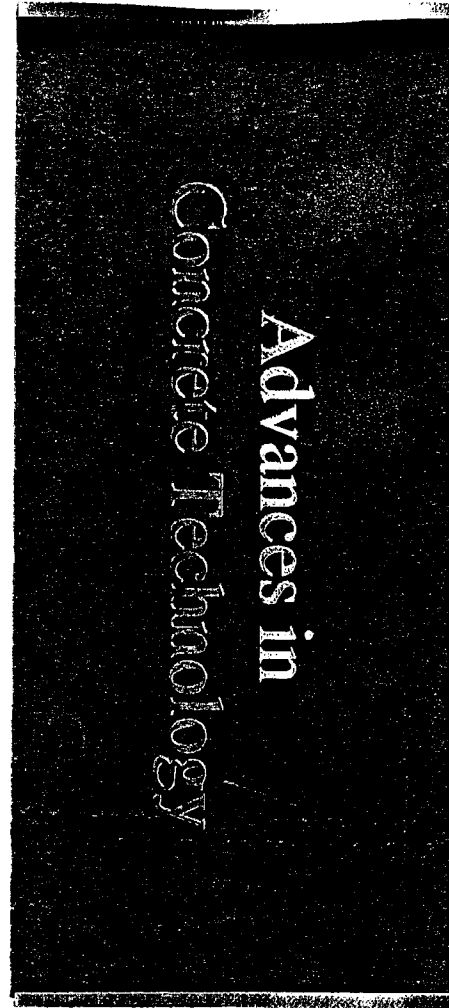


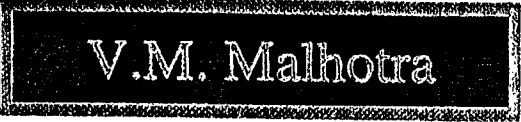
Malhotra



SP-179



international



international

Influence of the Sulfate Level in the Clinker Phase on the Performance of Superplasticized Concretes

by L. Coppola, R. Troli, P. Zaffaroni and
M. Collepardi

Synopsis: Portland cement contains sulfur compounds from the clinker phase and from added calcium sulfate (e.g. gypsum) which acts as a set regulator. The purpose of this investigation was to study the influence of the sulfate content in the clinker phase on the performance of superplasticized concrete mixtures in terms of initial slump level at a given water-cement ratio (0.45), slump-loss rate, and compressive strength at early and later ages.

Two batches (*A* and *B*) of clinker from the same kiln source were studied, the main difference being the content of sulfate (SO_3) in the clinker (0.72% and 1.40% respectively). Different percentages of natural gypsum, as set regulator, were interground in a laboratory mill to manufacture portland cements: A_1 , A_2 , A_3 from clinker *A*, and B_1 , B_2 , B_3 from clinker *B*. Three levels of total sulfate content in terms of SO_3 were set: 3.0% in portland cements A_1 and B_1 ; 3.5% in portland cements A_2 and B_2 ; 4.0% in portland cements A_3 and B_3 .

At a given sulfate content in portland cement, the lower the clinker sulfate content, the more effective is the slump increase of the concrete caused by the superplasticizer addition. Moreover, the lower is the clinker sulfate content, the lower is the slump-loss rate of the superplasticized concrete mixture. Finally, at a given water-cement ratio, there is a reduction in the compressive strength at early ages (≤ 3 days) when the low sulfate clinker is used to manufacture portland cements.

These results are related to the effect of the clinker sulfate content on the degree of cement hydration: the lower the clinker sulfate content, the lower the early cement hydration in terms of gypsum consumption, ettringite formation, and tricalcium silicate (alite) hydration.

Keywords: clinker; compressive strength; gypsum; slump; superplasticizers

Luigi Coppola is a research civil engineer and technical director of Enco, Spresiano, Italy. He has authored numerous papers on various aspects of concrete technology, durability and mix-design.

Roberto Troli is a research civil engineer and director of the Enco laboratory. He is author of several papers in the field of concrete technology and in particular of chemical and mineral admixtures.

Pasquale Zaffaroni is the R&D manager of the Building Materials Division, Mapei, Milan, Italy. He has authored several technical papers on concrete technology. He is member of the European Norms Committee for polymer or cement repairing mortars.

Mario Colleparidi is Professor of Materials Science and Technology in the Ancona University, Italy. He is author or co-author of numerous papers on concrete technology and cement chemistry. He is also the recipient of awards for his contributions to the fundamental knowledge of superplasticizers and their use in concrete.

