GEO-POLYMERS- An Alternative to Cement Based Materials

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Introduction

- Developments in the field of Concrete Technology have been phenomenal in the last decade
- Several radical changes have also occurred in this field
- Self compacting Concrete, Self curing Concrete, Regulated sleeping Concrete, High volume Fly ash Concrete etc.., have all revolutionized the concrete Industry
- The latest in the series is the development of Geopolymer Concrete

Portland Cement and Geopolymer

- ➢ Portland Cement → synthesis of high CaO minerals, main product is C-S-H gel from the hydration process; water is needed for the hydration process.
- ➢ Geopolymer → results of polymerisation process of minerals containing Si-Al; water is released <u>during the chemical process.</u>

GEOPOLYMERS

- Geopolymers are alkali activated Alumino silicate binders formed by reaction of silica and alumina rich materials with alkaline solutions.
- The reaction results in a mixture of gels and crystalline compounds which harden into a strong matrix.
- A relatively low elevated temperature environment of about 60-80 Deg C is sufficient for geopolymerisation, unlike organic polymers which often require higher levels of temperature.



Metakaolin, Rice husk ash,

MECHANISM OF GEOPOLYMERISATION

• One of the 'visualised mechanism' of Geopolymerisation' is

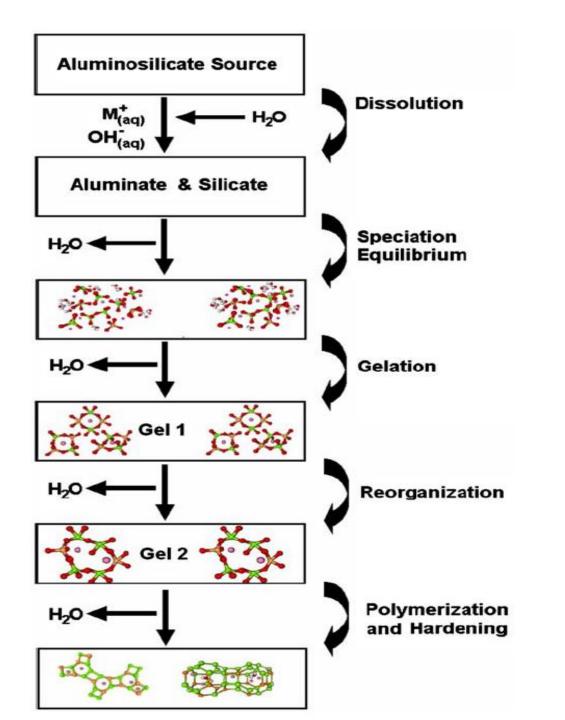
Dissolution

Gelation

Reorganisation

Polycondensation

Reaction takes place through an exothermic process



CONCEPTUAL MODEL The polymerization process involves a chemical reaction under highly alkaline conditions on Al-Si minerals, yielding polymeric Si-O-Al-O bonds, as described by

 $M_n [-(Si - O_2)_z - Al - O]_n .wH_2O$

 Where M is the alkaline element, the symbol – indicates the presence of a bond, z is 1,2 or 3 & n is the degree of polymerization.

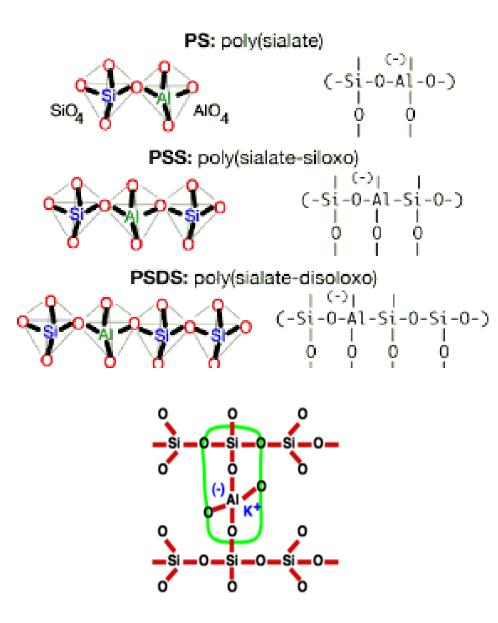
Schematic Formation of Geopolymer

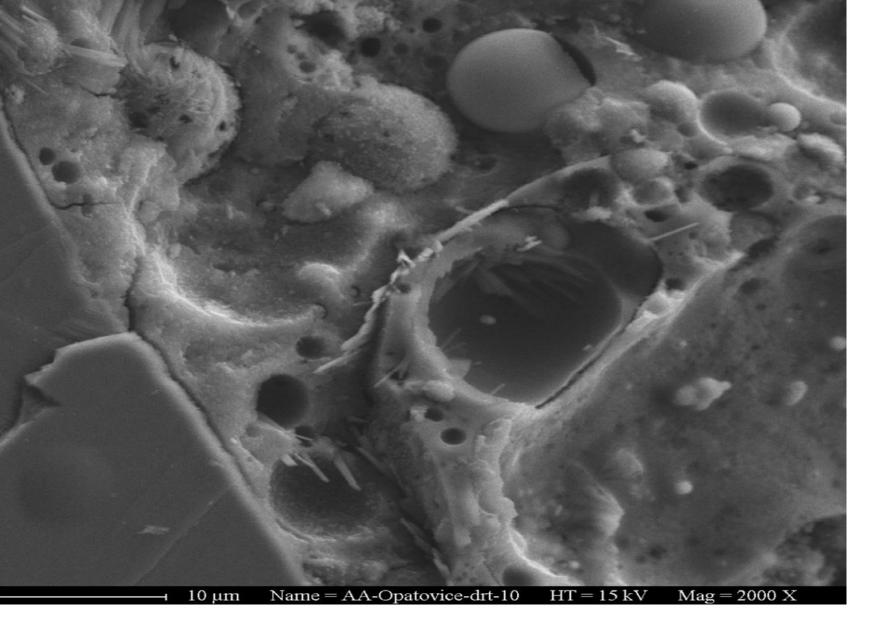
n(Si₂O₃-Al2O3)+2nSiO₂+4nH₂O+NaOH or KOH → Na⁺,K⁺+n(OH)₃-Si-O-Al-Si-(OH)₃ Si-Al materials (OH)₂ Geopolymer precursor

Geopolymer backbone

The rate of polymer formation is influenced by parameters such as curing temperature, alkali concentration, initial solids contents, etc.

CHEMICAL STRUCTURE





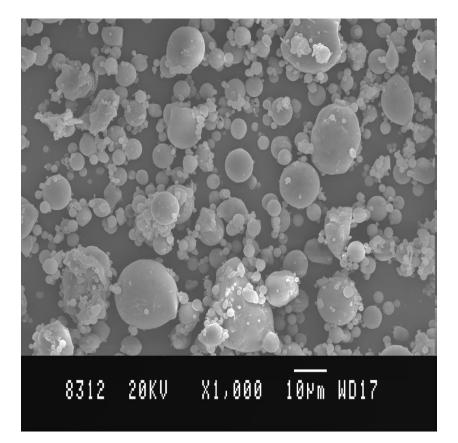
GEOPOLYMER- SEM

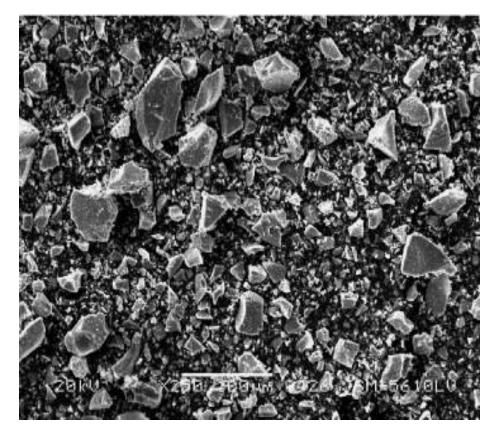
GPC with Fly ash/Slag – Some studies..

