

Effect of phosphor on the formation of Alite-Rich Portland clinker

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Abstract:

The anions HPO_4^{3-} , F^- , SO_4^{2-} and their composition were mixed with some industrial waste into the raw meals of alite-rich portland clinkers (ARPC). The effects of the anions and the waste on the burnabilities of the raw meals, properties of the clinkers and polymorphisms of the alite were studied. And volatilities of the anions in sintering progress were also investigated. The burnability could be improved whether HPO_4^{3-} was added solely or with F^- , $\text{F}^-/\text{SO}_4^{2-}$ synchronously into raw meals of ARPC. The burnability could be improved remarkably when HPO_4^{3-} , F^- and the industrial waste were added synchronously in the raw meals. The strengths were heightened when the clinkers were doped with HPO_4^{3-} or $\text{HPO}_4^{3-}/\text{F}^-$. And the strengths of the clinkers were further heightened if the raw meals were added HPO_4^{3-} , F^- and the industrial waste together. The reasons are that the content of alite was increased in the ARPC and the symmetries of the alites changed. The symmetries were heightened when the alites in the ARPC doped HPO_4^{3-} , F^- . The polymorph of the alite extracted from normal clinker was monoclinic (M3) form. The alite extracted from ARPC doped phosphorus and fluorine was rhombohedral (R) form. In ARPC phosphorus was mainly dissolved into alite. The concentration of phosphorus was about twice more in the alite than in the matrix. The volatilities of the anions can be expressed in the following decreasing order: $\text{SO}_3 > \text{F}^- > \text{P}_2\text{O}_5$.

Keywords: alite-rich Portland clinker (ARPC); anions; industrial waste; properties;

1. Introduction

C_3S (Ca_3SiO_5) is the primary crystal phase of cement clinker. Its concentration, crystal size, crystal shape and crystal structure impact the properties of clinker greatly. The clinker containing more C_3S has higher strength and is more excitative to mineral mixture. With Alite-rich Portland Clinker (ARPC), the concentration of alite $\geq 70\text{wt}\%$, more mineral waste powder can be mixed in cement or concrete. Mixing ARPC with more mineral waste is an ecology way to manufacture high performance cement. But manufacture of ARPC is difficult because of its bad burnability. Some foreign ions besides the normal compositions of portland clinker can affect the burnability and properties greatly, so that more attention has been paid to them, especially to some anions which can improve the burnability and strength of clinker. The mineralizers of combined fluoride and sulfate have positive effects on

the burning process and properties of clinker. They have been investigated and utilized in industry for many years [1,2,3]. But sulphate mineralizer is harmful to environment because of its great volatility in clinkering process. More effective and lower volatilizable mineralizers were needed for the formation of ARPC. K.Kolovos et.al [4] reported the effects of Cl^- , SO_4^{2-} , F^- , HPO_4^{3-} , SiF_6^{2-} , PO_4^{3-} , they believed that these anions lowered the viscosity and surface tension of liquid phase by affecting the acid-base equilibrium of the amphoteric ions (Al^{3+} , Fe^{3+}). As a result, the diffusibility of CaO was changed. Phosphor has a complicated effect, sometimes even completely reversed in relation to the type of compounds used. The addition of $\text{Ca}_3(\text{PO}_4)_2$ has a negative effect on the reactivity of the raw meal, while the addition of CaHPO_4 has a positive one. Bauchi[5] considered that phosphate could remarkably accelerate all reactions in the sintering process, thus, lime combination in the solid phase became easier and crystal grew quicker. The clinker with lower volume of phosphorus .0.5~1.0%. put up higher hydraulic activity. Stephan and his group[6] studied that the crystal type was influenced by doping with different Cr, Ni, and Zn contents by analyzing diffraction peaks of especial 2. angles for Cuk. of C_3S . The results showed that the addition of Cr up to 0.5wt.% didn't have any effect on the modification of C_3S , at concentration of 2.5wt.% Cr at least part of the C_3S was in the T_2 modification, and some of the C_3S was decomposed into C_2S and CaO. The addition of Ni caused a gradual transformation from the T_1 to the T_2 polymorph. With more than 2.5wt.% Ni, no further change in the XRD pattern was found. The hydration was also increased when it was doped with Cr of 2.5 wt.%. All the heavy metals only have an influence on the structure and reactivity of the C_3S when their dosages much higher than in ordinary portland cement. Dosages are 20 times higher for Cr and NI or 10 times higher for Zn than in ordinary portland cement had no influence on C_3S .

