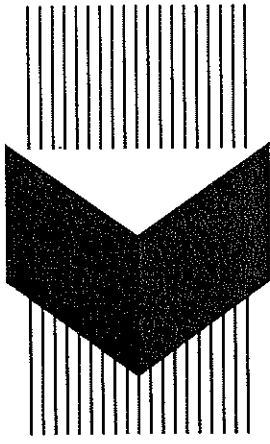


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INFLUENCE OF THE SULPHATE LEVEL IN THE CLINKER PHASE ON RHEOLOGICAL AND MECHANICAL BEHAVIOUR OF SUPERPLASTICISED READY-MIXED CONCRETES

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ABSTRACT

Portland cement contains sulphur compounds from the clinker phase and from added calcium sulphate (set regulator). The purpose of this investigation was to study the influence of the sulphate content in the clinker phase on the performance of superplasticised concretes in terms of initial slump, slump-loss, and compressive strength.

Two batches of clinker from the same kiln source were studied, the main difference being the content of SO_3 (0.72% and 1.40% respectively). Different percentages of gypsum were interground in a laboratory mill to manufacture Portland cements. Three levels of total sulphate content in terms of SO_3 were set: 3.0%, 3.5% and 4.0%.

At a given sulphate content in Portland cement, the lower the clinker sulphate content, the more effective is the slump increase caused by the superplasticizer. Moreover, the lower is the clinker sulphate content, the lower is the slump-loss rate. Finally, at a given water/cement, there is a reduction in the compressive strength at early ages when the low sulphate clinker is used to manufacture Portland cements.

Keywords: Clinker sulphate content, Compressive strength, Gypsum, Slump, Slump-loss, Superplasticizer.

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1. INTRODUCTION

Portland cement contains a mixture of sulphur compounds from the cement clinker and from added calcium sulphate (e.g. gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which acts as set regulator. The sulphates from different sulphur sources have different water-solubility kinetics: sulphate from the gypsum dissolves sufficiently fast to participate in the regulation of the setting of the cement, whereas sulphate from the clinker phase is usually unavailable for the setting regulation (1). Therefore, cements with the same *total* sulphate content, but with different proportions of sulphate from the clinker phase and that from the gypsum source, may perform in different ways.

In many present-day clinker kilns there are poly-functional burning systems which are capable of using either gaseous or liquid hydrocarbons, as well as solid small-particle coals, depending on the cheapest source of available fuels. The sulphur content of these different fuels can change and cause unwitting variations from one day to another of sulphate incorporated in the clinker phase. Moreover, the clinker sulphate content may increase with the use of high-sulphur organic residues - such as tires - burned in cement kilns to destroy environmentally harmful products in a safe and cost-effective way.

According to Hime (2) present-day cements, produced in kilns that burn sulphur-rich fuels or waste materials, can incorporate large amounts of sulphates, up to 3% by clinker mass. When high sulphate levels are not balanced by a high alkali content, the excessive SO_3 may occur as CaSO_4 or react with calcium aluminates or even occur as interstitial impurity in the alite and belite phases. According to Hime (2) all these forms of sulphate in the clinker phase are slowly soluble in the mixing water and, therefore, they can act as late sulphate release which is essential for the delayed ettringite formation (DEF)-related damage (2, 3). However, the DEF-induced damage is not the point of the present paper.

The purpose of this work was to study the influence of the sulphate content in the clinker phase on the performance of superplasticized concrete mixtures in terms of initial slump level at a given water-cement ratio (w/c), slump-loss rate, and compressive strength at early and later ages. In other words it was assumed that the erratic behaviour of superplasticized concretes which occurs under certain circumstances, even by using cements from the same source and in particular characterised by the same *total* sulphate content, could be related to an unwitting change in the sulphate content of the clinker phase.

2. MATERIALS AND METHODS

2.1 Materials

Two batches (*A* and *B*) of clinker coming from the same kiln source were examined, the main difference being the type of fuel used. The sulphate content of the clinker *A* (0.72%) was 50% of that in clinker *B* (1.40%). Table 1 shows the chemical composition of clinker *A* and *B*.

Natural gypsum, with about 81% of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, was used as set regulator. The chemical and mineralogical analyses of this material are shown in Table 1.