Materials



GGBS





Physical properties of Fly ash and Slag

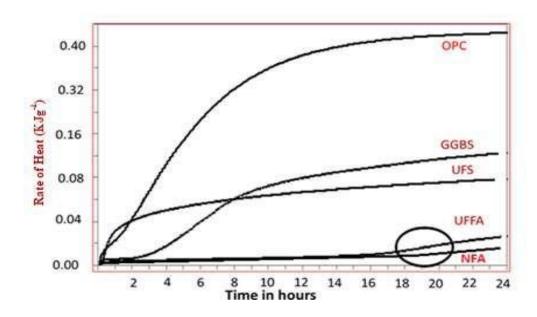
Parameters Tested	UFFA	NFA	UFS	GGBFS
Glass content (% by mass)	36.60	19.20	94	96.5
Specific Gravity	2.28	2.12	2.88	2.81
Surface Area, m ² /kg	486	328	12,000	358
Material Retained on 45µ Sieve (%)	2.20	6.44	Nil	6.50
Bulk Density, kg/m ³	684.0	646	1190	1120
Lime Reactivity	7.50	4.90	16.50	14.50
Particle shape	Irregular	Irregular	Irregular	Irregular
Comparative Compressive Strength %				
168±2 hour			67	58.0
672±4 hour	104	90	88	70.0

Chemical composition

Parameters Tested	UFFA	NFA	UFS	GGBFS	
Reactive Silica	36.38	21.12	35.22	32.10	
Total Silica (SiO ₂)	65.62	55.98	36.22	33.80	
Alumina (Al_2O_3)	22.92	27.44	18.60	17.36	
Reactive Alumina(r -Al ₂ O ₃₎	10.18	11.64	13.82	17.80	
Iron Oxide (Fe_2O_3)	4.98	5.94	0.86	1.36	
Calcium Oxide (CaO)	1.88	4.82	35.40	38.30	
Magnesium Oxide (MgO)	0.86	1.38	6.87	7.38	
Sulphur Trioxide (SO_3)	0.08	0.28	0.02	0.02	
Insoluble residue (IR)	96.74	88.92	0.62	0.23	
Sodium Oxide (Na_2O)	0.33	0.39	0.20	0.21	
Potassium Oxide (\overline{K}_2O)	0.80	0.92	0.80	0.72	
Loss on Ignition (LOI)	0.48	1.34	Nil	Nil	
Titanium Dioxide (TiO_2)	0.14	0.18	0.08	0.10	
Phosphorous pent oxide (P_2O_5)	0.27	0.36	0.22	0.24	
Manganous oxide (Mn_2O_3)	0.14	0.13	0.11	0.22	
Activator ratio of pozzolana and slag					
Reactive Silica/Al ₂ O ₃ ratio	1.59	0.77	1.84	1.85	
Total Silica/Al ₂ O ₃ ratio	2.84	2.04	1.94	1.95	
Total Ca/Al ₂ O ₃	0.08	0.18	1.90	2.20	
Ratio of Na/Al	1.40	1.52	1.54	1.46	

Ref: Dinesh et al.,

Heat evolution during early alkali activation period of geopolymers



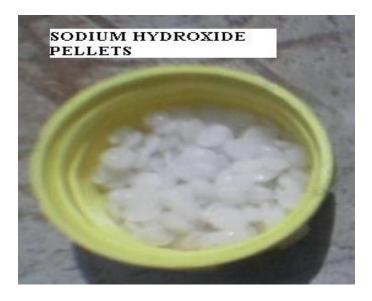
Observations

- Heat Evolution in OPC is Very High
- Heat Evolution in GGBFS is Moderately high
- Heat Evolution in UFS is Moderately high
- □ Heat evolution in UFFA is low
- Heat evolution in NFA is very

low

Development of heat in early reaction of reactive silica based geopolymer composites of alkaliactivated NFA, UFFA, GGBFS, UFS and hydrated OPC for 24 hours.

Alkaline liquid: sodium hydroxide and sodium silicate solution, used as alkaline liquid.





Sodium silicate(Gel form)

Alkali Activator Solutions(AAS):

1. Sodium hydroxide (NaOH)

Sl. No	Parameter	Test Results	Parameter	Test Results
1.	Appearance	White colour solid	Specific Gravity	1.690
2.	Solubility in aqueous	111 a / 100 ml	Density	2.1 g/cm ³
	media	111g/100 ml	Purity	99.98%
3.	Basicity (p Kb)	-2.42	Iron (Fe_2O_3)	0.001
4.	Heat of solution	44.12 kJ/mole	Alumina(Al ₂ O ₃)	Nil
5.	Molar mass	39.9972 g/mol	Carbonates($CaCO_3$)	1.80
6.	Melting point	318°C, 591 K	Lead	0.02

Physico-chemical properties of NaOH



2. Sodium silicate -

<u> </u>	Na Concentration of AAS at 10Molar.		
Sl. No.	Alkali metal ion (M) present in AAS	Na	
1.	Ratios of weight	1:1	-/
2.	Molar Ratio	2.50	
3.	Metal Type	M-Na ₂ SiO ₃	10000
4.	Mol .mass of M ₂ O	60	1
5.	Mol. mass of Silica	60	
6.	Percentage of M ₂ O	15.2	
7.	Percentage of SiO ₂	33.6	the case area
8.	Percentage of Solids	38.2	
9.	Density, g/mL	1.61	View of wate study- Wate
10.	[OH-] mol /L	7.72	
11.	pH Value	12.62	

View of water glass (Sodium silicate) used in the experimental study- Water Content 2

MIX PROPORTIONING OF GPC

B.V.Rangan (Curtin Univ) has carried out significant research on Geopolymer Concrete mixes, short and long term properties.

The guidelines for mix design was:

- Ratio of sodium silicate solution-to-sodium hydroxide solution, by mass, was fixed at 2.5 for most of the mixtures.
- Molarity of sodium hydroxide (NaOH) solution in the range of 8M to 16M.
- A lower water content will result in a stronger mix.

- Ratio of activator solution-to-Fly ash, by mass, in the range of 0.3 to 0.4.
- The quantity of coarse and fine aggregates, 75% to 80% of the entire mixture by mass. This value is similar to that used in Cement concrete.
- Super plasticizer dosage in the range of 0% to 2% of Fly ash, by mass.
- Extra water, when added, in mass.

Parameters governing Geopolymer Concrete Mix

- Molarity of Alkaline Solution and concentration of silicate solution.
- Water to Source material Ratio.
- Duration of Curing.
- Quality and Amount of Fly ash/ GGBS.
- Water content in the mix.

MIX PROPORTIONING METHOD (BMSCE)

Mix proportioning procedure, developed in BMSCE laboratory based on number of trial mixes:

Step 1: The wet density of geopolymer concrete is taken as 2400 kg/cum.

Step 2: Ratio of sodium silicate solution to sodium hydroxide solution is chosen (normally 2.5).

Step 3: Total water content is chosen, considering workability needs, in terms of Percentage mass of total volume of concrete (110 to 140 litres per cum). Step 4: Total quantity of alkaline solution is then calculated, since the molar ratio of sodium hydroxide solution is known and the percentage solids in sodium silicate solution is also known.

