The role of gypsum in cement

Shreesh Khadilkar reviews the present situation of gypsum, and takes us through a variety of gypsum products, its merits and demerits.

Gypsum (CaSO$_4$.2H$_2$O) is used widely in various industries either as gypsum, i.e., the gypsum di-hydrate crystalline variety or as the gypsum hemi hydrates, also known as plaster of Paris (POP) or bassinite mineral. Gypsum is a colourless, transparent, naturally occurring crystalline variety of gypsum and is used extensively in ceramic industry and for manufacturing surgical grade plaster of Paris, whereas alabaster is a fine-grained, massive variety, white or shaded in colour. The Silky and fibrous variety of gypsum is called satin spar. It also occurs in nature as water soluble natural anhydrite (CaSO$_4$) as a massive or fibrous mineral. This variety does not much occur in India but countries like Turkey, Egypt, Oman, Thailand, etc. have substantial occurrence of natural anhydrite.

In general the gypsum that occurs in nature is called mineral gypsum. In addition to mineral gypsum occurring in gypsum mines, gypsum is recovered from salt pans during production of common salt in coastal region, particularly in Gujarat and Tamil Nadu. This variety is known as marine gypsum. The washed marine gypsum with lower chlorides (as NaCl content) is usable in cement manufacturing.

The total reserves/resources of mineral gypsum in India as on 1.4.2015 have been estimated at 1,330 million tonnes of which 37 million tonnes have been placed under ‘Reserves’ and 1,293 million tonnes under ‘remaining resources’ category. Of the total reserves/resources, fertilizer/pottery grade accounts for about 80 per cent and Cement/Paint grade 13 per cent. Unclassified and other grades together account for 5 per cent of total resources. The remaining two per cent of resources is shared by surgical plaster and soil reclamation grades. By States, Rajasthan alone accounts for 81 per cent resources, Jammu & Kashmir (14 per cent) and Tamil Nadu with 2 per cent resources. The remaining 3 per cent resources are in Gujarat, Himachal Pradesh, Karnataka, Uttarakhand, Andhra Pradesh and Madhya Pradesh.

India’s cement production capacity stood at around 502 million tonnes per year (mtpa) in 2018 and is expected to reach 550 mtpa by 2025. Typically, manufacturing cement uses 2 to 4 per cent gypsum per tonne of cement. Thus the country requires importing substantial gypsum to cater to the requirements of cement industry. This has made the cement industry to look at the usage of different varieties of gypsum such as by product/chemical/synthetic.

This paper discusses to begin with the role and necessity of use of gypsum in cement manufacturing and assesses the available avenues of using other types of available chemical/by-product/synthetic gypsum available in the country.

ROLE OF GYPSUM IN CEMENT

In the absence of gypsum, the reaction of C$_3$A in ground clinker (cement) with water is very rapid. The C$_3$A is converted to calcium aluminate hydrate (4CaO.Al$_2$O$_3$.19H$_2$O), which forms interlinking bridges of solid material between the cement particles. These interlinking bridges reduce the mobility of the cement particles and produce a hard structure, which results in flash-set (sudden hardening of cement paste) of the cement mixture, this is irreversible hardening. The presence of gypsum in cement slows this reaction of hardening the C$_3$A.

These crystals are too small to bridge the gaps between the particles of cement. The cement mix therefore remains plastic and workable. After the initial hydration reactions of cement, a dormant period occurs during which the rate of hydration of cement is greatly reduced.

It is observed that the optimum addition of gypsum will also enhance the hydration of alite (C$_3$S) leading to increased early strength and reduced shrinkage. Thus gypsum has a dual role, it helps to retard the setting of cement thus providing working time/application time for cement on the other hand it also enhances hydration of C$_3$S content due to which it contributes to increased Compressive strengths at early ages. The optimum quantity of gypsum (% SO$_3$) would depend mainly on:

- C$_3$ A content and its reactivity (clinker)
- Fineness and particle size distribution of the cement
- Alkali content and presence of soluble sulphate

