NATURAL POZZOLANS

by
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Korhan Erdogdu

- Civil engineer, specialised in cement and concrete material science.
- Worked for Turkish Cement Manufacturer's Assoc. R & D Institute as a Chief Researcher for 6 years.
- Have several papers, state of the art reports and booklets on the below mentioned topics.

<u>Field of Activity and Research:</u>

- Usage of slag, pozzolan, limestone, fly ash etc. in cement.
- Grindability and design of grinding plants
- Durability of cementitious systems
- Microstructure in relation with cement properties.

Object and Scope of This Session

The aim of this session is to present facts about natural pozzolans (NP) based on the literature and Turkish experience.

Topics:

- Basics on NPs,
- Impacts of NPs on cement properties,
- Economical aspects of NP usage in cement,
- Sulfate resistance by NPs,

Abbreviations

NP	Natural Pozzolan
PC	Portland Cement
CH	Calcium Hydroxide, CH, $Ca(OH)_2$, portlandite
SR	Sulfate Resistant

"Cementitious systems" refers to
- Concrete
- Mortar
- Paste

KE Korhan Erdogdu, when giving references to his academic studies

Introduction - What is Natural Pozzolan?

According to ASTM C 618 & EN 197-1

Pozzolan is a siliceous or siliceous + aluminous material which has little or no cementitious value. However,

- at ordinary temperatures,
- in finely ground form,
- in the presence of moisture

it reacts with $Ca(OH)_2$ and yields compounds possessing cementitious properties.

Accordingly, natural pozzolan (NP) is a natural material which exhibits this property. Generally, NPs are the rocks of volcanic origin and usage of them as a cementitious material has a history of more than 2500 years.

Introduction - Pozzolanic Reaction

Pozzolanic Reaction (ultra simplified):

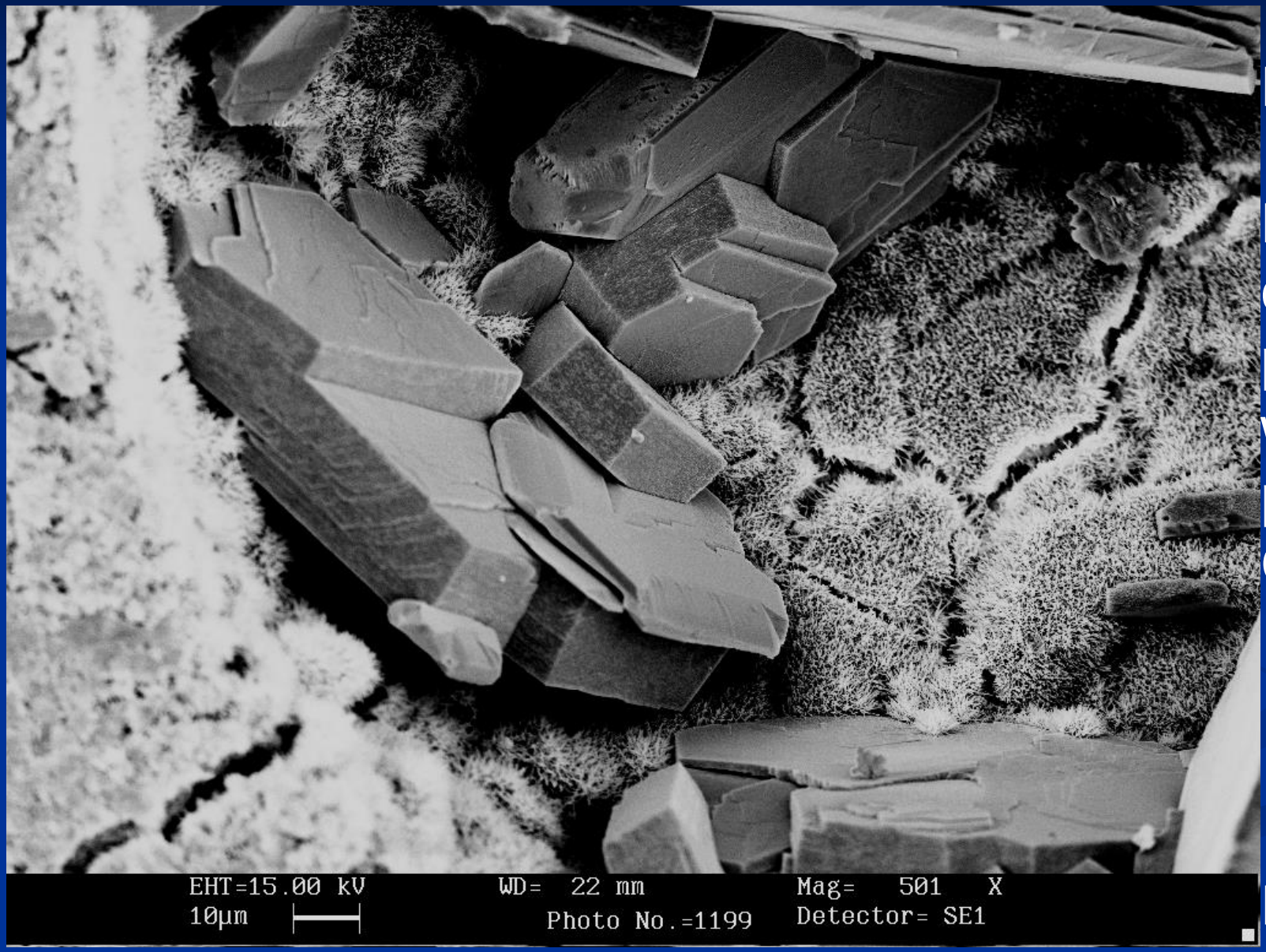
Pozzolan + Water + $Ca(OH)_2$ $\xrightarrow[\text{Slow Reaction Rate}]{}$ C-S-H Gel + others