Step 5: Combined quantity of base material (Fly ash and Slag) and aggregate are then determined.

Step 6: Source material (Fly ash and Slag) is assumed as certain percentage of total solids (20-30%).

Step 7: The respective quantities of fine aggregates and coarse aggregates are then determined.

Procedure Adopted:

• MIXING:

Dry material is mixed initially for 2-3 minutes, and then all the solution is added, mixing is continued for another 3-4 minutes.





Workability

 Fresh Geopolymer concrete and mortar, has a good consistency, and is generally cohesive.



Sticky MIx



CURING OF GEOPOLYMER CONCRETE

Purpose of Curing is two fold –

- a. To promote activation; and
- b. To preserve water in the mix, from the atmospheric hazards

Curing is generally carried out at elevated temperatures, in the range of 50 to 80 Deg C. Adequate humidity to be ensured or the product is to be insulated to preserve water in the mix

Curing of Geopolymer...

- Studies on three different lines have been carried out -
- a. Curing at elevated temperatures (ensuring humidity), right from the time water and activation source material are added to the base material
- b. Curing at elevated temperatures (ensuring humidity or insulation) after about one day of mixing (Curing period 24 hours)



Curing of Geopolymer...

c. Curing at normal temperatures in traditional way(7-10 days).

Established curing regime is keeping samples in humid conditions for 24 hours, demoulding and then curing at 60-80 Deg C for 24 hours. Specimens wrapped with coarse plastic cover during curing at elevated temperature in an oven to prevent excessive evaporation

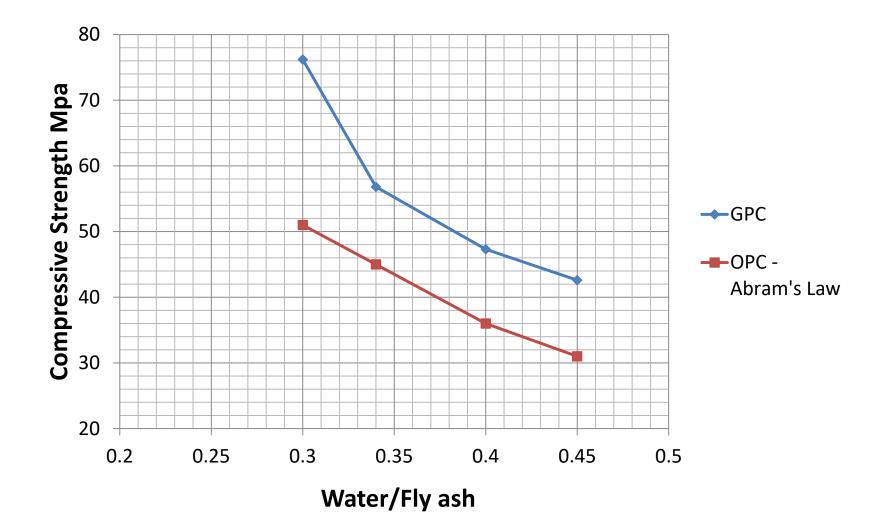


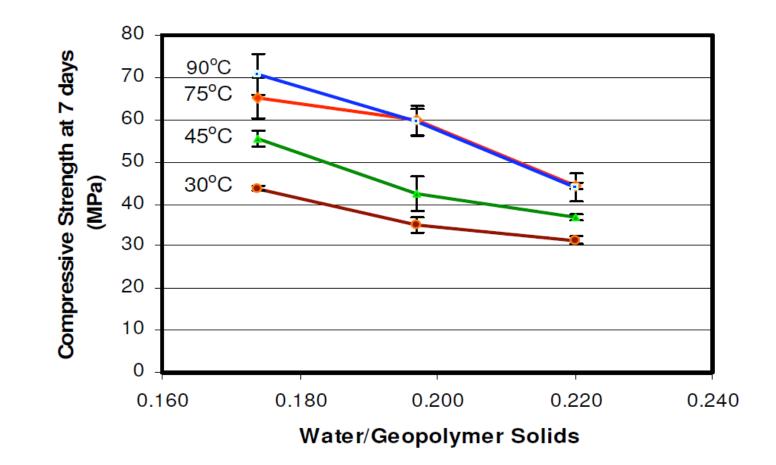


6388 20KV X1,000 10Pm WD17

 Some Properties of Typical GPC Produced in Laboratories using Flyash...

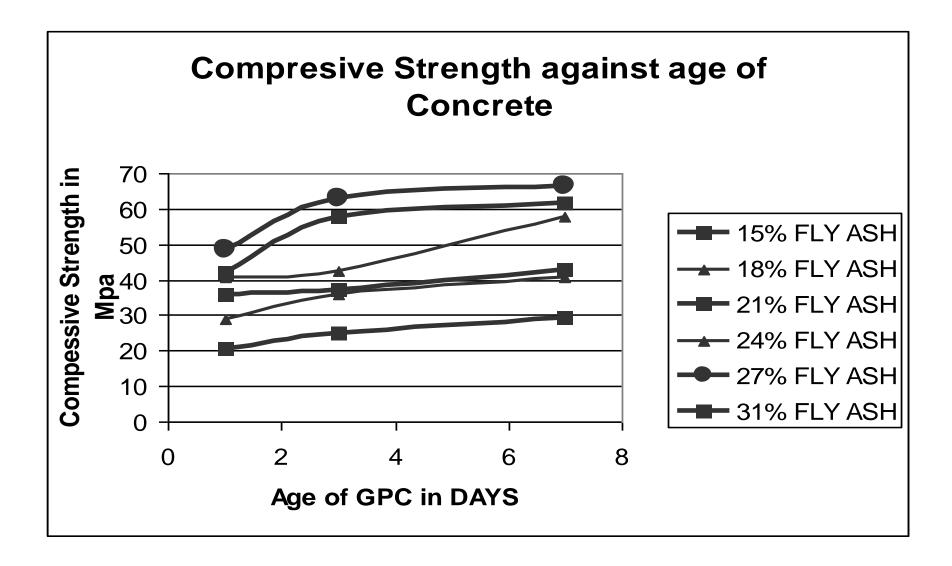
Comparison of OPC and GPC

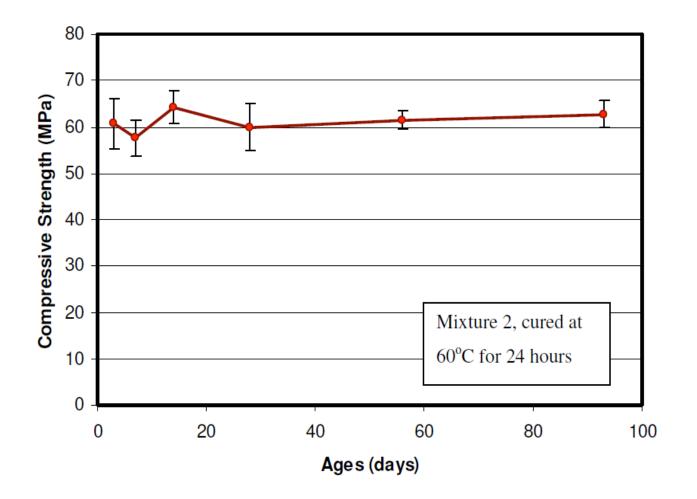




Strength Vs geopolymer solids ratio (Rangan)

Compressive strength of GPC with Age





Comp Strength Vs Age (Rangan)

