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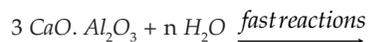
Dual role of gypsum: Set retarder and strength accelerator

N. Bhanumathidas and N. Kalidas

Gypsum plays a crucial role in cement. Though it is used in a small quantity, in the range of 2.5-3.0 percent in terms of SO₃, gypsum's role in cement is significant, more predominantly at early ages. Gypsum renders workability to mortar or concrete by keeping the cement in plastic state at early age of hydration. This is achieved by changing the course of hydration of calcium aluminate that manifests as retardation in cement hydration. This is how gypsum is identified as a set regulator or retarder, as known popularly. Nevertheless, gypsum also contributes for strength acceleration in the early stages of hydration. This dual role of gypsum is discussed in the feature.

Gypsum is the set retarder for ordinary portland cement (OPC). Without gypsum, ground clinker exhibits flash setting in a few minutes, due to the rapid hydration of calcium aluminates to form calcium aluminate hydrate (CAH). The hydration of C₃A releases profuse exothermic heat making the matrix stiff, minimising the chances for remixing. The CAH, thus formed, does not contribute for strength of the matrix and, moreover, hampers the hydration of calcium silicate. The sequence of

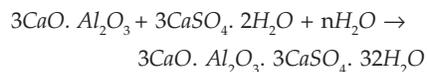
reactions, in the absence of gypsum, totally vetoes the commercial use of cement. The following chemical reaction, in the absence of gypsum, is explanatory in this regard.



CAH + profuse exothermic heat

Hence, it was found essential to change the reaction course of C₃A, and this was met by the use of sulphate salts. Due to its affinity with SO₃, aluminate tends to react readily with the former and in this process the reactions of aluminate with water are prevented. Ultimately, gypsum was identified as the most effective form of sulphate to control hydration reactions of C₃A that incidentally resulted in better workability for a longer duration.

Chemical reaction in the presence of gypsum is given below



(Ettringite : calcium trisulpho aluminate hydrate) + moderate exothermic heat

Many in the cement and concrete industry know the role of gypsum as set retarder or set regulator. But the complementary role of gypsum, as accelerator to render high early strengths, is generally unnoticed. This knowledge gap

lead to a misunderstanding that the addition of more gypsum means additional retardation in setting, which is not true. The formation of ettringite at threshold levels accelerates the hardening process and thus hastens strength gain at early ages. In view of this behaviour, the latest European code on cement — ENV 197 - 1 stipulates higher dosages of SO₃ (between 3.5 to 4 percent by mass)¹. As against this, the Indian specifications on both 43 and 53 OPC grade (IS 8112 : 1989² and IS 122269 : 1987³) specify the maximum SO₃ content of 2.5 percent by mass (for C₃A < 5 percent) and 3 percent by mass (for C₃A > 5 percent). The specification on portland pozzolana cement (IS 489 : 1991⁴) and that on portland slag cement (IS 455 : 1989⁵) stipulates SO₃ level of 3 percent by mass.

In the manufacture of blended cements, by virtue of reactive aluminates from fly ash and slag that leads to ultimate cement, the chances for existence of resultant calcium aluminate hydrates are more than what is generally available in OPC, as shown in the Table 1.

Hence, the increasing positive threshold levels of gypsum is one of the solutions to overcome the weakness of strengths at early ages in mortar/concrete with blended cements. This aspect is also of significance when the blending is done in ready mix

Table 1: Need of SO₃ corresponding to calcium aluminates formation in the blends

Type of cement	C ₃ A	CA	As monosulphate 3CaO.Al ₂ O ₃ .CaSO ₄ .12 H ₂ O	Need of SO ₃ for final phase
OPC	5.00	9.28	11.50	1.47
OPC(70) + FA(30)*	3.50	16.70	29.40	6.40
OPC(50) + Slag(50)**	2.50		38.40	8.35

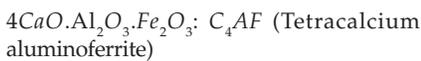
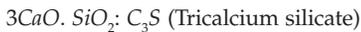
Note: CA - Reactive calcium aluminosilicate, *Fly ash with 30 percent reactivity containing 25 percent Al₂O₃, **Slag with 90 percent reactivity containing 14 percent Al₂O₃.

concrete plants. While all fly ashes may not need additional gypsum, care has to be taken not to deprive those fly ashes in need of additional gypsum.

