

THE PREPARATION AND COMPOSITION ANALYSIS OF ALITE-YE'ELIMITE WITH INDUSTRIAL WASTES

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Abstract: Alite-ye'elimite clinker is a high cementing clinker that is prepared by introducing calcium sulfoaluminate, a non-silicate mineral, into cement clinker. The industrial residue was used to produce cement clinker. The relationship of the aluminate modulus (IM) and the mineral composition and mechanics of tricalcium silicate-rich sulfur aluminate cement is reported. The effects of the aluminate modulus on the phase compositions, morphology and compressive strength were investigated. The phase morphology was analyzed by optical microscopy. The results show that the increase of IM in the clink can accelerate the formation of calcium sulfoaluminate; calcium sulfoaluminate can form at the temperature of 1250°C when the IM value is lower than 2.50, while it exists at a temperature of 1300°C without reheating when the IM value is higher than 2.50.

INTRODUCTION

Ye'elimite (C_4A_3S) is a mineral with rapid hydration, high early strength, small volume shrinkage during hydration and corrosion resistance [1-3]. Hence, a new clinker named alite-ye'elimite clinker was proposed by introducing ye'elimite into Portland cement clinker [4-7]. However, C_4A_3S decomposes at 1350°C, while much C_3S begins to form at 1400°C [8-12]. To enable the coexistence of alite and ye'elimite, university researchers in Jinan improved the decomposition temperature of ye'elimite by using the ions of Sr and Ba to partly replace the Ca ions. Based on thermodynamic principle, they cannot coexist. The decomposition kinetics of calcium sulfoaluminate have been investigated by Ma Suhua [13]. Shen Xiaodong et al. [14] prepared alite-ye'elimite cement clinker by reheating. I. Odler and H. Zhang [15, 16] showed that the clinker can be produced at temperatures between 1250 ~ 1300°C by adding gypsum and fluorite as mineralizers. Ma Suhua [17] reported that a small amount of metal oxide (MnO_2 , ZnO, CuO) could expand their coexistence range. Also, 0.1% MnO_2 added into the raw meal could improve the decomposition temperature of C_4A_3S by 100°C and enlarge the coexistence temperature scope between alite and C_4A_3S by 57°C. Upon the addition of 1 % ZnO to the raw meal, alite is detected in the sample at 1300°C, as the

temperature range of the coexistence of C_4A_3S and alite was broadened to 50°C. The addition of CuO (0.1 % in mass) to the raw meal could lower the burn temperature of the clinker, promote the coexistence of C_3S and C_4A_3S , and increase the strength of the clinker.

Based on the above research, industrial wastes were used as a raw material to make alite-ye'elimite by adding a small amount of metal oxide to decrease the formation temperature of the alite and promote the coexistence of the two phases. In this paper, the influence of IM on the preparation and mechanical properties of the cement made from alite-ye'elimite clinker was investigated, which can be useful for industrial applications.

EXPERIMENTAL

Raw materials

Limestone, sandstone, copper slag, phosphorus slag, fly-ash and gypsum were used as raw materials. Their chemical compositions are shown in Table 1.

Preparation of the clinker

The raw materials were ground in a laboratory ball mill to obtain a fineness of 6 - 8 % over an 80 μm sieve. The raw meals were made by mixing these raw

Table 1. Chemical components of the raw materials measured by X-ray fluorescence (XRF).

	LOSS	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	CuO	SO ₃
Limestone	42.24	2.63	0.83	0.44	52.16	1.46	0.08	0.01	–	–	–
Sandstone	1.55	86.21	5.02	5.50	0.62	0.20	0.82	0.02	–	–	–
fly-ash	2.72	49.86	31.84	4.45	5.41	0.98	0.98	0.85	–	–	–
copper slag	–	26.48	9.01	38.77	11.89	2.25	0.61	0.23	–	0.25	–
phosphorus slag	–	39.32	4.14	0.86	48.16	1.93	0.59	0.17	1.65	–	–
Gypsum	20.16	13.10	4.85	1.73	23.68	2.84	0.95	0.54	–	–	31.47

materials in the laboratory ball mill according to control parameters including a lime saturation factor (KH) of 1.00 ± 0.02 , silicate modulus (SM) of 2.40 ± 0.02 and IM of 1.50, 2.00, 2.50, 3.00 and 3.50. The raw meal was mixed with water and pressed under a pressure of 15 MPa into a disk with $\Phi 40 \text{ mm} \times 25 \text{ mm}$. The dried disks were calcined in a resistance furnace at different temperatures (1250°C, 1300°C, 1350°C, 1400°C, 1450°C) for 60 min, then removed from the furnace immediately and cooled rapidly by a fan to produce clinker. To avoid the effect of the specific area, the specific area was controlled within a set range ($360 \pm 18 \text{ m}^2 \cdot \text{kg}^{-1}$).

Experiment methods

The content of free lime (f-CaO) was determined chemically after dissolving the clinker in ethanol-glycerin. A thermal analysis was performed on a METTLER TOLEDO 1600LF instrument with a combined TG and DSC system to investigate the physical and chemical changes to the raw meals during the heating. The raw meals were heated from 30°C to 1450°C with a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ under N₂ atmosphere. X-ray diffraction (XRD) analysis was used for phase identification and quantification. The XRD patterns was recorded on a Rigaku SmartLab 3000 A diffractometer with CuK α radiation ($\lambda = 0.15406 \text{ nm}$). The X-ray tube was operated at 35 kV and 30 mA. The optics configuration includes a fixed divergence slit ($1/2^\circ$) and a D/teX Ultra detector. The measurements were collected using θ - θ reflection geometry. Data were collected from 10° to 70° (clinker) and 5° to 65° (the hydration of cement) in the continuous mode. The mineral content of clinkers were be calculated by GSAS (Figure 1a,b).

To investigate the hydration of the clinker produced at temperatures of 1450°C and 1300°C, cement pastes were prepared with water/cement ratios of 0.50. All hydration experiments were performed at 20°C.

