RESEARCH ON USING WASTE SLUDGE OF SMELTING LEAD AND ZINC TO SINTER CEMENT CLINKER

Wu Qingren,[1] He Qiongyu,[1] Lai Hongguang,[2] and Zhang Yongjun[2]
[1]South China University of Technology, Guangzhou, Guangdong, 510640, PRC
[2]Zhong Jin Ling Nan Lead and Zine Holdings Ltd., Shaoguan, Guangdong, 512325, PRC

Abstract

The chemical property of waste sludge of smelting lead and zinc and the application of the sludge in sintering of cement clinker are studied. The experimental and practical production results show that the waste sludge of smelting lead and zinc can be successfully used for replacing 50% siliceous materials and 100% ferrous materials so as to sinter cement clinker. High quality cement clinkers are fired by wet process kiln system, and the performance of the cement satisfies the requirements of the Chinese national standard.

1. Introduction

For environmental protection, the limitation of waste production and the use of waste materials have aroused worldwide concerns and initiatives. The heavy metal zinc (Zn) and lead (Pb) industries occupy the forth and fifth position in the world's metal industries, respectively. According to the manufacturing processes of lead and zinc, the amount of sludge of smelting lead and zinc is almost equal to the product of lead and zinc. More and more sludge of smelting lead and zinc are being produced with the development of zinc and lead industries. It is estimated that now about 3 million tons of waste sludge for Zn and Pb heavy metal is generated every year in China. It

will have certainly great scientific and technical significance and grand social and economical benefits to use the sludge of smelting lead and zinc rather than disposal of it as waste. Unfortunately, up to present the detailed relevant information can hardly be referenced [1, 2]. In this study, therefore, the chemical property of waste sludge of smelting lead and zinc and its application in the sintering of cement clinker are investigated.

2. Chemical Property of Sludge of Smelting Lead and Zinc

The sludge of smelting lead and zinc is the residue on smelting lead and zinc in which fine mineral of lead and zinc sulfides is smelted in the metallurgical furnace and watered out of the furnace. A typical chemical constitution of the fine minerals of lead and zinc sulfides is shown in Table 1.

Table 1: Typical chemical constitution of the fine minerals of Zn and Pb sulfides (%)

Kinds	Pb	Zn	Sn	S	Fe	Cd	Cu	Sb	As	SiO_2	CaO
Fine mineral Zn	1.58	47.98		30.82	10.38	0.25	0.42	0.03	0.27	3.21	1.09
Fine mineral Zn	0.97	55.00		31.15	5.85	0.14	0.04	0.01	0.02	3.17	0.99
Fine mineral Pb	62.52	4.43	0.04	16.88	8.70	0.04	0.58	0.17	0.34	2.79	0.72
Fine mineral Pb	71.50	4.55	0.08	15.80	5.20	0.06	0.17	0.05	0.02	2.50	0.89

Table 1 shows that there are kinds of color heavy metal in the fine minerals of lead and zinc sulfides such as Cd, Cu, and S. In the sintering process of the fine minerals of lead and zinc sulfides, the sulfides are changed to the oxides and then reduced by carbon. The chemical components for the typical waste sludge of smelting lead and zinc made up by oxidation-reduction method are showed in Table 2.

Table 2: Chemical components for typical waste sludge of smelting lead & zinc (%)

Smelting furnace	SiO_2	Fe_2O_3	CaO	MgO	Al_2O_3	S	C	Cu	Pb	Zn
Zinc blast furnace	20.90	26.80	19.50			3.40		0.45	0.51	6.50
Lead blast furnace	22.50	27.20	13.40			0.55		0.50	1.80	16.30
Smelting rotary kiln 1	28.17	39.97	6.05	5.20	17.27	3.25	20.38		0.014	0.003
Smelting rotary kiln 2	28.06	39.42	5.26	5.56	17.27	3.47	15.33		0.067	0.008

Table 2 shows that the chemical components of waste sludge of smelting lead and zinc in different smelting furnaces are not the same. They are mainly SiO_2, Fe_2O_3, CaO, MgO, Al_2O_3, S, and C, in addition to a small amount of Pb and Zn especially for the sludge from smelting rotary kiln 1 and 2. Therefore, they can be used not only as a substitute for siliceous materials and ferrous materials to sinter cement clinker, but also as the mineralizer and fuel.

3. Proportioning Optimization of Raw Materials and Meal

Due to the high SiO_2, Fe_2O_3, S, and C content of sludge of smelting lead and zinc in the smelting rotary kiln, the proportion and quality of calcareous, siliceous and ferrous raw materials and fuel should be controlled. The chemical components of raw materials and combined coal ash and main apparatus used in Fanghou cement plant are shown in Tables 3 and 5, respectively. The industry analysis of combined coal (which combination ratio is one-third of bituminous coal to two-thirds of anthracite coal) is showed in Table 4.