FaL-G technology, developed by the authors, achieved its breakthrough by tapping the potential of calcium aluminates towards the formation of ettringite and mono-sulphate; thus changing the pace of lime-fly ash chemistry. Gypsum plays a predominant role as the strength-accelerator in the context of hydrated mineralogy in FaL-G. Moreover, gypsum works as set-accelerator in lime-pozzolana binders in contrast to its role as set-retarder in OPC.

Calcium aluminate sulphate chemistry

Before getting into the details of the mineralogical formations, it is essential to briefly go through the chemistry and hydration of OPC, which is a product of four principal mineralogical phases, namely,



Upon adding water, the anhydrous mineralogy gets dissociated as CaO, SiO₂, Al₂O₃ and Fe₂O₃ for associating into hydrated mineralogy. Setting is the interface for this transformation. Soroka⁶ gave sequential illustrations for working period, initial setting and final setting for cement paste, by graphic representation of the mineralogical phase formations as shown in Fig 1.

As explained by Soroka in the first phase, when water is added to cement, as a result of the hydrolysis of the calcium silicates, a super-saturated solution of calcium hydroxide is formed. Sulphate and alkali ions, as well as small amounts of silica, alumina and ferric oxide are also present in the solution. Calcium hydroxide

and ettringite precipitate out and a dense C-S-H gel coating is formed on the cement grains. This coating as well as ettringite coating on C₃A grains retard further hydration, and this explains the existence of dormant period, that is, the period of relative inactivity lasting for one to two hours. During this dormant period the paste remains plastic and workable. The end of the dormant period can be identified as initial set. This is attributable to the break up of C-S-H and ettringite coatings, and the resultant continuation of hydration process. Due to the osmotic pressure the gel coating gets ruptured, exposing the cement grain, wherein hydration is resumed and setting takes place.

Consequently, as the hydration proceeds, the hydration products gradually fill in the spaces of the cement grains. Points of contact are formed resulting in stiffening of the paste, which is identified as the setting. At some later stage, the concentration of hydration products and resultant concentrations of points of contact restrict the mobility of cement grains to such an extent that the paste becomes rigid, reaching the state of final set.

The volume of the hydration products, through the process of crystallisation and matrix formation, is more than twice to that of the anhydrous cement. The dissociation and association of mineralogy continue as long as the moisture is available and release of lime is continued in the

matrix. This activity was sustainable for longer ages in low grade cements, accredited for their durability, which is explained in terms of heat bank and lime bank by the authors⁷. In contrast, accelerated reactions take place in high grade cements for relatively shorter periods, leading to the complications and decrease in durability.

Ettringite in pre-hardened and post-hardened concrete.

It is observed that the ettringite formed in pre-hardening stage is conducive for the matrix formation in comparison to the same formed in post-hardening stage. The simple reason is its volume expansion by taking almost 32 molecules as water of crystallisation. As already mentioned, in a hydrated cement paste, the level of impermeability increases through volume expansion of hydrated phases and the resultant densification through the process of curing. In the initial ages of hydration this expansion contributes for the internal compaction of matrix, resulting in densification and strength. These phenomena lead ultimately to impermeability of the matrix. However, if the same expansion occurs after the matrix attains volume stability then the matrix is subjected to in-