A conduction calorimeter (Thermometric TAM Air) was used to determine the rate of hydration heat liberation during the first 72 h. A total of 4.00 g of the cement was weighed into a flask, and the corresponding amount of water was added using a needle. The flask was then capped and placed into the calorimeter until the reading was stable. The mixing was performed by a stirrer for approximately 1 min. Due to the internal mixing, the early thermal response of the samples could be measured.

The total heat of hydration after 72 h was determined by the integration of the heat flow curve between 0 and 72 h.

The porosity and pore size distribution were measured on fragments of the specimens by mercury intrusion porosimetry (MIP). Samples of both cements, paste hydrated ($w/c = 0.5$) and shaped cylindrical discs, were cured for times ranging between 1 d and 28 d. Before the test, at the end of each aging period, the sample was broken, treated with ethanol to stop the hydration and stored in a desiccator to protect against water and carbon dioxide. For each sample, two plots can be obtained from the porosimetric analysis: (a) cumulative and (b) derivative Hg intruded volume vs. pore

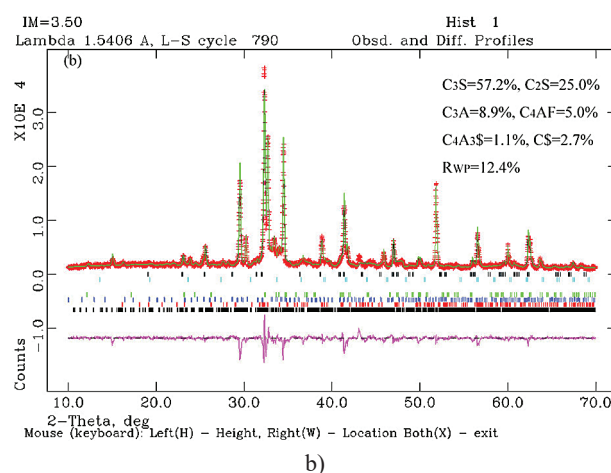
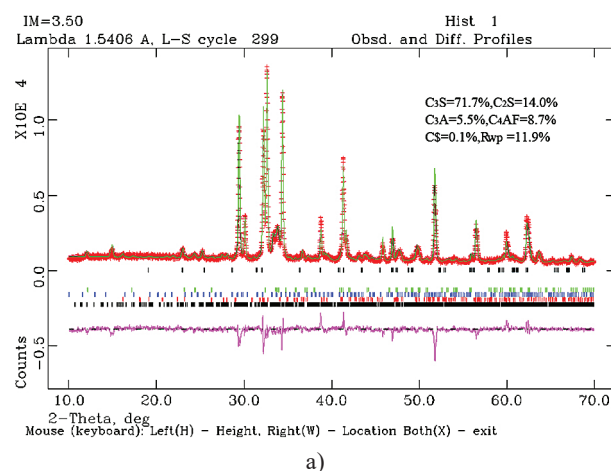


Figure 1. Rietveld refinement of the powder patterns of the clinker used: a) clinker produced at 1450°C, b) clinker produced at 1300°C.

To analyze the phase morphology, optical microscopy (Olympus LEXT OLS 4000) was used. Before that, the clinkers were embedded with epoxy and kept for 1 d; then, the clinkers were polished and etched for 15 s in a nital solution (1 ml conc. HNO₃ + 99 ml 99.5 vol. % ethanol). The compressive strengths of the cement mortars were measured according to EN 196-1.

RESULTS AND DISCUSSION

The burnability of the cement clinker

The burning of the clinker is reflected by its free lime (f-CaO) content. The f-CaO contents are shown in Table 2 for clinkers burned at different temperatures. The IM governs the ratio of the aluminite to ferrite phases in Portland cement, which has important effects on the cement properties, and so determines the quantity of liquid formed at relatively low temperatures. At 1338°C, the quantity of liquid reaches its minimum at an IM of 1.38 in Portland cement [1]. Table 2 shows that the addition of copper slag and phosphorus slag accelerates the burning of the clinker and promotes the absorption of f-CaO at a relatively low temperature (1250 - 1350°C) and with the increase of IM, f-CaO can be reduced specially at low temperature although an IM of more than 3.00 has an adverse effect on the burning of the clinker. It is suggested that the IM causes an increase in the liquid viscosity when it is more than 3.00, although it enhances the amount of liquid. On the other hand, the optimal value of IM decreases with the increase of the burning temperature in this temperature range. At high temperatures (1400 - 1450°C), IM has little effect on the burning of the clinker.

Table 2. f-CaO content vs. IM and temperature (%).

	1450°C	1400°C	1350°C	1300°C	1250°C
IM = 1.50	0.05	0.06	0.09	0.36	4.49
IM = 2.00	0.06	0.10	0.21	0.30	3.79
IM = 2.50	0.06	0.06	0.29	0.34	3.62
IM = 3.00	0.03	0.03	0.29	0.41	4.73
IM = 3.50	0.08	0.12	0.41	0.53	4.32

Previous research [18] showed that the addition of copper oxide did not reduce the decomposition temperature of calcium carbonate, but it decreased the formation temperature of C₄AF and promoted the formation of C₃S at low temperature. It has been reported [9] that a small amount of P₂O₅ (< 1.0 %) could improve the burnability of the raw mix by decreasing the surface tension of the liquid. However, it would inhibit the crystallization of C₃S and the preferential formation of the C₂S-P₂O₅ solid solution when the dosage of P₂O₅ exceeds the solubility limit of P in the C₃S phase (1.1 % P₂O₅). Sulfur forms an independent liquid in the process

of burning. The addition of the copper slag, phosphorus slag and gypsum could improve the burnability of the raw mix. Compared to the sintering temperature of ordinary Portland cement clinker (1450°C), the sintering temperature is reduced to 1300°C for the clinker using copper slag, phosphorus slag and gypsum as raw materials.