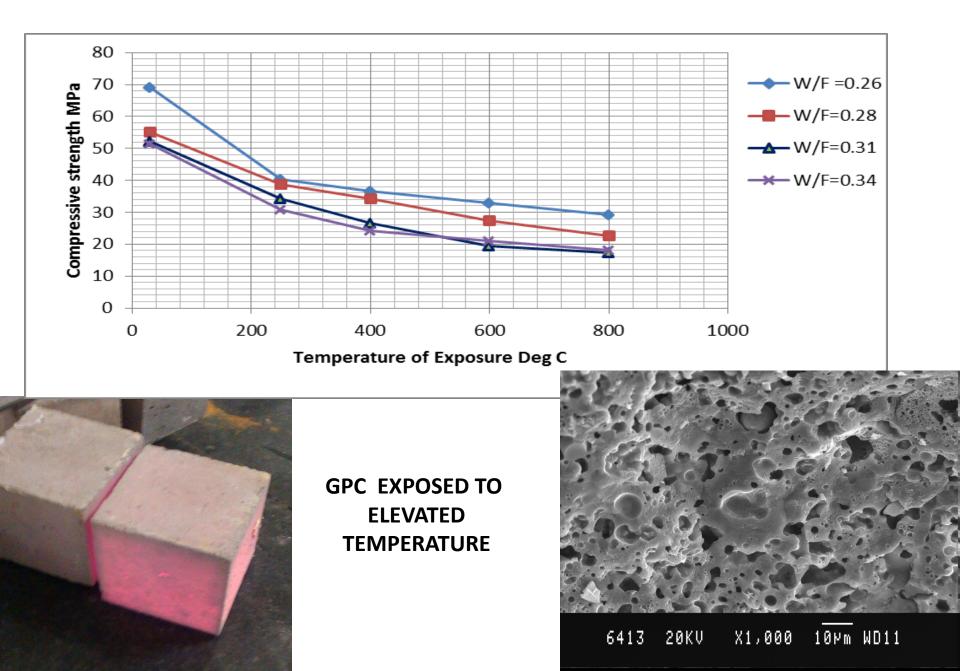
Modulus of Elasticity (Rangan)

f _{cm}	E _c measured (GPa)	E _c (Equation 4.1) (GPa)	E _c (Equation 4.2) (GPa)
89	30.8	39.5 ± 7.9	38.2
68	27.3	36.2 ± 7.2	34.3
55	26.1	33.9 ± 6.8	31.5
44	23.0	31.8 ± 6.4	28.9

GPC AUS STD ACI STD

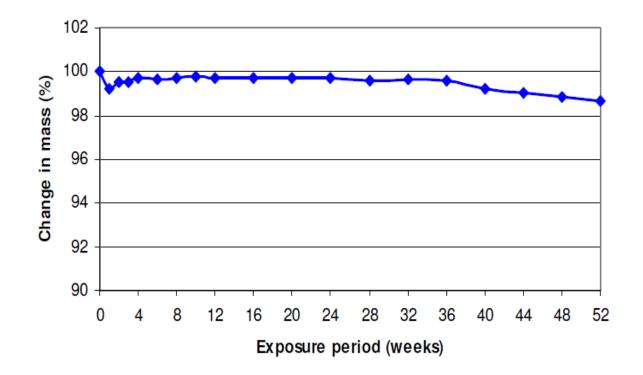
Durability Issues

- Resistance to Elevated Temperature
- Sulphate Resistance
- Acid Resistance



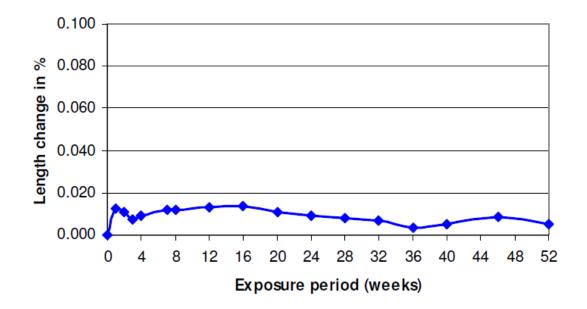
RESISTANCE TO ACID ATTACK





Change in Mass of Geopolymer Mortar Cubes Exposed to 1% Concentration of Sulfuric Acid Solution

ACID RESISTANCE OF GPC



Change in Length of Geopolymer Concrete Specimens Exposed to

Sodium Sulfate Solution

SULPHATE RESISTANCE OF GPC (< 0.5%)

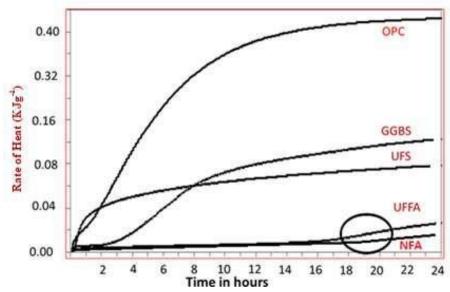
The Research Studies have established geopolymer concrete as an excellent alternative to Cement Concrete with:

- Similar mix design procedures.
- Comparable short term and long term Properties.
- Low drying shrinkage.
- Excellent resistance to sulphate attack.
- Good acid resistance.

GPC is a durable concrete for aggressive environment.

GPC WITH FLY ASH AND GGBS

- It is possible to combine the use of Fly ash and GGBFS in Geopolymer concrete.
- The reactions may involve both hydration as well as geopolymerisation, which are complimentary to each other.
- During hydration, the heat produced by the exothermic reactions is useful for geopolymerisation to proceed and the alkaline environment provided by the alkaline solutions will help in enhancing the hydration.

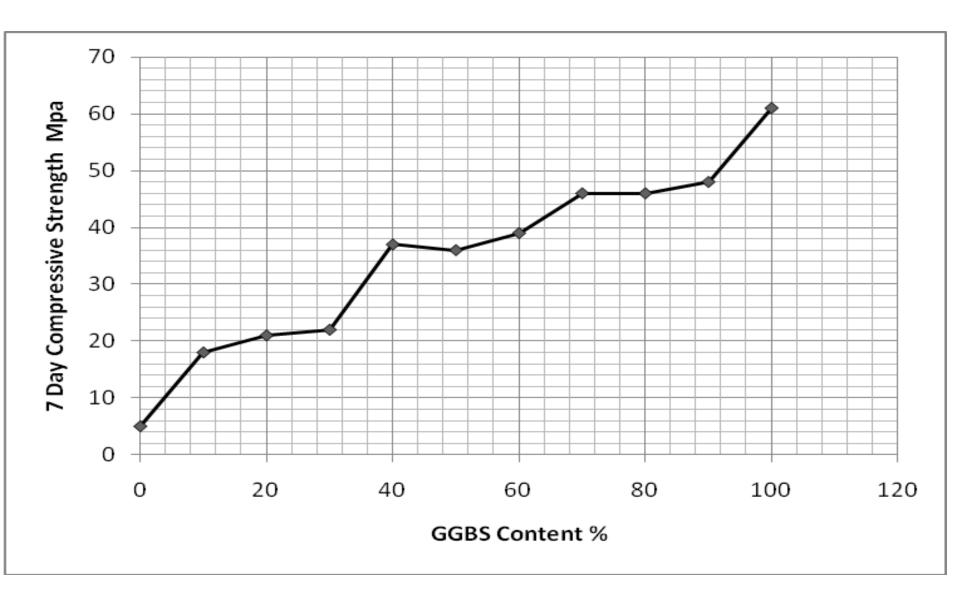


• Further, the presence of calcium ions is believed to improve geopolymerisation when alkaline solutions of low concentrations are used in the mix.

