Supplementary Report to the Paper on "Supersulphated Alumina-Belite Cements"

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Abstract

This paper provides the additional data to the paper submitted to 7th International Congress on the Chemistry of Cement¹⁾ and comprises the data to which the author could not refer due to the restricted pages. Some parts have been corrected in minor on the basis of several latest new findings, especially on the formation of sulphospurrite in clinkers and on the stability of gehlenite hydrate during hydration.

1. Introductory review

In 1974 Zakharov reported on the properties of "alumina-belite cement" which consists of β-C_2S, CA and $C_{12}A_7$ associated with minor presence of $C_4A_3\bar{S}$ and $C_5S_2\bar{S}$. This cement has peculiar features of high strength and high resistance to aggressive media²⁾. Probably, this is the first success in joining Portland cement and aluminous cement systems as illustrated in Figs. 1 and 2, and his invention may promise the effec-

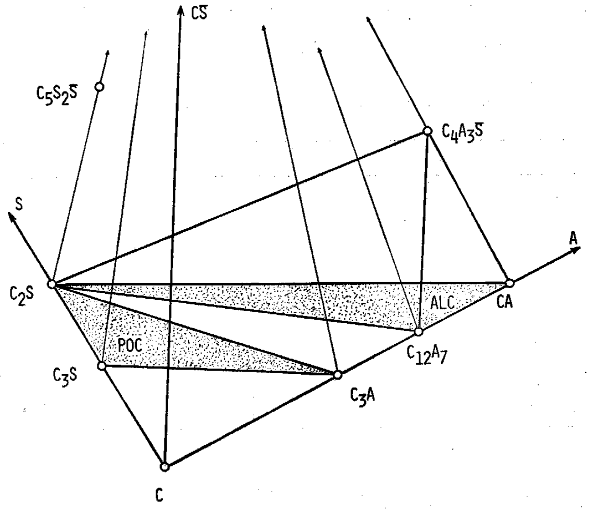

Fig. 1 Relationship between traditional cement systems and "supersulphated alumina-belite cement system" located along the join $C_4A_3\bar{S}$–C_2S including the vicinity of this join — POC, Portland cement system, ALC aluminous cement system. CA_2 is also a constituent mineral for aluminous cement, but it was omitted for simplification as well as C_2AS.

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Cement chemical notations are used in this paper: C CaO, A Al_2O_3, S SiO_2, $\bar{S}$ SO_3 and H H_2O.

tive utilization of low grade clays, coal ashes, blast furnace slags and so on containing considerably large amount of alumina.

In 1978 Viswanathan et al. extended this idea and made "Porsal cements" from anorthosites, prevailing in India, as one of the sources for raw materials[3]. Their cements have a little higher content of $\bar{S}$ than the cement of Zakharov as seen in Fig. 2 and consist of β-C_2S, CA, $C_{12}A_7$ and $C_4A_3\bar{S}$. Slight CaF_2 was introduced as a mineralizer. Emphasis was also placed on the resistance to aggressive media. The cements were named after representative characteristics of the cements, *Portland cement, Sulphate resistance* and *Alumina cement.*

Ordinary Portland cement, one of the most popular and widely used cements in the world, reveals a stable development of strength in harmony with the advance of hydration. However, initial strength and resistance to aggressive media are rather low. On the contrary, aluminous cement gives high initial strength and high resistance to aggressive media. Therefore, mixing ordinary Portland cement with aluminous cement would be more convenient to get a cement possessing both characteristics of Portland cement and aluminous cement at once. If we intend to utilize the mix-cement, energy loss due to separate burning should be conquered. This idea was applied to regulated set cement utilizing the join C_3S–$C_{11}A_7 \cdot CaF_2$. In the same way we can make another type of cements called "supersulphated alumina-belite cements", utilizing the join $C_4A_3\bar{S}$–C_2S, whose bending strength and compressive strength are summarized in Table 1[1].

Table 1. Bending strength and compressive strength of "supersulphated alumina-belite cements" — MPa, pastes with W/C 0.40. Top, 1200°C series. Bottom, 1300°C series.