Thermal Analysis

The thermogravimetric results carried out on blends were used to obtain information on the decomposition of chemical compounds during calcination. Figure 2 shows the DSC curves, establishing the decomposition process of the compounds present in the raw material. The first endothermic peak (about 130°C) was attributed to the gypsum in the raw mixtures. The second endothermic peak observed at approximately 782°C was proven to be the endothermic decomposition of CaCO₃, while the third endothermic peak was proven to be the formation of liquid. As the IM increases, the formation temperature of the liquid increased because of the decreasing of Fe₂O₃ amount.

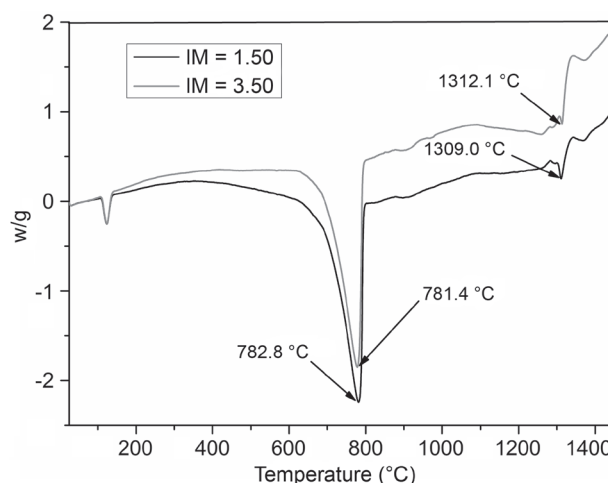


Figure 2. DSC curves obtained from different clinker raw doped with industrial residue, using an atmosphere of N₂ and a heating rate of 10°C·min⁻¹.

XRD study

An X-ray diffractometer was used to analyze the phase composition of samples burned at different temperatures (1250, 1300, 1350, 1400 and 1450°C). In this paper, the XRD patterns of the samples burned at 1250, 1300, 1350 and 1450°C are provided in Figures 3. At 1250°C, every sample contains six main phases, C₃S(A), C₂S(B), C₃A(C), Ferrite(F), f-CaO(f), C₄A₃\$ (CA\$) and CaSO₄ (C\$), whose diffraction peaks are shown in Figure 3a,b,c,d. The intensity of characteristic diffraction peak (d = 0.375 nm) for C₄A₃\$ was enhanced with the

increase of IM, while the intensity of characteristic diffraction peaks ($d = 0.263$ nm, $d = 0.348$ nm) of the ferrite phase and CaSO_4 seem to decrease. In addition, the diffraction peak of the C_3A phase is not observed at this temperature. With the ongoing increase of the temperature, the characteristic peak of $\text{C}_4\text{A}_3\text{S}$ disappears for the samples with an IM of less than 2.50 due to its decomposition at 1300°C . At the same time, the characteristic diffraction peak of C_3A appears and increases with the increase of IM. When the temperature is more than 1350°C , $\text{C}_4\text{A}_3\text{S}$ completely disappears, and the phase composition includes C_3S , C_2S , ferrite, C_3A and CaSO_4 for all of the samples.

Microstructure

To investigate the phases morphology, pictures taken by light microscopy are shown in Figure 4 for the samples with IM = 3.50 at temperatures of 1450°C

and 1300°C . Crystals of alite and belite are embedded in a matrix of aluminate and ferrite phases. In general, alite crystals are angular, often pseudohexagonal, and belite crystals are rounded and normally striated. In this paper, the alite and belite crystals are blue for samples burned at 1300°C due to the use of 1.0 % HNO_3 as the etchant. Compared with the DSC analysis, the quantity of the liquid phase was less at this temperature, and the alite does not crystallize well and does not show significant angles. The belite appears rounded, and the alite and belite cluster together. At 1450°C , alite crystals show a pseudohexagonal structure due to complete crystallization. Their average size is larger than that at 1300°C . In addition, little belite was found. Most of the silicate phases are alite, which distributes homogeneously in the matrix of the aluminate phase and ferrite phase without clustering. Figure 4a has a lower porosity than Figure 4b because the high temperature causes easy sintering and consequently lowers the porosity.

