Engineering Fly Ash-based Geopolymer Concrete

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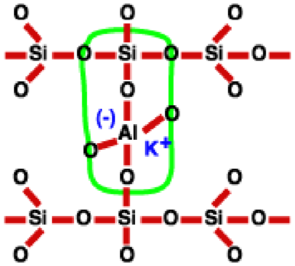
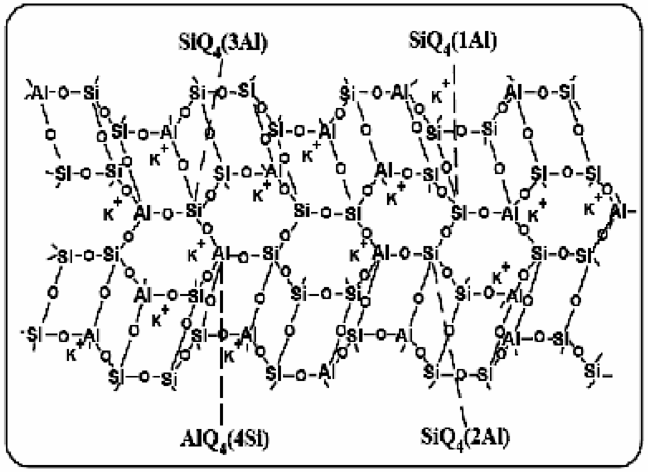
OUTLINE

- Geopolymers
  - Structure
  - Reactions
  - Properties
- Sustainability
- Engineering fly ash-based GPC
- Results
  - Fly ash analysis
  - Mechanical characterization of GPC
  - Data analysis
- Conclusions

Geopolymers

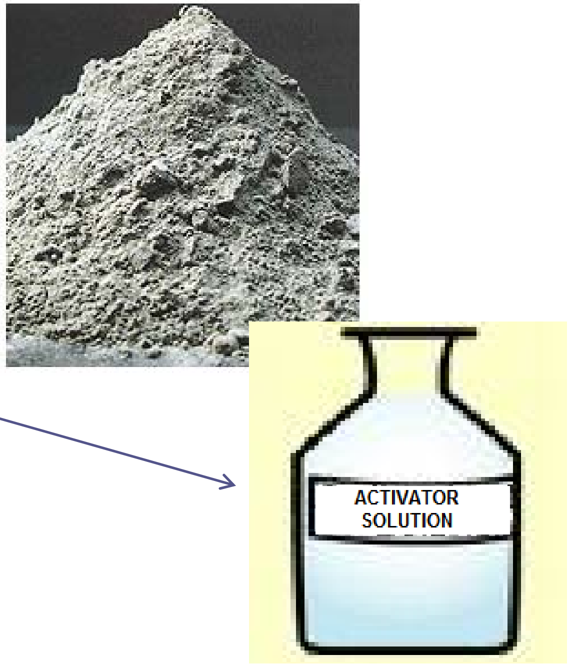
- Geopolymers are cementitious materials that do not require the presence of OPC to harden or gain strength.
- Geopolymers are formed by a 3d network of Si & Al mineral molecules linked through covalent bonds with oxygen molecules.
- A positive ion must be provided to allow aluminum to become tetravalent.





Geopolymers

- The source of Si & Al for geopolymers can be any mineral (e.g. metakaolin) or by-product (e.g. fly ash)
- The positive ion is usually provided by a hydroxide solution of Na or K, etc.
- Water glass provides the monomers from which the polymeric chains grow.
- In most cases a slightly elevated temperature is required to kick start the geopolymerization reaction



Geopolymerization

Geopolymeric reaction occurs can be divided into three steps:

1. Dissolution of species - Si and Al dissolve in the alkaline media providing monomers.
2. Transportation/Initial gelation- Orientation of the precursors takes place.
3. Condensation/setting- Hydrolyzed aluminate and silicate species policondensate and harden.

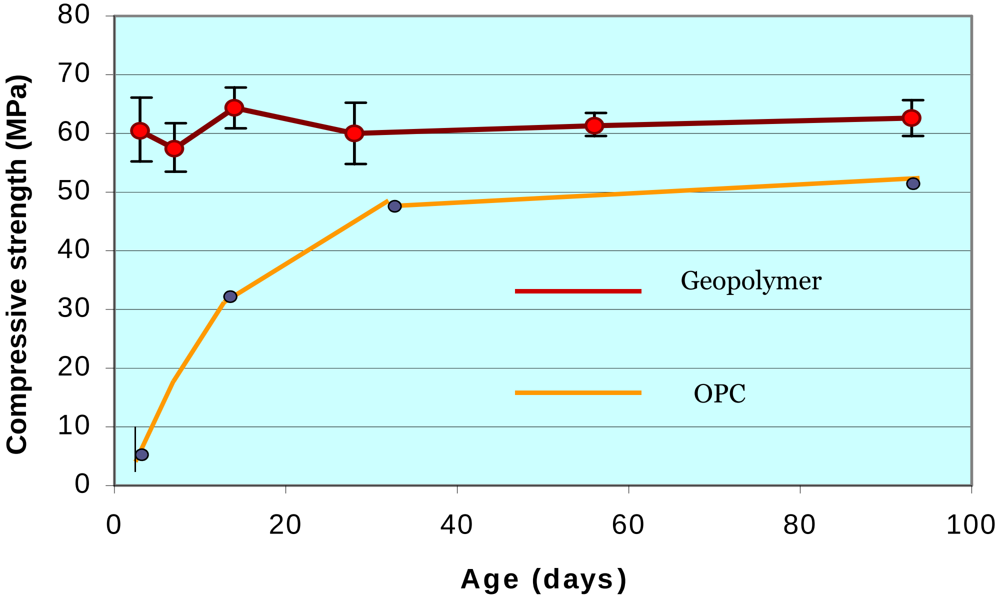
MIXING

Geopolymer paste can be mixed with the same aggregates used for Portland cement, for its use as mortar or concrete.