Such a concrete which does not require elevated temperature curing and also water curing will be a promising alternative to tropical countries like India, which is blessed with good ambient sun dry conditions during most part of the year when average temperatures could vary anywhere between 25 to 35°C, across the country.

GPC WITH FLY ASH AND GGBS

Sample No	Proportion (%)		Fly ash kg/cum	GGBFS kg/cum	Fine Aggregate kg/cum	Coarse Aggregate	Alkali Solution(kg/cum)	
	Fly ash	GGBFS				kg/cum	NaOH	Na_2SiO_3
1	100	0	423	0	744	947	82	204
2	90	10	380	42	744	947	82	204
3	80	20	338	84	744	947	82	204
4	70	30	296	126	744	947	82	204
5	60	40	253	169	744	947	82	204
6	50	50	211	211	744	947	82	204
7	40	60	169	253	744	947	82	204
8	30	70	126	296	744	947	82	204
9	20	80	84	338	744	947	82	204
10	10	90	42	380	744	947	82	204
11	0	100	0	422	744	947	82	204





Sun curing for 28 days-

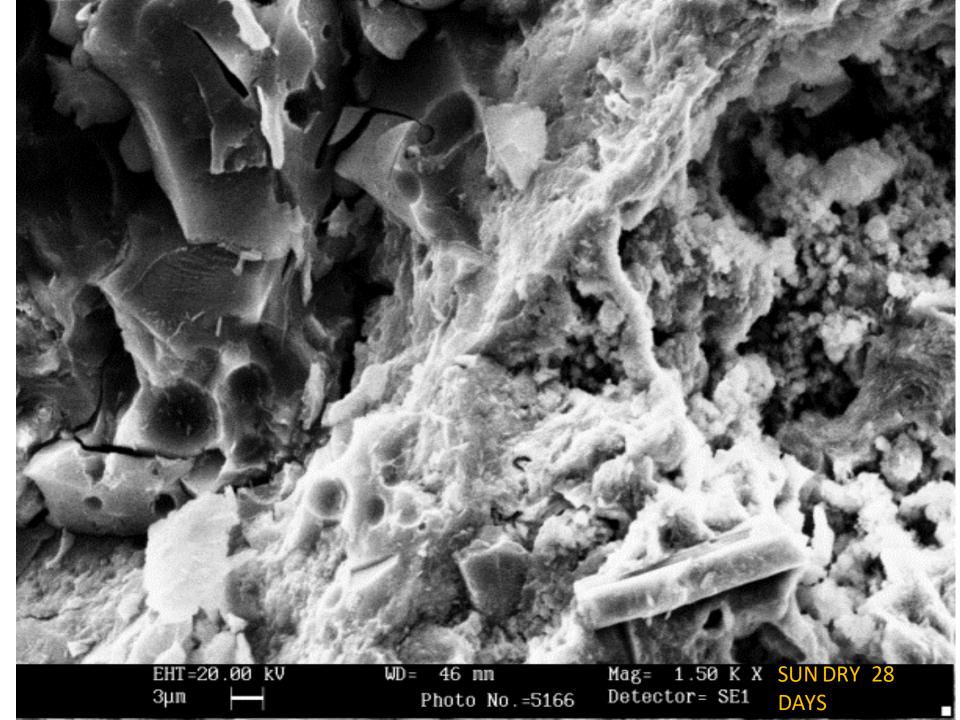
-Sun curing for 2 days with mould



SEM OF GPC WITH FLY ASH AND SLAG- SUN CURED 28 DAYS



50 µm -



STRUCTURAL APPLICATIONS

STRUCTURAL APPLICATIONS

• Certain studies on structural strength and behaviour of Geopolymer Concrete (fly ash based) reinforced columns have been carried out at curtin University

• At present, the structural applications are with respect to both precast components and in-place Concrete.



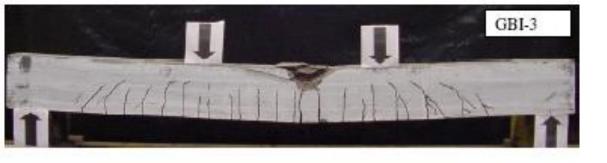
Casting of A Geo-Polymer Concrete Structural element (Typical)

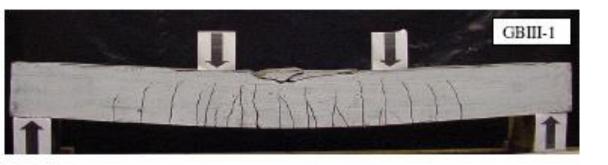


Beams after Demoulding

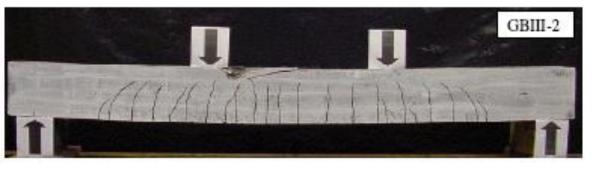


Column in Testing Machine





Crack patterns and failure Modes of the Testing Beam





PRECAST BOX CULVERTS



STONE ARCHES WITH GEOPOLYMER FERRO CEMENT



Figure 5a: Load testing of a 10 metre precast geopolymer beam.



The Global Change Institute which will be a showcase of sustainable construction.

FIRST APPLICATION OF GPC IN BUILDING. 10.8M x 2.4M WIDE PRECAST FLOOR ELEMENT OF GRADE M40



10.8 metre geopolymer beam with vaulted soffit being craned into position.







2012

Composite pultruded girder and Grade 40 geopolymer deck bridge in Brisbane.





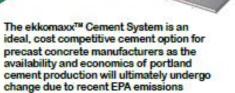
Boat ramp constructed with both precast and in-situ geopolymer concrete.

GPC(M40) WITH GFRP BARS AS REINFORCEMENT FOR SEVERE ENVIRONMENT EXPOSURE - 2011

Placing of pavement for weighbridge using geopolymer concrete.

GPC(M32) PAVEMENT CONCRETE- 2010





rulings.



ekkomaxxTM is the worlds only, truly green sustainable, high performance cement. It is derived entirely from coal ash and manipulated with CERATECH's line of rapidly renewable proprietary liquid activators to create an extremely versatile and robust cement system.

Concrete produced with the ekkomaxxTM cement system meets or exceeds all ASTM-C-1157 and 1600 specifications, is exceptionally durable and posses superior mechanical properties as compared to ordinary portland cement

The Roman contains was construction within possible contains technology similar to nature to estionees?

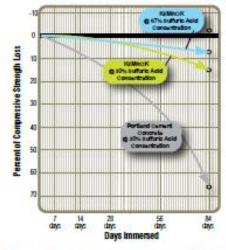
The ekkomaxx[™] Production Process





Correntee resistant, process concrete manhole risers made from wee-Partland, non-trianely commit.

> Comparison of Portland Cement Concrete & KEMROKTM Cement Concrete Compressive Strength Loss Through 84 Days Sulfuric Acid Immension



- Provide superior corrosion resistance, potentially, without requiring coatings or liners (See our chemical resistance data)
- · Provide reduced maintenance and repair costs
- · Superior service life
- Has superior compressive, tensile and shear strength versus conventional portland cement based concrete
- Reduced shrinkage on oure (reduces or elimitates issues caused by drying cracking shrinkage)

For more information, contact us at: 800-581-6397 info@ceratechino.com www.ceratechino.com



A PARTY

The requirement to cost commts surfaces with supervise spery spectrum can be derivated in most ranse. by officing (EMEQ)¹⁰ servert hand servert hand

Produce Corrosion Resistant PRECAST CONCRETE

Offer extended infrastructure life cycles while reducing maintenance costs.