Different percentages of the natural gypsum were interground in a laboratory mill with clinker *A* or *B* in order to manufacture Portland cements - all at a Blaine fineness of $380 \text{ m}^2/\text{kg}$ - with

three levels of total sulphate content. According to the European norm (ENV 197/1), the maximum sulphate content in Portland cements is 3.5% or 4.0% for ordinary (32.5 and 42.5 MPa) or high-strength (52.5 MPa) level respectively. Typical sulphate contents in commercial Portland cements are in the range of 3-4%. Table 2 shows the composition of Portland cements A_1 , A_2 , A_3 from clinker A, and Portland cements B_1 , B_2 , B_3 from clinker B. The total SO_3 content was: 3.0% in Portland cement A_1 and B_1 ; 3.5% in Portland cements A_2 and B_2 ; and 4.0% in Portland cements A_3 and B_3 . Due to the lower sulphate level in the clinker A, a higher amount of gypsum was required, for a given total sulphate level, in manufacturing Portland cements A_1 , A_2 and A_3 with respect to Portland cements B_1 , B_2 and B_3 respectively.

Table 1 - Chemical and mineralogical composition of clinkers and natural gypsum added as set regulator.

Chemical Composition: (%)	Clinker A	Clinker B	Natural gypsum
SiO ₂	22.49	22.36	2.01
Al ₂ O ₃	5.05	5.13	0.68
Fe ₂ O ₃	2.24	2.07	0.28
CaO	65.47	65.21	34.05
MgO	1.93	1.80	0.72
SO ₃	0.72	1.40	37.63
K ₂ O	0.95	0.86	0.18
Na ₂ O	0.07	0.11	0.05
l.o.i	0.47	0.43	23.18
Mineralogical Composition: (%)	Clinker A	Clinker B	Natural gypsum
C ₃ S*	53.6	53.3	-
C ₂ S*	25.2	25.1	-
C ₃ A*	9.6	10.1	-
C ₄ AF*	6.8	6.3	-
CaSO ₄ ·2H ₂ O**	-	-	80.9
CaCO ₃ **	-	-	14.1

* By Bogue calculation

** By thermogravimetric analysis

Table 2 - Composition of Portland cements from clinker A and B sources.

Portland cement	Clinker A	Clinker B	Natural gypsum	SO ₃ from clinker	SO ₃ from gypsum	Total SO ₃
A ₁	93.95	-	6.05	0.676	2.324	3.00
A ₂	92.62	-	7.38	0.669	2.831	3.50
A ₃	91.28	-	8.72	0.657	3.343	4.00
B ₁	-	95.75	4.25	1.341	1.659	3.00
B ₂	-	94.42	5.58	1.322	2.178	3.50
B ₃	-	93.09	6.91	1.303	2.697	4.00

Concrete mixtures with and without superplasticisers were manufactured all at $w/c = 0.45$. The following concrete composition was adopted:

- Portland cement	455 kg/m ³
- natural sand (0-4 mm) with F.M. of 2.6	1005 kg/m ³
- natural gravel (4-9 mm)	670 kg/m ³
- water	205 kg/m ³

Acrylic polymer (*AP*) based admixture, as well as sulphonated naphthalene- and sulphonated melamine-based admixtures were used as superplasticisers. The influence of the clinker type (*A* or *B*) on the performance of superplasticised concretes containing naphthalene- or melamine-based admixtures was similar to that recorded for the *AP*-based superplasticiser. Therefore, for the sake of brevity, only the results concerning the plain mixtures and those with the *AP*- based superplasticizer will be examined in the present paper. Details on the *AP*-based admixture can be found in other papers (4, 5). The dosage rate of the *AP*-based admixture - 30% aqueous solution - was 0.8% by cement mass so that the initial slump level, which was in the range of 40-110 mm for the plain mixtures, was in the range of 170-250 mm for the superplasticised concrete mixtures.

2.2 Methods

Measurements of the initial slump were carried out after mixing and then later at 20, 40, and 60 min to determine the slump-loss characteristics. Concrete mixtures were placed into cubic forms (100 mm) compacted by vibration, and cured at 20°C and 95% R.H. Compressive strength was measured 1, 3, 7, and 28 days.

X-ray diffraction (XRD) analysis on the corresponding cement paste specimens ($w/c = 0.45$) was carried out at different curing times from 6 hours to 28 days at 20°C and 95% R.H.

3. RESULTS

Figure 1 shows the initial slump level and the slump-loss rate for plain and superplasticised concretes with different Portland cements. For the same cement sulphate content, lower clinker sulphate contents produced higher initial slump levels and lower subsequent slump-loss, whether or not the superplasticizer was present. For instance, with 3.0% cement sulphate content, the initial slump of the concretes with cement A_1 were 95 mm or 225 mm for plain or superplasticised mixture respectively, whereas the corresponding values of the concretes with cement B_1 were 35 mm and 165 mm. The average slump loss was 60 mm/hr in the superplasticised mixture with cement A_1 and 90 mm/hr in the corresponding concrete with cement B_1 .