PC Hydration (ultra simplified)

PC + Water $\xrightarrow[\text{Fast Reaction Rate}]{}$ C-S-H Gel + $Ca(OH)_2$ + others

C-S-H Gel Gives strength.
$Ca(OH)_2$ Not a desirable product.

Introduction - Basic Info on CH



PC at 2 days

Large CH crystals in previously water filled pores and CSH Gels.

Ref. KE

Introduction - Basic Info on CH

Why $Ca(OH)_2$ is not a desirable product of PC hydration?

- No contribution to strength.

- Highly water soluble. Thus, it leaves the matrix upon water movements and releases empty open pores. This fact increases permeability.

- Most of the harmful mechanisms to concrete needs presence of CH as a precondition.
  (Ex: sulphate attack, alkali-silica reaction, carbonation etc.).

Conclusion:

The less CH means the better durability and the less permeable structure.

Introduction - Pozzolanic Reaction

Accordingly,
PC - Pozzolan mixture is a perfect combination.

At first, PC hydration gives undesired $Ca(OH)_2$ together with desired C-S-H.

Then, pozzolan reacts with this $Ca(OH)_2$ and yields extra C-S-H which further increases strength and decreases permeability by filling the empty pores.

This is the technical base for using pozzolans in cement,
and
accordingly, producing more durable cements.

Introduction - Results of NP Usage

- "Proper usage" of NPs in cement provide with
  - Technical,
  - Economical,
  - Ecological advantages to cement factories.

However, there are some disadvantages also.

"Proper usage" means usage of good quality NPs in the hand of experts.

Now these advantages and disadvantages of using NP in cement will be presented in detail.

Technical Advantages - Durability

Durability is Improved Considerably by NP

Why?

- CH consumption,
- Lower permeability in the cementitious system,
- Dilution of PC which is the vulnerable part of concrete,
- Better distribution of hydration products throughout the system

Results (in comparison with reference system with PC alone):

- Less chloride penetration,
- More resistance to alkali silicate reaction,
- Less corrosion of reinforcement in concrete,
- Better resistance to acidic waters,
- Better sulfate resistance, etc…….

