Study on the Mercury Migration in Clinker-Producing

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Abstract. Mercury is one most important global pollutants in the environment. The article studied the mercury migration according to the mercury migration in the cement process, in which a model for the relationship between the mercury input, internal circulation and output is built. In the model, mercury concentration in each stage of the process was calculated and characterized with different input, which were Consistent with actual verification, and then the reasonable method was advised to prevent the mercury pollution. The simulation showed that the mercury input is below 0.1 g/t.cli, and the mercury gas emission concentration is below 0.05 mg/Nm3 whenever the mode of raw mill is on or off. But once the mercury input is over 0.23 g/t.cli, the mercury gas emission concentration is over 0.05 mg/Nm3 although the mode of raw mill is on. The mercury content in ERM and KA is almost ten times higher than raw material, and the mercury content in KA is almost ten times higher than raw meal extraction, and multiples increase with higher mercury input as well. Even if mercury is continuously enriched internal, there is no limit of mercury concentration saturation.

1. Introduction

Since the Minamata disease happened in 1953 in Japan[1], mercury has been regarded as a highly dangerous global pollutant by United Nations Environment Programme and World Health Organization[2,3,17]. Mercury has become one of the most important global pollutants due to its toxicity, volatility, long-distance transport, persistence and bioaccumulation in the environment[4]. The cement and clink production reached to $2.38 \times 10^9$ t and $1.58 \times 10^9$ t respectively in 2019. So it is important for reducing mercury emissions and developing control strategies[5].

China is the largest cement producer and consumer in the world. Mercury emission factor has been studied to estimate the atmospheric mercury emissions from the cement industry in China by measuring concentration and speciation of mercury in flue gases or by calculating the mercury input. Some scholars in China have published a wide range of emission factors, ranging from 0.001 to 0.190 g/t clinker[6-10]. Based on a mass balance method, Cui JX et.al[11] thought that the best estimated emission factor was 0.092 g/t clinker and the best estimate of atmospheric mercury emissions from the cement industry obtained is 118 tons.

Research[12] showed that the mercury emission factors were influenced by a range of factors, such as the mercury input, the raw mill operation conditions, and the methods for kiln tail ash treatment. Then the single influence factor was researched such as the input of raw or fuel, dust treatment, raw mill operation mode and so on, while the relationship between them are less researched and the efficient method to Prevent mercury pollution is lack.
Previous studies have confirmed mercury cycling. In the pre-calciner process, the milled raw materials are preheated, pre-decomposed, and roasted in a rotary kiln system with coal. So in the process mercury is vaporized into the flue gas in high-temperature rotary kiln systems and captured in low-temperature facilities. The captured mercury is subsequently cycled back to the rotary kiln system with solid materials, especially the collected kiln dust. Therefore, during the mercury migration, mercury was discharged by flue gas and clinker solidified, and cycled back in the process.

The role of raw mill on flue gas temperature and mercury concentration was also found in cement plants in plants[13-15]. The mode of on and off situation accounted for approximately 80% and 20% of production time in respectively. The mercury cycling between the kiln system and the raw mill system was the most important aspect and contributed 57–73% to the total amount of mercury emitted from the kiln system and the dust treatment can efficiently reduce approximately 31–70% of atmospheric mercury emissions in the two plants, so the mercury mass flows internal were found 10 times as high as the emitted. Another study found that the mercury concentration in the flue gas emitted from the kiln system reached 15 and 4 times as high as the equivalent mercury concentration based on mercury input from raw materials and coal, respectively. The mercury concentration in a stack will experience a high peak when the raw mill is shut off because less mercury in the flue gas is captured in low-temperature facilities. The method that the collected kiln dust is treated outside the process was suggested. But the amount of the collected kiln dust which is about 5% of the raw input is so much that it has not been taken in cement plans so far.