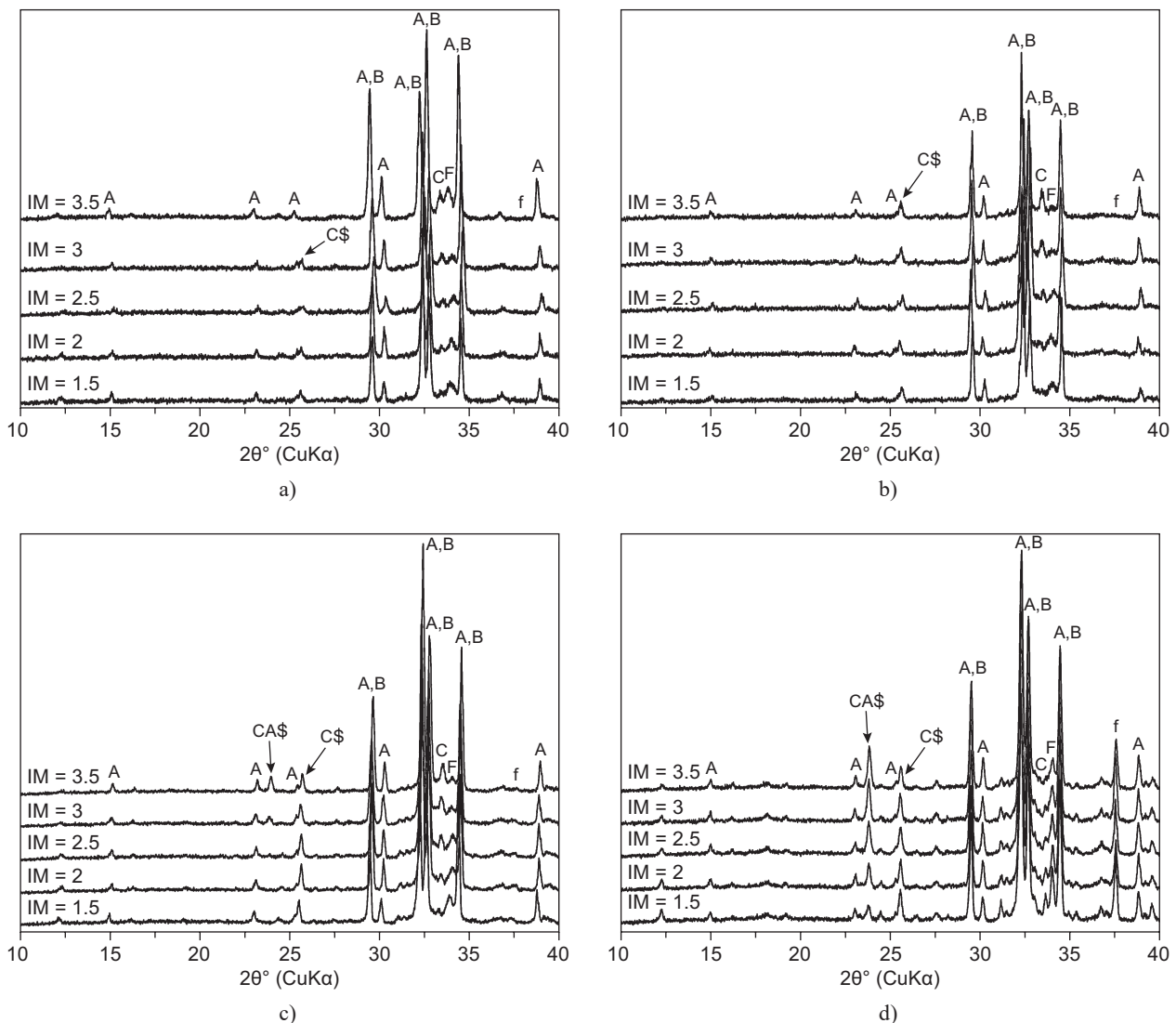
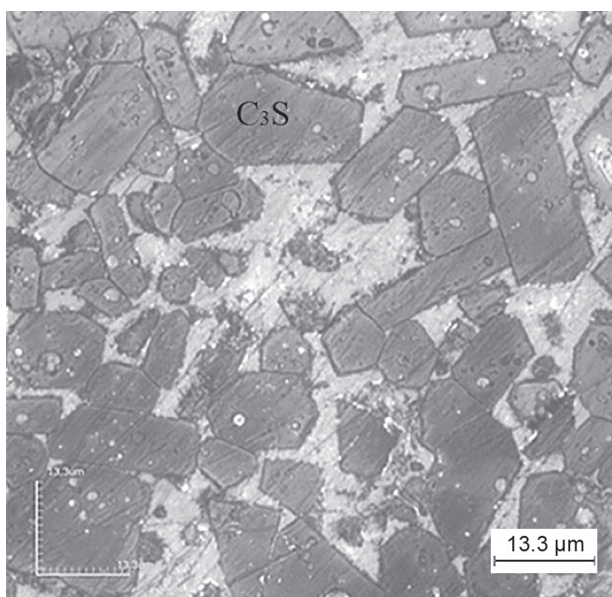
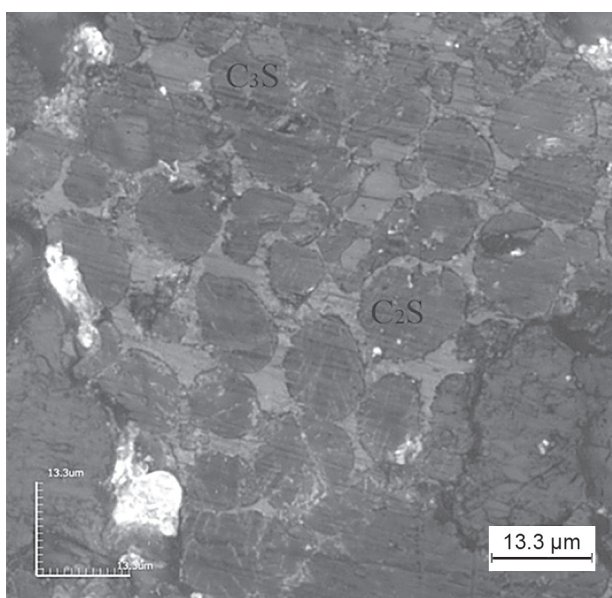


Figure 3. The XRD patterns of the samples burned at 1450°C (a), 1350°C (b), 1300°C (c), 1250°C (d).



a)



b)

Figure 4. Microscopic view of the clinker heated with IM = 3.50 at the temperatures of 1450°C (a) and 1300°C (b).

Compressive strength

The P.II 52.5 cement selected as a reference was provided by a Chinese cement company. It has a typical phase composition including C₃S (alite), C₂S (belite), C₃A (tricalcium aluminate), C₄AF (tetracalcium

ferroaluminates) and some calcite. Two cements were made of two clinkers and gypsum. With the higher quantity of C₄A₃\$, the IM = 3.5 is chosen for the two clinkers. However, one clinker is synthesized at 1300°C and the other at 1450°C. The dosage of gypsum is 5 % by weight of the cement. Their compressive strengths are shown in Figure 5. The compressive strengths of the two cements synthesized are higher at early ages and lower at later ages compared to cement P.II 52.5. C₄A₃\$ has some good properties with early strength and little expansion because its hydration leads to the formation of an initial ettringite (AFt) network and the subsequent infilling by mixtures of ettringite, calcium monosulfoaluminate (AFm) hydrate, alumina and ferrite gels. The XRD results demonstrate that C₄A₃\$ exists in the clinker burned at 1300°C, apart from C₃S, C₂S, C₃A and C₄AF. Hence, the introduction of C₄A₃\$ may cause the increase of the early strength at early ages for the cement burned at 1300°C. The early compressive strengths were increased by approximately 27 % and 17 %, respectively, for the cement burned at 1300°C. The increase of the early strength may be attributed to the change of phase composition and crystal structure for the cement burned at 1450°C. In addition, the compressive strength was higher for the cement burned at 1300°C compared to that burned at 1450°C.