(Reference: Mehta, Massazza, Gjorv, Neville, Swamy)

Technical Advantages - Durability

Romans employed NP-CH reaction in engineering structures.

Colleseum
72-80 AD

~ 50m
~ 16 storeys residential

Elliptical ~188x157m

Technical Advantages - Durability

Durability is Improved Considerably by NP

EN197-1 introduces NPs as one of the main raw materials for sulfate resistant (SR) common cements.

This topic will be covered later separately in the following slides.

Technical Advantages - Grindability

Cement with NP is Ground More Easily

Almost all NPs are easier to grind than clinker. This increases the grinding capacities of cement factories.

Example:
5-10% capacity increase is easily possible in most of the cases for the production of similar strength cement to reference PC.

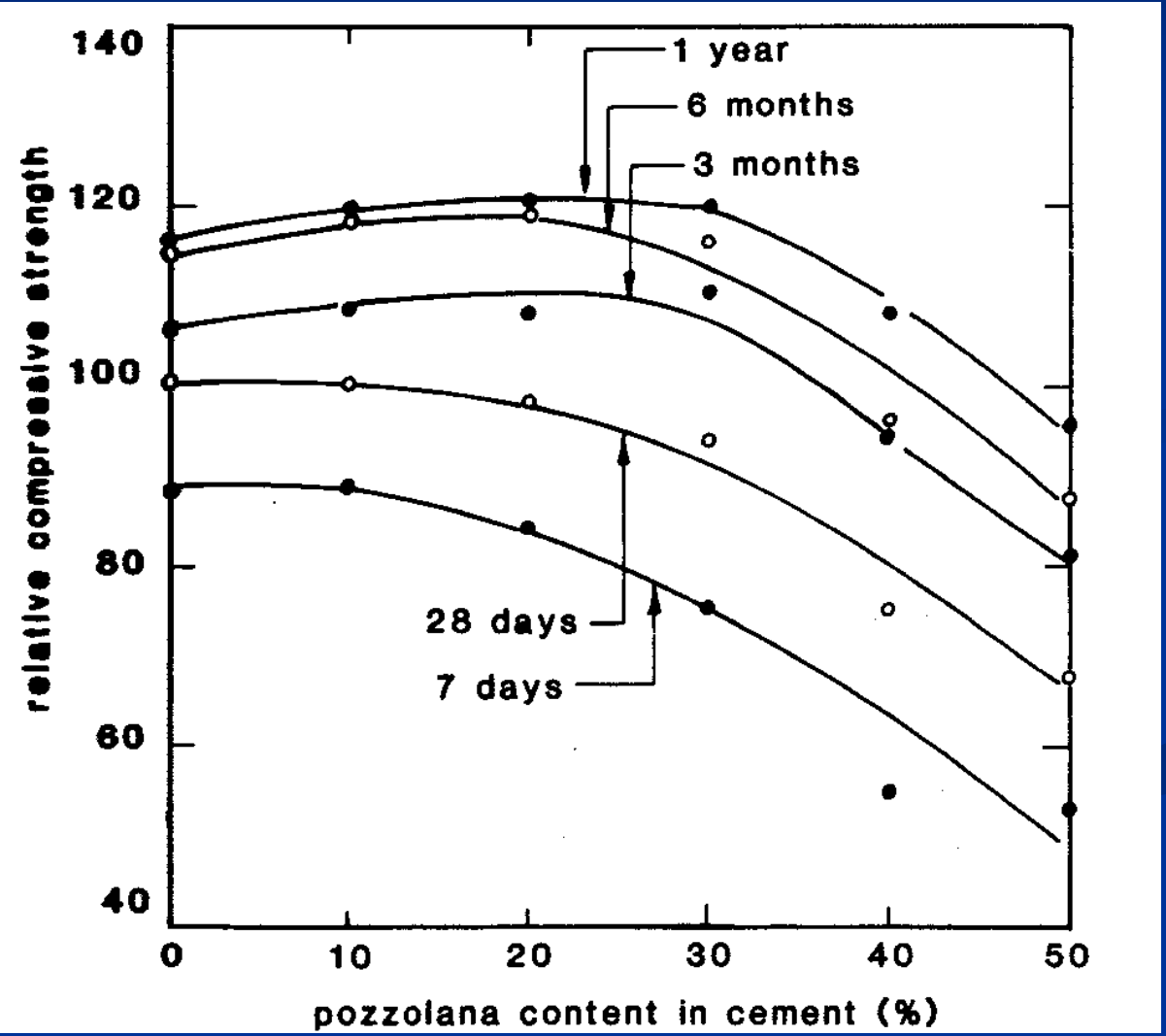
Grinding energy to reach the same fineness with PC is less.

