry flue gas desulfurization and dedusting can significantly remove heavy metals. Because heavy metals mainly gather in fine particle matters in fly ash, dedusting technology can effectively and collaboratively control Hg, Cr, Pb, and Cd in flue gas. Semi-dry desulfurization in combination with bag dedusting can improve the removal efficiency for Hg and Cr gathering on fly ash.

To the best of our knowledge, there are much more studies regarding control over conventional pollutants of sintering machines than regarding heavy metal pollutants. Considering this, this study into the efficiency of pollution control facilities on removing heavy metal pollutants may provide a basis for selecting ULE control measures.

Acknowledgements

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