Research on the Resource Utilization of the Sewage Sludge in Silicate Industry

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***Abstract*—With modulus (KH = 0.89, SM = 2.42, IM = 1.70), substituting the sludge for the shale in the calculation of the cement burden, we studied the influence of different amount of sludge on the cement raw meal sintering, mineral composition, compression strength and the leaching value of heavy metal element. The result indicates that as the proportion of the sludge increased, the free calcium oxide reduced first and increased later, while the compression strength increased first and then reduced. When the proportion of the sludge was 2.56%, the amount of the free calcium oxide in clinker was lowest, and the 28day-compression strength reached the maximum which was 1.37 times as large as the cement clinker without sludge. The XRD and SEM test results also show that the composition of clinker and mineral structure remains unchanged when shale replaced by sludge. When the sludge proportion is 12.18%, free calcium oxide and compression strength are nearly the same as the cement clinker without sludge, and leaching value of heavy metals could satisfy the concentration limits of hazard constituent in the lixivium**

Keywords- sludge; cement clinker; sintering; compression strength; heavy metals

I. INTRODUCTION

Urban sewage sludge, which has the high productivity and complicated composition, is the byproduct of the sewage treatment process. The annual production of the sludge is about 30 million tons (the moisture content is 80%) in China, and it is predicted that the annual production of the sludge will be 60 million tons in 2020 [1]. At present, the sludge is not fully effectively controlled. By the end of 2011, only about 10% of the sludge was disposed through composting technology, 20% was treated by the sanitary landfill, very few of the sludge was burned or used as the building material, and the rest was outward transported, simply landfilled or piled[2]. Thus, the resulting environmental problems cannot be ignored. To effectively dispose the sludge in large-scale and high level, the resource utilization of urban sewage sludge must be achieved to change the waste into the valuable.

The argillaceous material, of which the clay is used the most, is one of the main raw materials in the manufacture of the Portland cement. With a rough estimate of 970 million tons of the cement in 2004, about 110 million tons clay was used, which amounts to digging out more than 30000 mu of land [3]. Since the urban sewage sludge meets the technology requirements of the argillaceous material [4], replacing the clay by the urban sewage sludge not only largely disposes the sludge, but achieves the resource utilization of urban sewage sludge in silicate industry, and it can also protect the cultivated land and save resources.

II. EXPERIMENT

A. Experiment Raw Material

1) Industrial raw material

Industrial raw materials such as the shale, sandstone, limestone, copper slag, coal ash (coal ash is fully burned coal powder solid remainder, which is involved in manufacture of the cement clinker) are from Hangzhou Tai mao sheng yuan Cement co., LTD. The industrial raw material chemical composition analysis results are shown in table Ⅰ.

TABLE I. THE CHEMICAL COMPOSITION OF RAW MATERIALS/(%)

	LOSS	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
Limestone	42.18	1.63	0.47	1.04	51.21	1.47
Shale	4.74	68.99	7.13	14.33	0.33	2.48
Sandstone	2.94	79.72	4.53	9.13	0.00	1.68
Copper slag	1.12	47.47	22.66	6.28	15.27	5.20
Coal ash	0.00	51.26	35.66	5.98	3.19	0.60

2) Sludge

The sludge is taken from the third project of Hangzhou Qige Sewage Treatment Plant. The moisture content of the sludge is about 80%. The analysis of sludge chemical composition follows GB/T176-2008 Cement Chemical Analysis Method, and table Ⅱ shows the analysis result. The analysis of the heavy metal content of sludge follows CJ/T221-2005 Urban Sewage Treatment Plant Sludge Inspection Method, measured by the Thermo X Series II inductively coupled plasma mass spectrometry instrument (SN01426C), and the result is shown in table Ⅲ.

TABLE II. SLUDGE CHEMICAL COMPOSITION/(%)

LOSS	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	total
40.39	41.19	8.56	2.63	3.03	1.93	1.13	0.94	99.80

TABLE III. HEAVY METAL CONTENT OF SLUDGE/(MG/KG)