This effect can be best evaluated by industrial tests instead of lab. studies.

Technical Advantages - Strength

By proper usage of NP, without having a considerable early strength loss, higher late strengths are obtained with respect to PC.

Mortars with separately ground NP-PC



Compressive strengths are expressed as percentage of the strength of PC at 28 day.

Ref. Massazza

Technical Advantages - Strength

Conclusion on Strength

By engineered usage of NP,

- Similar or generally better compressive strength to those of PC can be obtained at late ages.
- However, lower very early strengths can be observed also.

Which age is late, which age is early?????

Depends on quality of clinker, quality of NP, fineness of the cement blend etc…….

In general, for the conclusion above, ages after 2-3 weeks can be considered as late (KE) under normal conditions for good NP and clinker.

How did Romans grind NP???

Technical Disadvantages - Early Strength

Early Strength Decreases by NP Usage

Why?

- There is no CH in the matrix at early ages available for NP to react with. First PC must hydrate to give enough CH for pozzolan. This takes time….

- By NP usage, PC is diluted. PC reactions are faster.

Technical Disadvantages - Early Strength

How to cope with potential early age strength decrease (which is actually the main potential disadvantage of NP usage)?

First measure is …… don't use NP excessively aiming profit only

Second measure is …… produce slightly finer PC-NP mixture than original reference PC (applied by all Turkish Cement Producers)

A Note on Strength

PC portion of PC-NP cement reacts faster. This is one of the factors limiting early strength loss. The reason;

Reaction products of PC (mostly C-S-H) accumulate on PC particles creating a relatively impermeable layer. Therefore, further reaction of PC particles gets slower with time.

In the presece on NP, these reaction products of PC are attracted by NP particles and precipitate on the surface of NPs.

As a result, further hydration of PC particles continue at a faster rate in PC-NP cements.

Another important result of this fact is that the reaction products are better distributed in the system. This also cause better strength and durability.

Technical Disadvantages - Humidity

NPs are natural materials with fluctuating humidity seasonally. This brings a cost of drying or if you dont dry decrease in grinding capacity depending on the level of water in NP.

How to cope with this?

Generally, Turkish cement factories do not purchase NP in winter and rainy seasons.

They purchase and make stocks in summer when the humidity content is tolerable. The stocks are either covered by plastic sheets or taken into closed areas. Even if it rains (for open air stockpiling), water can not percolate easily and the core of stockpile will not be so much affected.

Also in summer humidity decreases considerably with time under the sun.

Summary Till Now & Next Session

- NPs increase durability of cementitious systems.
- NPs increase late strength.
- NPs increase the reaction rate of PC portion in cement.
- NPs may decrease early strength. The measures are slightly finer grinding and not using NP at excessive amounts.
- NPs increase grinding capacity.
- NPs have humidity which can be avoided mostly by not purchasing in rainy seasons.

In the next session; Economical Aspects, NP Usage for SR Cements + General Notes

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Economical Advantages of NP Usage

Economical advantages arise from;

1- Saving clinker for the production of similar cements to reference PC (Primary Saving) - Based on EN 197-1

For a cement factory with 1.000.000 ton annual clinker production, 50.000 ton/year clinker saving is a very easy target even by a very conservative usage of an average quality NP (assuming that 60% of production is PC).