ACTIVATOR SOLUTION + FLY ASH + FINE & COARSE AGGREGATES

PROPERTIES

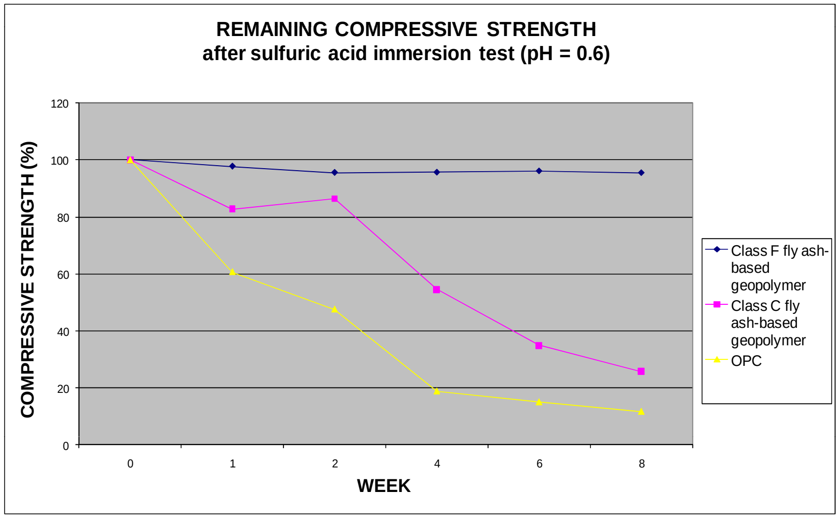
COMPRESSIVE STRENGTH

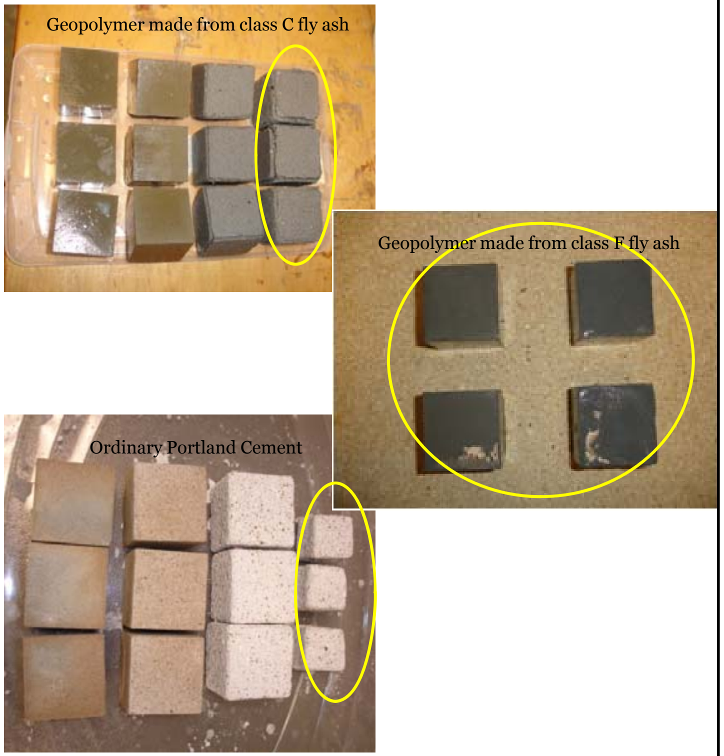


Typical compressive strength curve of Geopolymer vs. Portland cement. Observe the high early strength of geopolymer (up to 12,000 psi after 3 day of curing).

PROPERTIES

CHEMICAL RESISTANCE





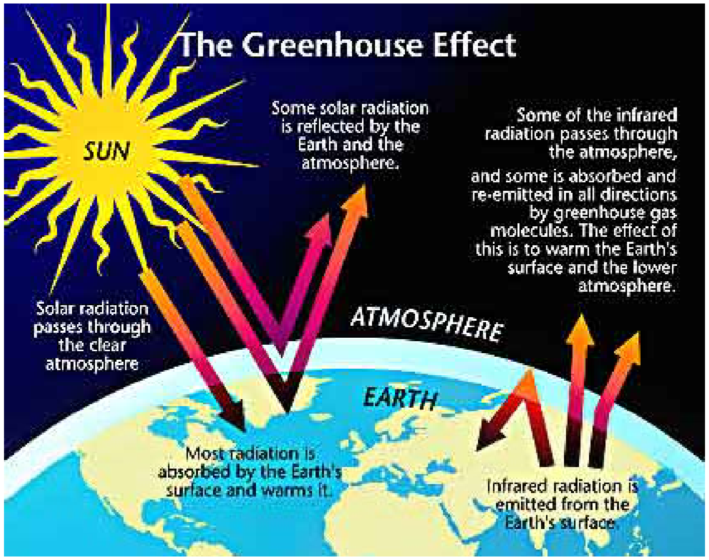
Geopolymer’s corrosion resistance to the attack of sulfuric acids is significantly greater than that of Portland cement. It is practically inert to sulfate salts attack.

Sustainability

POLLUTION AND ECOLLOGICAL FOOTPRINT

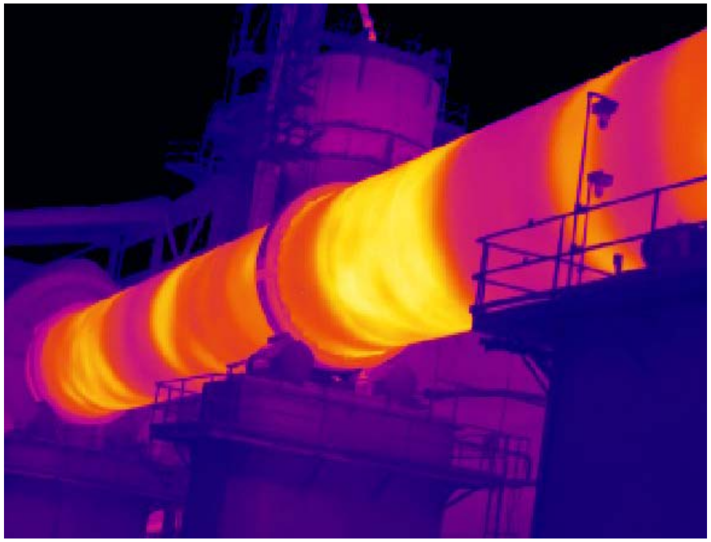
Actual production of Portland cement contributes 13.5 billion tons of CO_2 per year. Approximately 5% of the total global emission of CO2 to the atmosphere.

