Achieving Lowest Clinker Factor in fly ash /slag Based Cements

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Reducing Clinker Factor , Challenges ?

Clinker Factor Reduction

- Lower Cost of the Cement
- Enhances Volumes of Cements, from the clinker , which has its benefits in sold out markets
- Increases the durability quotient of the Blended Cement Product in Concrete

Challenges ?

- Low Clinker Factor could Affect Cement Quality and Performance
- Increased fineness of Cement , result in Increased Power Consumption
- Decrease Cement Mill Thru-puts
- May affect Concrete Performance at site and against Competitor Products in Market

Avenues for Reduction in Clinker Factor

Clinker Factor Reduction can be achieved through :

- **Improving Clinker Quality (Reactivity)**
- **Selection & Optimisation of Type & % use of Gypsum**
- **Characteristics of Fly ash / Slag used & Optimization of PPC /PSC**
- **Use of Cement Additives.**

Improving Clinker Quality

Improving Clinker Quality (Reactivity)

- **Optimising the Chemical Composition and clinker phase composition**

- Judicious Raw Mix Optimisation with existing or alternative corrective materials (with the fuel mix used by the plant) so as to have clinker with improved reactivity / hydraulic potential .
- In a running plant the approach has to be by attempting small gradual changes to clinker composition and assessing the impact of the changes on kiln Performance & clinker Quality .
  - The changes to be attempted could be indicated **through data analysis.** ***In each plant the QC & Process has a detailed analysis data of the Day Average clinkers along with its lab ground Cement Test Results .***
  - ***Additionally the article suggests : "to test at least one spot clinker per day for chemical parameters and physical tests of Lab ground Cement"***

Data analysis Mode :

- ✓ **why ? On some days or in some spot clinkers , the clinker reactivity is suddenly very good ?.** *In absence of an XRD some guiding indication could come from the comparison of the chemical composition of such clinkers* ***if XRD is available the phase composition of such clinkers by XRD could indicate the possible reasons .***

Improving Clinker Quality (Reactivity).....

- ✓ *It could also indicate at times* ***the impacts of changes in Fuel ,/ Sources of Coal / Proportions of Coal & Petcoke (even source of Petcoke) / AFR usage***

- *For The* Lab Ball mill grinding of average/spot clinker with fixed Time , it is preferable to select a grinding time to achieve **Blaine's of around 300 - 320 M^2/kg with the residue on 45 microns of the Cement in range of 18 to 20% , at this fineness, the clinker is observed to depict changes in clinker reactivity in terms of changes in 1 Day strengths of cements (± 3 to 5 MPa) .**
- At lower grinding Blaine's (of around 250 M^2/kg) , presently practiced by many Cement Plants , one does not observe the changes in clinker quality / reactivity as the changes in **1 Day compressive strengths is only ± 1 MPa**

Typically Clinkers with Good reactivity are observed to show 1 Day strengths in Lab ground Cements of 30 to 35 MPa (Higher values being observed when clinker alkali sulphates are high)

In the ball Mill grinding the achieved Blaine in the fixed grinding time is also indicative of clinker grindability.

Improving Clinker Quality / Reactivity -------

▪Process / Quality fluctuations :

- **Changes in fuel proportion & residue on 45 microns : If Mixed fuel (Petcoke + Coal) is used by inter grinding** , two fuels substantially different in their grinding characteristics *and so in mixed grinding , petcoke tends to concentrate on coarser fractions of ground mixed fuel.*
- **The fineness (lower the residues better) , check the impact of reducing residues on Kiln performance /clinker quality**
- *Coarser fuel residues in calciner / kiln increases the occurrence of frequent coatings / build ups*
- **Flame Momentum . With petcoke used in Kiln higher flame momentum is preferred >10 .**
- Typically using 100 percent coal or Petcoke is most suited , however from optimized cost mix a combination has to be used , the two fuel should be ground separately **with petcoke as kiln fuel** , this produces a consistent clinker phase composition and reactivity and stable kiln conditions
- *Frequent forming and falling of BZ coating / or ring in BZ / pre -Transition or Transition Zone is due to formation of low temperature Eutectics reasons for which need to be searched*