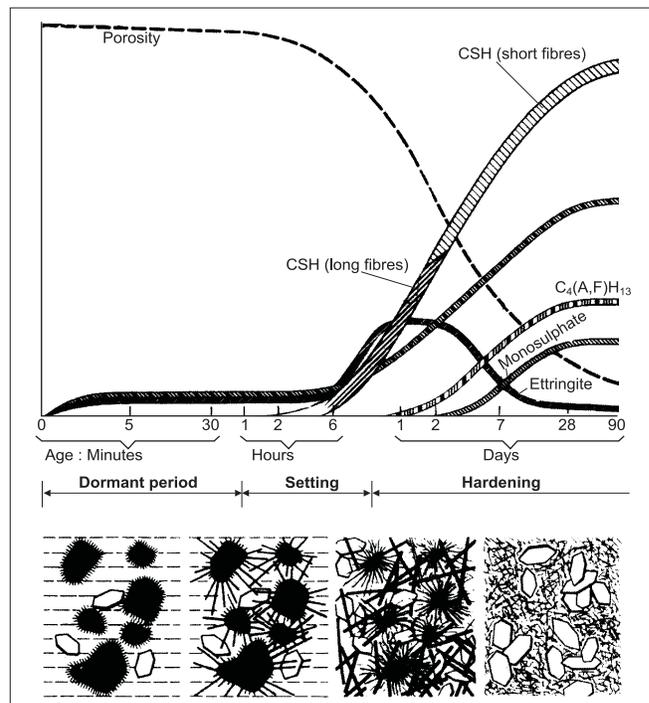


Fig 1 Schematic description of the hydration and structure development in cement paste (after Locher and Richartz) (from reference 6)

Table 2: Relation of strength and heat of hydration to increase in SO₃ in OPC

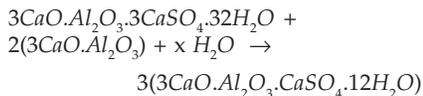
SO ₃ , percent	Setting time, min		Compressive strength, MPa				Heat of hydration, kCal/kg				
	Initial	Final	1-day	3-day	7-day	28-day	12-hour	1-day	3-day	7-day	28-day
1.80	115	150	17.7	37.4	53.8	61.6	22.5	33.2	45.4	59.3	67.2
2.10	130	165	20.9	40.2	59.0	65.4	28.2	33.2	44.5	63.0	65.7
2.40	135	180	20.9	32.1	47.8	62.0	46.0	54.2	63.2	80.3	88.5

Surface area of OPC : 320 kg/m²

ternal expansive pressures that result in cracking of the concrete.

If the hydration chart of Soroka is observed for the formation of various mineralogies, the formation of sulphoaluminate hydrates is predominant till the final set that is followed by calcium silicate hydrates. As ettringite descends from its peak of formation by first or second day, the formation of monosulphate does commence. What does it mean? It means that gypsum gets largely exhausted for the formation of tri-sulphate. At this stage calcium aluminate hydrates continue to be available with affinity to form sulphoaluminate hydrates. Due to their affinity for sulphate ion these aluminate hydrates react with ettringite. This is manifested as the commencement of monosulphate formation. These reactions concur with the physical status of the matrix where porosity of the matrix is largely filled up by ettringite at early age, beyond which the reduced porous spaces are progressively occupied by monosulphate. Thus, the three-day strength is largely attributable to the formation of calcium sulphoaluminate hydrates.

The transformation of ettringite to monosulphate is as follows:



This is a slow reaction that either leaves monosulphate as the ultimate mineralogy of sulphoaluminates or makes the same into hexagonal plate solid solution with CAH, probably C₄AH₁₃, to result in a stable stage. In the sequence of calcium aluminate hydrate chemistry, ettringite (trisulphate) formation is an in-built mechanism or a boon to render high early strengths to the matrix. This can be achieved only in the presence of gypsum, which also hastens the CSH chemistry⁸. This is how gypsum's role is upheld as early-strength accelerator.