In 2009[16-17], the EU was revising the "Guidelines for Best Available Techniques for Pollution Prevention and Control in the Cement Industry" (BAT), 306 on-site surveys and statistics were conducted in 27 EU countries, and the results showed that the average mercury emission of cement kiln flue gas was 0.02mg/m³, which was in line with the current EU standards. In China the mercury emission limit of cement industry is 0.05 mg/Nm³ by GB4915 and GB30485.

In normal conditions of less mercury input such as less than 0.10g/t.cli, the mercury emission of cement kiln flue gas will meet the standard requirements. But more mercury input such as more than 0.23g/t.cli or the raw mill is off, the mercury emission will be over standard limit. Then how much would be reasonable for mercury emission standard and why in china, the research about which is lack.

Knowledge generated from this study is useful for the mercury cycling characteristics and the mercury enrichment in cement production to obtain the relationship between influence factors of mercury emission factors. And it is feasible that less kiln dust was treated outside to prevent the mercury emission pollution.

2. Materials and Methods

2.1. Materials
Experiment materials are limestone, sandstone, coal, converter slag (CS), fly ash from Coal-fired power plant (hereinafter referred to as CFIFA), fly ash from incineration plant of municipal solid waste (hereinafter referred to as MSWIFA), Raw meal (hereinafter referred to as RM), Raw meal extraction(hereinafter referred to as ERM), and kiln ash from bag dust collector (hereinafter referred to as KA).

Solid samples are obtained from plant A where no MSWIFA is co-processed and plant B where MSWIFA is co-processed respectively. ERM and KA are sampled three times a day at random time from process section, and the other samples are sampled three times a day at random time from storage location. About 0.5–1.0 kg of samples were collected each time. The mercury concentration of samples from plant A and plant B, and whose amount used per day is showed in table 1 and table 2 respectively.
Table 1. Mercury input different samples from plant A.

| Item                              | limestone | sandstone | CS          | CFIFA      | coal        |
|-----------------------------------|-----------|-----------|-------------|------------|-------------|
| Hg concentration (mg/kg)          | ~0.06     | ~0.10     | 0.01~0.06   | 0.10~1.12  | ~0.50       |
| Median Hg concentration (mg/kg)   | 0.03      | 0.05      | 0.035       | 0.61       | 0.25        |
| Amount used per day (t/d)         | 2600      | 350       | 100         | 50         | 400         |
| Hg input per ton clink (g/t.cli)  | 0.017     | 0.004     | 0.001       | 0.007      | 0.019       |
| Ratio of Hg input (%)             | 35.54     | 7.97      | 1.59        | 13.90      | 41.00       |
| Total Hg input per ton clink (g/t.cli) |           |           |             |            | 0.047       |

Table 2. Mercury input different samples from plant B.

| Item                              | limestone | sandstone | CS          | CFIFA      | MSWIFA      | coal        |
|-----------------------------------|-----------|-----------|-------------|------------|-------------|-------------|
| Hg concentration (mg/kg)          | 0.01~0.06 | 0.04~0.11 | 0.01~0.06   | 0.10~1.12  | 18~28       | 0.08~0.45   |
| Median of Hg concentration (mg/kg) | 0.035     | 0.075     | 0.035       | 0.61       | 23          | 0.265       |
| Amount used per day (t/d)         | 2600      | 350       | 100         | 50         | 100         | 400         |
| Hg input per ton clink (g/t.cli)  | 0.019     | 0.005     | 0.001       | 0.006      | 0.479       | 0.022       |
| Ratio of Hg input (%)             | 3.56      | 1.03      | 0.14        | 1.19       | 89.94       | 4.15        |
| Total Hg input per ton clink (g/t.cli) |           |           |             |            | 0.533       |             |

Table1 shows that the main mercury input contrition with 41% in plant A is coal, and followed by limestone and CFIFA with 35.54% and 13.9% respectively. But in plant B showed in table 2, the main mercury input contrition with 89.94% is MSWIFA, and followed by coal with 4.15%. Total mercury input per ton clink in plant B is over ten times than plant A.