Geopolymer made out of waste materials like fly ash not only have a smaller footprint but help reduce the footprint of other industries namely, coal-fired power plants.



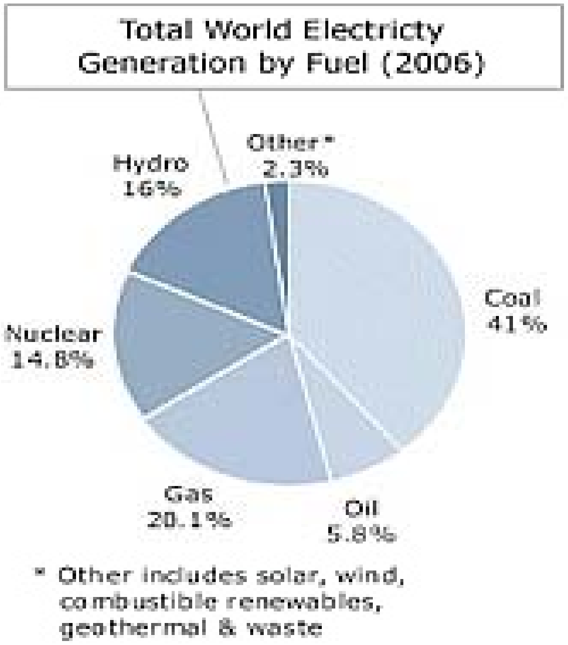
Sustainability

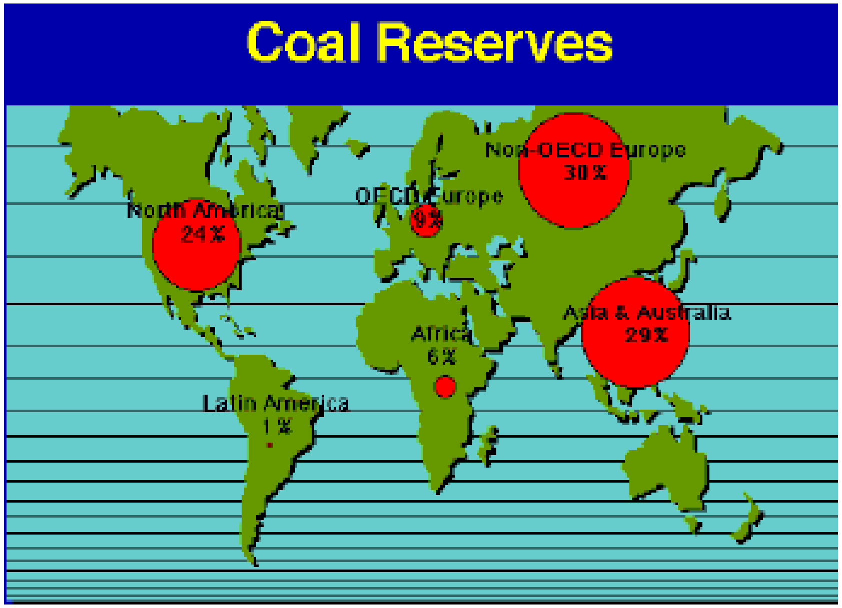
ENERGY CONSUMPTION



- Portland cement production requires heating raw materials over 2550 F
- Fly ash based-geopolymers are a much less energy consuming alternative.

Sustainability

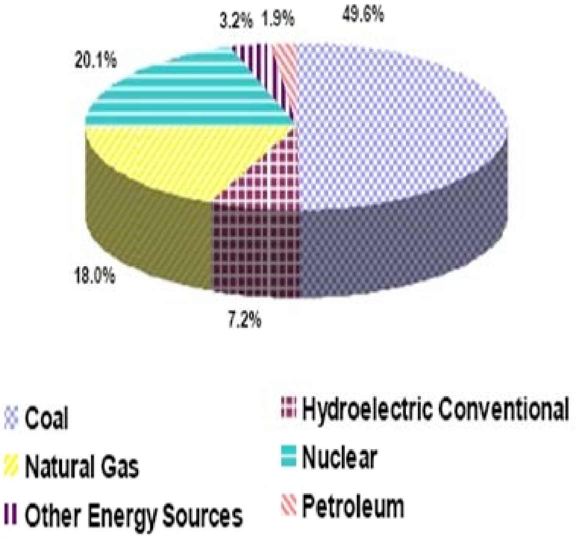




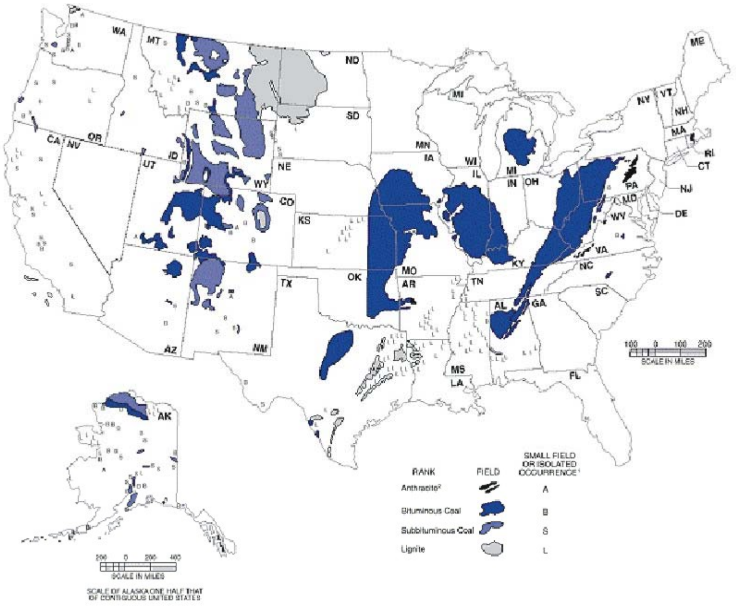
- 480 Million Tons of fly ash produced in 2001
- World wide utilization ranges 20 to 80%