The aim of this work is to investigate the influences of the anions HPO_4^{3-} , F^- , SO_4^{2-} and its combination on ARPC. The results indicate that a little content of phosphate and fluorite doped in clinker can improve the burnabilities and properties of the ARPC. The anions with one kind of industrial waste have further improvement on the ARPC clinkering and its properties could be improved fatherly when the anions added with one kind of industrial waste.

2. Experimental

2.1 Materials

Some industrial materials, such as limestone, clay, iron powder and gypsum were used in this experiment. Some calcium salts containing the anions SO_4^{2-} , F^- and HPO_4^{3-} were added into the samples, and they were all at the pure analytical reagents grade. Simply, they were named

as S, F and P in table 2. One industrial waste was used for the raw meals of ARPC preparing. Its chemical composition is almost same as that of clay. And it bore F.P and some other trace elements. Its mineral composition is mainly glass. The XRD pattern of the waste was shown in Fig. (1).

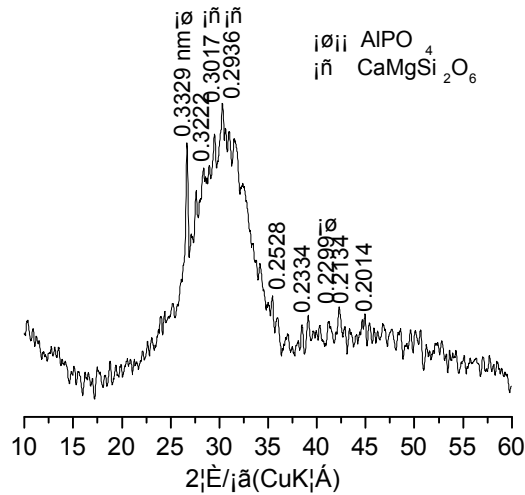


Fig. 1 The XRD pattern of the waste used in this work

2.2 Experimental methods

Samples preparation: All the raw materials were ground in a ball mill to 0.080 mm sieve residue lower than 10%. Raw meals were prepared with the raw material powders according to designed proportions. Then, the meals were homogenized, watered and pressed to little cylinders, 20×5mm. These cylinders were burnt at 1250.1300.1350.1400.1450 and 1500. and treated for 30min respectively for burnability test. For other tests the prepared meals were watered and pressed to big cylinders, 80×15mm. Then the cylinders were dried and burnt at 1450. for 1 hour. The all samples clinkered in a shift electrical stove, and cooled quickly to room temperature in air after treated.

Test program: Free CaO in all clinkers was determined by the ethylene glycol method. The mineral composition was analyzed by X-ray diffraction (XRD) with CuKα radiation (38KV, 40mA). The chemical composition and contents of foreign ions in the raw meals and in the clinkers were determined by chemical analysis routine.

The clinkers were ground in a taper ball mill (.350mm) after 5 wt% gypsum added. The strength tests of the cements were performed according to Chinese standard GB/T17671-1999 (equiv. ISO679: 1989), and standard denseness water requirement, setting time and soundness were tested according to Chinese standard GB/T1346-2001 (equiv. ISO9597: 1989).

The mineral phase was analyzed with a light microscopy and a

scanning electron microscopy (SEM), and the concentrations of the foreign anions in clinker minerals were determined with energy dispersive spectrometer (EDS). The clinker was crushed (<5mm) and then a fraction was embedded into epoxy resin. The samples were ground with SiC powder and then polished with Al₂O₃ powder. For reflect optic microscopy analysis the samples were washed by alcohol in an ultrasonic washer and then etched with nitric acid alcohol solution. Then the samples were coated with carbon for SEM and EDS test.

For the polymorphism analysis, the clinkers were milled (<10.μm), and the alites were extracted from the clinkers with KOH sugar solution. The clinker powders were separately put into the solution churn up at 95. for about (20~30) minutes so that the matrix could be dissolved completely, and no matrix diffraction peaks could be defined by XRD. Then the residues were filtrated and washed. The XRD was carried out on the extracted alites with CuK. radiation and at especial scanning range of 2θ: (28~31)°, (31~33)° and (51~53)°. The scanning speed was 0.5°per minute.