The optimum gypsum usage in cement is a function of type of milling system as well as on the type of milling system.
cement (OPC, PPC and PSC). The optimisation should always be carried out in plant grinding system as the optimum gypsum is also a function of particle size distribution of the cements. While the lower threshold limit of the gypsum is governed by the necessity to avoid a quick set, the upper limit is governed by the considerations of maximising the early strengths and avoiding undesirable expansion in the hardened mortar/concrete. The sulphate content in the cement may be added in the form of:

- Gypsum - calcium sulphate dihydrate CaSO$_4$.2H$_2$O
- Plaster of Paris calcium sulphate hemi hydrate CaSO$_4$.0.5H$_2$O and / or
- Anhydrite calcium sulphate anhydrite CaSO$_4$.0 - 0.5H$_2$O

Because of the differences in solubility between hemihydrates (highly soluble), gypsum (moderately) and anhydrite-I (highly soluble) and anhydrite-II (poorly soluble), the nature of the sulphate-bearing compound added to the clinker during cement grinding is of significant importance.

### Table-1 – Solubility of various sulphates (adapted from Bensted)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Solubility (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>CaSO$_4$.2H$_2$O</td>
<td>2.4</td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>CaSO$_4$.0.5H$_2$O</td>
<td>~6</td>
</tr>
<tr>
<td>Soluble anhydrite</td>
<td>CaSO$_4$.0.001 - 0.5H$_2$O</td>
<td>~6</td>
</tr>
<tr>
<td>Insoluble (nature) anhydrite</td>
<td>CaSO$_4$</td>
<td>2.1</td>
</tr>
<tr>
<td>Syngenite</td>
<td>K$_2$Ca(SO$_4$)$_2$.H$_2$O</td>
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</tr>
<tr>
<td>Potassium Sulphate</td>
<td>K$_2$SO$_4$</td>
<td>1.36</td>
</tr>
</tbody>
</table>

The actual extent of transformation would depend on a combination of temperature, time and humidity. It can be seen from above that in cement grinding process if the cement grinding temperature is not appropriately controlled the added gypsum would convert to hemi-hydrate. It has been observed that when gypsum dehydrates completely to hemihydrate the cement shows false set due to rapid reaction of the high Hemi hydrate with hydration water precipitating the hemi hydrate as gypsum which results in fast setting of the cement, termed as false set, because if this hardened cement paste if travelled again, the gypsum formed dissolves in hydration water and makes the cement plastic again showing a normal setting of the cement subsequently. The set observed is due to reaction of hemi hydrate with water to precipitate as gypsum.

It has also been observed that if the hemi hydrate content is more than 30 per cent, the bagged cement shows soft/hard lump formation on storage. This necessitates cement grinding temperature needs to be controlled judiciously. As the interaction of the sulphate with the clinker is mediated through the liquid phase solubility is a key issue. The solubility of various sulphate forms is given in table-2.

### AVENUES OF USING OTHER TYPES OF AVAILABLE GYPSUM

In India many varieties of gypsum are generated such as:

- Chemical gypsum generated from the neutralization of effluent containing sulphuric acid
- Fluorgypsum: Gypsum generated in manufacture of HF
- Phosphogypsum: Generated in the manufacture of phosphoric acid
• Boro-gypsum generated from boric acid manufacture
• Titano-gypsum from TiO₂ production
• FGD gypsum: Generated in fluidised gas-desulphurising process (thermal plants using sulphurous coal/pet coke
• Synthetic gypsum: Synthesised from lime source and sulphuric acid

The Boro-gypsum and Titano gypsum are available in negligible quantities in the country. Chemical gypsum (from dyes/chemical Industries) and phosphor-gypsum (fertilizer Industries) are available in considerable quantities.

Chemical gypsum generated primarily by dyes manufacturing industries using sulphuric acid in the manufacture of dye intermediates. The waste/effluent containing sulphuric acid is neutralised with limestone to produce large quantities of chemical gypsum in these industries. This gypsum exhibit similar performance to mineral gypsum however the gypsum is available as wet cake with moisture contents up to 25 to 30 per cent, the cement plants have to handle the wet chemical gypsum appropriately. One of the main quality issues faced by cement plants using the chemical gypsum was the presence of contamination with azo dyes in the gypsum which resulted in market complaints on observation of different colours in concrete at customer site.