Bending strength					Compressive strength			
1	3	7	28 days	A/S	1	3	7	28 days
2.7	3.5	2.6	3.1	0.4	8.4	9.4	10.6	11.8
4.2	6.5	6.7	5.3	1.0	16.1	25.7	27.6	34.2
6.3	9.6	10.5	7.3	2.0	27.2	32.5	37.7	58.0
7.1	9.4	10.6	10.7	3.0	30.9	50.4	56.4	60.2
—	1.3	1.8	2.5	0.4	—	3.3	4.4	7.0
—	6.1	7.1	6.5	1.0	—	25.6	32.7	39.0
—	10.2	10.3	5.6	2.0	—	36.6	42.9	75.5
—	10.4	12.6	6.3	3.0	—	45.1	64.4	63.9

The new type of cements consists of $C_4A_3\bar{S}$ and C_2S theoretically. However, contrary to expectation, resulting clinkers contained considerable amounts of CA and slight $C\bar{S}$ in addition to $C_4A_3\bar{S}$ and C_2S. The C_2S was found to be in α'-form and this would be the result of some incorporations of $\bar{S}$ component in the C_2S, although the effect of other impurities was suspected. Blast furnace slag and JIS 1st grade chemicals of $CaCO_3$, Al_2O_3 and $CaSO_4 \cdot 2H_2O$ were used as source materials. The chemical composition of the slag and the mixing proportions for each cement are given in Tables 2 and 3, respectively. For the measure of mixing A/S wt ratios were set in

Table 2. Specifications of the slag — wt %, sulphur as SO_3.

SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	MnO	TiO_2	Total
32.90	13.45	43.05	6.51	2.37	0.65	0.31	1.02	100.26
Fineness 3950 cm^2/g, Blaine, S.G. 3.26, Glassy.								

Table 3. Mixing proportions of raw materials by weight. In brackets weight after heating is shown to make total 100.

A/S	Slag	Gypsum	Alumina	Ca-carbonate
0.4	80.13	6.12 (4.84)	—	26.83 (15.03)
1.0	61.16	11.36 (8.98)	11.87	32.13 (18.00)
2.0	43.67	16.18 (12.79)	22.81	37.02 (20.74)
3.0	33.96	18.84 (14.90)	28.88	39.72 (22.26)

0.4, 1.0, 2.0 and 3.0. The 0.4 is the case without addition of extra alumina. Cements were burnt at 1200°C and 1300°C and as a consequence eight kinds of cement were prepared. The development of strength was different each other between 1200°C series cements and 1300°C series cements. The former showed high initial strength depending on the content of alumina, whereas the latter showed slow development of strength, but reached high strength in 3-day curing except mix 0.4. Ultimately, in 28-day age, the cements in both series acquired very high compressive strength except the mixes 0.4. In bending strength some depressions were noticed, probably due to the trisulphate-monosulphate conversion that would be prevented by the addition of some gypsum or anhydrite beforehand. For the details of the results readers are kindly requested to see the reference(1).

2. Supplement to clinker minerals

In Table 4 theoretical mineral proportions for each mix are shown, consisting of only two clinker minerals $C_4A_3\bar{S}$ and C_2S with the residues as mineralizers. XRD analyses on the resulting clinkers, however, revealed the presence of CA and $C\bar{S}$ in

Table 4. Theoretical potentials of clinker minerals for each mix — mole %. MgO is included in CaO. $CA \cdot 1/3C\bar{S}$ is taken as a unit molecule of $C_4A_3\bar{S}$. Mineralizers indicate the potentials estimated to be incorporated and others comprise Fe_2O_3, MnO and TiO_2.

A/S	Clinker minerals		Mineralizers	
	$C_4A_3\bar{S}$	C_2S	$C\bar{S}$	Others
0.4	17.8	74.2	4.1	3.9
1.0	34.7	58.9	3.2	3.2
2.0	51.5	43.6	2.4	2.5
3.0	61.6	35.0	1.9	1.5

Table 5. Amounts of clinker minerals resulted in 1200°C series — mole %. Amounts of CA and $C\bar{S}$ were only determined by QXRD and amounts of other minerals are recalculated ones on the basis of the QXRD results.

