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Industrial trial production of low energy belite cement

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Abstract

The Portland cement industry consumes large amounts of energy and produces huge quantities of carbon dioxide, which contribute to global warming, the so-called "Greenhouse Effect". Industrial trials are reported for the production of belite cements (≈3000 t) at lower temperatures and with lower lime saturation factors than for ordinary Portland cement. Belite cements with reasonably good properties have been made on an industrial scale from limestone, burnt clay, volcanic ash, pyrite ash and gypsum. A rapid rate of cooling improves the hydraulic activity, and also the physical–mechanical properties by stabilising reactive forms of belite. Such low energy cements provide a cheap alternative to Portland cement with properties that are acceptable for many applications and the additional benefit of possible improved durability.

Keywords: Low energy cement; Belite cement; Klein's compound; Low lime saturation factor cement; Reactive Belite Cement

1. Introduction

The Portland cement industry is known to be a consumer of large amounts of energy because it involves the sintering of raw feed at about 1450 °C followed by grinding the clinker with addition of 3–5% gypsum. The most energy consuming stage in the cement industry is the clinkering process that takes 60% of the total energy involved. The calcining process for the $CaCO_3$ component of the raw feed absorbs a large amount of the heat (≈1350 kJ/kg clinker). The net heat balance for ordinary Portland cement clinker (OPC) manufacture has been calculated to be 1674–1799 kJ/kg clinker for different raw mixes by various authors [1–3]. The heat required in practice (3100–3600 kJ/kg) is considerably greater than the theoretical value, on account of the heat lost in the stack with exit gases and from the hot clinker discharged from the cooler, as well as radiation–convection losses from the kiln.

One approach to the reduction in energy consumption in the production of cements is to reduce the lime saturation factor (LSF) of the raw feed. The substitution of a high lime by a low lime cement should lead to energy saving and also to a reduction of CO_2 emission from the decarbonation of the limestone. A reduction in LSF leads automatically to an increase in belite content and a decrease in alite content [3,4], with the added benefit that formation of C_2S (65.1% CaO) occurs at lower temperature than the formation of C_3S (73.7% CaO). When the LSF is reduced to 75%, a virtually alite-free clinker is formed.

The depletion in the $CaCO_3$ content reduces the energy demand by 15–20% for a Lime Saturation Factor of 80–85% and allows satisfactory clinker formation at lower temperatures by 100–150 °C. Substitution of some natural raw materials by suitable waste materials also leads to decrease in the energy demand. To produce a low energy cement with adequate strength development and LSF below 85%, belite must be formed with improved reactivity [3,4]. Dicalcium silicate (C_2S) exists in several polymorphic forms that are stable in different temperature ranges.

Stabilisation of the active forms of dicalcium silicate (α' and β-C_2S) in the belite clinkers can be realised by very quick cooling, at least 500 °C/min in the range 1300–700 °C, or by inclusion of an appropriate mineraliser.

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To compensate for the lower reactivity of belite compared with alite, there is considerable current interest in the benefit to be obtained by the incorporation of Klein's compound, $4CaO \cdot 3Al_2O_3 \cdot SO_3$, in low energy cement clinkers, as successfully carried out in China. These cements are often collectively referred to as calcium sulfoaluminate cement [4], but there are large differences in the amount of Klein's compound contained in them. Those reported in this paper have only low contents of Klein's compound.

Two industrial trials are reported in an effort to produce a reactive belite cement that could be made commercially. The objectives were to avoid increased costs and to remain close to normal conditions of production.

2. Industrial trial

An industrial experiment was carried out in the Câmpulung plant of CIMUS in Romania to obtain belite-rich Portland cements using raw materials from the surrounding area. The oxide compositions of the selected raw materials are shown in Table 1.

The limestone had calcite as its principal component (above 92%). The siliceous material was burnt waste coal-clay and represents the residue from the burning of coal with clay inclusions from the mining industry. This burning is, in fact, a natural process, resulting in a clay containing 35% content of metakaolinite. Its use is advantageous during clinkering, because many energy consuming reactions had already occurred.

Gypsum (5–7%) was introduced in the raw feed as a mineraliser. Pyrite ash was added in small amounts to increase the Fe_2O_3 content of the raw mix. It is a waste product resulting from sulfuric acid manufacture by burning pyrite.