Many of the cement plants subsequently have evolved simple colour tests of the water dispersion of the chemical gypsum and only those consignments which show colourless water dispersion were accepted. Some other chemical gypsum are white/dirty white as wet cake but on drying in gantry/storage, the gypsum tends to become dark brown to reddish in colour which reduces its usage levels as it would affect colour of cements. Having appropriate performance tests on the receipt chemical gypsum would help the cement plants to overcome the cement quality issues in use of chemical gypsum and would result in usage of higher percentage of the chemical gypsum.

Fluoro-gypsum is another variety of chemical gypsum, which is produced in the manufacturing of hydrogen fluoride/hydrofluoric acid. The manufacturing process is by the reaction of CaF₂ (Fluorspar) with concentrated sulphuric acid in reactors at around 350 to 400°C.

\[ \text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{2HF} \]

The CaSO₄ produced is water soluble Gypsum anhydrite (CaSO₄ (x H₂O) where x = << 0.3 per cent). The reaction mass is cooled in air when unreacted conc H₂SO₄ fumes with moist air till it is cool. This anhydrite gypsum has higher solubility than Gypsum di hydrate / hemi hydrate gypsum. Usage of the anhydrite gypsum shows higher early strengths in OPC as well as PPC/PSC. The anhydrite gypsum has higher SO₃ contents of 51 to 53 per cent due to which its optimum usage level would be much lower that imported mineral gypsum/chemical gypsum, its usage also helps to increase % fly ash / % slag in PPC/PSC. In OPC its usage gives higher early strengths with lower setting time. It may be noted here that the cement using this gypsum does not show false set (like use of hemihydrate gypsum).

It is classified as hazardous material like any other chemical gypsum and necessities proper storage preventing any leachates going to ground water. When freshly removed from reactor it tends to liberate fumes in air. The gypsum has around 2 per cent CaF₂; however the fluorine is not water soluble and does not retard cement setting time of the cements. Most of this variety of gypsum is used by cement plants to advantage. Experience with this anhydrite gypsum has also resulted in import of natural anhydrite gypsum by many cement plants so to have the indicated advantages in cement properties.

Phosphogypsum: Phosphogypsum is a by-product from the wet manufacturing process of phosphoric acid (used for ammonium phosphate, fertilizer) by the action of sulphuric acid on the rock phosphate. Approximately 4.5-5.5 tonnes of phosphogypsum are generated per tonne of phosphoric acid production using wet process. The manufacturing steps in the production of phosphoric acid by this process are as follows:

Acidification of finely ground rock phosphate with sulphuric acid to form phosphoric acid and gypsum. The chemical reaction is detailed below:

\[ \text{Ca}_{10} \text{F}_2 \text{(PO}_4\text{)}_6 + 10 \text{H}_2\text{SO}_4 + 10 \text{n H}_2\text{O} \rightarrow 6\text{H}_3\text{PO}_4 + 10 \text{(CaSO}_4\text{.nH}_2\text{O)} + 2\text{HF} \]

Rock phosphate sulphuric acid water phosphoric acid gypsum hydrogen fluoride. Where n = 0, ½ or 2 depending on the hydrate form in which the calcium sulphate is crystallised.

• Filtration and separation of gypsum from the acid
• Washing of the gypsum filter cake to remove phosphoric acid
• Concentration of the acid by evaporation to the desired concentration.
The phosphogypsum filter cake is washed to recover as much phosphoric acid as possible without excessive dilution of the acid. The dilute acid is recycled to the first stage filter cake washing and is concentrated by indirect heating by steam in a vacuum evaporator. The by-product phosphogypsum is disposed off in dry or slurry form.

There are two distinct processes for manufacture of phosphoric acid, namely, the di-hydrate process and the hemi-hydrate process. Combination of di-hydrate and hemi-hydrate processes is also used for production of phosphoric acid to achieve higher degree of P₂O₅ recovery.