Sustainability

Energy production sources in the



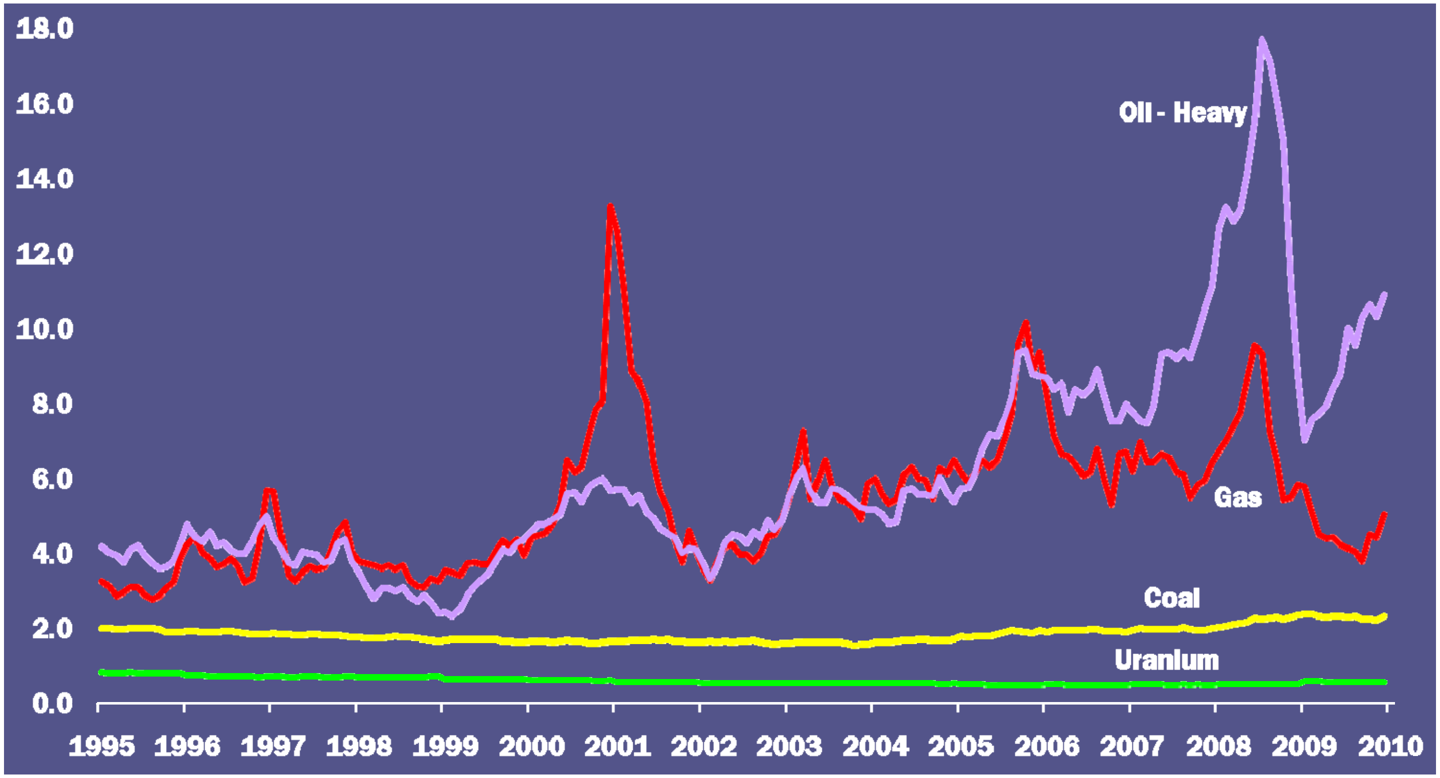
Coal reserves in the U.S.



- 72 million tons of fly ash produced in 2008
- Only 30 million tons were used sending around **42 million tons to the landfills**

Sustainability

Monthly Fuel Cost to U.S. Electric Utilities
1995 – 2009, *In 2009 cents per kilowatt-hour*



Source: Ventyx Velocity Suite

Updated: 5/10

Sustainability

POTENTIAL RISKS OF FLY ASH STORAGE LAGOONS

- In December 2008 a TVA's fly ash storage lagoon ruptured in Kingston, TN
- 1.1 billion gal. of fly ash slurry were spilled into the Emory and Clinch Rivers
- 300 acres of the surrounding land were contaminated
- Estimated clean-up costs:

  675 to 975 million

New Opportunities in the US

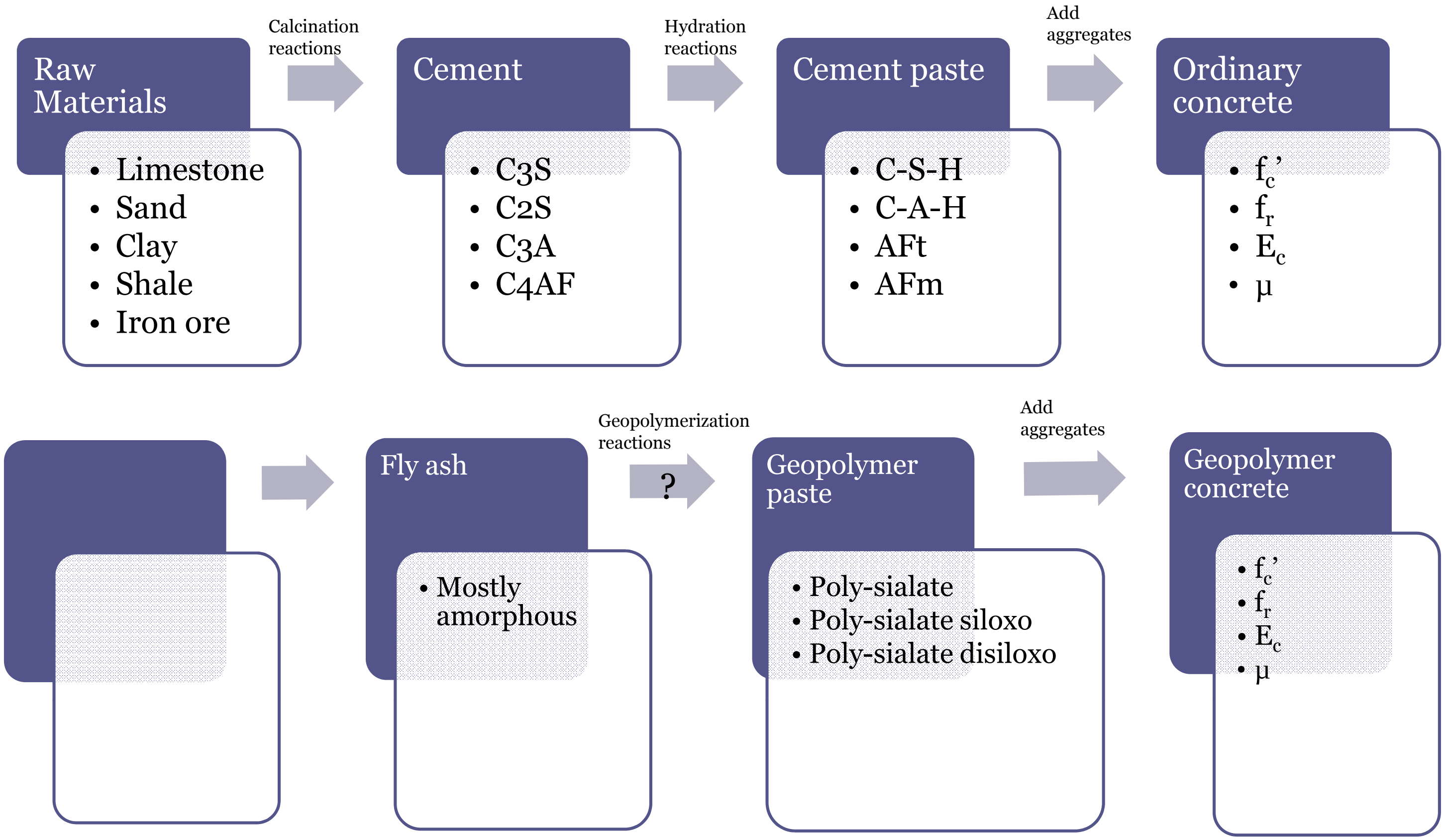
- Increasing Cost Of Fly Ash Disposal
  - New regulations proposed by the EPA are expected to tighten fly ash disposal requirements increasing its cost.
- Fly Ash Only For Encapsulated Applications
  - EPA's new regulations may only allow fly ash to be recycled in encapsulated applications.
- Green Construction Boom
  - LEED Certification is aimed at improving performance across all the metrics that matter most: energy savings, water efficiency, **CO_2 emissions reduction**, improved indoor environmental quality, and stewardship of resources and sensitivity to their impacts.
- Carbon Trading
  - Geopolymer offers the possibility to offset carbon emissions.

Challenges of fly ash-based geopolymer concrete

- Fly ash Variability

Component	Bituminous	Subituminous	Lignite
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	10-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO_3	0-4	0-2	0-10
Na_2O	0-4	0-2	0-6
K_2O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

Challenges of fly ash-based geopolymer concrete



Raw Materials
- Limestone
- Sand
- Clay
- Shale
- Iron ore

Calcination reactions

Cement
- C3S
- C2S
- C3A
- C4AF

Hydration reactions

Cement paste
- C-S-H
- C-A-H
- AFt
- AFm

Add aggregates

Ordinary concrete
- f_c'
- f_r
- E_c
- μ

Fly ash
- Mostly amorphous

Geopolymerization reactions

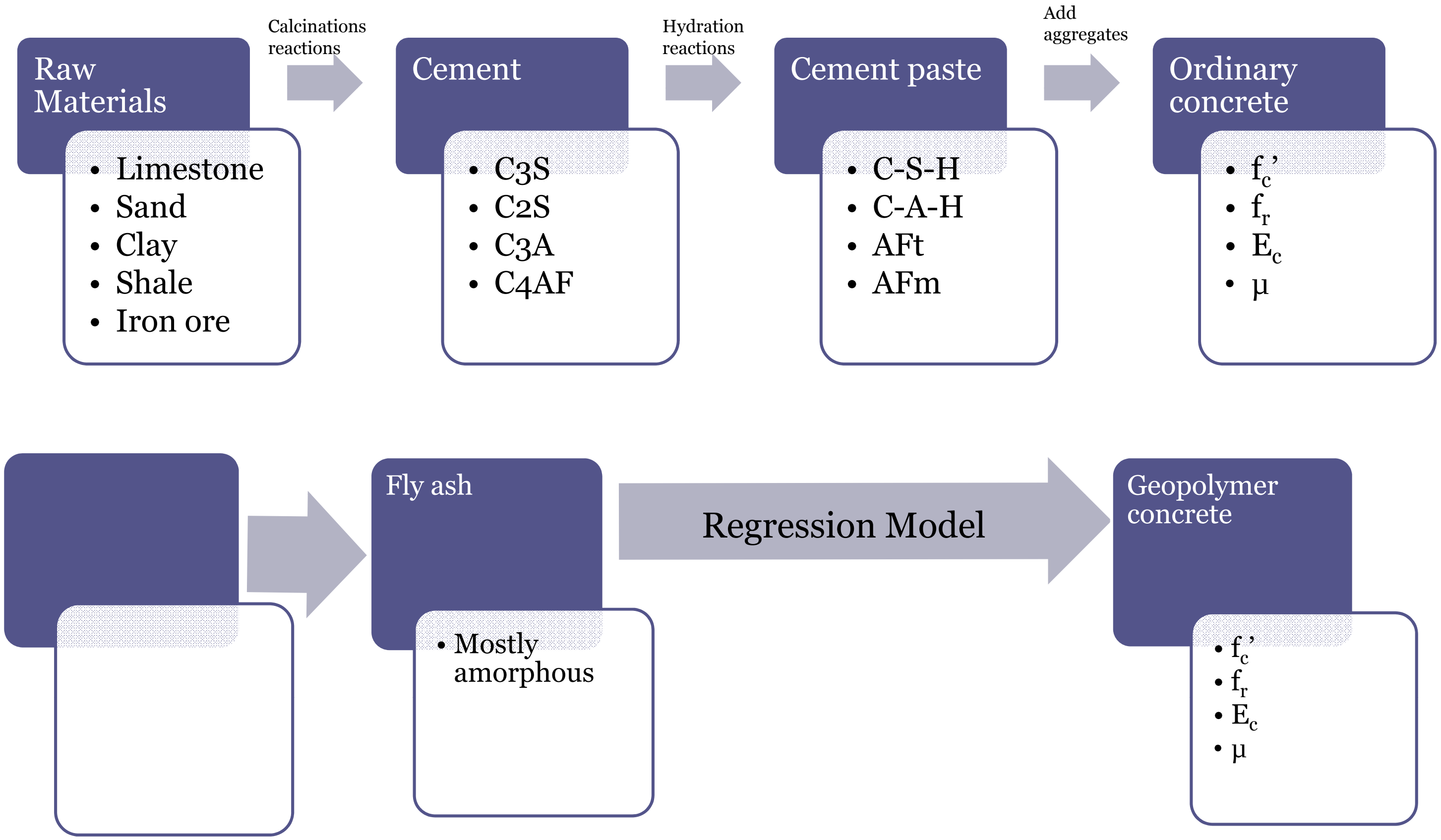
?