Improving Clinker Quality / Reactivity -------

- ***Check Clinker Nodules : <u>When free Lime is high whether the coarser nodule show higher free lime or show Brownish – yellowish core ? .</u>***
- *This occurrence could be due to the fluctuations in clinker liquid content as well as Liquid viscosity , or could be due to reducing conditions or falling of low melting coatings from kiln inlet /riser duct* ***etc Fluctuation in degree of calcination /variability of composition of the two strings (calciner) etc***
- *In some plants****, in some cases such observations are also reported due to fluctuations in usage levels of Shale / Low grade limestone / Clays (low meting materials from quarry) in the formation of limestone pile***
- *Plants with AFR co-processing , liquid wastes co processing necessitates monitoring of Hot Meal Volatiles , sudden changes in co-processed tonnages causes fluctuations in clinker quality indicated by clinker SO3 fluctuations , For solid wastes co-processing ,* ***the % ash content and waste ash compositions should be monitored*** *, higher fluctuations, affect kin performance and clinker quality .*
- *In case the Plant observes drastic decrease in day average clinker quality, the P2O5 contents in Clinker (also spot clinkers) should be analysed , if clinker P2O5 contents >0.3% , for the same clinker compositions , the 1 day strengths can be substantially reduced).*

Improving Clinker Quality -------

- Typically , the target clinker composition to give a good hydraulic potential of clinker would be : with LSF of 93 to 95 with a bogues potential C_3S of >55% , with C_3A (6.5 to 8.5%) (if the clinker is used for PPC/PSC and also for OPC (especially if OPC is supplied to RMX customers) and **SM 2.2 to 2.4 A/F 1.2 to 1.4).**

- In plants where clinker MgO is higher (3.5 to 4.5%) , besides having the above target modulii Values , the minimum clinker lime targeted should be between 62.5 to 64% for good clinker reactivity (lower value of CaO , for higher MgO in clinker)

- If the Plants raw Materials have low MgO , and the quarry limestone is siliceous , use of low silica dolomitic limestone or choice of low silica correctives such as low silica Iron Ore / Bauxite /Laterite etc is always advantageous .

- Use of fluoride based Mineralizers (CaF_2, SSF etc) , are observed to substantially improve the clinker reactivity , however from cost benefit angle presently it is not attractive .

Selection &Optimisation of Type & % use of Gypsum

The sulphate content (%SO3) of the cement should be such that it is consumed for the initial reactions and not later than 24 hrs after mixing with water. (Fig 1 & 2)

The optimum quantity of Gypsum (%SO3 usage)depends on

- **C_3A content and its reactivity. (Clinker) Fineness &**
- **Particle size distribution of the cement**
- **Alkali content and presence of Soluble sulphates in Clinker**

<u>For each type of Cement Type (OPC/PPC/PSC /PCC) and for every Milling system. as well as Type of Gypsum , Gypsum optimisation needs to be carried out at the Plant under stabilised conditions of the Milling system</u>

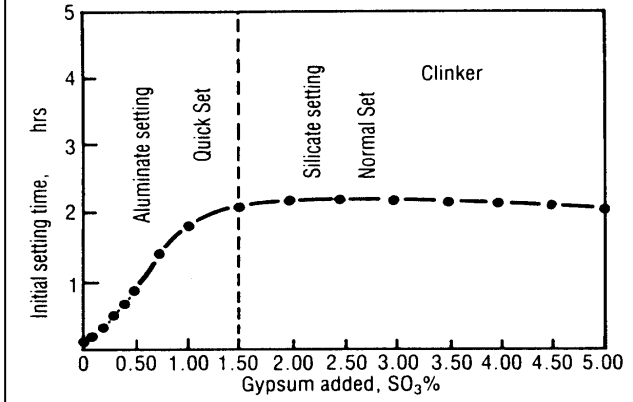
Optimum SO3 content in various types of cement