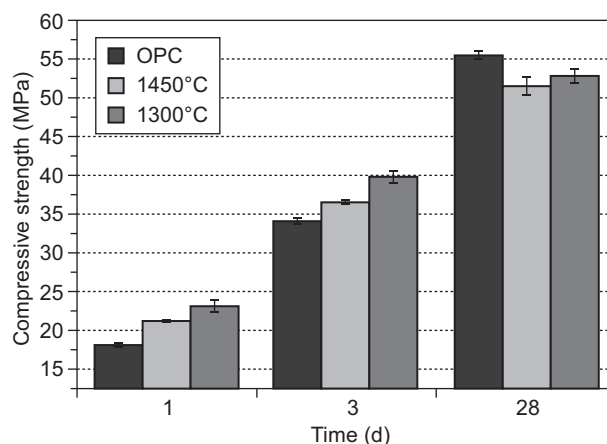


Figure 5. Comparison of the compressive strength of OPC and clinkers burned at different temperatures.

Isothermal calorimetry

The conduction calorimetry results are shown in Figure 6. Figure 6a shows that the heat release during the initial period (0 to 0.4 h) was more quickly for the

Table 3. Chemical composition of P.II 52.5 cement and IM = 3.50 burning at the temperature of 1450°C.

	LOS	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₄	MgO	SO ₃	Na ₂ O	K ₂ O
P.II 52.5	2.2	63.8	19.8	4.4	3.2	1.6	3.8	0.2	0.3
IM = 3.50	–	64.6	19.4	6.4	1.8	2.6	3.7	0.1	0.4

clinker produced at temperature of 1450°C than for the clinker produced at temperature of 1300°C due to the minerals of C_3A (1450°C) and C_4A_3S (1300°C) in the clinkers. The first peaks of two clinkers were dissolution peak followed by an induction period, and then a re-acceleration of hydration is observed. The second peaks of the curves were attributed to alite hydration. The difference from the clinker produced at the temperature of 1450°C, the peak three come from the presence of the C_4A_3S phase and its reaction with gypsum.

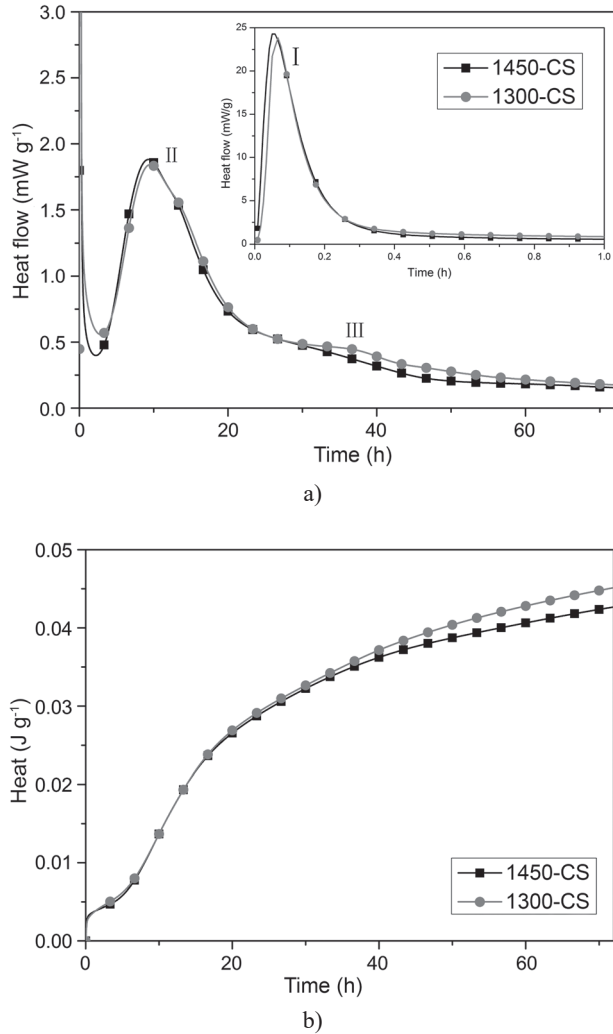


Figure 6. Heat flow development of clinker (IM = 3.5) produced at the different temperatures (a) and cumulative heat, as a function of time, between 0 to 72 h (b).

Figure 6b displays the cumulative heat of hydration that reflects the previous observation: compared to the clinker produced at 1450°C, more heat of the clinker produced at 1300°C was observed.

X-ray diffraction of hydration products

Figure 7c shows the hydration of the cement clinker after 1 day. The diffraction patterns of the cement clinkers