Three cement clinkers have been made from combinations of these raw materials:

- one corresponding to the normal Portland cement that is usually fabricated in Câmpulung, Romania;
- a second corresponding to a high ferro-belite cement;
- a third corresponding to a sulphoferroaluminate-belite cement.

It was necessary to use a narrow particle size distribution of the raw meal, because of the tendency to increase dust loss by entrainment in the exhaust gas. The coarse particles also had to be controlled and these were kept below 100 μm with no more than 1% in the range 100–150 μm, to ensure good burnability and to avoid excessive fuel consumption.

The fineness of the raw meal has been investigated using laser granulometry and grinding was continued to obtain a minimum 7500 ± 50 cm^2/g Blaine specific surface area. The grinding was carried out in a closed system, using a single cell mill with a static separator. The fineness was adjusted by dampers and gas flow in the circuit, and was evaluated by residue at 90 μm sieve, as normally used in the cement industry.

The burnability of the raw meal was tested in the laboratory using the free lime method [5]. The result showed a good preparation and homogenisation of the raw meal to improve the decarbonation in the kiln preheater and to confer a good burnability at the lowest possible temperature.

The raw materials were burnt in a dry process clinker installation, equipped with a 4-stage cyclone suspension heat exchanger and 2 grate plate coolers. An industrial scale rotary kiln was used with a production capacity of 3000 t per day. The sintering temperatures were 1260–1330 °C for high ferro-belite clinker (HFBC) and sulphoferroaluminate-belite clinker (SFAB) and 1420 °C for OPC.

The burning zone temperature was measured using an infrared technique and was stabilised adjusting the oil fuel rate ID fan speed (damper action), the raw meal feed and speed of kiln rotation (rmp). The kiln was operated to the limit of the ID fan. The oxygen level was corrected by reducing both fuel and feed. The fuel oil in all cases was preheated at 125 °C.

The cooling process was monitored using an infrared technique. The industrial installation for clinker cooling consisted of two-inclined grate coolers, 16 m long and

Table 1
Chemical analysis of the raw materials

No.	Characteristic	Content (%)			
		Limestone	Siliceous material	Gypsum	Pyrite ash
1	SiO_2	3.99	52.19	3.05	12.32
2	Al_2O_3	1.05	21.59	1.07	3.24
3	Fe_2O_3	0.74	7.58	0.47	67.27
4	CaO	52.19	4.89	32.77	0.68
5	MgO	0.41	3.21	1.01	2.85
6	SO_3	0.14	0.05	43.16	1.98
7	Na_2O	0.24	1.16	0.22	0.23
8	K_2O	0.23	2.14	1.80	0.47
9	TiO_2	0.11	0.41	–	–
10	Loss on ignition	40.90	6.78	16.02	10.94

2.45 m wide and some fans for compressed air. The clinker was transported on the grates with approximately 0.5 m/s and the air was passed through the clinker layer. In this way some of the heat from the clinker was recovered by the air, which was subsequently used in the firing process. The more the clinker is cooled, the higher is the temperature of the air exit. Thus the efficiency of the cooler is dependent on the total heat recovered from the clinker.

3. Results

Nearly 3000 tonnes of each of three types of clinkers were produced. The first was OPC, to act as a control for comparison purposes. The second clinker (HFBC) had high contents of belite and brownmillerite, while the third (SFAB) incorporated sulphate ions.

The chemical composition of the clinkers obtained and their mineralogical composition (Bogue computation) are presented in Table 2. Also, in brackets, are the actual mineral contents determined by X-ray diffraction and chemical analysis. Some differences are to be expected because of the limitations of the Bogue computation and the failure to reach equilibrium in the clinkering process, especially that carried out at ca.1300 °C.

There was a notable increase in the belite content, and an accompanying decrease in the alite content, in the sequence OPC, HFBC, SFAB. The content of brownmillerite also increased in the same sequence, whereas C_3A was only present in the OPC. Klein's compound, $3CaAl_2O_4 \cdot CaSO_4$, was present in the SFAB cement, but in only a small amount in HFBC (see Fig. 1).