Phosphogypsum generation in the country is around 6 to 7 million tonne a year, large quantities of stocks are also available at the production sites. The impurities of phosphates and fluorides (especially the water soluble forms) present in phosphogypsum have a substantial retardation effect on setting time and also decrease the early strengths of the cements. The extent of retardation depends on the percentages of the two water soluble impurities either singularly or both together.

The phosphogypsum has the water soluble impurities of phosphates (0.05 to 1.0 per cent) and fluorides (0.3 to 0.9 per cent depending on the source). The retarding effect on setting time is more pronounced in the Blended cements (PPC & PSC). Its usage not only retards the setting time but also substantially decreases the early strengths in cements (especially at 1 day and 3 days) the effects on 28 days compressive strengths is negligible. The extent of retardation in PPC/PSC is also a function of % fly ash/% slag and the retardation in initial setting time could be even 8 to 10 hours or more, this extent of retardation is also a function the site temperatures.

In OPC, the retardation effects are less and the usage levels could be possible up to 60 per cent or more in total gypsum used, but for OPC going into high strength concretes the impurities at times may or may not be compatible to the admixtures used and the concretes may require higher dosages of admixture or changes to the admixture used, these aspects need to be assessed so as to maximise the use of phosphogypsum in OPC. More acidic is the pH of phosphogypsum higher is its retardation tendency; the acidic pH is due to water soluble phosphate and fluoride ions.

Avenues for maximising use of phosphogypsum
Several alternatives have been reported in literature

<table>
<thead>
<tr>
<th>Industry</th>
<th>Type of Process</th>
<th>Insoluble P₂O₅</th>
<th>Insoluble F</th>
<th>Soluble P₂O₅</th>
<th>Soluble F</th>
<th>Moisture</th>
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<tr>
<td>TCL, Haldia, West Bengal</td>
<td>DH</td>
<td>0.5</td>
<td>0.25</td>
<td>0.3</td>
<td>0.6</td>
<td>15</td>
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<td>PPL, Odisha</td>
<td>DH</td>
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<td>-</td>
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<td>0.8</td>
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<td>4.5</td>
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<td>0.5-1.0</td>
<td>-</td>
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<td>Hindalco Industries (HIL) P.O. Dahej, Gujarat</td>
<td>DH</td>
<td>0.5-1.6</td>
<td>0.45-0.65</td>
<td>0.05-0.6</td>
<td>0.03-0.06</td>
<td>18-22</td>
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<tr>
<td>Indian Farmers Fertilizer Co-Operative Ltd. (IFFCO) Musadia, Odisha</td>
<td>DH</td>
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<td>0.2-0.5</td>
<td>0.04-0.1</td>
<td>0.04-0.06</td>
<td>6-12</td>
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<tr>
<td>Rashtriya Chemicals And Fertilizers, (RCFL), Mumbai</td>
<td>HDH</td>
<td>0.2-1.2</td>
<td>0.06-0.2</td>
<td>0.05-0.6</td>
<td>0.02-0.16</td>
<td>15-20</td>
</tr>
<tr>
<td>Range</td>
<td></td>
<td>0.2-1.6</td>
<td>0.06-0.65</td>
<td>0.04-1.0</td>
<td>0.02-0.16</td>
<td>6-24</td>
</tr>
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Phosphogypsum generation in the country is around 6 to 7 million tonne a year, large quantities of stocks are also available at the production sites. The impurities of phosphates and fluorides (especially the water soluble forms) present in phosphor-gypsum have a substantial retardation effect on setting time and also decrease the early strengths of the cements. The extent of retardation depends on the percentages of the two water soluble impurities either singularly or both together.

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Avenues for maximising use of phosphogypsum
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for either removing the water soluble phosphate and fluoride for phosphogypsum. Such beneficiated or treated phosphogypsum is usable to higher levels without affecting the setting time and early strength properties of cement. Washing of the phosphogypsum with warm water reduces to large extent the water soluble impurities. Such washed gypsum is usable to very high levels in OPC and up to 10 to 15 per cent in PPC/PSC without much effect on setting time and early strengths.