Pb	Cu	Cd	Ni	Cr	Zn	As	Hg
36.7	198	0.76	60.4	275	720	10.2	1.8

B. Sample Preparation and Test Methods

Mix the shale and sludge respectively at the ratio of (9:1) (7:3) (5:5) (3:7) and set aside. With modulus (KH = 0.89, SM = 2.42, IM = 1.70), use the rate formula method[5] to operate the mixture calculation of the shale, mixture of sludge and shale, sludge separately with the limestone, sandstone, copper. Prepare 6 samples with codes from P0 to P5, and table Ⅳ shows the mixing-ratio of all samples. Adopt the temperature control program, which can heat to 1450℃ in 150min and then keep the temperature constant for 30min. After the high-temperature burned, put the sample in the air and use the air fan to form quenching, and then corresponding clinker samples can be produced. Following the standard GB/T176-2008 Cement Chemical Analysis Method, measure the proportion of free calcium oxide and SO_3. Test the compressive strength of clinker following the standard GB/T17671-2005 Cement Mortar Strength Testing Method. Measure the heavy metal proportion of clinker P5 following GB5085.3-2007 Identification Standards for Hazardous Wastes-Identification for Extraction Toxicity.

TABLE IV. MIXING-RATIO OF SAMPLES

	P0	P1	P2	P3	P4	P5
limestone	82.72	82.43	81.75	80.95	80.01	78.13
shale	7.60	7.8	5.98	4.69	3.09	0.00
sludge	0.00	0.79	2.56	4.69	7.22	12.18
sandstone	5.95	5.89	5.78	5.61	5.43	5.10
Copper slag	3.74	3.80	3.93	4.07	4.25	4.58
total	100	100	100	100	100	100
Coal ash	2.55	2.54	2.53	2.51	2.49	2.45
KH	0.89	0.89	0.89	0.89	0.89	0.89
SM	2.42	2.42	2.42	2.42	2.42	2.42
IM	1.70	1.70	1.70	1.70	1.70	1.70

III. EXPERIMENT RESULTS AND DISCUSSION

A. Analysis of Free Calcium Oxide (f-CaO) in Clinker

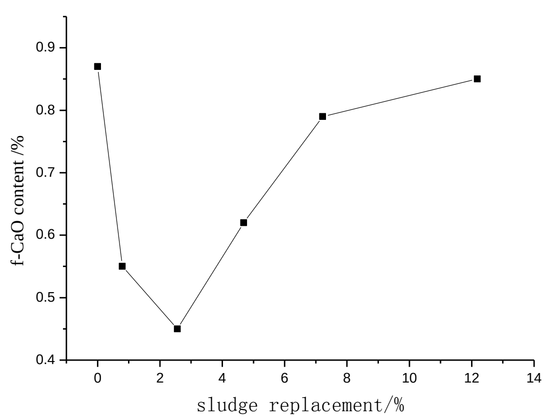


Figure 1. The relationship of f-CaO and sludge proportion

Figure 1 is the test result of f-CaO in the sludge-mixed clinker sample. The figure indicates that in the sample the f-CaO content is low, and as the amount of the sludge increases, the f-CaO content decreases first then increases. Furthermore, the f-CaO content reaches the minimum when the proportion of sludge is 2.56%. When all of the shale is replaced with the sludge, the proportion of sludge is 12.18%, the f-CaO content is almost the same as in the non-sludge-mixed situation.

The f-CaO changing trend, on the one hand, may result from the slight amount of alkali metal ion K and Na in the sludge (Seen in Table Ⅱ). Because of the low melting point of those metals, the addition of them decreases the minimum eutectic temperature. The low proportion of those metals has the flux function, which has positive influence on the clinker burning, whereas when the proportion reaches to a certain degree, the liquid viscosity of the clinker grows and hinders the spread of CaO. As a result, the f-CaO content grows. On the other hand, the addition of heavy metals enhances the mineralization and also has flux function, and it changes the physic property of the clinker in molten state. Consequently, it changes the dissolution rate after CaO and C_2S in liquid phase [6].