Geopolymer paste
- Poly-sialate
- Poly-sialate siloxo
- Poly-sialate disiloxo

Add aggregates

Geopolymer concrete
- f_c'
- f_r
- E_c
- μ

Challenges of fly ash-based geopolymer concrete



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- Limestone
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Calcinations reactions

Cement
- C3S
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Hydration reactions

Cement paste
- C-S-H
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Add aggregates

Ordinary concrete
- f_c'
- f_r
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- μ

Fly ash
- Mostly amorphous

Regression Model

Geopolymer concrete
- f_c'
- f_r
- E_c
- μ

Engineering fly ash-based geopolymer concrete

1. Identify the fly ash characteristics that significantly impact GPC
    - Collect fly ash samples
    - Keep mix design constant
    - Full mechanical characterization of GPC samples
2. Evaluate the mechanical behavior of GPC made from each of the fly ash samples
    - Compressive vs. tensile strength
    - Compressive vs. elastic modulus
    - Density vs. fly ash fineness
3. Determine the feasibility of establishing a regression model to predict GPC's mechanical properties using the characteristics fly ash

COLLECTION OF FLY ASH SAMPLES

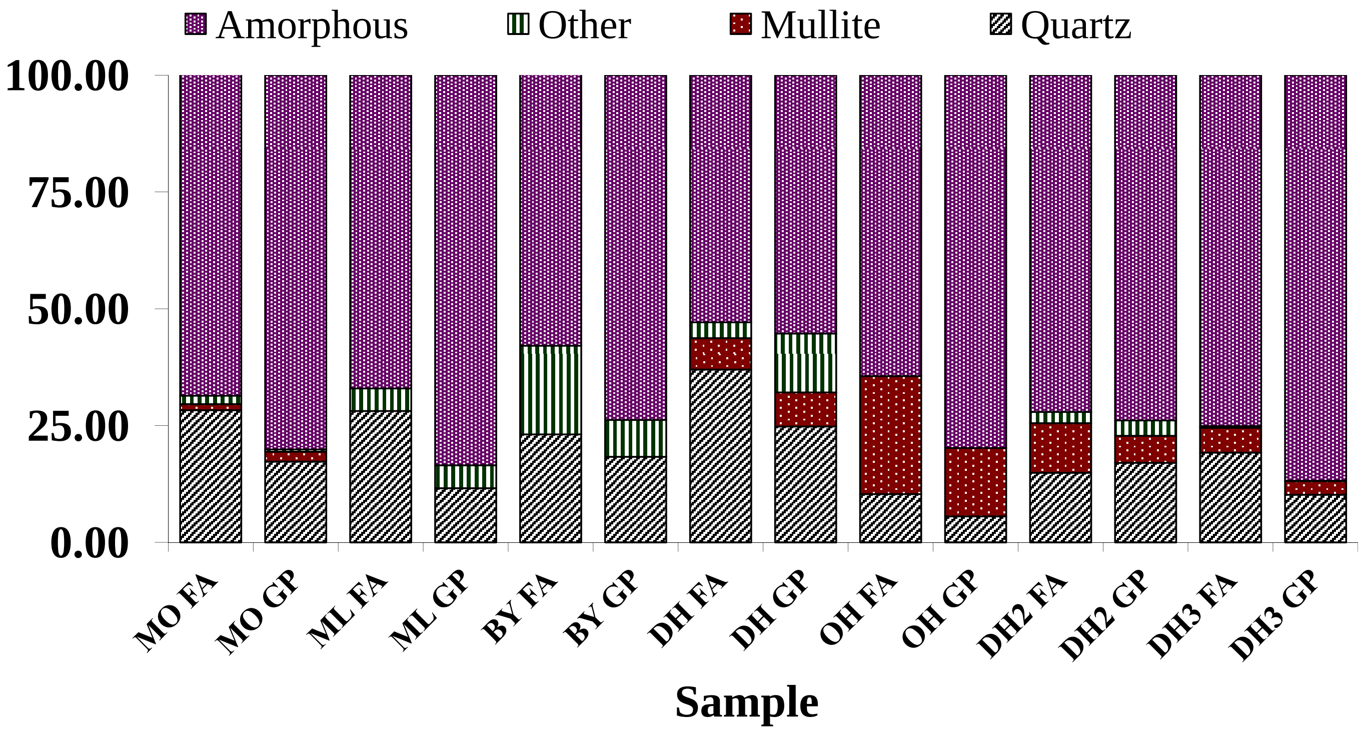
SAMPLE	FLY ASH ORIGINS	LOCATION	ID CODE	CAPACITY (MW)	FLY ASH PRODUCTION PER YEAR (TONS)
1	RODEMACHER PP	BOYCE, LA	BY	963	438,000
2	RODEMACHER PP 2ND BATCH	BOYCE, LA	BY2	1871	1,092,664
3	MONTICELLO PP	MOUNT PLEASANT, TX	MO	1,880	1,097,920
4	DOLET HILLS PP	MANSFIELD, LA	DH	750	438,000
5	DOLET HILLS PP 2/09/09	MANSFIELD, LA	DH 2		
6	DOLET HILLS PP 3/16/09	MANSFIELD, LA	DH 3		
7	DOLET HILLS PP 07/01/09	MANSFIELD, LA	DH 4		
8	DOLET HILLS PP 08/10/09	MANSFIELD, LA	DH 5		
9	MARTIN LAKE PP	TATUM, TX	ML	2,250	1,314,000
10	AVON LAKE PP	AVON L., OHIO	OH	745	435,080
11	SAN JUAN PP (LANDFILL)	FARMINGTON, NM	SJLF	1,800	1,051,200
12	SAN JUAN PP UNIT 1	FARMINGTON, NM	SJ1		
13	SAN JUAN PP UNIT 2	FARMINGTON, NM	SJ2		
14	SAN JUAN PP UNIT 3	FARMINGTON, NM	SJ3		
15	SAN JUAN PP UNIT 4	FARMINGTON, NM	SJ4		
16	COUTLAND PAPER MILL	COURTLAND, AL	CL	-	
17	TENNESSE	TENNESSEE	TN	-	
18	TENNESSE REBURNED	TENNESSEE	TNRB		
19	MERRIMACK STATION UNIT 1	BOW, NH	NH1	459	1,097,920
20	MERRIMACK STATION UNIT 2	BOW, NH	NH2		
21	SAN MIGUEL ELECTRIC COOP.	TILDEN, TX	SM	390	227,760
22	GIBBON'S CREEK PP	BRYAN, TX	GC	454	265,136
23	COLETO CREEK PP	FANIN, TX	CC	600	350,400
24	PIRKEY PP	HALLSVILLE, TX	PK	721	421,064
25	WELSH PP	HALLSVILLE, TX	SE	1,674	977,616
26	FLINT CREEK PP	GENTRY, AR	FC	528	308,352
27	NORTHEASTERN STATION U 3&4	OOLOGAH, OK	NE	946	552,464
28	W.A. PARISH PP	THOMPSON, TX	WA	3,565	1,040,980
	TOTAL				**11,108,556**