Economical Advantages of NP Usage

Economical advantages arise from;

2- Grinding energy saving (Secondary Saving).

Example (from lab. ball mill) - (Ref. Master Thesis of KE) :

Grinding energy (kW.h/ton) required for cements to reach 4.000 cm^2/g from 3.500 cm^2/g.

100% PC	19,8	
80% PC + 20% NP1 (hard)	16,9	(15% less energy than PC)
80% PC + 20% NP2 (grindable)	8,7	(56% less energy than PC)

Economical Advantages of NP Usage

Economical advantages arise from;

2- Grinding energy saving (Secondary Saving).

PC-NP mixtures should be ground finer than PC to compansate early age strength loss.

Increasing fineness of PC-NP blend;

- is not as much costly as you expect for PC.
- will not decrease grinding capacity as you expect for PC.

(According to the test results given in the previous slide).

Instead, even at a higher fineness, a gradual capacity increase or grinding energy saving could be achieved with NP.

Economical Advantages of NP Usage

Comparison between Limestone and NP

Opposite to NP; limestone

- is almost an inert material in cement,
- has no contribution to durability
- has detrimental effects for sulfate resistance.
- does not have a positive impact on permeability,
- decreases all age strengths more than NP.

Based on this information;

- With NPs, higher clinker savings are possible with respect to that achieved by limestone,
- Limestone can not be used in systems extensively where durability is of main concern (Ex: SR cements)

NP Usage in Turkey

Thanks to geologically recent volcanic activities, Turkey has vast NP sources which are used extensively. Accordingly, Turkey is a well experienced country on NP usage.

Almost all the cement factories in Turkey use NP at high amounts.

<u>Turkish Bagged Cements with NP:</u>

Almost all the bagged cements of Turkey contain NP as a major addition. The most common bagged cement types and compositions are;

CEM II A 32.5 R average 14-15% NP + 0-5 % limestone.

CEM II B 32.5 N average 23-24% NP + 0-10 % limestone.

NP Usage in Turkey

Turkish Bulk Cements with NP:

CEM II A 42.5 R	contains more than 7% NP + limestone
CEM II A 42.5 N	contains more than 12% NP + limestone

The first cement above is being sold to ready mix concrete plants as an alternative to PC. Consumption of this cement increases remarkably with time.

Generally, the first cement above is used by ready mix concrete plants belonging to cement factories.

NP Usage in Turkey

Cement factories mostly dont buy any NP during the period of November-March (wet season) due to high humidity.

NP Usage in Turkey

In Turkey, European Standards (EN) are compulsory, and accordingly, NPs with min. 25% reactive silica are used. Generally, NPs exploited by Turkish factories have reactive silica content in between 25-29%.

Turkish factories are ready with good experience for new EN 197-1 which introduces NP as an important raw material for SR cements.

NP Usage in Turkey

The same NP that is supplied by Cemtech Global Engineering Inc.

Properties of Commercial Cements (Monthly Average)

Cement Type	PC 42.5R	CEM II A 42.5R	CEM II B 32.5R
Composition			
Clinker	95,0%	81,5%	65,0%
NP	0,0%	12,8%	27,5%
Limestone	5,0%	5,7%	7,5%
Gypsum	4,0%	3,5%	3,0%
Blaine (cm^2/g)	3.570	4.420	4.670
Comp. Strength			
2 Day (MPa)	22,5 - 24,4	21,9 - 24,6	17,0 - 18,5
28 Day (MPa)	47,1 - 49,2	45,9 - 48,5	35,4 - 38,0

SR Cements in prEN 197-1rev. (2008.06.23)

According to EN 197-1, SR cement can contain:
- Granulated Slag,
- NP,
- Siliceous Fly Ash,

Granulated slag is not widely and reliably available.
Prices are increased to unfeasible levels due to high demand.