OPC - % SO3 -~2.2%

PPC - % SO3 -~2.3 – 2.6%

PSC - % SO3 -~2.4 – 2.6%

Fig 1. Effect of gypsum added on setting time



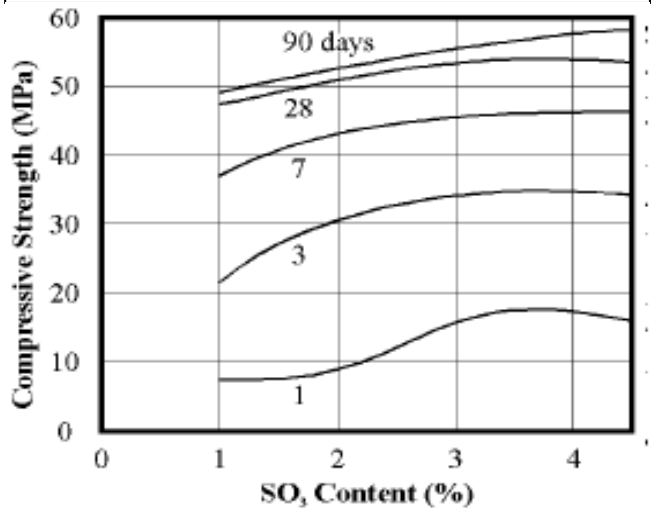


Fig 2 Effect of % SO_3 on compressive strengths of Cement

Optimisation of % use of Gypsum

- As and when there is decreased availability of fly ash , the Plant tends to reduce % fly ash in PPC , and decrease the fineness of PPC so as to maintain the Mortar quality norms of the Product.
- Such actions would affect the PPC performance in Concrete at the applications sites , it also increases the variable cost of the Product , due to increased clinker factor .
- For such instances the plant should use lower purity Gypsum (kept in stock) which would help to relatively maintain the clinker factor of PPC. Use of cement grinding aid accelerator would help in such cases .
- In general use of anhydrite Gypsum (synthetic / Natural) , is advantageous for PPC / PSC as it increases the early strengths and there by assists in increasing % Fly ash / % slag in PPC/PSC
- With Petcoke as fuel the clinker tends to have higher SO3 , in which case if Imported / high Purity Gypsum is used to achieve % SO3 in Cement less percentage of Gypsum will be used . In such cases also using low purity Gypsum helps to increase usage percentages and there by helps reduce clinker factor

Characteristics of Fly ash used & Optimization of PPC

Characteristics of fly ash used

- **Combustibles in fly ash**
- **Chemico–Mineralogical properties of fly ash**
- **Effect of amorphous phase composition of the fly ash**
- **% Use of CPP Fly ash (Crushed Coal fired (AFBC/CFBC) boilers)**
- **% Use of Pond ash**
- **Fineness (Particle size Distribution of fly ash) received from Power Plants (pulverized coal fired) .**

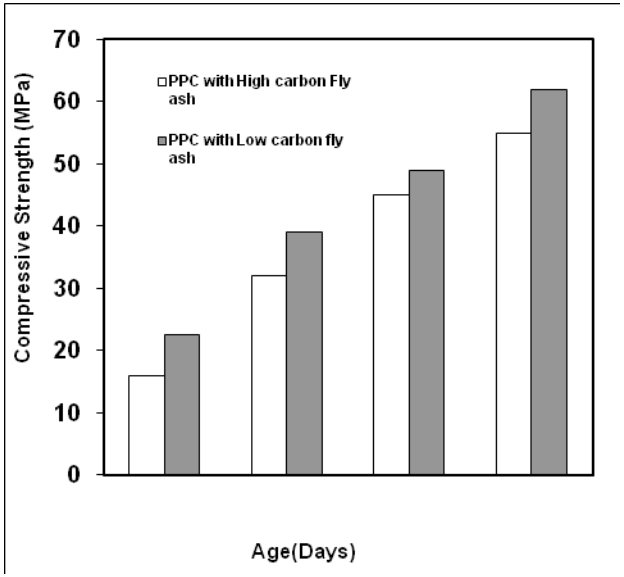


Fig.3 : Effect of high carbon content in fly ash on compressive strength

Combustibles in fly ash

The carbon or combustible contents of fly ash can be determined by loss-on-ignition (LOI, a measure of carbon mass).

The high-carbon fly ash tends to demand more water thus affect the compressive strength characteristics of the resultant PPC Mortar and resultant Concrete .

The Fig.3 depicts the physical properties of PPC (Indian standards)produced with 20% of high carbon (12.5%) and low Carbon (2.5%) fly ash.

Chemico–Mineralogical properties of fly ash.

In India the chemico - mineralogical characteristics of dry fly ash produced, has been observed to vary. The mineralogy of fly ash has 15 -30% Mullite, 15-45 % Quartz, 1-5% Magnetite, 1-5% Hematite and around 25 – 50 % of amorphous glassy alumino - silicate phase.