The chemical proportions of the clinkers: In order to demonstrate the effects of these anions, we designed a reference sample, and took that mixed with deferent anions or mixed some industrial wastes in raw meals as experimental groups. The concentration of SO₃, P₂O₅, and CaF₂ is less than 1.0wt% in the clinkers. Surely the essential chemical and mineral compositions of every group were just kept the same. We designed each group's lime saturation factor (LSF) about 1.0. The reference clinker's chemical and mineral composition is given in Table(1). Addition of foreign anions and wastes in series groups were shown in Table(2).

Table1. The chemical and mineral composition of the reference clinker

chemical composition		mineral composition (according to Bogue)		modulus	
SiO ₂	21.16	C ₃ S	72.2	LSF	0.99
Al ₂ O ₃	5.18	C ₂ S	6.2	SM	2.53
Fe ₂ O ₃	3.19	C ₃ A	8.3	IM	1.62
CaO	66.98	C ₄ AF	9.7		

Table2. Admixture in series clinkers

Sample	Composition
1	Reference
2	Reference +F
3	Reference +S+F
4	Reference +P

5	Reference +S+P
6	Reference +F+P
7	Reference +S+F+P
8	Reference +F+ more P
CM1	Reference with mixed waste
CM2	Reference with mixed waste+P
CM3	Reference with mixed waste+P+F

3. Results and discussion

3.1 Effect of HPO_4^{3-} compared to SO_4^{2-} , F^- on the burnability

The effects of phosphate, sulphate and fluorite on the burnability are shown in Fig.(2). It can be seen that the effect of phosphate is not as good as fluorite or fluorite-sulphate mineralizer when the temperature is at 1300. and 1350. . At the temperature of 1400., their effects are almost same as each other. However, above 1450. the effect of phosphate on the sintering is better than adding fluorite singly or fluorite-sulphate mineralizer. So the conclusion could be reached that flourite-sulphate mineralizer is applicable for low temperatures while phosphate is more suitable for higher temperatures.

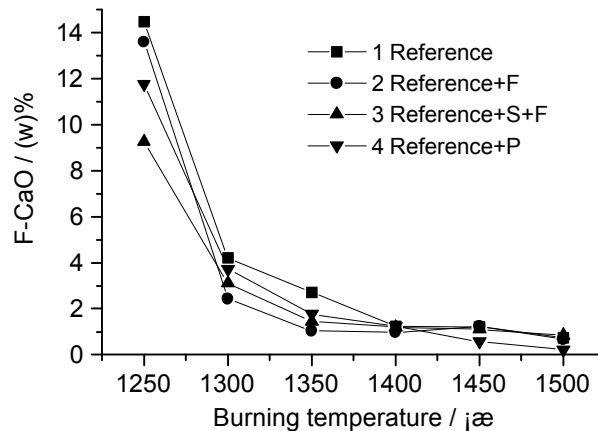


Fig. 2 Effects of HPO_4^{3-} , SO_4^{2-} and F^- on the burnability

In order to look for a kind of composite mineralizers that can improve burnability not only in lower temperature but also in higher temperature, we investigated comparatively the effect of phosphate and the effect of phosphate compounded with fluorite or/and sulphate. The result is shown in Fig.(3).

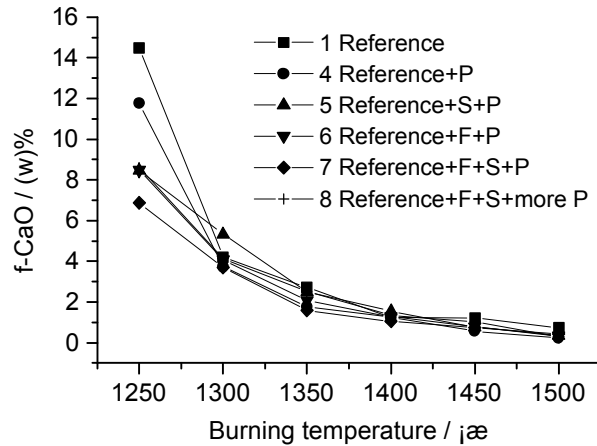


Fig. 3. The effect of phosphate compounded with fluorite or/and sulphate on burnability

