Emission of Heavy Metals during Cement Calcinations by Utilizing Waste Materials*

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Abstract: Emission pollution of Pb, Cd, Zn, Cu and Hg during cement calcinations was investigated by means of atomic absorption spectroscopy (AAS). The samples of raw materials, clinker and soil were collected from several cement plants utilizing waste materials such as Pb-Zn tailings, Pb-Zn smelter slag and electronic arc furnace dust. The emission rate of Hg during cement calcinations is very high, in the range from 89% to 96%; the emission rates of Pb and Cd are in the range from 63% to 90%; those of Zn and Cu are in the range from 29% to 47%. The emitted Pb, Cd and Hg pollute the soil nearby during the cement production by utilizing the waste materials. The contents of Pb, Cd and Hg in the soil 500 m leeward are 2~3 times of those in the soil 2000 m leeward and 1000 m windward. The fluorite mineralizer promotes the emission of Pb, Cd, Zn and Cu.
Key words heavy metals; calcinations; emission pollution; fluorite

1 Introduction

Utilizing waste materials to produce cement clinker is the important trend of sustainable development of cement industry[1-3]. But when utilizing the waste materials with high contents of heavy metals such as Pb-Zn tailings, Pb-Zn smelter slag and electronic arc furnace dust, the emission pollution of Pb, Cd, Zn, Cu and Hg should be noticed. This paper explored the emission pollution of Pb, Cd, Zn, Cu and Hg during cement calcinations.

2 Experimental materials and methods

2.1 Materials

Industrial materials: limestone, clay, iron powder and coal.

The samples of raw materials and clinker were collected from MX, YH, MS, CS and FK cement plants.

The samples of soil were collected from YH, MS and FK cement plants.

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2.2 Methods

Clinker calcinations: The raw materials were conglobated with water. After drying at 105 , the samples were sintered at 1400 for 30 minutes in an electrical furnace. Then the samples were fast cooled in air.

Determination of contents of Pb, Cd, Zn, Cu and Hg: The contents of Pb and Cd were detected by means of KI-MIBK extraction flame atomic absorption spectroscopy (AAS). The contents of Zn and Cu were detected by means of flame atomic absorption spectroscopy. The content of Hg was detected by means of cold atomic absorption spectroscopy.

3 Results and discussions

3.1 Emission of heavy metals in cement kiln

The samples of raw material and clinker from MX, YH, MS, CS and FK cement plants were collected, which utilize Pb-Zn tailings and Pb-Zn smelter slag to produce cement clinker. MX, YH and MS plants use shaft kiln, CS and FK plants use wet process rotary kiln. T he raw material includes raw meal and coal. The kiln dust all goes back into the kiln, and that is an internal circulation. The contents of Pb, Cd, Zn, Cu and Hg were detected, and the emission rates were calculated according to the material balance of kiln. The results are shown in Tab 1.

Table 1 Contents of heavy metals and their emission rates

		MX	YH	MS	CS	FK
Hg	Raw materials /mg·kg^{-1}	0.189	0.161	0.202	0.240	0.253
	Clinker /mg·kg^{-1}	0.011	0.007	0.009	0.014	0.027
	Emission rate /	94.18	95.65	95.54	94.17	89.33
Pb	Raw materials /mg·kg^{-1}	379.5	88.6	162.8	202.4	69.5
	Clinker /mg·kg^{-1}	45.1	13.4	20.6	52.7	23.4
	Emission rate /	88.12	84.88	87.35	73.96	66.23
Cd	Raw materials /mg·kg^{-1}	1.09	1.89	1.74	2.79	2.99
	Clinker /mg·kg^{-1}	0.11	0.30	0.26	0.75	1.08
	Emission rate /	89.91	84.13	85.06	73.12	63.88