The ternary phase diagram of SiO_2-Al_2O_3-CaO (Fig 4) indicates the relative positions of different materials . As the lime in fly ashes increases their relative position moves towards the center of the ternary diagram so does the reactivity .

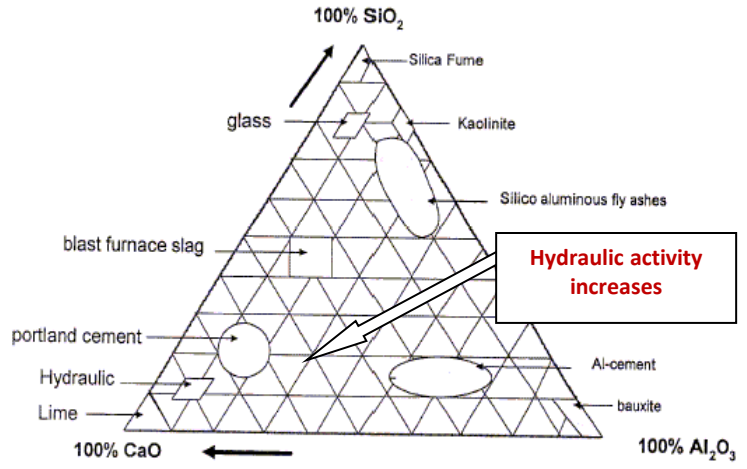


Fig.4: SiO_2-Al_2O_3-CaO system showing relative positions of cement & cementitious materials

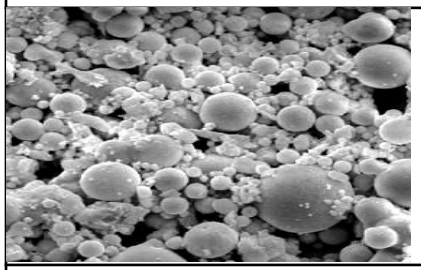
The amorphous phase in fly ash is the reactive part in fly ash responsible for the pozzolanic hydration reaction. The crystalline **phases of fly ashes such as Mullite, α-quartz, hematite, magnetite are non hydraulic ,In Class F fly ash (low lime) the alumino-silicate amprphous phse is Pozzolanic (most of the Indian Fly ash)**

In Class C Fly ash with higher Lime , the calcium alumina silicate glass , crystalline calcium aluminate phases present makes the fly ash cementitious in nature .***Thus the chemico-mineralogical properties would determine the reactivity of the fly ash and their by influence the % clinker factor in PPC***

% Use of CPP Fly ash (Crushed Coal fired (AFBC/CFBC) boilers)

These fly ash constitute 10 to 40% of Total fly ash used for PPC manufacture in many plants , Depending on **consistency of supply of Dry Fly ash** generation of CPP Fly ash , the % use of CPP Fly ash increases .

This CPP fly ash produced at lower over board Temp. show higher water demand and show much lower early strengths in PPC . There by Increasing the Clinker Factor for achieving quality compliance at Early ages .

Boiler Type	
Pulverised coal fired	Crushed Coal fired (CFBC/AFBC)
	
High temperatures (1300 to 1500 °C)	**Low temperatures 850 – 900 °C**
Workability	
Increases	**Reduces**

It has been observed ***that lower is the percentage use of CPP fly ash lower would be the clinker factor achieved in PPC (i.e high would fly ash absorption***

Use of Pond ash : Pond ash has higher absorbed & adsorbed moisture , the wet storage agglomerates the finer size particles , it also has varying percentage of bottom ash which is pumped to the same fly ash ponds . Use of Pond ash affects the water demand and early strengths of PPC there by tends to increase the clinker factor .

In both the above cases use of *suitable Cement additive combination could help to reduce the water demand of PPC , thus would help achieve Lower clinker factor in PPC ,and would also enhance the performance of PPC Mortar & Concrete .*