B. Analysis of the Clinker Compressive Strength

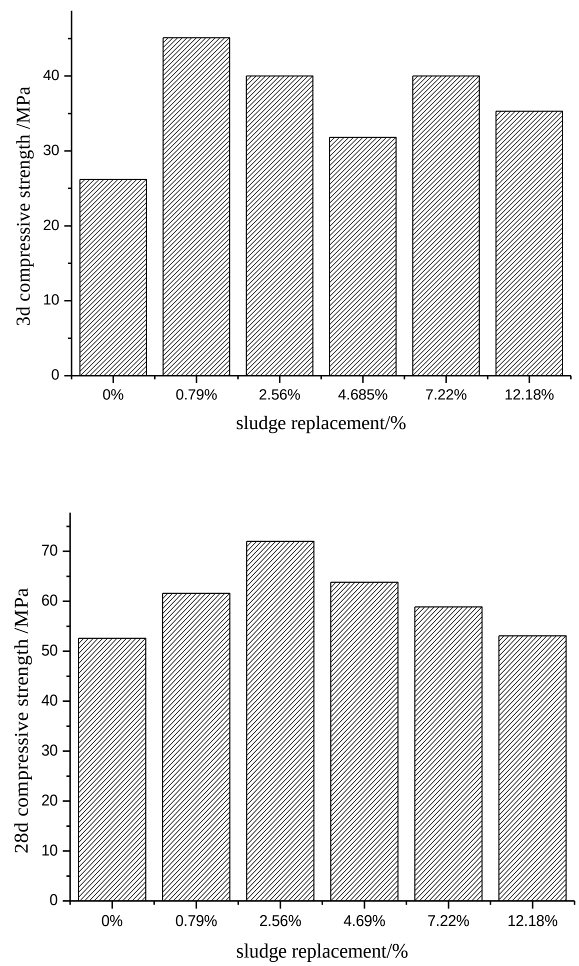


Figure 2. The relationship of compressive strength of 7-day and 28-day sample and the sludge proportion

As the figure 2 shows, the compressive strength of all clinker samples dramatically increases with the increasing age. The compressive strength of all clinker samples that mixed with the sludge is higher than the compressive strength of both 3-day and 28-day clinkers. As the proportion of the sludge increases, the compressive strength increases first and decreases later. When the proportion of sludge is 0.79%, the compressive strength of 3-day sample is 1.74 times as much as the compressive strength of non-sludge-mixed sample and reaches the maximum. When the proportion of sludge is 2.56%, the compressive strength of 28-day sample is 1.37 times as much as the compressive strength of non-sludge-mixed sample and reaches the maximum. In the situation that all of the shale is replaced with the sludge, that the proportion of sludge is 12.18%, the compressive strength of 3-day and 28-day clinker are slightly higher than the compressive strength of non-sludge-mixed sample. Results above indicate that substituting the sludge for shale helps improve the burnability of raw material and the strength of clinker. Results above also correspond to f-CaO measure results, in which the amount of f-CaO increases first then decreases and reaches the minimum with the proportion of sludge is 2.56%.

C. Analysis of Clinker SO_3

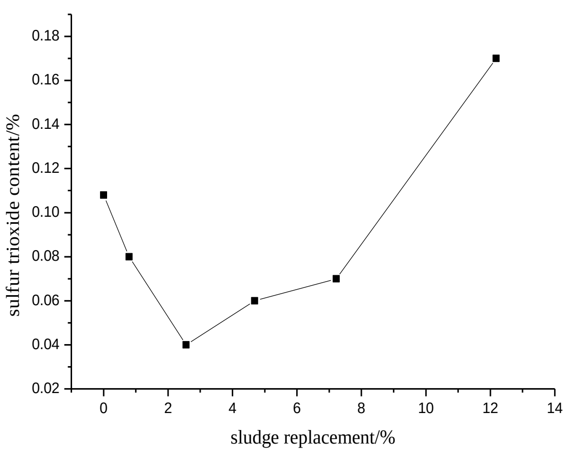


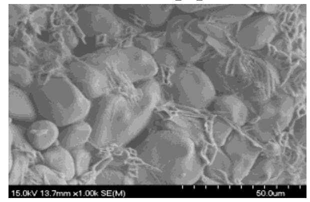
Figure 3. The relationship of SO_3 and sludge proportion

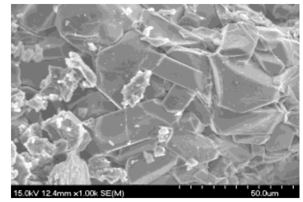
The figure 3 indicates that the proportion of SO_3 is generally low, and far beyond the requirement of SO_3 proportion (≤1%) in the standard GB/T21372-2008 Portland Cement Clinker.

D. Analysis of Clinker SEM

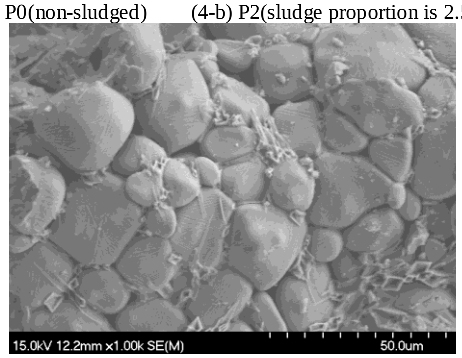
The figure 4 shows that the mineral morphology of clinker sample P0 and P5 are almost the same. However, the clinker sample P5 has better uniformity, compactness, and the granule of sample P5 is slightly larger than sample P0. Compared with sample P0 and P5, the clinker sample P2 has more pseudo-hexagonal and platy crystal, which means more A crystal. Therefore, appropriate mixed sludge can improve the burnability of sludge, whereas the opposite effect will appear if the quantity of sludge is too large.