Fig.(3) supports that the compounded addition of phosphate-sulphate can improve burnability greatly at 1250. But the effect is not very obvious when temperature is at 1300. and 1350., or even become worse when the temperature is at 1400.. The reason may be the volatilization of SO_3 . The burnability of the both samples of adding phosphate-fluorite and phosphate -fluorite-sulphate can be improved remarkably. phosphate -sulphate-fluorite group exerts the best effect and improved the sintering greatly in the temperature range of 1250-1450.. But above 1300., the f-Cao of sample 7 was nearly same as sample 4 and sample 6. and adding more phosphate into sample 6. such as sample 8. was not more efficiency on the burnability. The conclusion can be done that phosphate and phosphate-fluorite are suitable for improving the burnability of ARPC in normal burning temperature range.

Fig.(4) shows the XRD patterns of the sample6. From the patterns we can see that the diffraction peaks of CaO is very feeble at 1300., and can not be distinguished at 1400., which correspond with the results of free lime analysis. All these suggest that the composite addition of phosphate-fluorite improve the burnability greatly.

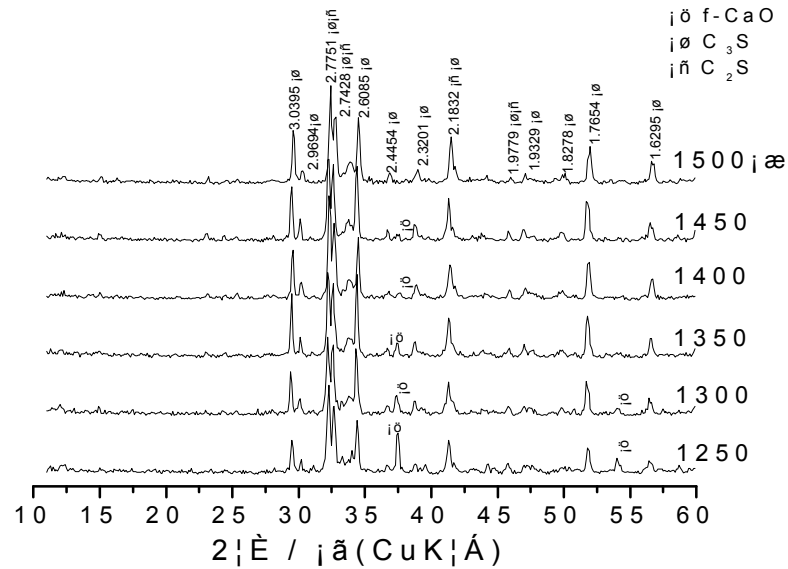


Fig. 4 The XRD patterns of sample 6 at different temperature

3.2 Influence of the industrial waste on burnability

Fig.(5) shows that the change of the free CaO in sample1 and sample CM3 with the temperatures after the thermal treatment at 1300 . to 1500 .. The raw meal of CM3 was mixed with the industrial waste and F⁻, HPO₄³⁻ anions. The results indicate that the content of free CaO in modified sample reduced much faster than the free CaO content in reference sample. The free CaO content of CM3 was much less than reference sample1 at every temperature. Above 1350. the free CaO content of CM3 was less than 1wt%, which denotes that clinking process was completed. The SEM picture is illuminated the conclusion too, which can be seen in Fig.6.

The Fig.(6a) and (6b) show that little C₃S was formed in sample1, then a lot of C₃S can be seen in sample CM3 at 1300.. At 1350, the formation of C₃S is starting in sample1, with large axes ratio and tine crystal shape. The crystal shape of C₃S in sample CM3 is more regular than in sample1, which can be seen in Fig. (6c and 6d). At 1400. and 1450., the formation of C₃S are finished either in sample1 or sample CM3. The edges of C₃S crystal in sample CM3 are straighter and their angles are sharper than that in sample1, which can be seen in Fig.(6 e. f.g and h).