A/S	Clinker minerals				Mineralizers	
	$C_4A_3\bar{S}$	C_2S	CA	$C\bar{S}$	$C\bar{S}$	Others
0.4	17.8	74.2	tr.	1.2	2.9	3.9
1.0	20.1	56.3	13.0	1.7	5.8	3.1
2.0	28.8	40.8	20.0	1.2	7.5	1.7
3.0	38.7	32.8	19.0	0.7	7.4	1.4

Table 6. Amounts of clinker minerals resulted in 1300°C series — mole %. Small amounts of glassy phases were disregarded.

A/S	Clinker minerals				Mineralizers	
	$C_4A_3\bar{S}$	C_2S	CA	$C\bar{S}$	$C\bar{S}$	Others
0.4	17.8	74.2	tr.	tr.	4.1	3.9
1.0	25.6	57.3	8.2	tr.	5.8	3.1
2.0	44.1	42.6	6.3	tr.	4.5	2.5
3.0	54.3	34.2	6.1	tr.	3.9	1.5

addition to $C_4A_3\bar{S}$ and C_2S as shown in Tables 5 and 6. In 1300°C series slight generations of glassy phases were estimated, but they were disregarded in the table. The C_2S was in α'-form, bredigite, different from ordinary β-form, larnite. In this section the author will try to explain the cause for the formation of CA.

The main clinker minerals, $C_4A_3\bar{S}$, C_2S and CA are plotted on the triangular diagram of Fig. 2 in molecule ratios. For convenience $C_{12}A_7$ was also taken into account in combination with CA in order to cite relevant references. In the diagram alignments between original compositions (theoretical) and clinker compositions (resulted) for 1200°C series and 1300°C series are noticed as well as mutual parallelisms among the alignments. It is also marked that mixes 0.4 do not contain any CA, meaning ideal complete reactions expected from the theoretical calculations. The presence of free $C\bar{S}$ is slight and negligible for these mixes.

For simplicity, let consider the 1200°C series cements first which contain no glassy phases. From the completion of the reaction of the mix 0.4, it is concluded that 74.2 mole C_2S in α'-form incorporates 2.9 mole $C\bar{S}$ at 1200°C, if this type of incorporation is permitted. This amount is correspondent to 2.2, 1.6 and 1.3 moles for mixes 1.0, 2.0 and 3.0, respectively, on the basis of the amount of C_2S in each mix. The reduction of these values from the values of $C\bar{S}$ being mineralizers gives 3.6, 5.9 and 6.1 moles for mixes 1.0, 2.0 and 3.0, respectively, which are in good agreement with the amounts of 4.3, 6.7 and 6.3 moles expected from the amounts of CA to form $C_4A_3\bar{S}$ for mixes 1.0, 2.0 and 3.0, respectively. These missing $C\bar{S}$ would form sulphospurrite, $C_5S_2\bar{S}$. Actually, slight presence of which is noticeable in XRD diagrams

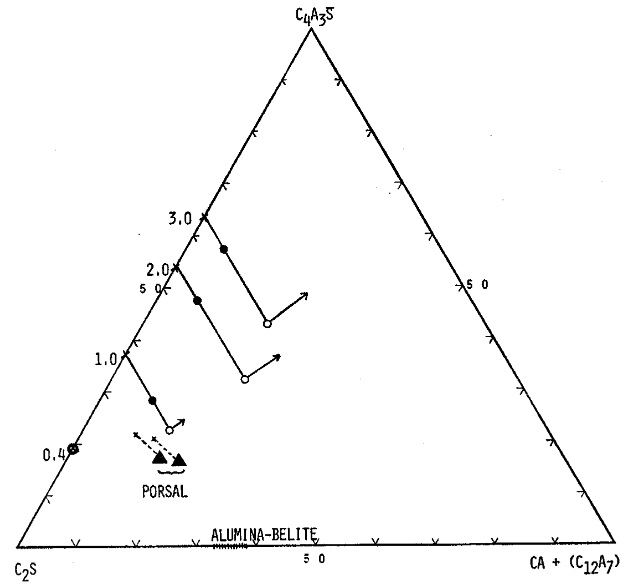

Fig. 2 Variations of molar ratio for major clinker minerals in "supersulphated alumina-belite cements". Notations; cross, theoretical points, open circle, points resulted in 1200°C series, solid circle, points resulted in 1300°C series. Arrows indicate the points, when the presence of sulphospurrite is taken into consideration in 1200°C series. Mixes 0.4 are superimposed in three. Points of Porsal cements[3] (cross, theoretical, and triangle, resulted) and of alumina-belite cement[2] are also plotted for comparison.