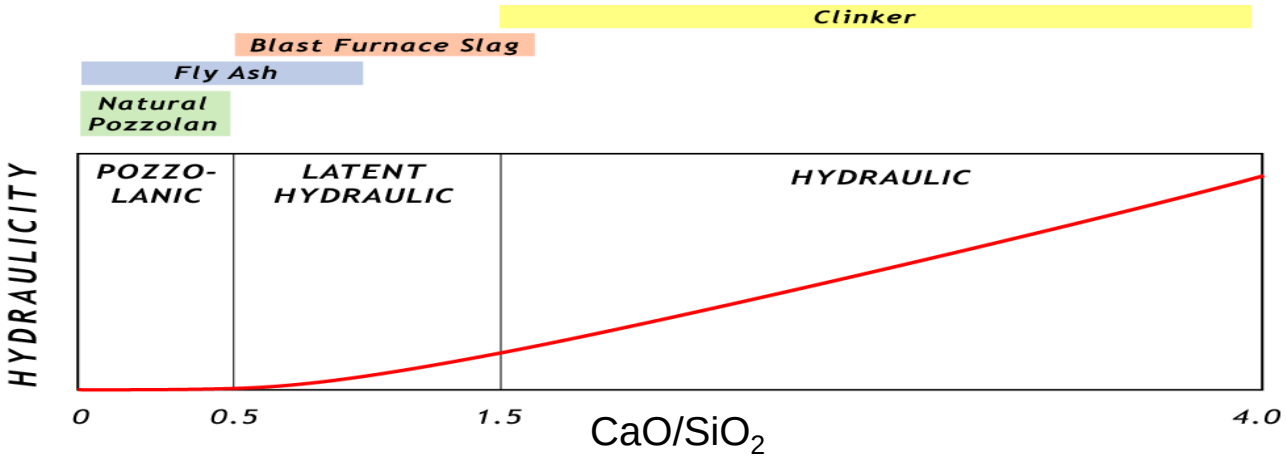
Granulated Slags / PSC

- Granulated slags of Glass content >85 % are used for PSC
- In most of the Modern Plants manufacturing PSC the slag is ground separately while the OPC is ground separately
- There are grinding aids used for slag grinding as well as for OPC grinding .
- Some of the plants also use strength accelerators along with grinding aids which should be chloride free
- ***% slag in PSC is more governed by the Particle size distribution of the ground slags and ofcourse on the clinker Quality***
- ***Typically OPC (clinker +Gypsum) should be ground to around R 45 of 10 to 12% (Blaines 360-380 M2/kg) while slag should be ground to around 70% passing 20microns with blaine's of around 400 – 420 M2/kg Blaine's , for slag control on 45 micron sieve has no relationship***
- Many plants today achieve **% slag up to 60 to 65% in PSC** .
- Cost economics depends on landed cost of slag to the Plant as well as the clinker costs

Characteristics of Granulated Blast Furnace slag (GBFS)
&
PSC optimisation .

Characteristics of Granulated Blast Furnace slag (GBFS)

The hydraulic property of different materials with increase in C/S ratio is indicated below .



As also seen from the ternary diagram in Fig 4 , with the increase in CaO in materials the hydraulic activity of the material increases.

The Granulated blast furnace slag (GBFS) is cementitious showing its own hydraulic potentials ,

In most of the Modern Plants manufacturing PSC .
The slag and OPC is ground separately and interblended to produce PSC .

The *% slag in PSC is more governed by the Particle size distribution of the ground slag and also of course on the clinker Quality .*

It may be noted here that the OPC component in the Portland Slag Cement is the alkaline activator