Another process is lime treatment of phosphogypsum, this process removes the water soluble fluoride and phosphate impurities, such a treatment however does not remove the water soluble impurities trapped in the crystal lattice it removes only the absorbed impurities. Lime treated phosphogypsum could completely replace mineral/imported gypsum in OPC and up to 25 to 30 per cent in PPC/PSC. As indicated this process does not remove the water soluble impurities trapped in the crystal lattice.

Literature and patents also report use of additions to phosphogypsum such as alkanolamines, High alumina cements, and water soluble aluminates with a large extent of retardation.
or without thermal treatments. Phosphogypsum treated with such additives can fully replace mineral/ imported gypsum even in PPC. In these methods, the surface as well as lattice impurities of water soluble fluorides and phosphates are made inert. It has been observed that the properties of cement with use of such a processed gypsum are even better that the properties of cements observed with use of imported mineral gypsum.

Considering 6 to 7 million tonnes of annual generation in the country and the large quantities of the material available in pond dumps at the generation sites, some of the above alternatives would have a good commercial potential especially if the processing is done nearer to generation sites.

**Gypsum: Generated in fluidised gas desulphurising process (Thermal Plants using sulphurous coal/pet coke). Globally, flue gas desulphurisation (FGD) systems have been installed in many thermal power plants in developed countries, FGD plants have been in operation in the US for the last 40 years. Proven technologies are available for FGD in power plants. The technologies are primarily based on limestone and lime products such as quick lime or hydrated lime. FGD plants-based wet process technology using limestone slurry is used most commonly in the US and China.**

In this process, the gaseous SOx is absorbed in limestone slurry and forms synthetic gypsum (SG) which can be a substitute for mineral gypsum by cement industry. FGD Gypsums of thermal power plants can become a major source of gypsum for the Indian cement industry. It can become a substitute for imported gypsum consumption by industry. The quality requirements of Limestone for FGDs are defined in FGD specification documents of the Central Electricity Authority (CEA). It is to be noted that the quality requirements are similar to the limestone quality requirement for clinker production. Higher the lime content in limestone, higher will be the purity of SG produced by FGDs.

Typically, the limestone requirement for FGD plant with sulfur content of 0.5 to 0.7 per cent in coal fired in power plants is about 0.23-0.30 TPD of limestone/MW installed capacity. It is estimated that limestone demand by FGD systems will be about 15 mtpa by 2022. FGD plants of wet process technology generate a solid product, which has similar chemical composition of gypsum i.e. CaSO₄·2H₂O. This product, in the form of slurry is collected at the bottom of the SOx absorption tower. The slurry passes through belt filters to generate filter cake of about 10-12 per cent moisture. The expected quality of per cent from wet FGDs is as follows:

- Gypsum purity (as CaSO₄·2H₂O, dry) is more than 80-90 per cent (depends on LS quality)
- Free moisture: 10-12 per cent
- Particle size: 100 per cent passing 200 microns

The above is similar to phosphogypsum, however the FGD gypsum does not have water soluble impurities, that affect cement Properties. In future the integrated cement units could have an understanding with power producers about supply of limestone to FGDs and in return and receive SG from power producers. This will benefit both the sectors as it optimises the landed costs at both ends. Such an initiative of course would necessitate revision of conditions of ML for Limestone by cement companies and hence, a joint initiative could be taken up CMA and CEA (Central Electricity Authority) for representation with concerned departments of State/ Central governments for relaxation of ML conditions cement and power producers can also jointly explore the possibility of installing SG dryers at power plants to reduce the handling, transport and dosing problems associated with wet FGD gypsum. This could be a win-win situation for both industries and would also help reduce the dependency of cement industry on imported gypsum.

**Synthetic gypsum:** Some of the cement plants in the have adopted this route of synthetic gypsum by reaction of concentrated sulphuric acid ground limestone/ESP dust. Commercially feasible at locations where the logistic cost of sulphuric acid is lower. Another off-shoot of this process could be through reaction of waste lime sludge from paper/fertilizer/textile industry and use waste sulphuric acid from chemical/battery industries to produce synthetic gypsum. Of course this option also would be feasible only for selected locations where both components are available.

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