The calcining process of raw material is high temperature heterogeneous reaction process. The burnability of raw material is influenced by many complicated factors. In those factors, the characteristic of material plays a decisive role in the reactivity of raw material high temperature reaction, and the degree of liquid amount and liquid viscosity decide the formation speed of cement clinker minerals [7].





(4-a) P0(non-sludged) (4-b) P2(sludge proportion is 2.56%)



(4-c) P5(sludge proportion is 2.56%)

Figure 4. Clinker SEM

E. XRD Pattern Analysis of Clinkers

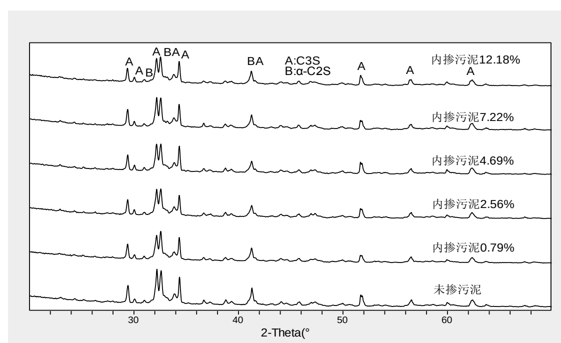


Figure 5. XRD pattern of clinkers

The quality of cement is reflected by the strength, which depends on the mineral composition of the clinker. Figure 5 indicates that the major mineral composition, that mainly is C_3S C_2S C_3A C_4AF, of all 6 samples are almost the same, while the height of peaks indicates that the proportion of minerals are different.

F. Analysis of the Heavy Metal Leaching Test Result

TABLE V. HEAVY METAL FILTER VALUE OF THE CLINKER (MG L-1)

Pb	Cu	Cd	Ni	Cr	Zn	As	Hg
＜0.001	0.012	＜0.001	0.046	0.46	＜0.01	＜0.004	＜0.0001

TABLE VI. CONCENTRATION LIMITS OF HAZARDOUS CONSTITUENT IN LIXIVIUM (MG L-1)

Pb	Cu	Cd	Ni	Cr	Zn	As	Hg
5	100	1	5	15	100	5	0.1

Notes: The concentration limits in table Ⅵ are from the concentration limits of hazardous constituent in leaching solution in GB5085.3-2007 Identification Standards for Hazardous Wastes- Identification for Extraction Toxicity.

Take the clinker containing 12.18% sludge and operate the leaching toxicity test following GB5085.3-2007 Identification Standards for Hazardous Wastes- Identification for Extraction Toxicity. Table Ⅴ and table Ⅵ indicate that leaching values of all heavy metals meet the concentration limits of hazardous constituent in lixivium.

IV. CONCLUSION

1) With modulus KH = 0.89, SM = 2.42, IM = 1.70, replace the shale with sludge. When the proportion of sludge reaches 12.18%, the property of clinker is almost the same as the non-sludge-mixed clinker, and the proportion of f-CaO, the compressive strength of 3-day and 28-day clinker and the proportion of SO_3 all meets requirements of the standard GB/T21372-2008 Portland Cement Clinker, and leaching values of heavy metals meet the requirements of Identification Standards for Hazardous Wastes- Identification for Extraction Toxicity. Since the proportion of sludge is high, the resource utilization of the sludge can be used.

2) Slight amount of sludge mixed in can improve the burnability of clinker, and to some degree improve the compressive strength of 3-day and 28-day clinker. When the proportion of sludge is 2.56%, the amount of f-CaO reaches the minimum, and the compressive strength of 28-day clinker is 1.37 times as much as the compressive strength of non-sludge-mixed sample; when the proportion of sludge is 0.79%, the compressive strength of 3-day clinker reaches the maximum which is 1.74 times as much as the compressive strength of non-sludge-mixed sample;

3) Since the resource utilization of the sludge has a high demand of the sludge, higher request are raised in the stability of the sludge quality and sustainability of supply. The sludge pre dry technology is supposed to be stable, and the cement plant should both improve the technique and equipment.

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