INTRODUCTION

Portland cement contains a mixture of sulfur compounds from the cement clinker and from added calcium sulfate (e.g. gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which acts as set regulator. The sulfates from different sulfur sources have different water-solubility kinetics: sulfate from the gypsum dissolves sufficiently fast to participate in the regulation of the setting of the cement, whereas sulfate from the clinker phase is usually unavailable for the setting regulation (1). Therefore, cements with the same *total* sulfate content, but with different proportions of sulfate 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 sulfur content of these different fuels can change and cause unwitting variations from one day to another of sulfate incorporated in the clinker phase. Moreover, the clinker sulfate content may increase with the use of high-sulfur 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 sulfur-rich fuels or waste materials, can incorporate large amounts of sulfates, up to 3% by clinker mass. When high sulfate 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 e belite phases. According to Hime (2) all these forms of sulfate in the clinker phase are slowly soluble in the mixing water and, therefore, they can act as late sulfate 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 sulfate 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 behavior of superplasticized concretes which occurs under certain circumstances, even by using cements from the same source and in particular characterized by the same *total* sulfate content, could be related to an unwitting change in the sulfate content of the clinker phase.

MATERIALS AND METHODS

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 sulfate 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 analysis 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 m^2/kg - with three levels of total sulfate content. According to the European norm (ENV 197/1), the maximum sulfate 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 sulfate 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 sulfate level in the clinker *A*, a higher amount of gypsum was required, for a given total sulfate 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.

Concrete mixtures with and without superplasticizers 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 sulfonated naphthalene- and sulfonated melamine-based admixtures were used as superplasticizers. The influence of the clinker type (*A* or *B*) on the performance of superplasticized concretes containing naphthalene- or melamine-based admixtures was similar to

that recorded for the AP-based superplasticizer. 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 superplasticized concrete mixtures.

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.

RESULTS

Figure 1 shows the initial slump level and the slump-loss rate for plain and superplasticized concretes with different portland cements. For the same cement sulfate content, lower clinker sulfate contents produced higher initial slump levels and lower subsequent slump-loss, whether or not the superplasticizer was present. For instance, with 3.0% cement sulfate content, the initial slump of the concretes with cement A_1 were 95 mm or 225 mm for plain or superplasticized 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 superplasticized mixture with cement A_1 and 90 mm/hr in the corresponding concrete with cement B_1 .

By increasing the cement sulfate 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 sulfate (clinker B). Therefore, the increase in the addition of natural gypsum reduced the difference in the slump characteristics between concretes with different sulfate 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 superplasticized mixtures.

Figure 2 shows the compressive strength of plain and superplasticized concrete mixtures with different portland cements. With the clinker at lower sulfate content (0.72%), the early compressive strength (1-3 days) of superplasticized concretes was lower with respect to the plain mixtures (cements A_1 , A_2 , and A_3). The difference in strength between plain and superplasticized 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 ($SO_3 = 1.40\%$). 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 ($CaSO_4 \cdot 2H_2O$), ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) 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.

When portland cements A_1 , A_2 and A_3 were used - all from the clinker phase A with a lower sulfate 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 superplasticized 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 sulfate content (1.40%) - the retarding effect caused by the superplasticizer was negligible or absent (Fig. 4).

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 sulfate 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).

CONCLUSIONS

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

1. At a given sulfate content in portland cement, the lower the clinker sulfate content, the more effective is the slump increase of the concrete caused by the superplasticizer addition.
2. The slump-loss rate of the superplasticized concrete mixture is lower when portland cements are used with a lower clinker sulfate content (0.72%).
3. At a given w/c , there is a reduction in the compressive strength at early ages (≤ 3 days), when low sulfate 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 sulfate 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 sulfate contents of the clinker phase affects not only the performance of the superplasticized 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 sulfate content in the clinker phase both in plain mixtures and superplasticized concretes.