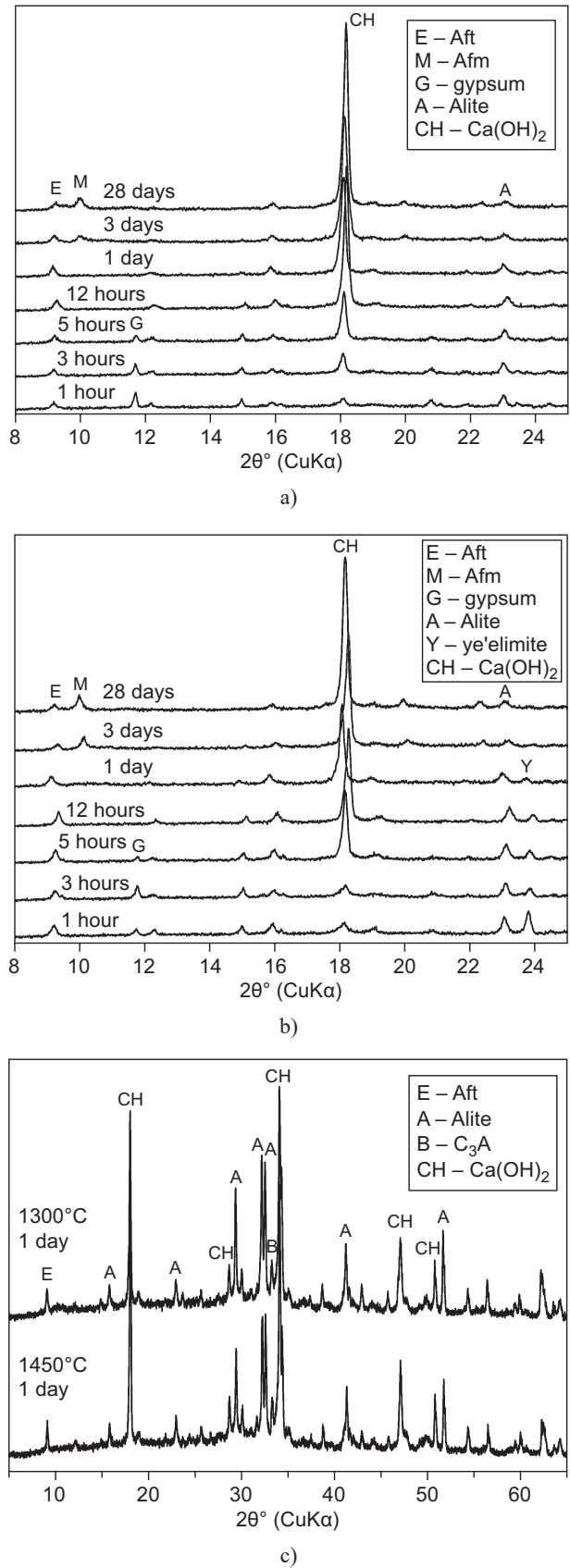


Figure 7. Observed diffraction patterns for hydrated clinker: a) clinker burned at 1450°C mixed with 5 % gypsum; b) clinker burned at 1300°C mixed with 5 % gypsum; c) hydration of cement clinker after 1 day.

were similar. The gypsum was consumed completely at 12 h, and AFm was found at 3 day, attributed to the lack of gypsum and the high IM (Figure 7a, b). In the sample with no ye'elinite (Figure 7a), ettringite and portlandite were the main crystalline products found by XRD at the early stages, regardless of the curing method. Over time, AFt phases increased in these samples (at 3, 5, 12 h and 1 d). After 1 day, the ettringite peaks weakened, while the AFm phases (monosulfoaluminate) appeared and became stronger at 28 days. The clinker phases were consumed at different rates, with alite, aluminate and ferrite reacting more quickly than belite. Compared to the sample without the ye'elinite, the hydration rate of the ye'elinite phase was greater than that of the aluminate phase. In one type of behavior, the ye'elinite peaks weaken at 24 h and ultimately disappear after 3 days (Figure 7b).

Mercury intrusion

According to previous research [18-21], mercury intrusion porosimetry plots do not represent the actual distribution of pore size in the hydration of cement. Large internal pores mostly open only to smaller pores communicating with the outside. They do not fill until the higher pressures that are needed for the mercury penetration into the smaller pores are reached. Therefore, almost all of the volume at larger pressures is mistakenly allocated to the size of the smaller ones. Moreover, the measured intrudable porosity does not coincide with the total porosity because, in addition to the pore space actually intruded by mercury, finer pores are present in cement pastes that require a pressure value for entry higher than the maximum available pressure of the commercial instrumentation. A few isolated pores that

are entirely sealed against intrusion may exist as well. In this investigation, the pore diameter and the total volume of intruded mercury can be taken as useful indicators of the processes of space filling and pore refinement.

Figure 8 shows the intruded Hg volume vs. pore diameter for cement pastes cured at various ages. Figure 8b, d showed that the pore size distribution of the pastes in mortar have the different shape between the clinker produced at the 1450°C and 1300°C. The lower total porosity of the cement paste produced at the 1300°C was contributed to the hydration of ye'elinite. The addition of gypsum substantially retarded reaction of the C_3A , this has been attributed to the protective action of a layer of ettringite. But the gypsum had no effect to the hydration of ye'elinite. The pore size distribution of the cement paste which clinker produced at the 1450°C was bimodal, while it was unimodal which clinker produced at the 1300°C. It was noted that as the pastes cured, the character of the porosimetry curves changed. As the hydration proceeded, the hydration products grew into the pore space of the hardened cement pastes. The initially sharp peak became less dominant, and a second more rounded peak represented the smaller pore sizes. The increase of the curing time resulted in lower total porosity values and smaller threshold pore widths (Figure 8a,c,e). Figure 8f showed the pore size distribution of the paste had the same shape. The initial peak corresponds to intrusion into a material phase with a distinct network of larger pores, and the roundness of the peak corresponds to a wide distribution of pore size in this material. The pore sizes of the clinker produced at 1450°C were larger than that of the clinker burned at 1300°C after 1 day. After 28 days, the pore sizes of the clinker burned at 1450°C decreased more quickly than those of the clinker burned at 1300°C.