Zn	Raw materials /mg·kg^{-1}	303.8	286.3	221.8	288.7	339.0
	Clinker /mg·kg^{-1}	174.4	153.5	132.1	187.7	212.4
	Emission rate /	42.59	46.38	40.44	34.98	37.35
Cu	Raw materials /mg·kg^{-1}	176.8	126.2	54.9	139.0	187.1
	Clinker /mg·kg^{-1}	106.9	72.7	35.0	98.1	129.3
	Emission rate /	39.54	42.39	36.25	29.42	30.89

It can be seen from Tab 1, the contents of Pb, Cd, Zn, Cu and Hg in clinker are lower than those in burnt raw materials. That is to say, quite a number of heavy metals emit and pollute the environment during cement calcinations except that part of them is solidified in clinker. Hg has high volatility, the emission rate of Hg during cement calcinations is in the range from 89% to 96%. The emission rates of Pb and Cd are in the range from 63% to 90%; those of Zn and Cu are in the range from 29% to 47%.

3.2 Soil pollution of Pb, Cd and Hg from cement kiln

During cement calcinations, part of heavy metals emit with exhaust gas and pollute the environment, especially the toxic Pb, Cd and Hg.

The soil samples were collected from the different positions around YH, FK and MS cement plants which produce cement clinker by utilizing the waste materials for several years. The contents of Pb, Cd and Hg were detected. The results are shown in Tab 2, Tab 3 and Tab 4.

Table 2 Contents of Hg, Pb and Cd in soil around YH plant

Sampling position	Hg /mg·kg^{-1}	Pb /mg·kg^{-1}	Cd /mg·kg^{-1}
North 500m leeward	0.353	72.2	1.91
North 1000m leeward	0.251	53.2	1.18
North 2000m leeward	0.162	25.4	0.76
South 500m	0.245	50.8	1.14
South 1000m	0.178	27.2	0.88

Table 3 Contents of Hg, Pb and Cd in soil around FK plant /mg·kg^{-1}

Sampling position	Hg /mg·kg^{-1}	Pb /mg·kg^{-1}	Cd /mg·kg^{-1}
North 500m leeward	0.328	56.0	1.46
North 1000m leeward	0.146	26.8	0.63
North 2000m leeward	0.106	19.5	0.49
South 500m	0.207	40.5	1.20
South 1000m	0.118	24.3	0.57

Table 4 Contents of Hg, Pb and Cd in soil around MS plant /mg·kg^{-1}

Sampling position	Hg /mg·kg^{-1}	Pb /mg·kg^{-1}	Cd /mg·kg^{-1}
North 500m leeward	0.387	82.3	1.78
North 1000m leeward	0.246	53.8	1.13
North 2000m leeward	0.166	29.7	0.63
South 500m	0.256	60.5	1.08
South 1000m	0.187	35.3	0.77

It can be seen from Tab 2, Tab 3 and Tab 4, the soil near the chimney stack and leeward is polluted worse. The contents of Pb, Cd and Hg in the soil 500 m leeward are 2~3 times of those in the soil 2000 m leeward and 1000 m windward. The contents of Pb, Cd and Hg in the soil samples which sampling at the position 500m away from the plant are all higher than the national standard maximum limit: 35 mg·kg^{-1}, 0.2 mg·kg^{-1} and 0.15 mg·kg^{-1}.

It is obvious that during cement calcinations the emission of Pb, Cd and Hg pollutes the soil nearby, the pollution prevention of Pb, Cd and Hg is very necessary.

3.3 Fluorite and the emission of heavy metals

The different content of fluorite mineralizer was mixed in the raw meal with same clinker modulus. And the content of CaF_2 in the fluorite mineralizer is 52.82%. After calcinations at 1400 for 30 minutes in electric furnace, the contents of Pb, Cd, Zn and Cu in clinker were detected, and the results are shown in Fig.1.