REFERENCES

1. Jøns, E., "Measuring the Sensibility of Sulphate in Cement", World Cement, pp 65-68, June 1996.
2. Hime, W.G., "Clinker Sulfate: A Cause for Distress and a Need for Specification", Concrete in the Service of Mankind, Concrete for Environment, Enhancement and Protection, pp. 387-395, Editors: R.K. Dhir and T.D. Dyer, E. & F.N. Spon, 1996.
3. Collepari, M., "A Holistic Approach to Concrete Damage Induced by Delayed Ettringite Formation", Mario Collepari Symposium, Ed. P.K. Mehta, Rome (Italy), 1997.
4. Collepari, M., Coppola, L., Cerulli, T., Ferrari, G., Pistolesi, C., Zaffaroni, P. and Quek, F., "Zero Slump-Loss in Superplasticized Concrete", Proceedings of the Congress "Our World in Concrete and Structures", pp 73-80, Singapore, 1993.
5. Collepari, M., "Superplasticizers and Air Entraining Agents: State of the Art and Future Needs", Concrete Technology. Past, Present, and Future, Mohan Malhotra Symposium, pp 399-416, Ed. P.K. Mehta, ACI-SP 144, 1994.

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

Fig. 1—Slump as a function of time for plain and superplasticized (SP) concrete mixtures