Traditional portland cement based concrete is inherently susceptible to deterioration if not protected with expensive, difficult to install epoxy coatings and/or polymer linings. Improper, inconsistent or discontinuity of these coatings or liners, especially at the joints of precast components creates opportunities for corrosive liquids to damage precast components. This damage leads to costly repair, reduced service life and premature replacement of these structures.

A new, non-portland cement based concrete using 100% flyash from CERATECH called KEMROK[™] addresses these issues with a base chemistry that has greatly reduced quantities of calcium hydroxide and calcium silicate hydrates. These two minerals are the main reason why portland cement based concretes are attacked by corrosive acids.





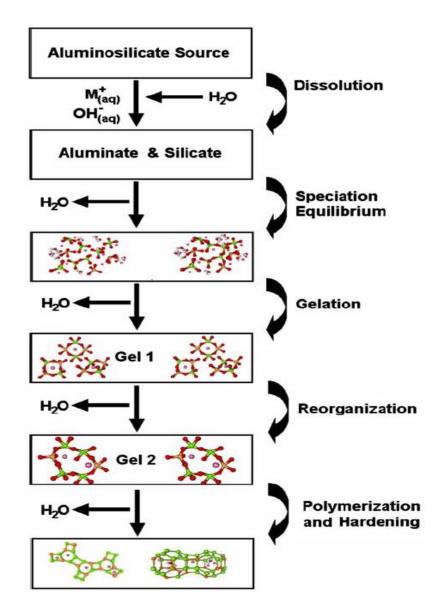
E-CRETE, ENVIRO CRETE, etc

Some Challenges..

Role of Water

- Sodium Silicate customisation for construction works...
- Flexural performance..
- ➤ Safety ...

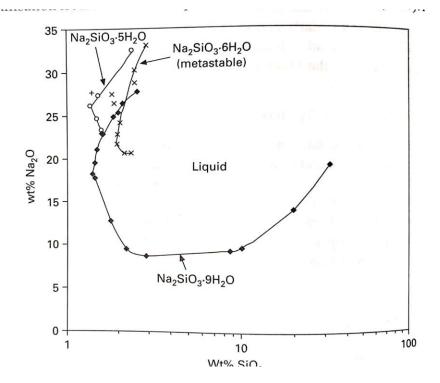
➢Role of Water



V Spot Magn kV 3.0 1000x Det WD Exp SE 10.1 2460 Pr. 10 20 µm V.

Water craters

Sodium Silicate





Chemical Composition of Sodium silicate (Available in Market)

LEGEND	% SiO ₂	% Na ₂ O	% H ₂ O	Grade
Α	39.18	17.81	33.9	2.2
В	37.85	14.02	43.81	2.7
С	30.88	9.35	53.73	3.3

Research Avenues..

- Mining/Industrial waste utilisation in Geopolymers
- Non-thermally activated Clays (Tank Bed soil)
- Immobilisation of toxic wastes in geopolymers

Mining/Industrial waste utilisation in Geopolymers

• Red MUD example....

Plantations done at the red mud pond



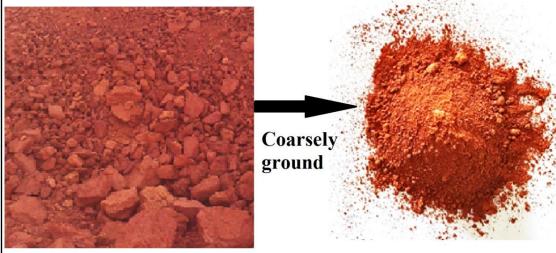
Location of red mud collection

Manmade water body developed around the red mud pond

Approach to the red mud pond

Alumina extraction plant

Characterisation-Red mud



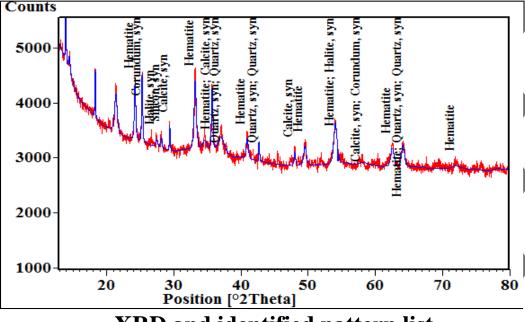
Red mud in the as collected state and then ground to pass through 300-micron sieve

Chemical Composition								
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	TiO ₂	P ₂ O ₅	V ₂ O ₅	L.O.I
9.93	18.1	42.9	2.3	5.58	9.03	0.35	0.31	10.5

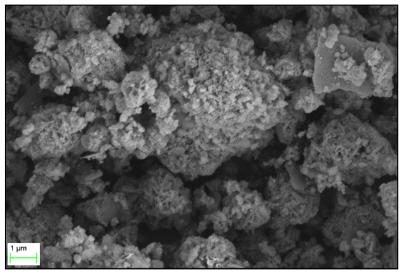
Properties

Specific gravity	Surface area (m2/kg)	Lime Reactivity (MPa)	рН	Reactive silica%
3.25	33,650	0.95	11.0	1.62

Ref: Smita et al.,



XRD and identified pattern list

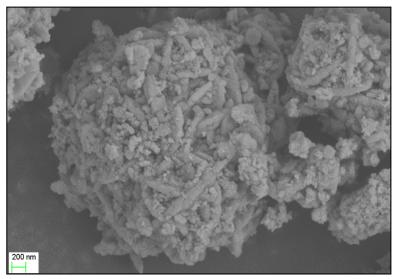


From XRD, the main phases present were calcite $(CaCO_3)$, hematite (Fe_2O_3) , corundum (Al_2O_3) , halite (NaCl) and quartz (SiO_2) .

Presence of sharp peaks indicated that the minerals were mostly in crystalline phase

From SEM, the sample consisted of lumps of irregular shapes (hematite), and each lump appeared to be made of much smaller particles

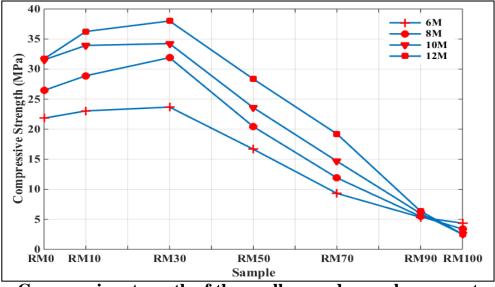
Irregular-shaped crystalline particles of size about 1 μ m lay scattered in the image, likely representing quartz crystals



SEM micrographs

Ref: Smita et al.,

Specimen	Binder composition (RM : FA : MS)%		
RM100	100:0:0		
RM90	90 : 0: 10		
RM70	70 : 20 : 10		
RM50	50 : 40 : 10		
RM30	30 : 60 : 10		
RM10	10 : 80 : 10		
RM0	0 : 90 :10		