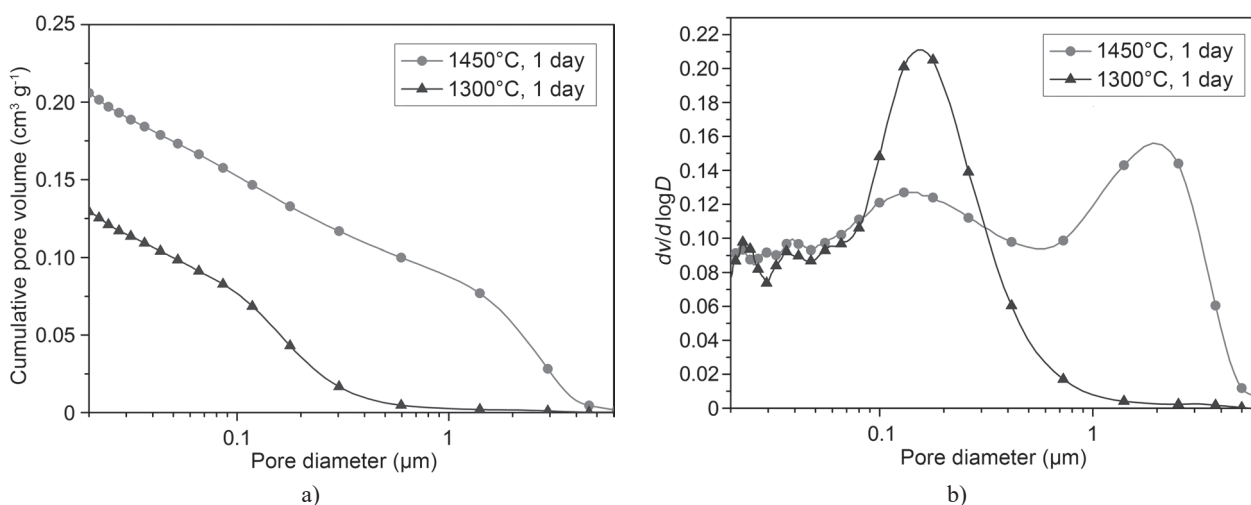


Figure 8. Intruded Hg volume vs. pore diameter for cement pastes cured at various ages: clinker (IM = 3.5) burned at 1450°C and 1300°C mixed with 5 % gypsum, cumulative plot (a, c, e); clinker (IM = 3.5) burned at 1450°C and 1300°C mixed with 5 % gypsum, derivative plot (b, d, f). *Continue on next page.*

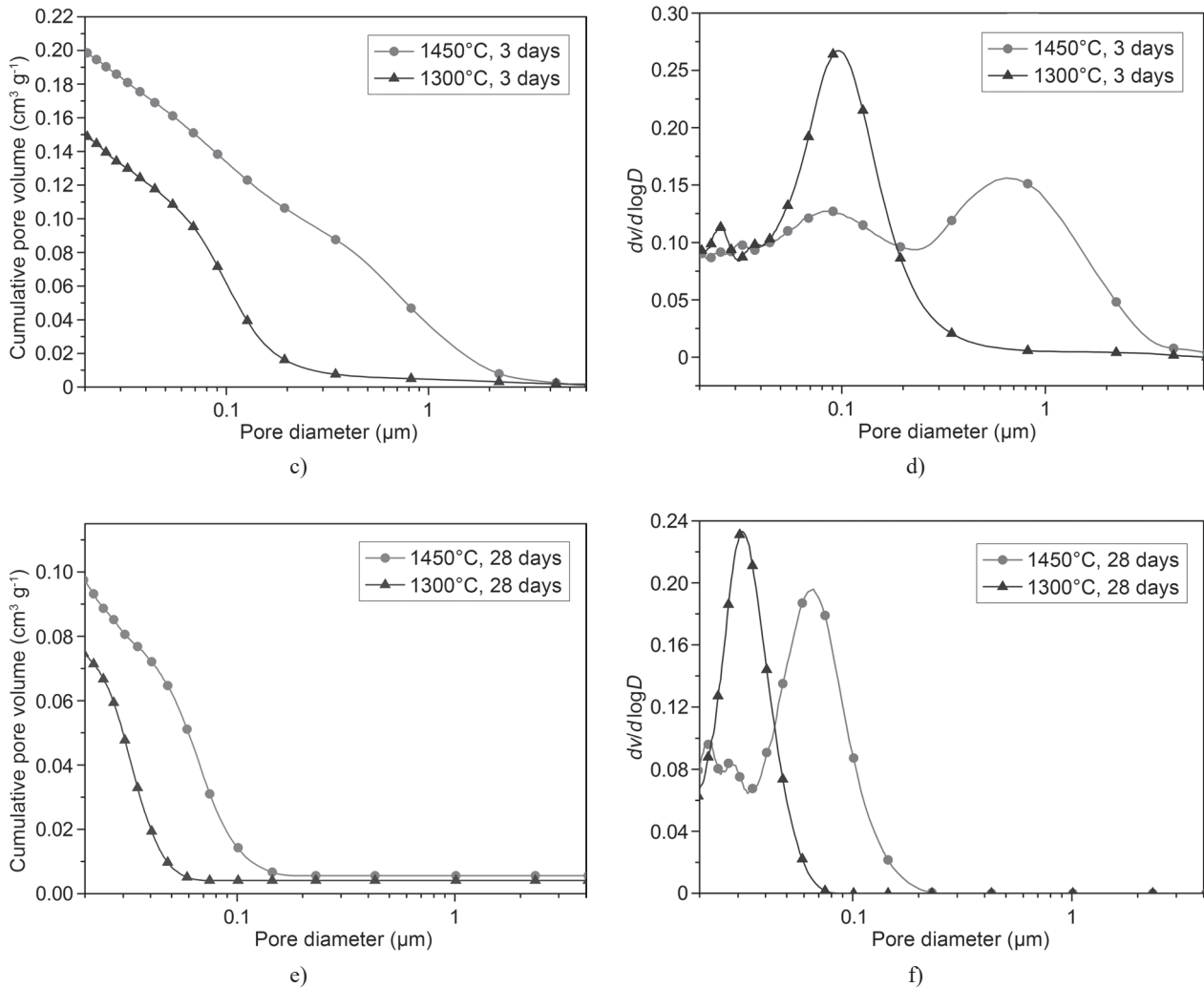


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CONCLUSIONS

The influence of industrial residue on the phase composition and formation of cement clinker under laboratory conditions was reported in this paper. Industrial residues (copper slag, phosphorus slag) have a distinctly positive effect on the alite crystal nucleation, and they stabilize alite by entering its structure. Ye'elinite formation is blocked by the IM and the temperature. IM changes the viscosity of clinker melt, while the Al content promotes the formation of ye'elinite. When the temperature is higher than 1300°C, ye'elinite is separated. The hydration rate of the ye'elinite was more rapid. The cumulative Hg volume and the pore threshold diameter of the alite-ye'elinite clinker decreased little as the curing time progressed from 3 days to 28 days. The compressive strength of the clinker was higher than that of ordinary Portland clinker at 1 and 3 days, but lower at 28 days.