At the early ages, the cementitious matrix needs heat for rapid hydration of chemistry. This is rendered by the hydration of C₃A, which is commensurately availed

as heat of formation. The threshold dose of gypsum regulates the heat of hydration as also the ettringite formation for progressive chemistry. In the anxiety of not to retard cement if the gypsum is reduced below the threshold level, heat of hydration is commensurately profuse leading to internal thermal stresses and incohesiveness. This is where the role of gypsum is evident as retarder.

Maximum amount of gypsum is engaged into ettringite in the first two to three days. Thus, matrix becomes more cohesive with improved strength development. Nevertheless, each clinker has its own optimum level of demand for gypsum that decides the other characteristics. The data in Table 2 elucidate the same.

In the above studies on OPC, addition of SO₃ beyond 2.1 percent is proving adverse both in strength and heat of hydration though the one-day strength is impressive. Hence, it would be highly inappropriate to decide the quality of cement based on one-day strength alone, which unfortunately is projected as a quality parameter by many.

Strength data of calcium aluminates to calcium sulpho aluminates

Gypsum in FaL-G

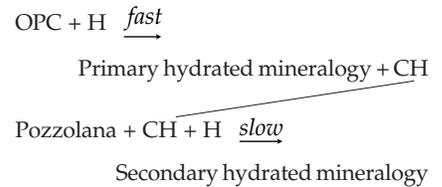
In FaL-G studies, two formulations were made for fly ash lime mixes with and without gypsum. The predominant difference is the formation of calcium aluminate hydrate where there was no gypsum; and the formation of calcium sulphoaluminate hydrate where gypsum was available. These mineralogical formations were substantiated by XRD. Notwithstanding these formations, the strength data also substantiate the observation both at 7-day and 28-day as shown in Table 3. In the light of moderate performance by calcium silicate chemistry in fly ash lime mixes at early ages, the credit of the early strength goes to ettringite.

Table 3 shows that LT fly ashes show higher reactivity than HT fly ashes. This could be

attributed to the presence of higher reactive amorphous aluminosilicates in LT fly ashes which produces CAH that can further form ettringite with gypsum.

Gypsum in blended cements

The hydration chemistry of blended cements is a two-phase mechanism. In the first phase, the OPC chemistry surfaces and in the second phase pozzolanic chemistry comes into force. This is represented as follows:



In pozzolanic reactions, alumina is noticed but the addition of commensurate gypsum is not given much weightage. Even the ASTM definition of pozzolanic chemistry is silent on this issue, which says, "Siliceous or siliceous and aluminous materials, which, though not cementitious themselves, react with lime, when in finely divided form, in the presence of water at ordinary temperature, and form stable and insoluble mineralogical phases, possessing cementitious characteristics".

But the principle behind use of additional gypsum in blended cements lies in the capability of SO₃ to break the glass of pozzolana. This occurs due to the affinity between SO₃ and alumina that facilitates the formation of calcium sulphoaluminate hydrates. The indirect benefit is the availability of reactive silica, freed from glass of pozzolana, for reactions. The formation of additional ettringite and CSH makes the cement matrix more densified and impermeable at early ages. The studies on fly ash blended mortars and concrete substantiate this phenomenon as shown in Table 4.

Table 3: Increase in strength upon addition of gypsum in fly ash-lime mixes both in LT and HT fly ashes

Source	Compressive strength MPa			
	Fly ash + lime		FaL-G	
	7-day	28-day	7-day	28-day
LT fly ash 1	9.0	17.9	25.0	32.0
LT fly ash 2	11.0	15.8	20.0	25.8
HT fly ash 1	2.6	7.8	8.4	24.0
HT fly ash 2	3.3	4.9	6.5	24.8

Table 4: Impact of gypsum on compressive strength at different inputs of fly ash

Fly ash	Compressive strength of mortar, MPa									
	7-day		14-day		28-day		60-day		270-day	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
50 : 50 (PPC-I)	24.4	20.0	32.4	22.8	40.8	29.6	50.8	44.4	56.8	48.0
40 : 60 (PPC-II)	21.2	15.2	29.6	22.0	38.0	34.0	45.2	44.4	56.0	47.8
100 : 0 (control mortar)	27.2		35.2		40.4		48.0		54.4	