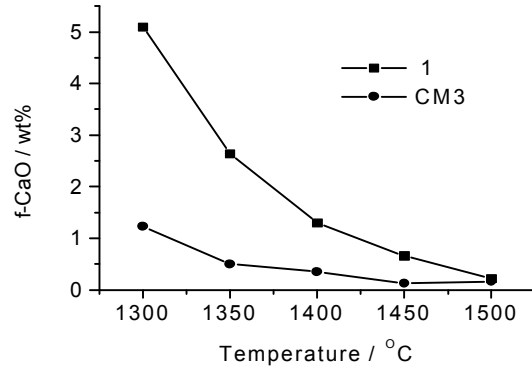
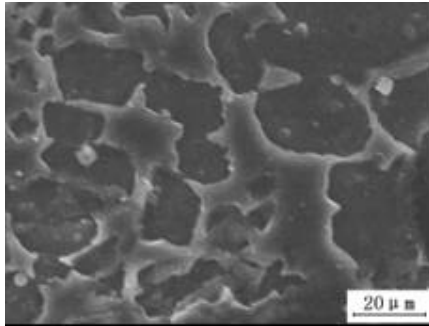
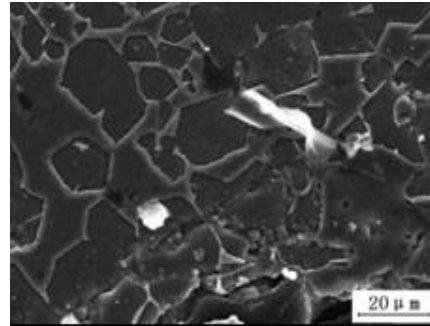


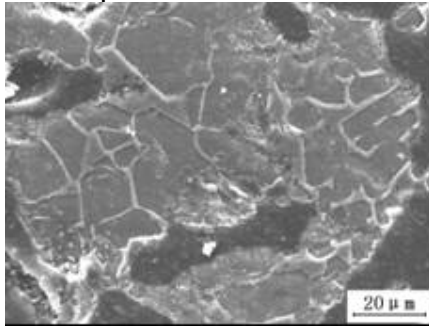
Fig. 5 Effect of industrial waste on the burnability of ARPC



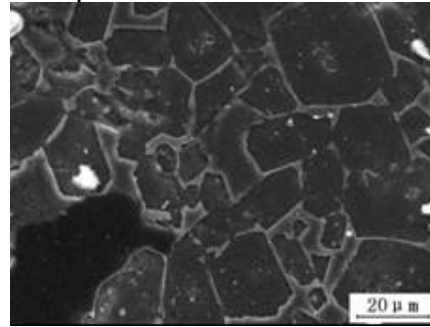
a. Sample 1 burnt at 1300.



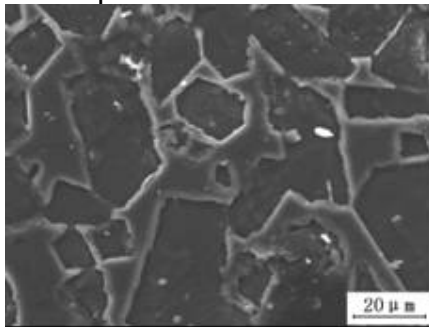
b. Sample CM3 burnt at 1300.



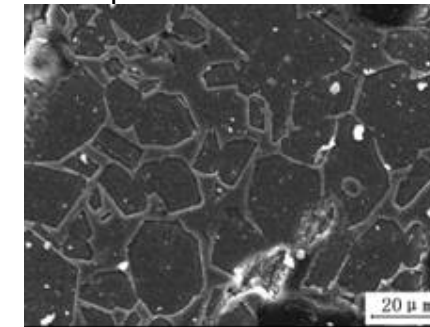
c. Sample 1 burnt at 1350.



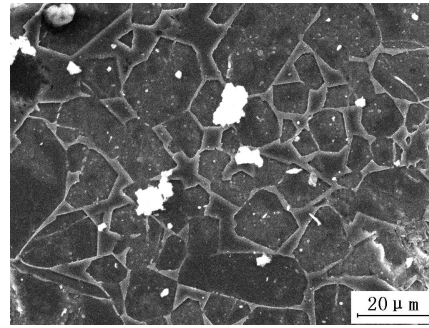
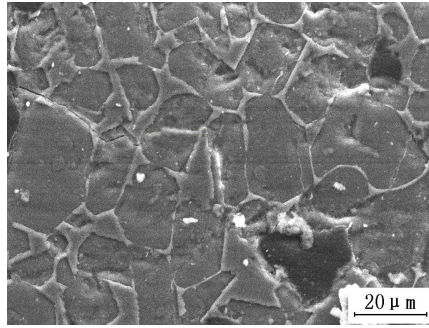
d. Sample CM3 burnt at 1350.



e. Sample 1 burnt at 1400.



f. Sample CM3 burnt at 1400.



g. Sample 1 burnt at 1450.

h. Sample CM3 burnt at 1450.