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REFERENCES

1. Taylor F. W. (1990). *Cement Chemistry*, 2nd ed. Thomas Telford Publishing, London.
2. Janotka I, Krajčič L È. (2000): Resistance to freezing and thawing of mortar specimens made from sulfoaluminate—belite cement. *Bulletin of Materials Science*, 23(6), 521-527. doi:10.1007/BF02903894
3. Álvarez-Ayuso E., Querol X., Tomás A. (2006): Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products. *Chemosphere*, 65(11), 2009-2017. doi:10.1016/j.chemosphere.2006.06.070
4. Knox E G. (2008): Atmospheric pollutants and mortalities in English local authority areas. *Journal of Epidemiology & Community Health*, 62(5), 442-447. doi:10.1136/jech.2007.065862
5. Péra J, Ambroise J. (2004): New applications of calcium sulfoaluminate cement. *Cement & Concrete Research*, 34(4), 671-676. doi:10.1016/j.cemconres.2003.10.019
6. Zhang L, Glasser F P, Zhang L. (2002): Hydration of calcium sulfoaluminate cement at less than 24 h. *Advances in Cement Research*, 14(4), 141-155. doi: 10.1680/adcr.14.4.141.38914
7. Miller F. M., Tang F. J. (1996): The distribution of sulfur in present-day clinkers of variable sulfur content, *Cement & Concrete Research*, 26(6), 1821-1829. doi:10.1016/S0008-8846(96)00171-8
8. Zhang T., Shang S., Yin F., Aishah A., Salmial A., Ooi T.L (2001): Adsorptive Behavior of Surfactants on Surface of Portland Cement. *Cement & Concrete Research*, 31(7), 1009-1015. doi:10.1016/S0008-8846(01)00511-7
9. Kolovos K., loutsi P., Tsivilis S., Kakali G. (2001): The effect of foreign ions on the reactivity of the CaO–SiO₂–Al₂O₃–Fe₂O₃ system: Part I. Anions. *Cement & Concrete Research*, 31(3), 425-429. doi:10.1016/S0008-8846(00)00461-0
10. Raina K, Janakiraman L K. (1998): Use of mineralizer in black meal process for improved clinkerization and conservation of energy. *Cement & Concrete Research*, 28(28), 1093-1099. doi:10.1016/S0008-8846(98)00082-9
11. Tsuboi T., Ito T., Hokinoue Y., Matsuzaki Y. (1972): The effects of MgO, SO₃ and ZnO on the sintering of Portland cement clinker. *Zement-Kalk-Gips*, 25, 426–430.
12. Juenger M C G, Winnefeld F, Provis J L, Ideker J.H. (2011): Advances in alternative cementitious binders. *Cement & Concrete Research*, 41(12), 1232-1243. doi:10.1016/j.cemconres.2010.11.012
13. Ma Suhua, Shen Xiaodong, Zhong Baixi (2006): Influence of CuO on the formation and coexistence of 3CaO·SiO₂ and 3CaO·3Al₂O₃·CaSO₄ minerals, *Cement & Concrete Research*, 36 (9), 1784-1787. doi:10.1016/j.cemconres.2006.05.030
14. Shen X., Ma S., Li X., Chen L., Zhou W. Deng S. (2013): *Secondary synthetic method for calcium sulfoaluminate mineral in Portland cement clinker*; US8404039B2.
15. Odler I, Zhang H. (1996): Investigations on high SO₃ portland clinkers and cements I. Clinker synthesis and cement preparation. *Cement & Concrete Research*, 26(9), 1307-1313. doi:10.1016/0008-8846(96)00128-7
16. Zhang H, Odler I. (1996) Investigations on high SO₃ Portland clinkers and cements II. Properties of cements. *Cement & Concrete Research*, 26(9), 1315-1324. doi:10.1016/0008-8846(96)00129-9
17. Ma Suhua, Shen Xiaodong, Huang Yeping, Zhong Baixi. (2008): Preparation and formation mechanism of calcium sulfoaluminate. *Journal of the Chinese Ceramic Society*, 36(1), 78-81. doi:10.14062/j.issn.0454-5648.2008.01.005
18. Kolovos K, Tsivilis S, Kakali G. (2002): The effect of foreign ions on the reactivity of the CaO–SiO₂ –Al₂O₃ –Fe₂O₃ system: Part II: Cations. *Cement & Concrete Research*, 32(3):463–469. doi:10.1016/S0008-8846(01)00705-0
19. Keith Quillin, Geoff Osborne, Amal Majumdar, Bahadur Singh (2001): Effects of w/c ratio and curing conditions on strength development in BRECEM concretes. *Cement & Concrete Research*, 31(4), 627-632. doi:10.1016/S0008-8846(00)00494-4
20. Ellis Gartner. (2004): Industrially interesting approaches to “low-CO₂” cements. *Cement & Concrete Research*, 34(9), 1489-1498. doi: 10.1016/j.cemconres. 2004.01.021
21. Arjunan P, Silsbee M R, Roy D M. (1999): Sulfoaluminate-belite cement from low-calcium fly ash and sulfur-rich and other industrial by-products. *Cement & Concrete Research*, 29(8), 1305-1311. doi:10.1016/S0008-8846(99)00072-1
22. Li H, Agrawal D K, Cheng J. (2001): Microwave sintering of sulfoaluminate cement with utility wastes. *Cement & Concrete Research*, 31(9), 1257-1261. doi:10.1016/S0008-8846(01)00579-8