for 1200°C series except mix 0.4. The amounts of clinker minerals finally normalized considering the presence of sulphospurrite are given in Table 7 for 1200°C series. No trace of sulphospurrite was found in 1300°C series due to higher burning temperature where sulphospurrite cannot survive owing to disintegration into α'–C_2S containing 1.1 mole% $C\bar{S}$ and α–$C\bar{S}$. The decomposition temperature is reported to be 1298°C or 1285°C[4,5]. According to Nakamura et al. the volatilization of $\bar{S}$ was negligibly small below 1250°C[5]. Viswanathan et al. also found the scarce depletion below 1280°C[3]. Therefore, the volatilization of $\bar{S}$ in present cements is estimated to be negligible. In 1300°C series the discrepancy of mineral assemblage of resulting clinker minerals from theoretical one can be explained in the same way, disregarding the

Table 7. Amounts of clinker minerals resulted in 1200°C series, when the presence of sulphospurrite is taken into consideration — mole %.

A/S	Clinker minerals					Mineralizers	
	$C_4A_3\bar{S}$	C_2S	CA	$C_5S_2\bar{S}$	$C\bar{S}$	$C\bar{S}$	Others
0.4	17.8	74.2	tr.	tr.	1.2	2.9	3.9
1.0	21.7	52.9	14.0	3.9	1.8	2.4	3.3
2.0	32.6	32.9	22.7	6.7	1.4	1.8	1.9
3.0	44.1	23.5	21.6	6.9	0.8	1.5	1.6

presence of small amounts of glassy phase. Missing amounts of $C\bar{S}$ probably dissolved in liquids are calculated to be 2.6, 2.1 and 2.0 moles on the basis of the mix 0.4 for mixes 1.0, 2.0 and 3.0, respectively, which are in very good agreement with the amounts expected from the observed amounts of CA to form $C_4A_3\bar{S}$, i.e., 2.7, 2.1 and 2.0 moles for mixes 1.0, 2.0 and 3.0, respectively.

3. Supplement to hydrates and hydration

Hydrates encountered during aging the cement pastes with W/C 0.40 in 20°C water are summarized in Table 8 for both 1200°C and 1300°C series up to 28-day age.

1) Ettringite, calcium aluminate trisulphate hydrate, $C_6A\bar{S}_3H_{32}$. This hydrate is an essential hydrate that is brought by the hydration of $C_4A_3\bar{S}$, sometimes associated with slight monosulphate hydrates both of 12 hydrate and 18 hydrate. The ettringite would be a solid solution with C_6AH_{32} component as considered in the following scheme:

$$3C_4A_3\bar{S}+85H=\begin{pmatrix} C_6A\bar{S}_3H_{32} \\ C_6A\ \ H_{32} \end{pmatrix}_{ss}+7AH_3$$

where ss denotes solid solution, if no association of monosulphate hydrates occurs or it is very small in amount. Then, the following reaction may proceed to form more C_6AH_{32} component which may further enrich the ettringite solid solution:

$$AH_3+6CH+23H=C_6AH_{32}$$

where CH comes out of C_2S due to hydration. Finally, when the supply reaches the limit of the solid solution, a part of ettringite solid solution may become stable in the form of monosulphate hydrate which may be also in form of solid solution, i.e., the trisulphate-monosulphate conversion may occur accompanied by the depression of bending strength happened around 28-day age1). The enrichment may also take place in consumption of CAH_{10}, C_2AH_8 and so on with the CH. Accordingly, it may be effectable to add certain amounts of gypsum or anhydrite to the cements to prevent the conversion, attaining more elevation of strength together6).