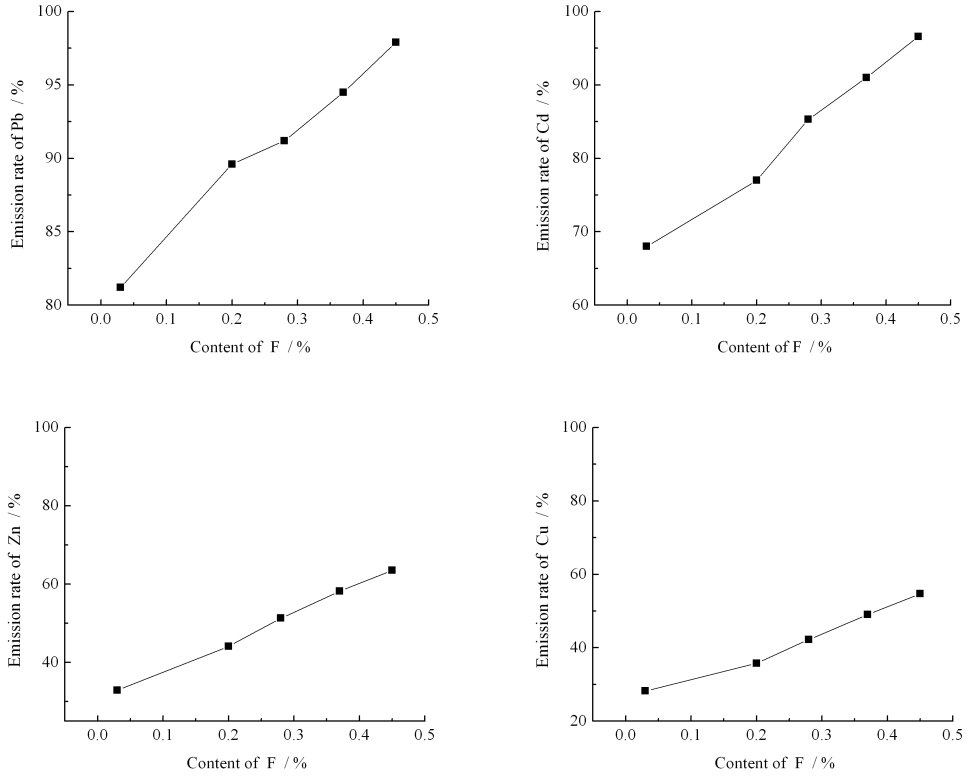

Fig.1 Emission rates of Pb, Cd, Zn and Cu with different mixing contents of F

It can be seen from Fig.1, during the cement calcinations at 1400 in the electric furnace, as the mixing content of fluorite increases, the contents of Pb, Cd, Zn and Cu in clinker reduce and the emission rates increase. As the content of F increases from 0.03 to 0.45 , the emission rate of Pb increases from 80 to 98 ; that of Cd increases from 67 to 97 ; that of Zn increases from 32 to 64 ; that of Cu increases from 28 to 55 .

The reason is that during cement calcinations Pb, Cd, Zn and Cu react with F to produce fluorides. The vapor tension of fluorides is comparatively high, it is difficult to be solidified in clinker mineral. Thus the fluorite promotes the emission of Pb, Cd, Zn and Cu.

The fluorite mineralizer is widely used in the cement production of shaft kiln in China, which is helpful to improve the output and quality of cement clinker [4,5]. But the fluorite promotes the emission of Pb, Cd, Zn and Cu. Thus the emission pollution of heavy metals should be noticed during cement calcinations by utilizing the fluorite mineralizer and waste materials with high contents of heavy metals.

4 Conclusions

During cement calcinations in shaft kiln and wet process rotary kiln, the emission rate of Hg is very high, in the range from 89% to 96%; the emission rates of Pb and Cd are in the range from 63% to 90%; those of Zn and Cu are in the range from 29% to 47%. Quite a number of heavy metals emit and pollute the environment.

The emitted Pb, Cd and Hg pollute the soil nearby during the cement production by utilizing the waste materials. The contents of Pb, Cd and Hg in the soil 500 m leeward are 2~3 times of those in the soil 2000 m leeward and 1000 m windward.

The fluorite mineralizer promotes the emission of Pb, Cd, Zn and Cu.

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