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Metabolism of cement chemistry

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In this 'Point of View', the authors present an interesting analogy between the metabolism of sugar in living organisms and the phenomenon of cement hydration. The authors hope that this will help to promote a better understanding of the chemistry of cement hydration.

Heat is an indispensable need for formations — may it be biological science or material science. The plants avail the energy associated with sunlight for photosynthesis. The organisms including human beings avail the heat out of metabolic reactions.

Similarly, the cement materials also avail heat during formation and emit the same as exothermic heat during hydration. This can be termed as the 'Metabolism of cement chemistry'. The rate of heat liberation (heat of hydration) has an impact on the soundness of cement concrete system. This is where understanding the metabolism of cement chemistry is meaningful.

Transition in cement

The ordinary Portland cement (OPC), during the early period of its introduction, was coarse and low strength class of grade 20-25. Subsequently, for attaining early strengths, OPC was upgraded to grade 32.5

or 33, which was also low grade compared to the grade of cements witnessed today.

Due to the devastation resulting out of World War II and the need to rehabilitate numerous cities and towns, there was great demand for speed of construction and, thus, the development of high strength-grade cements took place.

Two approaches were adopted to increase the grade of cement which were:

- (i) increase in ratio of C_3S to C_2S and
- (ii) increase in fineness.

The fine particles of cement trigger off a higher rate of hydration and commensurate liberation of heat, causing the exhaustion of the lime bank and heat bank lavishly much before the need, leading to premature deterioration. This has boomeranged the belief that higher the strength, higher the durability. Subsequently, durability was regarded as independent of strength and many investigations took place to identify the issues of durability.

At this juncture, attention was paid to the age-old lime-pozzolan chemistry accredited for durability over millennia. The construction speed could not be sacrificed and, at the same time, the soundness of progressive cement chemistry associated with pozzolanic chemistry was earnestly sought for. Thus, rapid construction and features of soundness rendered by OPC in association with complementary cement materials have increased the credibility of blended cements.

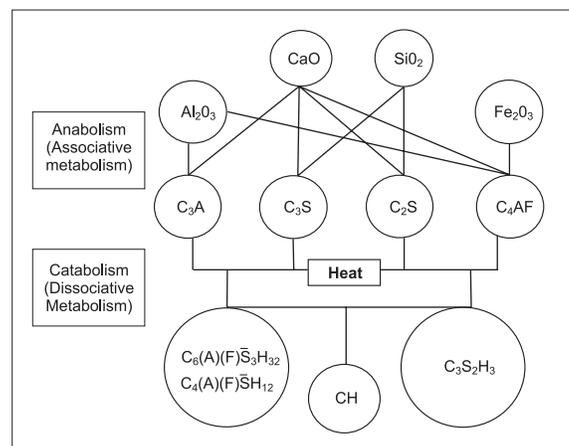


Fig 1 Metabolism of cement chemistry

Table 1: Heats of solution for various cementitious materials

Cementitious materials	Heat content, kcal/kg
OPC	612
Fly ash	358
GGBS	616
Silica fume	562
RHA	546
Metakaolin	684

Metabolism of cement chemistry

It is necessary to understand the chemistry of cement before comprehending the role of complementary cementitious materials (CCM) in blended cements. With reference to the release of heat and lime, cement chemistry has close analogy to metabolism in life system that consists of two phases, as illustrated in Fig 1.

In the first phase, called anabolism or constructive metabolism, the cells combine molecules to assemble new organic matters. This is identified in cement chemistry as associative metabolism during which the compounds of raw materials associate into anhydrous mineralogy, entrapping endothermic heat.

In the second phase called catabolism the cells break down molecules to obtain energy and release heat. In cement, this phase is identified as dissociative metabolism. Water or moisture triggers off reactions in anhydrous mineralogy of cement, by which heat is liberated and, simultaneously, compounds are dissociated from mineralogy. Presence of heat and water helps the compounds to associate into hydrated mineralogy that contributes strength to the mortar or concrete.

The cells of organisms and particles of cement have close parallel in their functions. A cell is intensely active and carries out life's functions including growth and reproduction. The cell is the source of heat; wherein mitochondria burn the fuel that a person eats. Similarly the cement particle is the heat source, but not with day-to-day generation. The difference is that the intake of food by organisms from time to time works as fuel for metabolism and heat generation, whereas, in cement the heat is tapped and entrapped in anhydrous phases right at the formation. In either case the heat results in growth and strength.