2) Tetracalcium aluminate monosulphate 18-hydrate, $C_4A\bar{S}H_{18}$. This hydrate is subordinate to ettringite and appears slightly in both early and late ages. The early age one may be metastable because of its disappearance in middle ages.

3) Tetracalcium aluminate monosulphate 12-hydrate, $C_4A\bar{S}H_{12}$. This hydrate is also subordinate to ettringite and the amount is slight. The early age one may be metastable as well as 18-hydrate. When this hydrate appears more intense at late ages, the bending strength of the pastes is weakened.

4) Monocalcium aluminate 10-hydrate, CAH_{10}. This hydrate sometimes appears metastable in early ages. It is stable and more intense at middle to late ages, especially in 1300°C series due to the hydration of the glassy phases present in the cements as well as CA. The abundance of this hydrate may lead the easy conversion

Table 8. Relative amounts of hydrates and clinker minerals remained — after XRD, notations; − nil, ± scarce presence suspected, + slight, ++ medium, +++ enhanced.

A/S	Minerals	1200°C series				1300°C series			
		Age, days				Age, days			
		1	3	7	28	1	3	7	28
0.4	$C_6A\bar{S}_3H_{32}$	+++	+++	+++	+++	+	++	++	++
	$C_4A\bar{S}H_{18}$	−	−	−	−	−	+	−	±
	$C_4A\bar{S}H_{12}$	±	±	−	−	+	+	−	−
	CAH_{10}	−	−	−	−	−	−	−	−
	C_2AH_8	−	−	−	−	−	+	+	−
	C_2ASH_8	−	−	−	−	−	−	−	−
	AH_3	−	−	±	±	−	±	±	−
	C–S–H	−	−	++	+++	−	±	+	+
	$C_4A_3\bar{S}$	+	+	−	−	+	+	+	−
	C_2S	+++	+++	+++	+++	+++	+++	+++	+++
	CA	−	−	−	−	−	−	−	−
	$C\bar{S}$	+	+	+	−	−	−	−	−
1.0	$C_6A\bar{S}_3H_{32}$	+++	+++	+++	+++	+	+++	+++	+++
	$C_4A\bar{S}H_{18}$	−	−	−	−	−	−	−	−
	$C_4A\bar{S}H_{12}$	+	+	−	−	−	+	+	+
	CAH_{10}	+	−	−	−	−	++	++	++
	C_2AH_8	+	−	−	−	−	−	+	+
	C_2ASH_8	−	−	−	−	−	−	−	+
	AH_3	±	±	±	±	−	−	−	−
	C–S–H	−	−	−	+	−	−	−	+++
	$C_4A_3\bar{S}$	++	±	−	−	+++	++	+	−
	C_2S	+++	+++	+++	+++	+++	+++	+++	+++
	CA	+	+	−	−	+	+	−	−
	$C\bar{S}$	+	−	−	−	−	−	−	−
2.0	$C_6A\bar{S}_3H_{32}$	+++	+++	+++	+++	+	+++	+++	+++
	$C_4A\bar{S}H_{18}$	−	−	−	±	−	+	+	±
	$C_4A\bar{S}H_{12}$	+	−	−	++	−	−	+	++
	CAH_{10}	−	+	−	−	−	++	++	++
	C_2AH_8	+	−	−	−	−	+	+	+
	C_2ASH_8	−	−	+	−	−	−	+	+
	AH_3	+	+	+	+	+	+	±	±
	C–S–H	−	−	−	+	−	+	±	+
	$C_4A_3\bar{S}$	++	+	−	−	+++	++	−	−
	C_2S	++	++	++	++	++	++	++	++
	CA	+	+	−	−	+	−	−	−
	$C\bar{S}$	+	+	−	−	−	−	−	−
3.0	$C_6A\bar{S}_3H_{32}$	+++	+++	+++	+++	++	+++	+++	+++
	$C_4A\bar{S}H_{18}$	+	±	−	+	+	+	−	±
	$C_4A\bar{S}H_{12}$	+	−	+	−	+	−	+	++
	CAH_{10}	−	+	+	+	+	+	++	++
	C_2AH_8	+	−	+	−	−	−	−	−
	C_2ASH_8	−	+	−	−	−	+	+	+
	AH_3	−	±	−	−	±	+	±	±
	C–S–H	−	+	++	++	−	+	+	+++
	$C_4A_3\bar{S}$	++	+	+	+	+++	++	++	++
	C_2S	++	++	++	++	++	++	++	++
	CA	+	+	+	−	+	−	−	−
	$C\bar{S}$	−	−	−	−	−	−	−	−