By increasing the cement sulphate content from 3% (A_1 and B_1 cements) to 4% (A_3 and B_3 cements) there was an increase in the initial slump level and a reduction in the slump-loss rate. However, this beneficial effect was more remarkable in the concretes with higher clinker sulphate (clinker *B*). Therefore, the increase in the addition of natural gypsum reduced the difference in the slump characteristics between concretes with different sulphate clinker sources. For instance, the difference in the initial slump level between concretes with cement A_3 and B_3 , was only 20 mm in both plain and superplasticised mixtures.

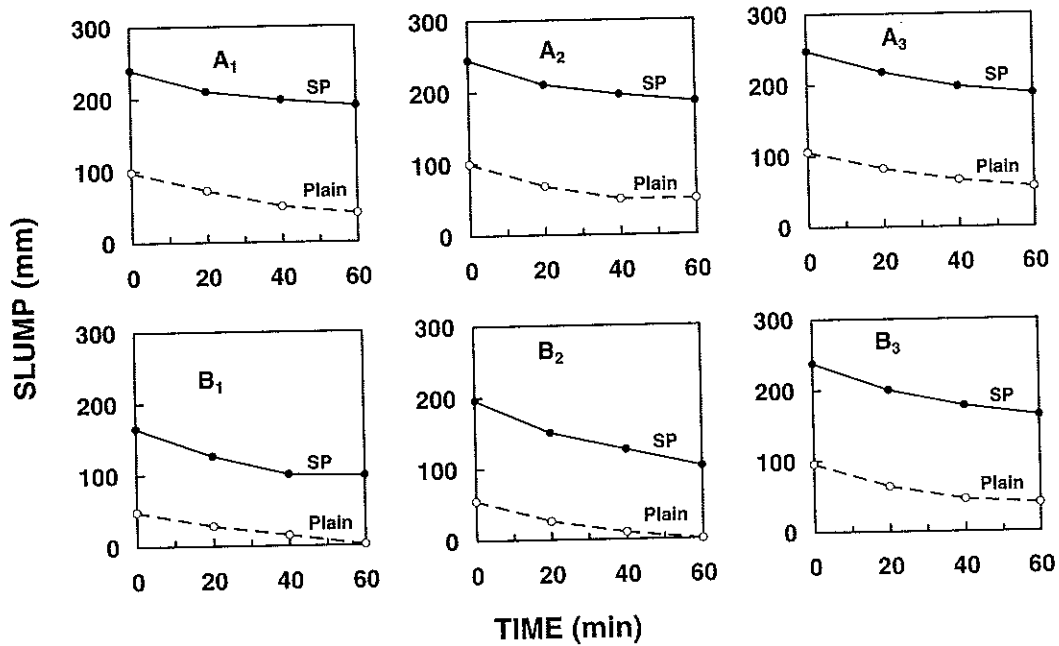


Figure 1 - Slump as a function of time for plain and superplasticised (SP) concrete mixtures.

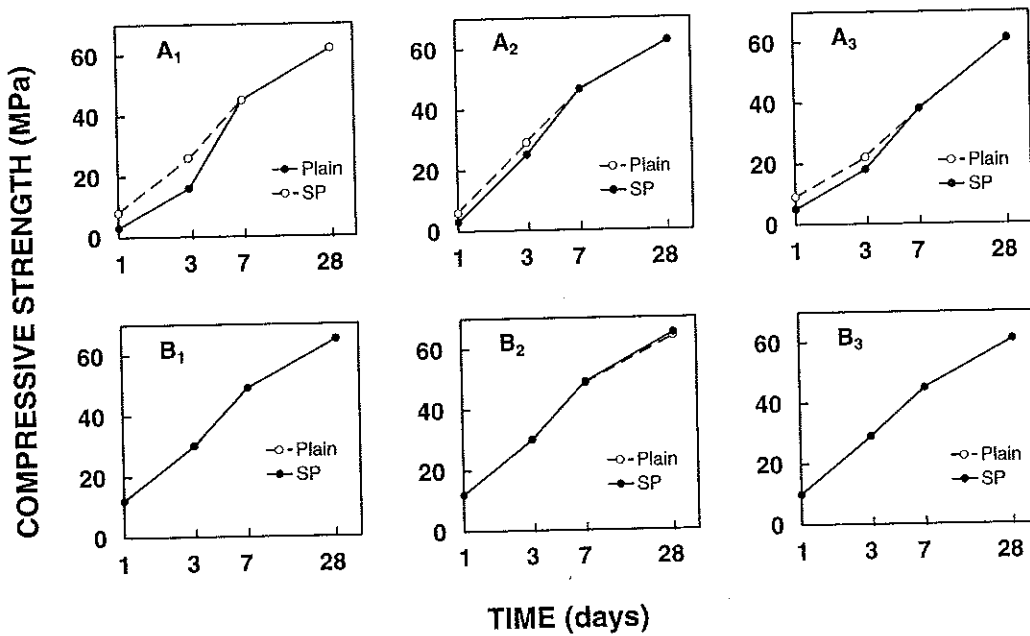


Figure 2 - Compressive strength as a function of curing time.