In addition to heat, lime of cement also draws parallel with sugar in life system. Both lime and sugar are basic needs and indispensable to their respective systems. When both of them are not engaged in catabolic reactions, they prove to be surplus and cause deleterious effects to their respective systems.

In this context, the authors present an interesting concept about the heat bank and lime bank of cement hydration system.

The hydraulic cements are associated with two performing features:

- heat bank
- lime Bank

In low-grade cements both heat and lime are available for hydration on progressive and sustainable basis for healthy performance. In high-grade cements the loci of these very performing features are disturbed, leading to durability problems.

Heat bank

Cementitious materials such as OPC or slag and, for that matter, complementary cement materials (CCM) such as fly ash, rice husk ash, silica fume and metakaolin do absorb some heat during the formations of anhydrous phases as indicated below in terms of heat of solution.

Heats of solution for different cementitious materials (studied on typical samples) is given in Table 1.

This heat, identified as endothermic heat during formation, manifests as exothermic heat during hydration. However, this heat does not get released instantaneously but spans to years together through progressive formation of hydrated mineralogy by reaction of lime with other compounds such as silica and alumina. In other words, the anhydrous constituents work as a heat bank to release the heat progressively over the ages for the formation of lime associated hydrated mineralogy. Thus, heat is one of the essential tools in the cement chemistry if it is maintained within the threshold levels. Excess heat of hydration of cement causes thermal stresses and microcracks in concrete leading to a durability crisis. In a way, controlled heat of hydration spells upon the formation of hydrated mineralogy, crystal growth, densification of the matrix and impermeability. It is the absence of this heat in lime-mortar which results in very slow formation of mineralogy, where, indeed, the external heat is availed from the environment.

The pozzolan that emerges out of volcanoes also contains some endothermic heat that renders relatively higher speed in the formation of hydrated mineralogy over that of lime mortars, when associated with lime and moisture. This observation resulted in the development of lime-pozzolan concretes used by Roman architecture that proved sustainable even after millennia of age.

With regard to blended cements, the heat values of CCM complement the heat bank of OPC by virtue of very slow and progressive hydration over years and decades.

In a nutshell, the above aspects can be summed up as follows:

- It is the sustenance of the heat liberation (exothermic heat) over prolonged ageing that is significant for sound performance of cement concrete through microstructure refinement and not the quantum of heat generated.
- The rate of heat emission depends upon the metabolic reactions of cement chemistry. Despite containing parallel quantity of heat, two cementitious materials liberate the heat at different ratings over different ages.
- The slower the rate of hydration-heat, higher the densification of microstructure; all resulting in impermeability and durability.

Lime bank

Lime is another principal constituent for the progress of cement chemistry. Lime is common constituent in age-old lime-pozzolan binders or lime mortars and modern-age OPC. The saturated lime solution, released out of cement hydration, incites reactions with anhydrous constituents whereby the mineralogical phases are dissociated along with release of heat. Presence of heat accelerates this phenomenon for the formation of hydrated mineralogy through re-association of compounds.

In age-old cements with coarse particle size and higher C₂S content, there was synergy between the release of lime and heat, commensurate to the progress of hydrated chemistry, without wasting either of them. In the process, the matrix used to get densified year after year rendering a relatively water impervious mass.

In contrast, in modern concretes with high-grade OPC the loci of lime and heat

are disturbed which raises several questions about the durability of concrete.

Complementary cement materials

Products such as fly ash, slag, rice husk ash, silica fume and metakaolin are identified as CCM for their ability to complement the engineering properties of OPC for improved durability. As explained already, there is a distinct difference in the heat content and rate of heat liberation between OPC and fly ash. In the production of OPC heat facilitates formation of calcium-associated mineralogy. The proportions of such mineralogy are monitored based on the desired grade. The same mineralogy exhibits rapid heat of hydration during setting and hardening of cement, liberating surplus lime.

As happens with OPC, the reactive phases of fly ash also absorb some endothermic heat during random formation of glass and reactive phases. Such heat absorption is more predominant while the fused fly ash is subjected to sudden temperature drop in economisers.

When fly ash is blended with cement, the reactive phases undergo reaction with liberated lime from cement, simultaneously liberating heat at a very slow pace in moderate quantities. In the process, fly ash compensates the heat bank of cement for sustained late-age reactions. Blast furnace slag also behaves on similar lines to fly ash in terms of progressive release of heat of hydration.

It is strongly believed that these studies would bring about a reorientation in understanding the chemistry of cement hydration. It is hoped to use this branch of science for characterising the cement materials from the point of view of reactivity and monitoring the scope of reactions at different ages of hydration interlinked with performance.



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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.

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