Compressive strength of thermally cured geopolymer paste



Thermally cured geopolymer cubes of RM30, RM50 and RM90

Compressive strength increased with molarity

Optimum of red mud % in the binder was 30%

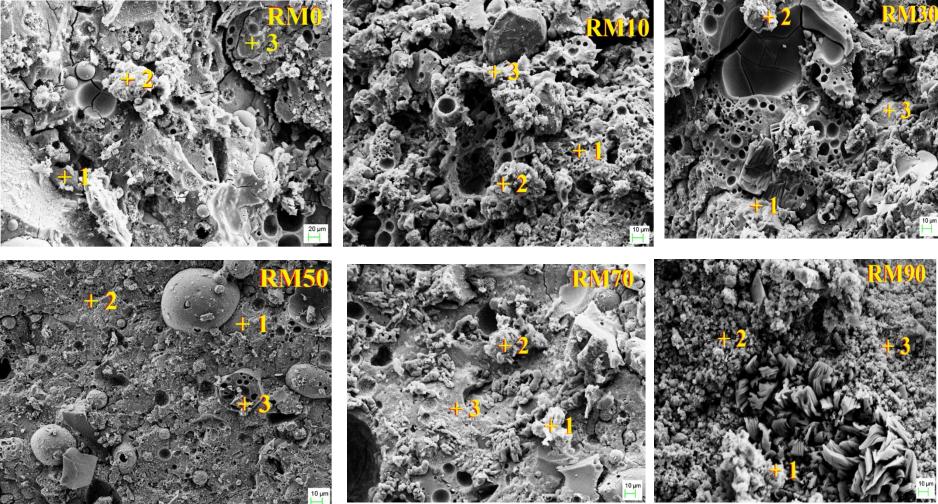
Red mud contribution to strength

Alkalinity

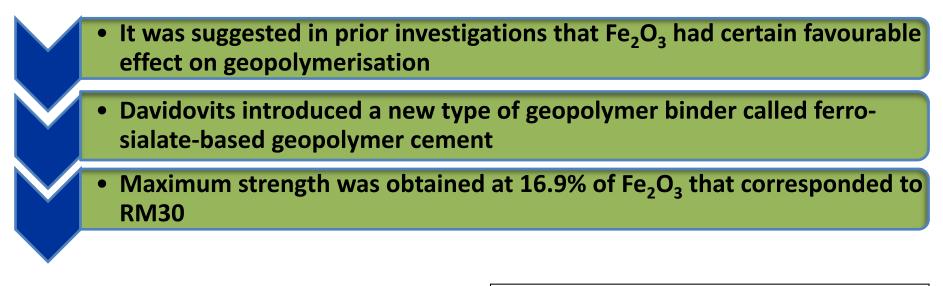
Ultra fine particles act as filler

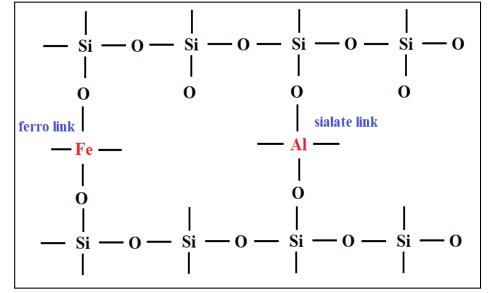
Ref: Smita et al.,

Microscopic Studies

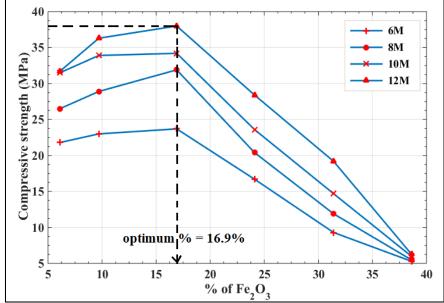


The unreacted phases of fly ash particles and quartz crystals were minimum when red mud % was 30 In RM30 and RM50, iron was traced as part of continuous matrix, thereby hinting the participation of Fe in geopolymerisation





Ferro-sialate geopolymer structure



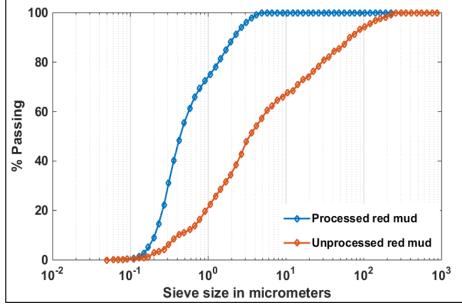
Variation of compressive strength with % of

Fe₂O₃

Ref: Smita et al.,

77

Characterisation of Pulverised Red Mud



Particle size analysis

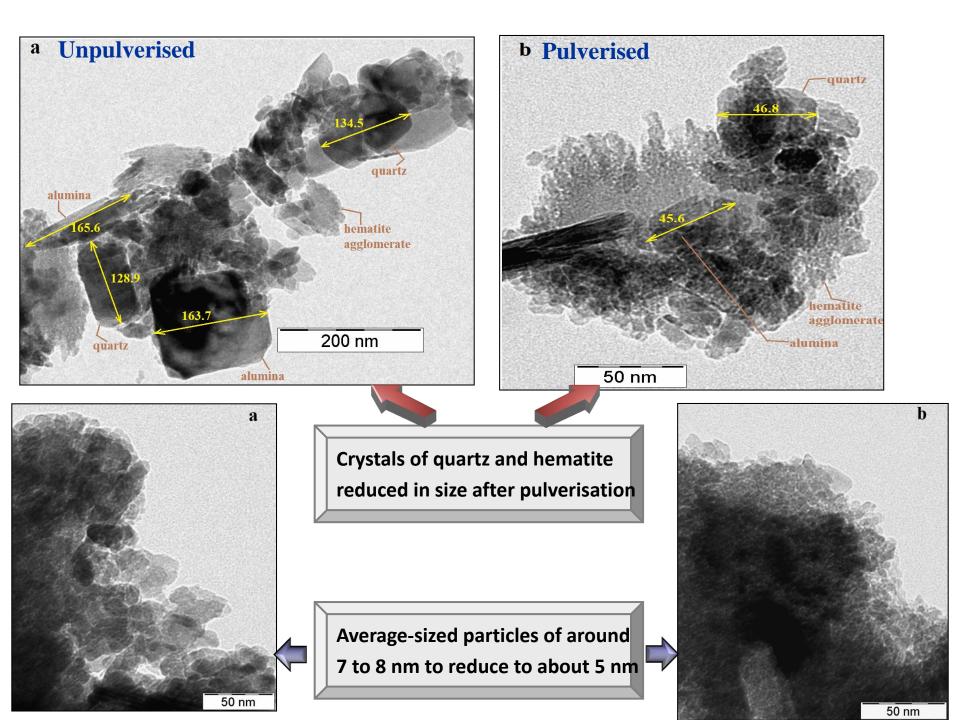
Particle size analysis test revealed that processed red mud consisted of ultrafine particles of size lesser than 5 µm

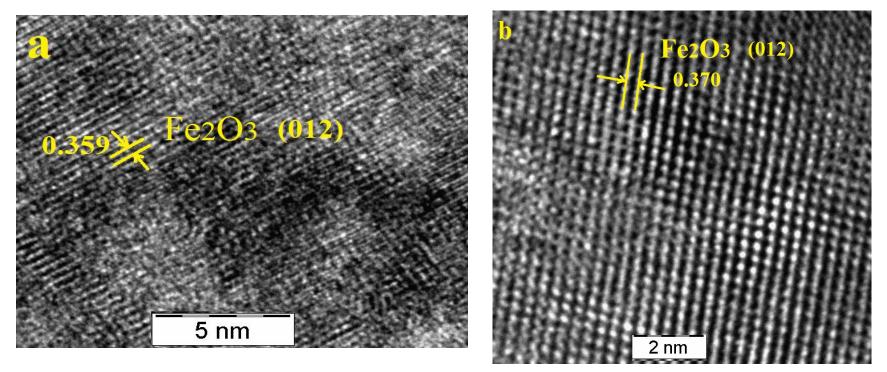
The processing of red mud increased its reactivity with lime from 0.95 MPa to 3.61 Mpa