Elemental analysis of fly ash via XRF

ID Code Oxide	BY	BY2	MO	DH	DH 2	DH 3	DH4	DH5	ML	OH	SJLF	SJ1	SJ2	SJ3	SJ4	CL	TN	TNRB	NH1	NH2	SM	GC	CC	PK
SiO2	37.77	32.41	55.61	58.52	61.01	61.23	62.12	59.32	48.70	55.07	56.60	56.22	56.39	57.11	57.35	37.99	23.48	44.56	40.75	36.18	66.50	39.25	33.02	59.25
Al2O3	19.13	18.40	19.87	20.61	20.06	19.20	19.59	19.72	16.60	28.61	25.68	27.15	27.36	28.18	27.78	17.37	13.15	24.79	22.79	17.70	18.80	21.09	19.82	18.43
SiO2/Al2O3	1.97	1.76	2.80	2.84	3.04	3.19	3.17	3.01	2.93	1.92	2.20	2.07	2.06	2.03	2.06	2.19	1.79	1.80	1.79	2.04	3.54	1.86	1.67	3.21
SiO2+Al2O3	56.90	57.90	75.48	79.13	81.07	80.43	81.71	79.04	65.30	83.68	82.28	83.37	83.75	85.29	85.13	55.36	36.63	69.35	63.54	53.88	85.30	60.34	52.84	77.68
CaO	22.45	28.07	12.93	5.00	5.48	5.64	5.01	6.90	18.72	1.97	5.73	5.43	4.69	5.18	5.57	18.46	2.30	4.39	4.64	2.26	4.91	23.53	26.19	9.23
Fe2O3	7.33	7.17	4.52	9.43	7.00	7.27	6.88	7.22	6.93	6.22	3.92	3.73	3.34	4.00	3.65	3.09	4.72	8.46	17.76	10.59	1.95	4.99	6.75	5.61
MgO	4.81	5.11	2.49	1.86	2.26	2.23	2.18	2.23	3.91	1.08	0.73	0.77	0.75	0.82	0.82	1.44	0.74	1.35	1.23	1.20	0.63	4.45	6.34	3.23
SO3	1.56	2.04	0.49	0.49	0.28	0.29	0.21	0.36	0.85	0.19	0.34	0.22	0.26	0.28	0.18	2.77	0.26	0.16	1.29	0.20	0.22	0.85	1.36	0.35
Na2O	1.80	2.28	0.67	0.52	0.82	1.13	0.88	1.11	0.71	0.38	1.30	1.47	1.50	1.53	1.42	0.22	0.31	0.63	1.33	0.73	2.90	1.47	1.92	0.50
K2O		0.41	0.86		1.27	1.28	1.37	1.27	1.22	2.63	1.00	1.00	0.95	1.05	1.01	3.46	0.93	1.73	2.19	1.59	2.63	0.57	0.35	1.63
TiO2		1.45			1.09	0.97	1.01	1.00	0.97	1.56	0.80	0.93	0.96	1.00	1.01	0.91	0.90	1.67	1.28	1.03	0.89	1.50	1.50	1.21
MnO2		0.03			0.14	0.16	0.16	0.18	0.21	0.02	0.05	0.04	0.03	0.03	0.03	0.54	0.02	0.04	0.03	0.03	0.09	0.02	0.03	0.06
P2O5		1.22			0.08	0.09	0.09	0.10	0.10	0.16	0.13	0.18	0.18	0.21	0.19	0.50	1.01	1.80	0.62	0.43	0.01	1.18	1.52	0.05
SrO		0.35			0.21	0.24	0.20	0.23	0.31	0.08	0.06	0.07	0.07	0.07	0.06	0.17	0.08	0.14	0.25	0.14	0.14	0.36	0.33	0.21
BaO		0.68			0.23	0.22	0.20	0.22	0.30	0.21	0.10	0.10	0.11	0.11	0.09	0.24	0.08	0.13	0.19	0.08	0.12	0.62	0.72	0.21
Moisture content	0.12	0.07	0.03	0.14	0.05	0.04	0.17	0.08	0.12	0.12	0.09	0.04	0.00	0.00	0.01	0.12	0.72	0.05	0.14	0.16	0.02	0.03	0.01	0.03
Loss On Ignition	0.17	0.38	0.23	0.05	0.08	0.06	0.10	0.15	0.49	1.82	3.50	2.69	3.41	0.44	0.83	12.83	52.01	10.14	5.72	27.84	0.26	0.11	0.16	0.04