Figure 2 shows the compressive strength of plain and superplasticised concrete mixtures with different Portland cements. With the clinker at lower sulphate content (0.72%), the early compressive strength (1-3 days) of superplasticised concretes was lower with respect to the plain mixtures (cements A₁, A₂, and A₃). The difference in strength between plain and

superplasticised concretes was completely cancelled at 7 days and later ages. This retarding effect, caused by the superplasticizer at early ages, was absent in concretes with Portland cement from clinker *B* ($\text{SO}_3 = 1.40\%$). So, it seems that the retarding effect in the early compressive strength is related to the higher effectiveness of the superplasticizer in terms of higher increase in the initial slump and lower slump-loss rate.

Figures 3 and 4 show the XRD-peaks of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), ettringite ($\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) and tricalcium silicate (C_3S) as a function of the hydration time in paste specimens ($w/c = 0.45$) with cements from clinker *A* and *B* respectively.

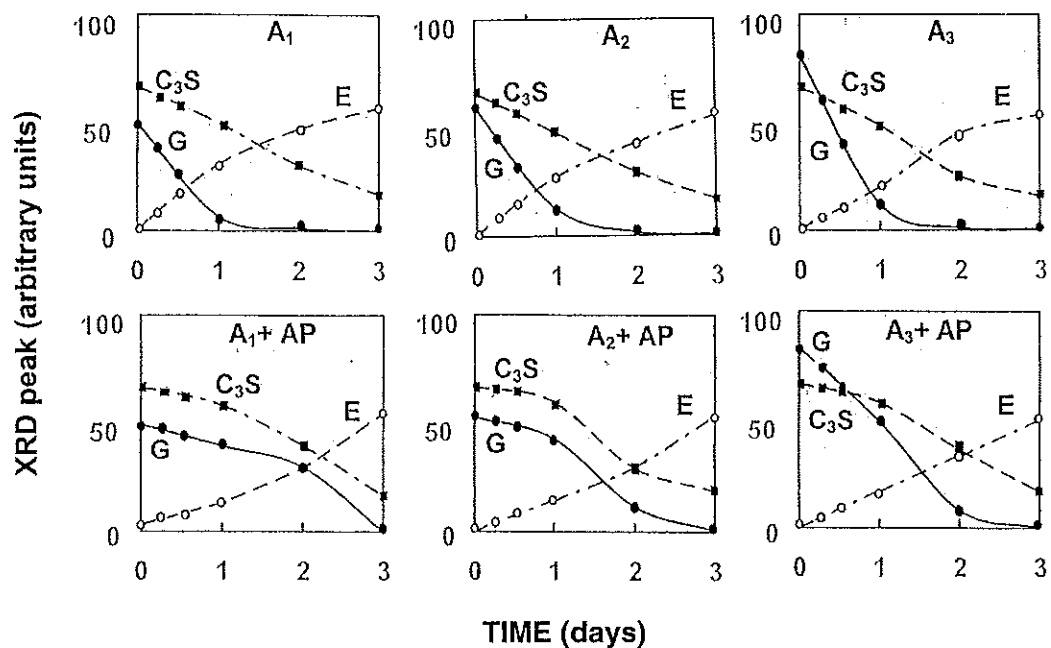


Figure 3 - XRD peaks of gypsum (G), ettringite (E), and tricalcium silicate (C_3S) as a function of hydration time for paste specimens with cements A_1 , A_2 , and A_3 without and with the AP-based superplasticizer.

When Portland cements A_1 , A_2 and A_3 were used - all from the clinker phase *A* with a lower sulphate content (0.72%) - the superplasticizer addition caused an early retardation on the gypsum consumption and the ettringite formation, as well as on the C_3S hydration (Fig. 3). For instance, with cement A_1 the consumption of gypsum was completed in less than 1 day in the plain cement paste, whereas it took about 3 days in the superplasticised corresponding sample. A similar trend was recorded with cements A_2 and A_3 , although the retarding effect on the consumption of gypsum, the formation of ettringite, and the hydration of C_3S was mitigated by the increase in the amount of gypsum added as set regulator. When Portland cements B_1 , B_2 and B_3 were used - all from the clinker phase *B* with the higher sulphate content (1.40%) - the retarding effect caused by the superplasticizer was negligible or absent (Fig. 4).