Fly ash is not available everywhere similar to slag,
Quality deviates considerably and have high amount of free carbon most of the time
Due to logistic problems, very difficult for sea transport,
Must be stocked in silos (no open air stocking)
Prices are increased by demand from concrete factories.

As a result, NP seems to be the best available material for SR.

SR Cements with NP

Current CEM IV cements with slight differences are accepted as SR cements by EN 197-1.

Rules for CEM IV SR cements with NP:

- Clinker must have max. 9% C_3A (acc. to Bogue formula).
- Sulfate content in cement as SO_3
  More strict (0,5% less than current limitations)
- CEM IV A (P) ---------- 21 - 35 % NP
  CEM IV B (P) ---------- 35 - 55 % NP
- Pozzolanicity test should give satisfactory results in 8 days (more strict)

SR Cements with NP

In general, the restrictions are not difficult to achieve and mostly ordinary CEM IV cements automatically conform to the given regulations.

Potential Problems of CEM IV A/B (P) SR Cements:

- Compressive strengths may fail due to high amount of NP,
  - . Use high quality NP,
  - . Use high quality clinker
  - . Increase fineness of cement,
  - . Dont use NP excessively aiming to save clinker.

- Pozzolanicity

  Sometimes despite you have acceptable strength, pozzolanicity test may fail for your cement at 8 days.
  - . Increase the fineness of cement,
  - . Use slightly more NP.

SR Cements with NP

Increasing fineness seems to have a key role in achieving SR. Also it has positive impact in decreasing permeability.

Will it cause loss in grinding energy?

Generally, easily grindable nature of NPs compansate grinding energy losses.

Despite this fact, there may be a loss. However, please note that this is a new cement with SR property and it has higher commercial value in the market.

Final Notes on NPs

- NP seems to be used in high amounts in the short run. Although the new cement standard (prEN197-1) is not valid now, many factories have started to act on this topic already.

- CEM IV (P) SR cement design need the highest level of experience and engineering w.r.t. design of other cements.

  Personally, I recommed to start with production of;
  CEM II A-M (P-L) 42.5 R / N (5 to 15% NP + Limestone)
  and/or
  CEM II A/B-M (P-L) 32.5 R / N (15 to 30% NP + Limestone)
  Then, shift to ordinary CEM IV A/B, and finally

  Based on strength results and experience on these, design your <u>CEM IV SR</u>.

Final Notes on NPs

- NPs with past records of usage should be preferred not to have surprises in usages.
- Conformity of any NP simply to EN 197-1 is not enough. The only criteria in EN for NP is the reactive Silica (min. 25%). An interesting note on this: The more reactive silica does not mean that NP is better for cement. Different reactive phases from different NPs have different reactivities.
- Dont rely on Blaine fineness measurements for cements with NP. Blaine test is not suitable for NP added cements especially at higher amounts than 10%. The best way for fineness measurement is sieve analyses by 0,045 mm sieve or by laser diffractometer.
- Dont trust on your laboratory tests only. Actually, industrial tests are the only reliable method to evaluate.

Final Notes on NPs

Very Important Final Note:

- Laboratory tests fail to reflect real conditions in the factory. Because, (particle size distribution differs remarkably)
  . No separator in the lab. (primary reason),
  . Difference in grinding media (minor reason),
  . Fluctuations in weighing in the factory (minor reason)

Therefore, the best way to evaluate a NP and to get clear idea about potential cements are to produce it in the factory and to test the real commercial cement.

SUMMARY & CONCLUSION

- Proper NP usage provides technical, economical and environmental advantages to cement factories.

- Humidity and very early strength losses are the disadvantages by usage of NPs.

- By NPs, more clinker replacements than limestone are possible.

- NPs are the most reliably and widely available raw material for EN197-1 SR cements.

- In determining the quality of a NP, industrial tests are more important than lab. tests which suffer from lack of reflecting real conditions.

THANK YOU FOR LISTENING…

Please dont hesitate to contact for further discussions…

Questions and comments to:
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