(a): Added with anhydrite commensurate to fly ash quantity, (b): Without anhydrite

Table 5: Improvement in lime reactivity strength with the addition of gypsum

Fly ash	Lime reactivity strengths MPa			
	Without gypsum		With gypsum	
	10-day	90-day	10-day	90-day
Sample 1	2.8	6.4	5.2	10.8
Sample 2	7.7	11.9	11.9	19.3
Sample 3	9.1	15.9	17.7	21.7

Durability aspects

Chloride permeability with change in dose of gypsum

When gypsum is added as a third component in lime reactivity studies, the LR value improves strikingly that indicates formation of quite cohesive matrix associated with improved strength as shown in Table 5.

Studies on blended concretes using Sample 3 have brought in interesting phenomena towards improved durability despite higher workability as shown in Table 6.

The rationale of gypsum in European codes:

Studies were conducted on OPC at different doses of gypsum mentioned in terms of SO₃. The heat of hydration diminishes up to a particular level beyond which, it is noted that, increase of SO₃ increases heat of

hydration also, which is evident from the data already given in Table 2.

This means, gypsum liberates more heat of hydration on account of rapid chemistry. However, beyond a threshold level of SO₃, such rapid chemistry would not contribute for strength gain. This explains the rationale behind the increase of gypsum for rapid hardening cements vide European code, keeping an eye on the threshold limits.

Conclusions

Gypsum works as a double-edged sword in cement chemistry. One needs to have comprehensive understanding of the cement mineralogy and hydration chemistry before deciding on the dosage of gypsum. As much one can get optimum results by judicious input of gypsum, so much so one may get disastrous results too by improper dosing. This is where the holistic knowledge on cement chemistry is of significance.

Acknowledgements

The authors acknowledge the guidance of Prof P.K. Mehta and his wealth of library made available. The authors also record their gratefulness to Madras Cements Ltd., for making available the laboratories to this research.

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Dr N Bhanumathidas is the director general of Institute for Solid Waste Research and Ecological Balance (INSWAREB), the research body dedicated to the utilisation of industrial wastes towards building material. After obtaining her postgraduate degree in physics from Andhra University, she did her doctoral studies in chemical engineering (inter-disciplinary). Dr Bhanumathidas has authored several technical papers in collaboration with her associate, Mr N Kalidas, and presented at several national and international seminars. FaL-G is the outcome of this teamwork. She is currently focussing on advanced concrete technology, use of industrial byproducts as complementary cementitious material and promotion of blended cements.



Mr N Kalidas is engaged in the pursuit of waste utilisation technologies for the last 18 years as a technocrat and by virtue of his assignment with certain overseas companies. In order to consolidate his work on waste utilisation, he along with his associate, Dr N Bhanumathidas, founded the research body, INSWAREB. He is the director of INSWAREB. His field of interest includes: advanced concrete technology, use of industrial byproducts as complementary cementitious material, promotion of blended cements. Along with Dr N Bhanumathidas, he has authored several technical papers and presented at various national and international seminars.



Table 6: Reduction in permeability upon addition of gypsum

Cementitious Content, percent	Slump, mm	Compressive strength, MPa							Chloride permeability material, Coulombs				
		3-day	7-day	28-day	90-day	180-day	360-day	28-day	90-day	180-day	360-day		
OPC	Sample 3												
100	—	14	21.6	31.2	43.3	47.2	51.4	54.7	3852	2451	2251	1912	
65	35	80	12.2	17.7	35.1	53.7	58.4	65.9	2529	313	166	155	
65	35*	139	13.1	18.8	35.7	54.9	61.3	63.7	2107	234	130	151	

*Added with 2.76 as SO₃.