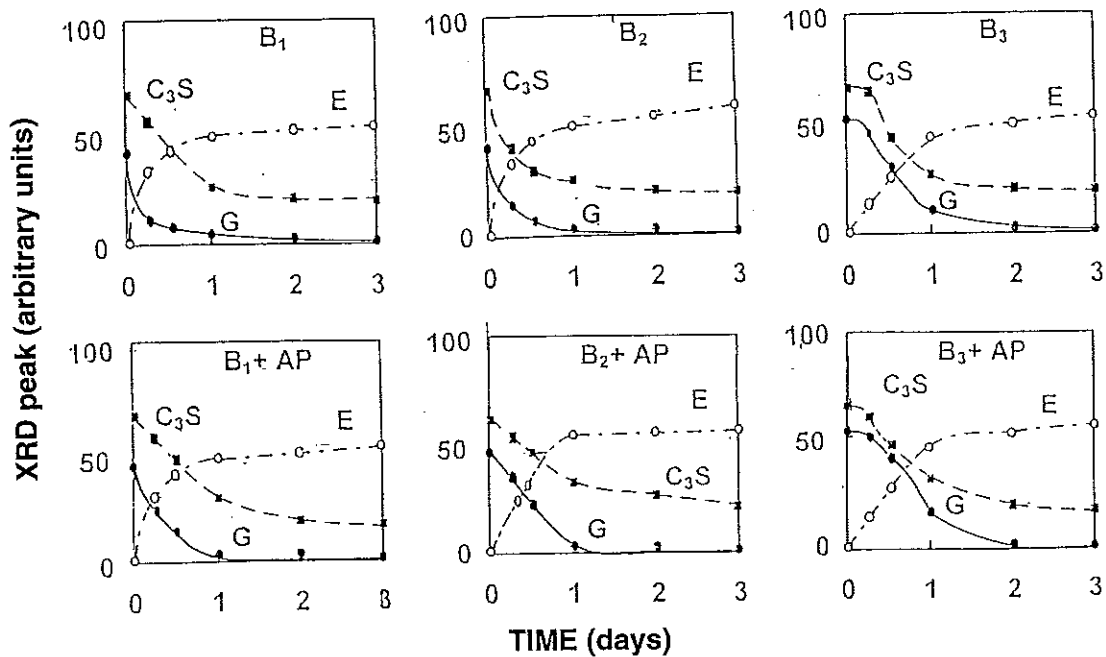


Figure 4 -XRD peaks of gypsum (G), ettringite (E), and tricalcium silicate (C_3S) as a function of hydration time for paste specimens with cements B_1 , B_2 , and B_3 without and with the AP-based superplasticizer.

It seems that the above XRD data agree with the slump results since the reduction in the slump-loss rate caused by the superplasticizer occurred only when cements from the clinker phase A were used, but it did not occur with cements from the clinker phase B at higher sulphate content (Fig. 1). On the other hand, the retarding action caused by the superplasticizer on the hydration of cements A_1 , A_2 , and A_3 (Fig. 3) is related to the lower compressive strength at early ages of these cements (Fig.2).

4. CONCLUSIONS

The results of the present investigation relate to Portland cements from two clinker phases (A and B) with different sulphate content (0.72 and 1.40% respectively). The following conclusions appear to be relevant to these results:

1. At a given sulphate content in Portland cement, the lower the clinker sulphate content, the more effective is the slump increase of the concrete caused by the superplasticizer addition.
2. The slump-loss rate of the superplasticised concrete mixture is lower when Portland cements are used with a lower clinker sulphate content (0.72%).
3. At a given w/c, there is a reduction in the compressive strength at early ages (≤ 3 days), when low sulphate clinker (0.72%) is used to manufacture Portland cement.

4. Although it is not very clear what is the exact role played by the two different sulphate sources - from clinker and from gypsum addition - it seems that there is a reduction in the cement hydration rate which is, to a certain extent, related to both the lower slump-loss and the early strength retardation.
5. The different sulphate contents of the clinker phase affects not only the performance of the superplasticised concrete, but also that of the plain mixture in terms of initial slump level, slump-loss rate, and early compressive strength.
6. The higher amount of gypsum addition mitigates the effect of the sulphate content in the clinker phase both in plain mixtures and superplasticised concretes.

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