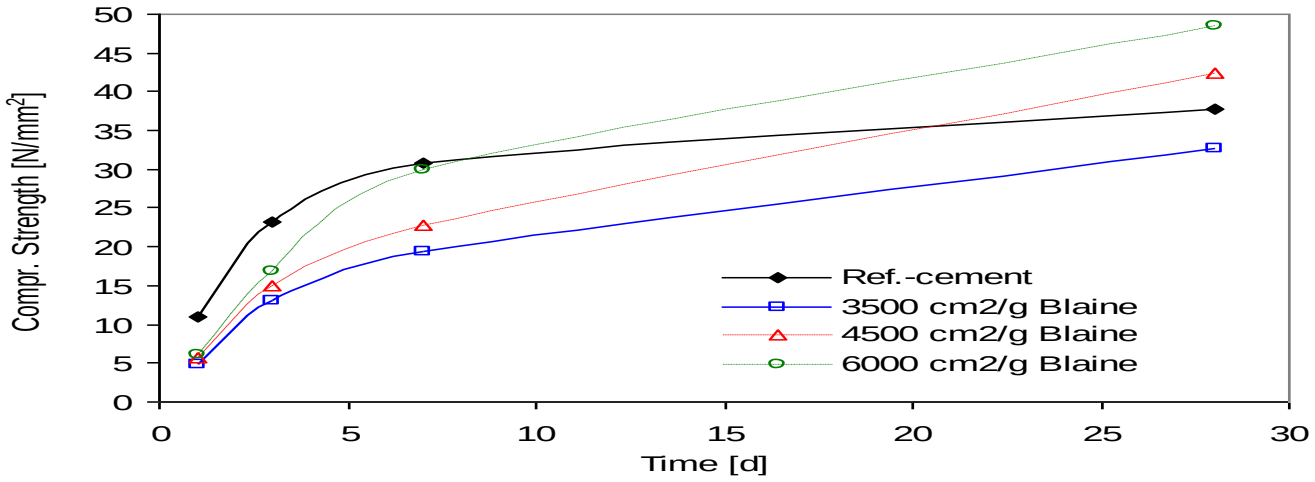
GBFS properties influencing reactivity

Parameter	Range observed	Ideal	Preferred	Comments
Chemical composition – Major elements				
CaO/SiO_2	0.85-1.3	~1.3	>1.0, ≤1.4	CaO controls dissolution,
Al_2O_3	7.5 - 20	13 -14	>10, <15	ettringite formation at early ages
TiO_2	0.4-2.5	Lowest	<0.5	Reduces dissolution
MgO	6.5-15.0	~10-	<12	Not as effective as CaO
Physical properties				
Bulk density, kg/l	0.6 -1.3	0.9-1.0	<1.2, >0.8	Low bd, higher reactivity, but high % moisture
Mineral	Melilite: Gehlenite (C_2AS_2) ,Akermanite (C_2MS_2),Merwinite: C_3MS_2			Merwinite in basic slags, indicates high reactivity
Glass content	85 to 96	~95	>90	increase dissolution
LOI (CO_2)	0.2-2.6	Lowest possible	<1.5	Due to aging & false Blaine“

The Alumina content has strong influence on GBFS reactivity, especially at early ages. Ideal Al_2O_3 Content being: 13-14%. , as the TiO2 content in GBFS increases the slag becomes denser and harder to grind and its reactivity is observed to decrease

Reactivity of ground GBFS & Fineness

Effect of increased fineness on reactivity of ground GBFS



typically the reactivity of GBFS slag increases with increase in Fineness

*For achieving **lowest clinker factor ,** typically in the inter blending mode :*

- *OPC (clinker +Gypsum) should be ground to around 380 to 400 M^2/kg (with 10 to 12 % residue on 45 microns)*
- *Slag (preferable slag + Gypsum) should be ground to around 70 to 75% passing 20 microns with Blaine's surface of around 400 – 420 M^2/kg .*
- Many plants have achieved by inter blending mode **% slag up to 64 to 67% with clinker factor of PSC at around 27 to 29% and the quality of PSC manufactured is competitive in Market**

Optimisation of PSC

In the inter-grinding mode with Clinker +Slag + Gypsum ground together :

- ***The clinker (with Gypsum) gets preferentially ground leaving slag relatively coarser .***
- ***Proper optimization of the distribution of slag in desired size fractions of Cement with or without cement additives could help achieve a clinker factor of around 35 to 40 % .***
- **There are grinding aids (combined with strength accelerators) , used for slag grinding , as well as for OPC grinding.**
- **For slag grinding with hot air the grinding aids should not be steam volatile.**
- **The strength accelerators along with grinding aids should be chloride free**

Achieving the lowest clinker factor in PSC is advantageous firstly from cost economics and also because it substantially increases the Cement volumes from the clinker , which is beneficial for a sold out market especially for Grinding Units .

Use of Cement Additives

Use of Cement Additives

The last and final step in achieving Lowest Clinker factor in PPC & PSC would be , use of Cement additives .