Reactive silica percentage from 1.62% to 5.12%

in spite of having 27.12% of reactive silica, the reactivity of fly ash with lime was lower than that of red mud

Properti	es			
Specific gravity	Surface area (m ² /	kg) Lime Reactivity (MPa)	рН	Reactive silica%
3.2	39400	3.61	10.8	5.12





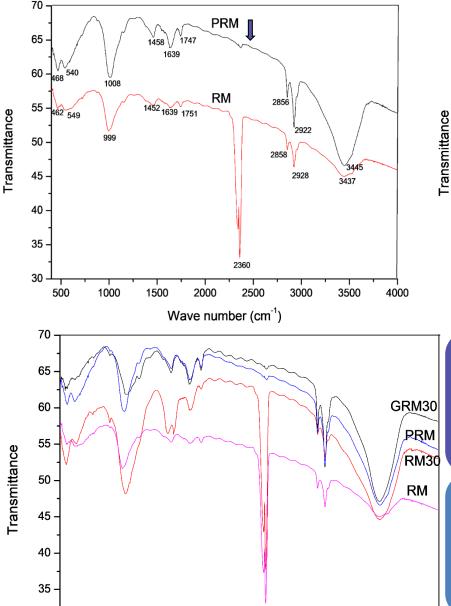
HRTEM and lattice spacing of a) unprocessed, b) pulverised red mud samples

The spacing d between the two lattice planes appeared to have increased after pulverisation

Appearance of ions seemed brighter, which indicated increase in crystallinity which complements the XRD results

Reactive silica % increased from 1.62% to 5.12%. **Increased lattice expansion** increased the ease of protonation or deprotonation of ions Ways in which pulver is atton of in which pulver is a to a city in which pulver is a city in the contract of t Sizes of all phases decreased, Hematite nanoparticles resulting in increase of their became more crystalline reactivity thus enhancing the reactivity

Fourier Transform-Infrared Spectroscopy



GRM30 ^V1746 RM30 Wave number (cm⁻¹)

Significant reduction of peak at 2360 cm-1 in PRM. The IR at 2360 cm-1 possibly represent the water molecules associated with the ferrihydrite and other hydrate phases of red mud which reduced considerably after pulverisation due to phase transition

GRM30 had only one hematite peak at 462 cm-1 and that too with diminished intensity, this indicated the dissolution of more Fe atoms from the crystalline hematite phase and their participation in the geopolymeric network

Non-thermally activated Clays

• Tank Bed soil.....



Guddaemaranahall i tank bed

Ghati tank bed

Harti tank bed

TBS BEING DRIED AND LUMPS BEING CRUSHED TBS SIEVED THROUGH 2.36MM SIEVE AND STORED

 Ref: Jyothi et al.,

Brick powder(BP)





Pulverizer used to crush to 75 micron

- Specific gravity was 2.67.
- 100% of materials passed thro 75Microns.



FLOW TEST

To find the optimum fluid content required for every mix proportions flow test was conducted.

Fresh mix of geopolymer composites



Flow table



Ref: Jyothi et al.,

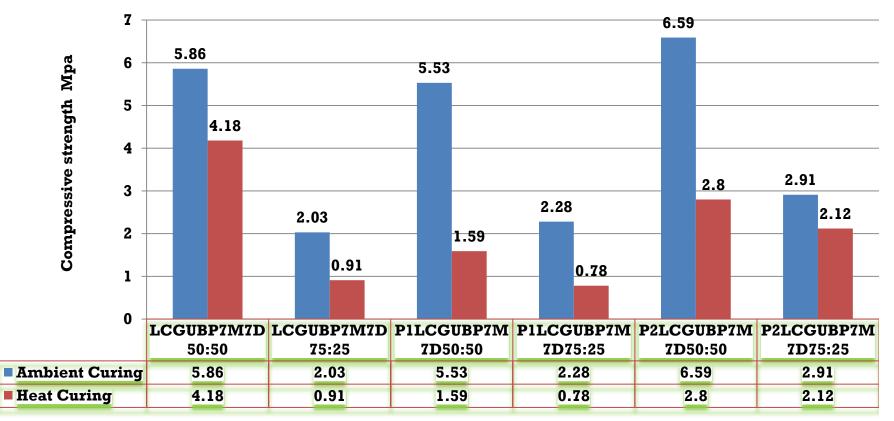
Flow test observation



GEOPOLYMER BLOCKS USING TANK BED SOIL & BRICK POWDER

1. Influence of curing conditions

CURING EFFECTS ON GEOPOLYMER BLOCKS USING GUDDAEMARANAHALLI SOIL



Ingredients used for LPC

Consistence paste

Paste on glass p

Briquettes

Kiln sealed for

burning

Kiln constructed for burning

Fuel arrangement



Ref: Jyothi et al., n during burning pr Chermosouple, used for material temperature peasurement

Production of Bricks



Dry mixing of materials Wet mixing of geopolymer Placing of fresh composite Cast brick composite



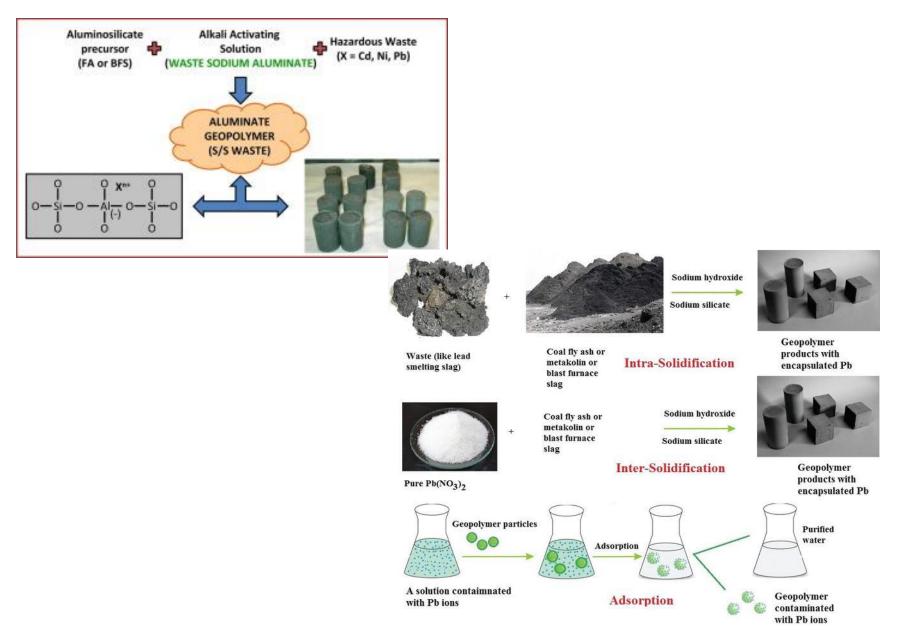
Bricks kept for curing

Ref: Jyothi et al.,



Capping of bricks with plaster-of-Paris.⁸⁹

Immobilisation of toxic wastes in geopolymers



IN CONCLUSION

Development in the field of concrete technology are far reaching

Paradigm shifts in concrete concepts are evident

Geopolymer concrete is emerging as one of the answers for developing 'greener concrete' for sustainable development