of the ettringite into monosulphate hydrate that causes the depression of bending strength.

5) Dicalcium aluminate 8-hydrate, C_2AH_8. This hydrate sometimes appears metastable in very small amount in early ages. In late ages it is also observed in some hardened cements. The late age one may be stable, but the amount is very small.

6) Dicalcium aluminate silicate 8-hydrate, C_2ASH_8. In some hardened cements of 1200°C series this hydrate appears slightly and is estimated to be metastable because of disappearance with the advance of curing time. On the contrary, in 1300°C series this is not the case and this hydrate seems to become stable at late ages, although the amount is slight. This point is different from the result obtained by Raina et al. on Porsal cement, in which C_2ASH_8 forms more intense7). This hydrate would be formed by the pozzolanic reaction of the glassy phases present in small amounts in 1300°C series clinkers. Consequently, it would be better to consider the stable formation of C_2ASH_8 for the hydration of 1300°C series cements as illustrated in Fig. 3.

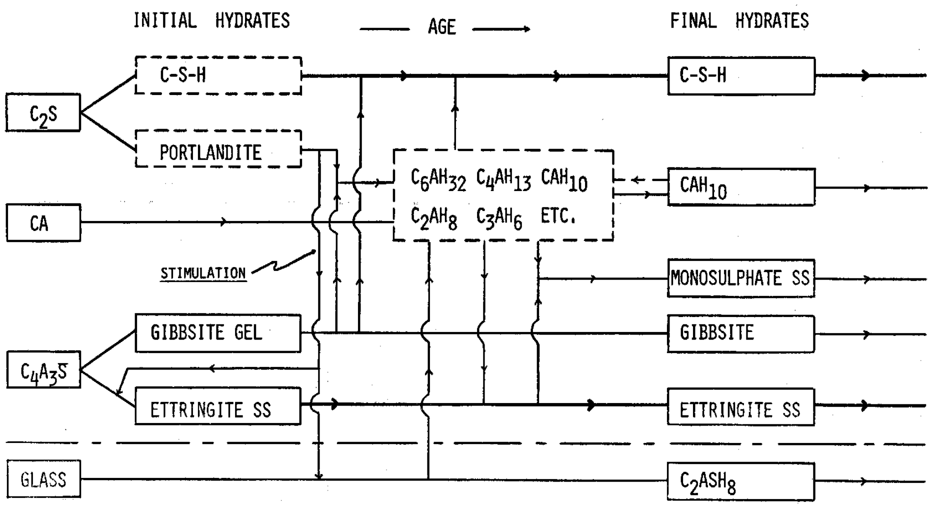

Fig. 3 Schematic hydration courses for "supersulphated alumina-belite cements". Stable formation of C_2ASH_8 should be considered in 1300°C series hydration owing to pozzolanic reaction of the glass. C_2AH_8 is included in CAH_{10} for simplification. Hydrates in dashed boxes are potential ones in solutions but not as precipitates. See also Table 8 together.

7) Gibbsite, AH_3. The detection of this hydrate is not so easy because of poor crystalline, especially in early ages. Accordingly, it is suspected that the presence may be more intense than the XRD observations shown in Table 8. However, more or less, this hydrate would be gradually consumed by the action of portlandite component out of C_2S.

8) C–S–H, poorly crystallized calcium silicate hydrate. This hydrate is also the essential hydrate as well as ettringite in present cements. The more abundant formation of this hydrate will bring the more elevation of the strength of the hardened cements in advanced ages.

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