Table 2
Chemical analysis and mineralogical composition of the clinkers

Oxide (%)	Type of clinker		
	OPC	HFBC	SFAB
Chemical analysis			
CaO	67.30	62.04	56.77
SiO_2	19.54	23.59	27.14
Al_2O_3	8.19	4.84	5.67
Fe_2O_3	3.94	7.54	8.73
SO_3	–	–	1.45
Other	1.03	1.99	0.24
Mineral, %	OPC	HBC	SFAB
Mineralogical composition			
C_3S	65[a] (67)[b]	30 (25)	– (7)
C_2S	7 (13)	45 (43)	61 (52)
C_3A	15 (11)	–	–
C_4AF	12 (7)	23 (18)	26.5 (23)
$C_4A_3\overline{S}$	–	Trace	11 (13)
Other	1	2	1.5

[a] From Bogue analysis.
[b] From X-ray and chemical analysis.

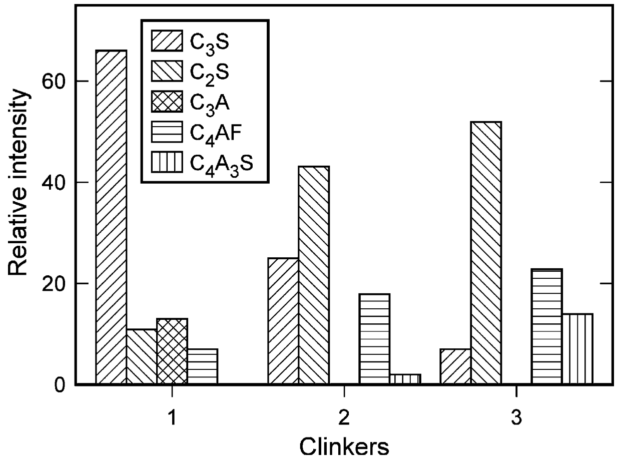

Fig. 1. Relative intensity of C_3S (2.78 Å), C_2S (2.60 Å), C_3A (2.70 Å), C_4AF (2.63 Å) and $C_4A_3\overline{S}$ (3.76 Å) in clinkers: 1-OPC; 2-HFBC; 3-SFAB.

The principal characteristics of the clinkering process for each type of clinker are shown in Table 3. In the presence of a high quantity of iron oxide and/or a small amount of sulphate ions, the clinkering temperature was modified and it became 120–160 °C lower compared with that of normal Portland cement clinker. The production of high ferro-belite clinker and sulphoferro-aluminate belite clinker saved around 500–540 kJ/kg compared with ordinary Portland clinker produced in the same plant. The total quantity of each type of cement produced was similar (2750–2800 t).

The granulometric distribution and the average dimensions of the clinkers differed as a function of their composition, as is shown in Table 4. Generally, the belite clinkers, even in the presence of a high iron oxide content, had smaller dimension particles than those in ordinary Portland clinker. A higher content of iron oxide in the raw meal led to a higher proportion of melting during the clinkering process, but the presence of a small amount of sulphate had a favourable influence on the granulometric distribution of the clinker, as indicated by the data for SFAB clinker in Table 4.

The clinkers obtained after cooling were stored for two days in a silo and then ground in an industrial closed mill circuit, in the presence of 5% gypsum. Only SFAB clinker was ground without gypsum. No special problems were detected during the grinding process, but a slow reduction in the grindability of HFBC clinker was noted. This clinker had a high content of brownmillerite, which has a low grindability, but the presence of Klein's compound, $C_4A_3\overline{S}$, in SFAB clinker had a positive influence on the grindability. The milling time needed to obtain the same Blaine specific surface area (310–320 m^2/kg Blaine specific surface) decreased in sequence:

HFBC (100%) > OPC (98%) > SFAB (72%)

Table 3
The clinkering characteristics

Type of clinker	Calorific power of fuel oil, kJ/kg	Clinkering temperature °C	Specific heat consumption kJ/kg	Tempertaure of exhaust gases °C	Consumption of fuel oil *l*/*h*
OPC	38911	1420	3845	357	3550
HFBC	37477	1300	3342	350	3400
SFAB	36819	1260	3305	347	3350

Table 4
Granulometric distribution of the clinkers

Particle size (mm)	% of granulometric fraction in clinker		
	SFAB	OPC	HFBC
0–2	18	2	3
2–3	20	2	5
3–5	30	3	6
5–7	20	13	15
7–10	9	21	21
10–15	3	17	20
15–20	0	19	16
20–30	0	15	10
30–40	0	8	4
40–50	0	0	0
Average (mm)	4.22	14.76	12.28

The characteristic properties of the resulting cements are presented in Table 5. The cement properties depend, as expected, on their mineral composition. Thus, the normal consistency water demand was higher for the sulphoferroaluminate-belite cement, but lower for the ferroaluminate-belite cement, in comparison with that required for the OPC.