Table 3: Chemical components of raw materials and combined coal ash (%)

Name	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	S	∑
Calcareous raw	39.31	7.26	1.29	0.90	48.69	1.29		97.45
Siliceous raw	10.35	64.69	15.42	6.63	0.81	0.62		98.52
Ferrous raw	14.13	11.33	7.47	61.82	2.48	1.44		98.67
Sludge of smelting		28.11	17.27	39.69	5.65	5.38	3.36	99.46
Combined coal ash		56.30	28.14	6.50	2.88	1.46		96.28

Table 4: Industry analysis of combined coal (%)

Name	W^f	A^f	V^f	C^f	Q^y_{DW} (kJ/kg)
Combined coal	1.19	28.04	13.80	56.97	23,052

Table 5: Main apparatus in Fanghou cement plant

Name	Specification and type	Amount	Ability of design (t/h)
Limestone crushing	Φ1.25 vertical crusher	2	50×2
Raw meal grounding	Φ2.4×13 tube mill	1	50
Sintering clinker	Φ2.5/3.0×90 wet process kiln	3	10×3
Coal grounding	Φ2.2×4.4	1	10
Cement grounding	Φ2.4×13 tube mill	1	30
Cement bagging	two-mount bag filler	1	30

The proportioning optimization of raw meal and experimental results show that the waste sludge of smelting lead and zinc is successfully used for replacing 50% siliceous materials and 100% ferrous materials to sinter cement clinker. Lime saturation factor (*LSF*) and alumina modulus (*AM*) are suitably decreased and silica modulus (*SM*) is increased, which may improve the quality of cement clinker. The comparison of the chemical components of raw meals before and after using the waste sludge of smelting lead and zinc is shown in Table 6.

Table 6: Comparison of chemical components of raw meal slurry before and after using sludge

	Chemical components of raw meal slurry (%)								Three ratios		
	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	S	∑	*LSF*	*SM*	*AM*
Before sludge	36.47	11.17	2.71	2.78	44.63	1.35		99.11	1.25	2.03	0.98
After sludge	35.83	11.72	2.60	2.75	44.21	1.33	0.25	98.69	1.19	2.19	0.95

4. Effect of Using Sludge of Smelting Lead and Zinc on Sintering Cement Clinker

(1) Influence of sludge of smelting lead and zinc on fluidity of raw meal slurry

Table 7 shows that when water of raw meal slurry is 33%, 34%, and 35%, using sludge of smelting lead and zinc, the fluidity of raw meal slurry can increase 2-3mm because of higher C of sludge of smelting lead and zinc.

Table 7: Effect of sludge of smelting lead and zinc on fluidity of raw meal slurry

	Proportion of raw materials			Sludge of	Water of raw	Fluidity
	Limestone	Clay	Ferric powder	smelting	meal slurry	(mm)
A	89	8	3	0	33	66
B	89	8	3	0	34	69
C	89	8	3	0	35	71
D	89	7	0	4	33	68
E	89	5	0	6	34	72
F	89	3	0	8	35	74

(2) Influence of sludge of smelting lead and zinc on sinterability of raw meal

According to GB9965-88 (experimental method for sinterability of raw meal), effect of using sludge of smelting lead and zinc on fluidity of raw meal is shown in Table 8. It can be observed from the table that sludge of smelting lead and zinc contains trace amounts of heavy metals and higher S and MgO, which improve the burnability of raw meal. The amount of 6% sludge of smelting lead and zinc is considered the best.

Table 8: Effect of sludge of smelting lead and zinc on firing behavior of raw meal slurry

	Pb	Zn	SO_3	MgO	f_{CaO} (%)		
	(%)	(%)	(%)	(%)	1350°C	1400°C	1450°C
C	0	0	0	1.54	5.89	3.85	0.83
D	0.0016	0.0002	0.13	1.71	4.67	2.65	0.79
E	0.0025	0.0004	0.20	1.80	4.18	2.01	0.63
F	0.0033	0.0005	0.27	1.90	4.37	2.29	0.75

(3) Influence of sludge of smelting lead and zinc on quality of cement clinker

The comparison of the chemical components, three ratios, mineral constitution and physical properties of cement clinkers before and after using the waste sludge of smelting lead and zinc are shown in Tables 9 and 10.

Table 9: Comparison of the chemical components and three ratios of cement clinkers

	Chemical components of clinkers (%)								Three ratios			
	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	f_{CaO}	*LSF*	*LSF'*	*SM*	*AM*
Before using	0.64	20.34	5.92	4.58	65.03	2.08		1.38	0.94	0.92	1.94	1.29
After using	0.58	20.91	5.71	4.65	65.17	1.51	0.37	0.57	0.92	0.91	2.02	1.23

Table 10: Properties of clinkers

	Mineral constitution (%)				Compression strength (MPa)			Flexural strength (MPa)			Specific surface	Setting time (h:min)	
	C_3S	C_2S	C_3A	C_4AF	3d	7d	28d	3d	7d	28d	(m^2/kg)	Beg.	End
Before using	58.74	13.99	7.92	13.92	5.3	6.4	7.8	28.5	43.8	60.7	302	2:38	4:41
After using	57.69	16.38	7.24	14.15	5.8	7.1	8.4	31.7	46.2	62.6	303	2:58	4:45

It can be seen in Tables 9 and 10 that after using the waste sludge of smelting lead and zinc, f_{cao} in the cement clinkers is decreased from 1.38% to 0.7%. The total amounts of silicate minerals ($C_3S + C_2S$) are further increased from 72% to 74%. At about the same of the specific surface, the strength of cement clinkers at 3, 7, and 28 days is promoted and the performance of cement satisfies the requirements of the Chinese national standard.

Conclusions

- The chemical components of waste sludge of smelting lead and zinc contain mainly SiO_2, Fe_2O_3, CaO, MgO, Al_2O_3, S, and C. The sludge can be used as a raw material for production of cement clinker.
- The proportioning optimization of raw meal and experimental results show that the waste sludge of smelting lead and zinc is successfully used for replacing 50% siliceous materials and 100% ferrous materials to sinter cement clinker.
- Using the waste sludge of smelting lead and zinc to fire cement clinkers can improve the fluidity of raw meal slurry and the burnability of raw meal and promote the strength and performance of the cement.

References

1. Q.R. Wu, H.G. Lai, and Y.J. Zhang. "Application of Wet Sludge of Smelting Lead and Zinc in Firing of Cement Clinkers." *Cement* 10, 2000, 16-17 (in Chinese).
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