In the test for plant B, mercury adsorption technology was running at the end of dust collection to prevent mercury emission via gas, because the mercury input per ton clink is over 0.23g/t.cli which is the technological specification requirement of HJ662.

2.2. Methods

2.2.1. Characterization of mercury of materials in gas. Tekran3300 (HG-CEMS330) with dilution sampling method is the on-line gas detector in the test, and mainly composed by 2537 mercury analyser, which works by atomic fluorescence and pure gold amalgam enrichment method to measure gas mercury content. The other parts of HG-CEMS330 are 3342 sampling probe, non-thermal dilution pipeline connected with 3340 dilution probe controller, thermal sampling pipeline connected with 3320 sample gas pre-treatment unit, 3315 ionic mercury calibrator, 3310 element mercury calibrator, 3305 central control unit, M9932B data acquisition instrument and other measurement devices. The sampling probe 3342 was set at the fixed sampling port of the exhaust Stack. The 3340 dilution probe controller is connected with the sampling probe 3342 via a non-tracing dilution line, and the sample gas gotten flues into 3320 sample gas processing unit passing high temperature tracing pipeline, and then different state of mercury was respectively input into 2537 mercury analyser, then total mercury (HgT) and elemental mercury(Hg0) is analysed respectively, and the difference between the two is the concentration of mercury oxide(Hg2+)\[18-19\].

2.2.2. Characterization of mercury of materials in solid. The detection instrument for solid sample is a JKG-205 cold atomic absorption mercury analysers. 0.1g sample each time is dissolved in a can under ultra-high pressure with 8ml aqua regia which is a mixture of concentrated nitric and hydrochloric acids. Then the mixture liquid and washing liquid of the can over three times are all poured into a 50ml volumetric bottle to the limit level for testing.
2.2.3. Simulation model. In cement plant, raw materials (limestone, clay, sandstone, Fe material, coal gangue, etc.) are first processed using grinder and homogenizing device, and then the commented and mixed raw materials are ground further in a raw mill to produce raw meal. After passing through the preheater and pre-calciner successively, raw meal is heated further by burning coal in a rotary kiln to produce clinker. Finally, in the production process of cement, clinker is blended with a certain proportion of additional materials (limestone, gypsum and CFIFA etc.) in the cement mill to produce various types of cements. During the process, mercury will volatilize at high temperature and condense at low temperature, so some will be absorbed by particulars such as raw meal, coal meal, KA and pre-heater[20]. Some will be solidified in the clinker, some was discharged as exhaust emission. First the Hg migration model was set according to the process and researches. In the model, some key parameters are set: The adsorption efficiency inner including raw-meal, coal meal, KA and pre-heater was set about 70% while the raw-mill is on, but about 30% while the raw-mill is off. The time with raw-mill on is set three times as long as raw-mill off. And the mercury concentration in clink is set about 10% of mercury input. And the amount of KA is 5% of raw material. So the mercury concentration in different section of process was calculated with different input level, assumed as 0.04g/t.cli, 0.10g/t.cli, 0.23g/t.cli and 0.6g/t.cli.

3. Results and Discussions

3.1 Hg Concentration in Different Process Parts is Simulated with Different Hg Input

The simulation results of mercury concentration of ERM, KA, and gas emission different input are showed in following Figures.

![Figure 1. Hg concentration of ERM with different Hg input(g/t.cli).](image1)

![Figure 2. Hg concentration of KA with different Hg input.](image2)

Figure 1 shows that mercury concentration of ERM will be about 0.1–0.6mg/kg with mercury input changes from 0.04 to 0.23 g/t.cli. If the Hg input is 0.6 g/t.cli, mercury concentration of ERM can be 1.6 mg/kg, which increases more with higher mercury input. In a normal plant, the level of mercury concentration in raw material and fuel is about 10⁻¹mg/kg. But that in ERM is about ten times than it. This indicates that the mercury concentration of the ERM can always get higher with higher Mercury input. The absorption of ERM is powerful and it is hard to reach the maximum or the limit. So mercury can be absorbed much in ERM and Mercury emission decreases much, and the cycling enrichment of ERM can’t reach saturation.