Although both low energy cements had setting times (Table 5) slightly longer than that of the ordinary Portland cement, the setting time of all three cements was acceptable for use in the construction industry. All the cements obtained had good dimensional stability, only the sulphoferroaluminate-belite cement exhibited a small expansion, about 0.15%, after 28 days of hardening. The high ferroaluminate-belite cement had the best stability, showing no change in volume after 28 days of hardening.

The compressive strength development of the cements, based on mortar prisms (40 × 40 × 160 mm) made from the three cements, is shown in Fig. 2 and indicates the very good behaviour of the SFAB and HFBC cements, particularly beyond 90 days hydration, when compared with OPC. These cements with an LSF ≈ 85 show a lower rate of increase in compressive strength only during the initial period of hardening, from 2 to 7 days. They have an acceptable compressive strength after 28 days and excellent strength after one year. Thus, after 28 days the following compresive strengths were obtained: OPC = 43.7 MPa, SFAB 35.6 MPa, and HFBC 34.2 MPa.

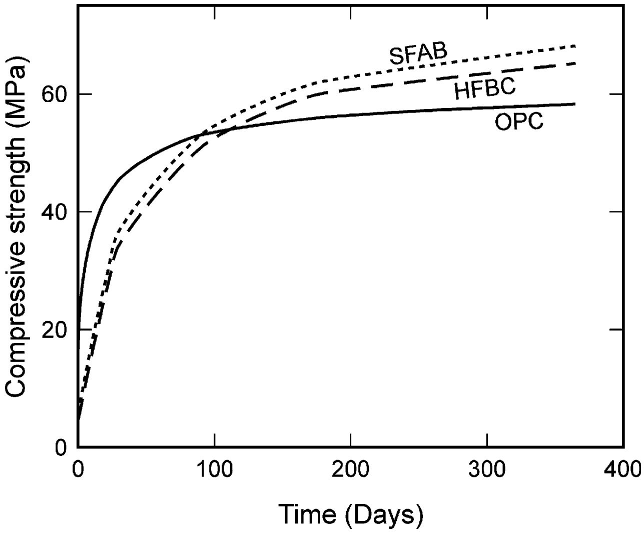

Fig. 2. Development of compressive strength of OPC, HFBC and SFAB cements.

The compressive strength development and other characteristics of the belite cements demonstrate the possibility of using these types of cement as Cement Class 32.5 according to the European Standard ENV 197-1, or to be blended with Portland cement, for Cement Class 42.5, in order to accelerate the initial rate of hydration. They have the potential to become useful alternatives to normal Portland cement for a wide range of applications, although the effect of the inevitable variability in composition of the waste raw materials

Table 5
Characteristic properties of the cements

Cement type	Specific surface area (m²/kg)	Normal consistency water (%)	Setting time (min)		Expansion after 1–28 days (%)
			Initial	Final	
OPC	315	28	120	185	0–0.03
HFBC	320	26	200	210	0
SFAB	310	30	135	195	0.10–0.15

on the resulting cement properties would need to be assessed.

4. Conclusions

- Industrial trials regarding the manufacture of belite cements show that there can be advantages in producing this kind of cement. The energy consumed during production of the clinkers was 500–540 kJ/kg clinker less than that consumed in producing the OPC usually made in the plant.
- Compared with the production of normal Portland cement, less limestone was consumed and less CO_2 evolved. The other raw materials were cheap waste products.
- The high quantities of Fe_2O_3 and SO_3 in the raw mixtures reduced the burning temperature to 1260–1300 °C without significant modification (except initially) of the mechanical properties in comparison with OPC. At longer hardening periods, after 90 days, the compressive strength of the belite cements was greater than that of OPC.
- The early hydration of the belite cements was somewhat slower than that of OPC. Blending these cements with OPC may produce a composite cement suitable for use for all purposes as a normal cement.
- The belite cements obtained can be used as Cement Class 32.5 according to ENV 197-1, or can be blended with OPC, for Cement Class 42.5, in order to accelerate the initial rate of hydration.

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