Fig.6 SEM picture of sample1 and sample CM3 burnt at different temperature

3.3 Effect of phosphate cooperated with other anions and the industrial waste on strengths of the clinkers

The effect of phosphate compounded with other anions and the industrial waste on the strengths of clinkers is shown in Table 3. The specific surface areas (Blaine) of the cements were controlled at $320 \pm 10 \text{m}^2/\text{Kg}$. The setting times were determined in condition of fixed ratio of water/cement at 26.5wt.%.

Table 3. Physical performance of series clinkers

No.	Setting time / min.		Bending strength / MPa.			Compressive strength / MPa.		
	Initial	Final	3d	7d	28d	3d	7d	28d
1	151	301	5.48	7.03	9.47	31.27	45.40	65.43
4	233	283	5.92	8.08	9.18	35.79	52.10	64.46
5	245	288	4.31	6.76	9.47	29.60	45.65	64.81
6	276	317	5.87	8.20	10.30	34.29	50.58	70.87
7	372	444	5.85	8.05	9.25	32.87	53.34	67.34
8	226	286	6.15	7.81	9.48	36.42	51.58	70.59
CM1	182	248	6.88	8.49	10.22	41.45	57.66	78.11
CM2	159	255	7.06	9.10	10.10	42.70	57.67	74.48
CM3	228	306	7.03	9.16	10.82	42.60	61.19	84.76

Data in Table (3) show that all the setting times accorded with the Chinese standard GB175-1999. Compared with reference group, the single addition of phosphate increases the bending strength and compressive strength of 3d and 7d to a great extent while keeps the 28d strengths equal approximately. But every age's strength of the sample doped phosphate and sulphate together is declined to different extent or retained its balance. That is to say that the single introduction of phosphate or compound introduction of sulphate and phosphate cannot heighten the strengths of the clinkers burnt at the normal burning temperature even reduce them, though the introductions can accelerate the combination of CaO with C_2S . The phosphate-fluorite group's strengths of any ages are enhanced greatly. The 28d's compressive

strength is heightened by 5Mpa. Comparing strengths of sample6 to sample8, we can find that when the more phosphate doped, the earlier strength is higher while the 28d's compressive strength is almost equal, and the 28d's bending strength decreases a little. Taking the results of sample4 in consideration, we can find that at normal burning temperature, adding phosphate into clinker can improve the earlier strengths. When adding phosphate-fluorite-sulphate, the strength of any age is higher than the strengths of reference sample except that the 28d's is almost equal. But when compared with sample4 their strengths of any ages are almost equal. At normal burning temperature, overmuch composition of the foreign anions is not good as phosphate-fluorite to increase the strengths of the clinker, though it may cause a positive effect on absorption of free lime. When mixed the industrial waste in raw meals all the burnt clinkers have very high strengths at all ages. It would be an efficient way to manufacture ARPC with inducing the industrial waste and a little of phosphate, fluorite in its raw meal.

3.4 Solid solution of phosphor in clinker minerals

The solid solution of phosphor in the alite and matrix of ARPC was identified by EDS, as shown in table (4). Each datum is the average of fifty testing results in order to decrease the larger error of EDS testing. The concentration of phosphor is about twice more in alite than in matrix. As the burning temperature heightened the phosphor content increases in matrix and reduces in alite. Then, the phosphor concentration is still much more in alite than in matrix. The conclusion can be reached that phosphor is mainly dissolved into alite in ARPC.

Table 4 Concentration of phosphorus in Portland clinker at different temperatures

Temperature / .	1300	1350	1400	1450	1500
In Alite / wt %	0.76	0.74	0.72	0.76	0.70
In matrix / wt %	0.30	0.35	0.41	0.33	0.45

3.5 Polymorphism of the alites extracted from the clinkers

To study the polymorphism of alites in ARPC doped with phosphor and fluorine, the XRD scanning at the especial angles $2\theta=(28\sim31)^\circ$, $(31\sim33)^\circ$, $(51\sim52.5)^\circ$ were examined. The pure C_3S was synthesized and tested at the same conditions as a comparison. The results are shown in Fig.(7).