These are substances added in very small proportions typically < 0.25 % to the cement mill to improve

- **Production capacity**
- **Cement flowability (avoid “pack set”)**
- **Cement properties (to achieve lower Clinker factor)**
- **For improved performance in Concrete**

In common language these are referred to as “grinding aids” or “quality improvers” , as per EN 197-1 they are called “additives” , the ASTM standard uses the term “additions”

Cement Additives

The materials could be further differentiated as below

- **As Grinding aids:**
  - **Bottlenecks in cement grinding capacity, such materials can enhance throughputs**
  - **High specific electrical energy consumption during cement grinding**
  - **"Pack set" problem i.e problems with cement handling due do its flowability .**
- **As Quality improvers:**
  - **Opportunity for further clinker factor reduction**
  - **Cement setting or strength development issues at early or later ages .**
- **Others: materials which are used for specific special cements like masonry Cements special premium Cements with special USPs , *Production of special cements/binders with better margins (masonry cement, road binder …*)**

Cement Additives

Action mechanism & Basis for the Additive Formulation

When Cement additives are used :

- **The additives reduce the inter-particle forces**
- **Reduces coating of grinding balls and mill internals ,due to creation of like charges on cement particles.**
- **There is decreased agglomeration , much improved flowability , higher generation of fines better dispersion of particles in separator feed .**
- **There is a reduction of mill filling level (decrease of residence time) .**
- **In VRM grinding , necessary actions need to be taken to have stable Bed formation on the grinding table.**

Commercially available Cement additives from National & International suppliers:

The additives are formulated mixture of compounds in aqueous solutions (40 to 50 % water). formulated:

- **as per the requirements of the customer,**
- **as per the cement components used by the customer .**
- **as per the desired objective of usage of the additives , which could be like increased thru puts , improved early and /or later age mortar strengths , improved concrete performance of the resultant Cements etc .**

Formulations Details : Basic Concept

There are many Cement plants / cement groups in the world , who have developed the cement additive formulation themselves ***so as to avoid a black box - Cement additive from suppliers*** .

These plants procure the individual compounds **(in their purer form)** , and create their own optimized formulations at site with adequate dilutions with water , for use in Cement grinding .It is **a cost saving option** on hand and on the other hand has a **flexibility of altering the formulations** as per the requirements

As reported in literature & also substantiated by a number of detailed evaluations of different cement additive formulations in market , The cement additive formulations are :

A Combinations of Different Chemical compounds **,** typically composed of :

1. Accelerator/s for the hydration reaction of Cements

- ✓*Dependent on the acceleration effect desired in* ***Mortar / Concrete compressive strengths at early or later ages*** *.*
- ✓ *Clinker quality and blending components (fly ash / slag) or a mix of both*

Formulations Details : Basic Concept---- continued ….

2. *Water reducer / workability / wet-ability / enhancer*

- ✓ *Which show impact on the resultant Cement mortars & concrete.*
- ✓ *Some of the compounds (retarders) like polysaccharide derivatives , gluconates etc show an initial retarding action towards hydration which result in reducing the water requirements for the Cements Mortars & concrete . thus act as water reducers*
- ✓ *It could be some appropriate polymeric molecules which show much improved wet-ability and reduce water demand .*

3. *Grinding aids*

- ✓ *Compounds that work as **Grinding Aid** i.e. which would enhance **Mill thru-puts** on one hand as well as would **increase the early strengths due to the higher** fines generation/ or activation of cement components .*
- ✓ *These compounds could be like alkanol-amines such as TIPA , DEIPA , TEA etc or could be compounds like glycols and other poly-ols , depending on whether it is a PPC or PSC manufacture*

Advantages & Applications of Cement Additives

***Cement additives with o**ptimal combination (either from suppliers or as formulated at site) , evolved for PPC/ PSC /PCC are observed to :*

- ✓ *Act as grinding aid cum accelerator combinations .*
- ✓ ***Enhances productivity of Cement grinding***
- ✓ *H**elp achieve lower clinker factor in PPC/PSC/PCC .***
- ✓ ***Exhibit a much improved concrete performance** of the blended Cements at application sites even at higher % fly ash / % Slags in the PPC/PSC/PCC .*

***Cement additives could be used** to create specific **niche properties** of the Blended Cements like*

- ✓ **Premium high strengths high Performance brands** of PPC/PSC/PCC
- ✓ Premium Brands with properties could be **water repellency , water proofing , much reduced water demand , self compacting , self leveling properties of Blended Cements** in concrete etc .

Conclusive Thoughts

- ***Cement additives could be used to over come in-efficiencies of clinker and grinding circuits .***
- ***However this would actually not realize the complete benefits from using Cement additives .***
- ***Thus as discussed above a judicious optimization , in the steps indicated above , would definitely help achieve lowest clinker factor in PPC/PSC/PCC***