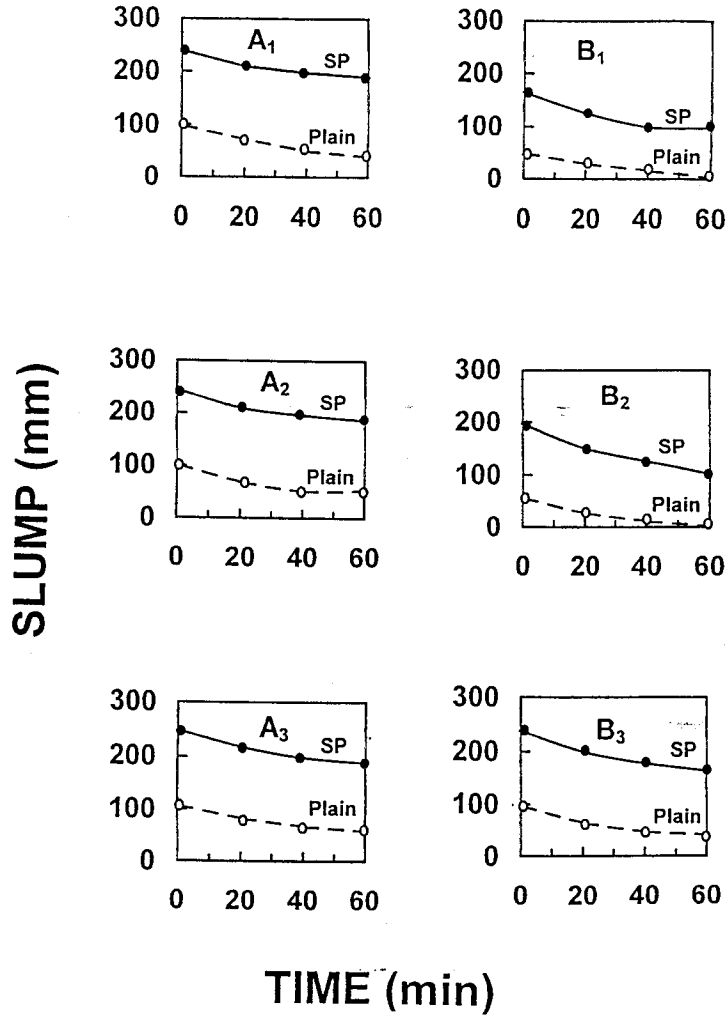


Fig. 2—Compressive strength as a function of curing time

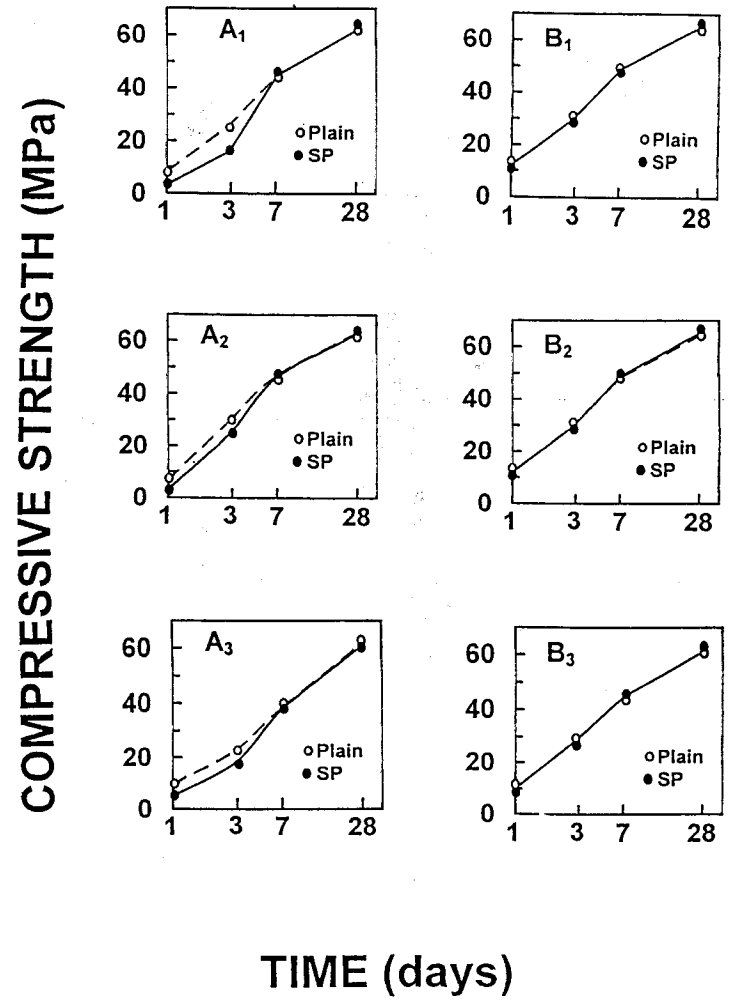


Fig. 3—XRD peaks of gypsum (G), ettringite (E), and tricalcium silicate (C_3S) as a function of hydration time for paste specimens with cements A_1 , A_2 , and A_3 without and with the AP-based superplasticizer

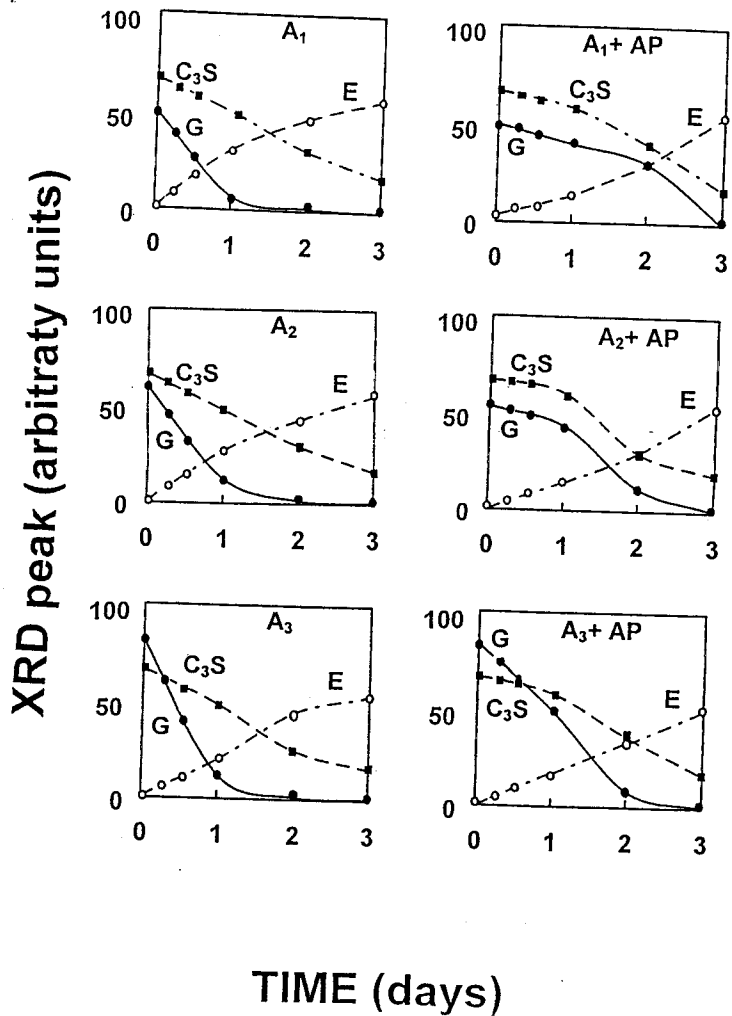


Fig. 4—XRD peaks of gypsum (G), ettringite (E), and tricalcium silicate (C_3S) as a function of hydration time for paste specimens with cements B_1 , B_2 , and B_3 without and with the AP-based superplasticizer