Mercury concentration of KA will be about 1–10mg/kg with mercury input changes from 0.04 to 0.23 g/t.cli showed in figure 2. If the Mercury input is 0.6 g/t.cli, mercury concentration of KA can be...
30 mg/kg, which increases more with higher mercury input. In a normal plant, the level of mercury concentration in ERM is about 1 mg/kg, but that in KA is about ten times than it. This indicates that mercury concentration of KA can always get higher with higher mercury input, and it is over ten times higher with raw-mill off than raw-mill on. The absorption of KA is powerful and it is hard to reach the maximum or the limit. So mercury can be absorbed much in KA, but because KA will return the process again, so mercury will recycle and enrich inner, except it was discharged. So if the KA during raw-mill off is discharged, much mercury could be avoided in gas emission.

Figure 3 and figure 4 shows that the mercury emission gets higher with higher mercury input, and the level with raw-mill off is higher than on. When mercury input is less than 0.1 g/t.cli, mercury concentration of gas emission can meet the standard requirements of GB4915 whenever the raw-mill is on or off. But when mercury input is over 0.23 g/t.cli, mercury concentration of gas emission can meet the standard requirement of GB4915 only during the raw-mill is on. It illustrates that mercury is always released during the process as long as the mercury is present. Mercury emission factor is lower 1/3 than mercury input with raw-mill on, but it is more than mercury input with raw-mill off and that is a peak during the first few hour of the raw-mill off. So mercury gas emission changes always because of fluctuating input, and the matter for mercury migration is conserved at whole period including raw-mill on and off. Most researches thought the average mercury emission factor should be about 0.04 g/t.cli, and Cui JX et.al[11] deduced it about 0.09 g/t.cli. Then mercury concentration of gas emission can meet the standard requirements of GB4915 according to the simulation.

Because the number of raw material and fuel in process is huge, while the number of mercury is at micro level, the mercury absorption efficiency of the process is hard influenced by the mercury circling and enrichment. Although the mercury in gas state is absorbed in the ash which is returned to the internal cycle, the level of mercury cycling enrichment isn’t a easily reachable limit. So the mercury is always absorbed inner by KA, ERM, coal, preheater pipeline and so on. Then the mercury equilibrium can’t be reached in the process and there isn’t enrichment saturation value. The mercury is always absorbed by the material partially, and discharged partially in the process.

3.2 Ratio of Mercury Between Different Factors is Simulated
The mercury is discharged by gas emission, KA and clinker. Because the Calcination temperature of clink is over 300°C, the mercury concentration of clinker is low. KA is returned as the part of the raw circularly, then the cyclic enrichment of mercury reappears in high temperature section, especially in
the preheater. Then the ratio of mercury between different factors is simulated showed as figure 5 and figure 6.

Figure 5. The ratio simulation of Hg concentration of KA to Hg input.

Figure 6. The ratio simulation of the mercury concentration of gas emission to input.

Figure 5 is the simulation of mercury ratio between KA and that of raw-fuel input, it shows that the mercury number of KA is times higher than that of raw-fuel input with the unit of g/t-cli. Because the volume of KA is generally five percent of raw material, the mercury concentration of KA is over hundred times raw material or fuel. Figure 6 is the simulation of ratio between the mercury concentration of gas emission and, it shows that 40% mercury is discharged by gas emission with the raw-mill turning on, and 90% mercury is discharged by gas emission with the raw-mill off, especially it is over 100% at the first few hours of raw-mill off.

3.3 Test Result in Manufacture
The simulation of ratio between the mercury concentration of KA and that of raw-fuel input in Figures 2-7 is consistent with kiln process showed as figure 7 and figure 8.