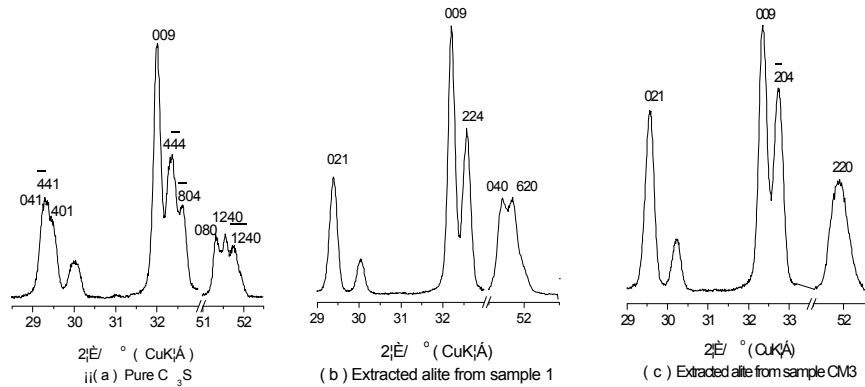


Fig. 7 XRD patterns of pure C₃S and extracted alites

The symmetry of pure C₃S is the lowest form in all of the polymorphs of C₃S and its solid solutions. Its modification is triclinic (T1). There are three furcations in the diffraction peaks at 2. angles = (29~30)°, (31~33)°, (51~52.5)°. The XRD pattern of alite extracted from clinker 1, which was clinkered with normal raw meal, is illustrated in Fig.6 (b). There is a diffraction peak of the (021) crystal side at the angle 2. = (29~30)° and two diffraction peaks of the (040), (620) crystal side at 2. = (51~52.5)°. Its polymorph should be monoclinic modification (M3). It can be seen from Fig.6 (c) that the symmetry of alite extracted from sample CM3 is improved when it doped with fluorine and phosphorus. Its polymorph turned into rhombohedral(R) form. There is no furcations in the XRD peaks at the angles 2. = (29~30)°, (31~33)°, (51~52)°.

3.6 Volatilities of these anions

The exhaust gas containing F⁻ and SO₄⁻ ions may erode the equipment of kiln system, form acid rain, and cause great pollution to environment. Therefore, the volatilities of these ions in the samples burnt at 1450 . for 30min were analyzed. Table 5 presents the percentages that have been volatilized during the thermal treatment.

Table 5 Volatilities of doped anions at 1450.

Doped anions	S	F	P
Volatility/ wt%	62.27	34.64	26.80

These data lead us to a conclusion that the volatility of sulphate is high, that of fluorite moderate, and phosphate's is low. All these can confirm the burnability turning to bad at higher temperature when phosphate and sulphate are added into the raw meal. The reason may be the high volatility of sulphate that causes the increase of the practical volume of CaO in the clinker. Considering the lowest acidity of phosphate, it will not bring serious pollution to environment when phosphate is used to improve the burnability and physical performance of ARPC.

4. Conclusions

(1) The burnability could be improved whether HPO_4^{3-} was added solely or with F^- , $\text{F}^-/\text{SO}_4^{2-}$ synchronously into raw meals of ARPC. The burnability could be improved remarkably when HPO_4^{3-} , F^- and the industrial waste were added synchronously in the raw meals. But it will turn over when SO_4^{2-} is induced singly or SO_4^{2-} and HPO_4^{3-} added synchronously at normal clinking temperature since the volatility of sulphate is high.

(2) The strengths are heightened when the ARPC doped phosphor or doped phosphor and fluorite. And the strengths are further heightened if the clinkers doped HPO_4^{3-} , F^- and the industrial waste synchronously. The reasons include that the content of alite in the ARPC is increased and the polymorphism of the alite is changed.

(3) In ARPC phosphor is mainly dissolved into alite. The concentration of phosphor in alite is about twice more than that in matrix.

(4) Its symmetry is heightened when the alite in the ARPC doped F^- and HPO_4^{3-} . The polymorph of the alite extracted from normal clinker is monoclinic (M3) form while the polymorph of the alite extracted from ARPC doped phosphorus and fluorine is rhombohedral modification.

(5) The volatilities of the anions can be expressed in the following decreasing order: $\text{SO}_3 > \text{F}^- > \text{P}_2\text{O}_5$.

Acknowledgments

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