The test is operated in plant A and B, Plant A is a normal plan with no co-processing and Plant B is a plant with MSWIFA co-processing The mercury concentration differs between samples. The test is showed as figure 7.

Figure 7. The mercury concentration tested of (a) ERM in plant A, (b) KA in plant A, (c) ERM in plant B, (d) KA in plant B.
In plant A, the mercury concentration of ERM is between 0.2mg/kg and 0.5mg/kg showed in figure 7(a). The mercury concentration of KA is between 3mg/kg and 7mg/kg showed in figure 7(b). It verifies that compare to 0.01mg/kg unit of the raw-fuel mercury concentration level, the simulation for a normal plant that it is 0.1 mg/kg unit of the ERM, and 1.0 mg/kg unit of KA. But in plant B, the mercury concentration of ERM is between 2mg/kg and 7mg/kg showed in figure 7(c). The mercury concentration of KA is between 28mg/kg and 50mg/kg showed in figure 7(d). So if the KA during raw-mill off is discharged, mercury can be avoided in gas emission.

We found that mercury emission concentration tested in plant A is always less than 50μg/Nm³, or its value is so low that it can’t be tested, which is consistent with the simulation results of mercury input that is no more than 0.1g/t.cli. Mercury emission concentration in plant B was monitored continuously on-line and the results were showed in Figure8. When the raw-mill was off during 4:30 to 6:30am and 18:30 to 21:20, mercury emission concentration increased from 20 to 400μg/Nm³ speedily and occurred the peak, and then decreased speedily from 450 to 20μg/Nm³ once the raw-mill was running. But the decreasing rate was higher than increasing. According to table 1, the mercury input was about 0.423~0.630 g/t.cli in plant B, and its average was about 0.533g/t.cli. The fact above verified the simulation results of 0.05g/t.cli and the trends.

![Graph showing Hg gas emission concentration](image)

**Figure 8.** Hg gas emission concentration tested in plant B.

When mercury input increases, mercury concentration different part of process including emission increases more, and the fact is more obvious while the raw-mill is stopping. And their trends are same with the simulation results also.

4. Conclusions

According to the kiln process, the mercury migration and emission was simulated, and It's been analyzed and compared with the process fact and literation, the conclusion were followings:

1) The model was set based on the matter conservation of input and output, and all parameters in the model for inner absorption including raw-mill and coal-mill, dust absorption, KA percent and the time space between raw-mill on and off, and mercury output of clink were thought about the process fact and previous researches.

2) The simulation showed When mercury input increased, mercury concentration different part of process including emission increased more, such as the mercury concentration in ERM was almost ten times higher than raw material, and the mercury concentration in KA was almost ten times higher than raw meal extraction, and multiples increase with high mercury input as well. And the fact above was
more obvious while the raw-mill was stopping. It indicates that mercury recycles and enriches internal, but there is no limit of mercury concentration saturation during inner enrichment.

3) In the test, in plant A with 0.047g/t.clim mercury input, mercury concentration of ERM and KA is 0.2~ 0.5mg/kg and 3~7mg/kg respectively. While in plant B with 0.533g/t.clim mercury input, it is 2~7mg/kg and 28~50mg/kg respectively. Mercury emission concentration in plant A is lower, but mercury emission concentration in plant B increased from 20 to 400μg/Nm³ speedily and occurred the peak, and then decreased speedily from 450 to 20μg/Nm³ when the raw-mill was running. The process fact above and the trends are same with simulations.

4) The model and the parameters are proved reasonable by the test fact in plant. The whole cycling period of mercury migration in kiln process should include the raw-mill on and off, so mercury gas emission monitored can't be as the data to calculate mercury gas emission factors. Discharging KA only in the mode of raw mill-off is easy to implement to avoid mercury gas emission, which can greatly reduce the amount of KA discharged.

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