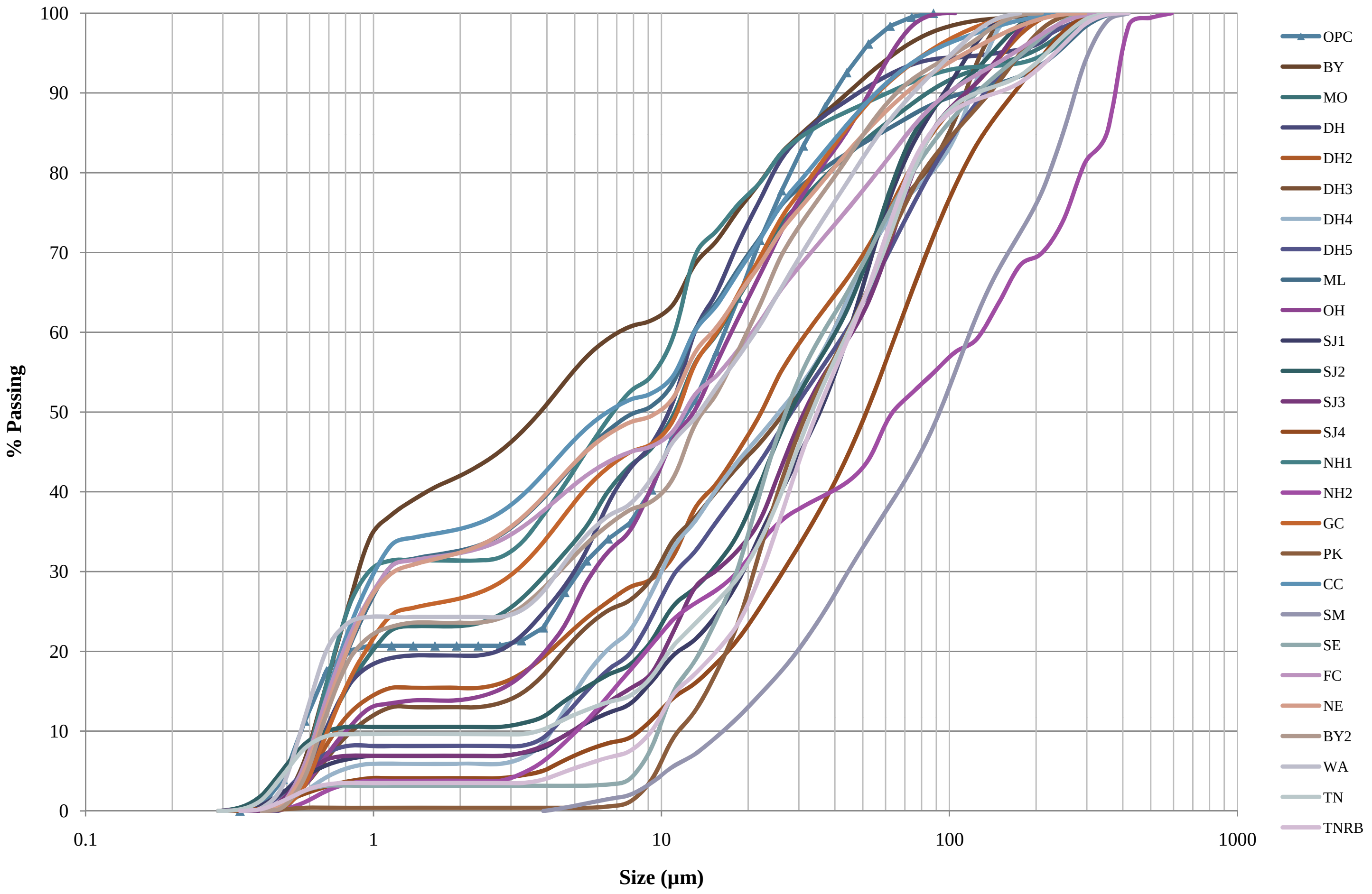
Parameter	Min	Max	Avg	Sta Div
SiO2+Al2O3	36.63	85.30	71.15	13.93
SiO2/Al2O3	1.79	3.19	2.35	.59
CaO	2.26	28.07	9.78	8.24

Crystallographic characteristics of fly ash



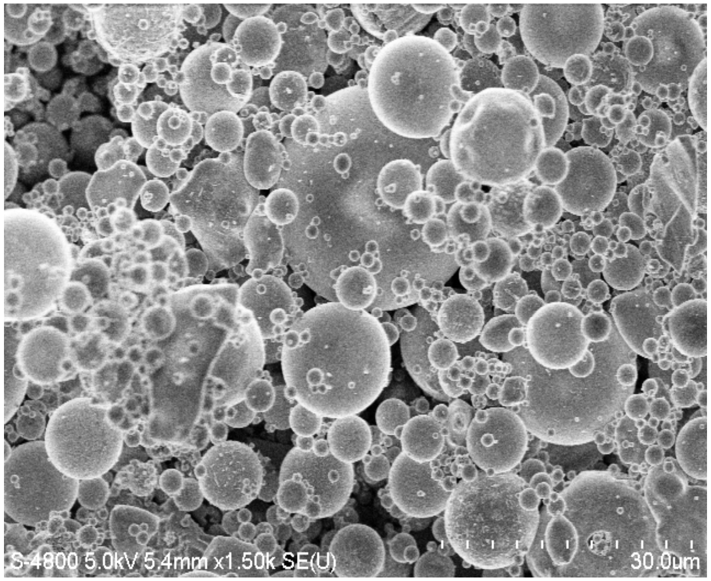
Parameter	Min	Max	Avg	Std Dev
Amorphous FA	27.9	75.1	62.41	12.46
Amorphous GP	55.3	86.8	74.44	8.3

Particle size distribution of fly ash

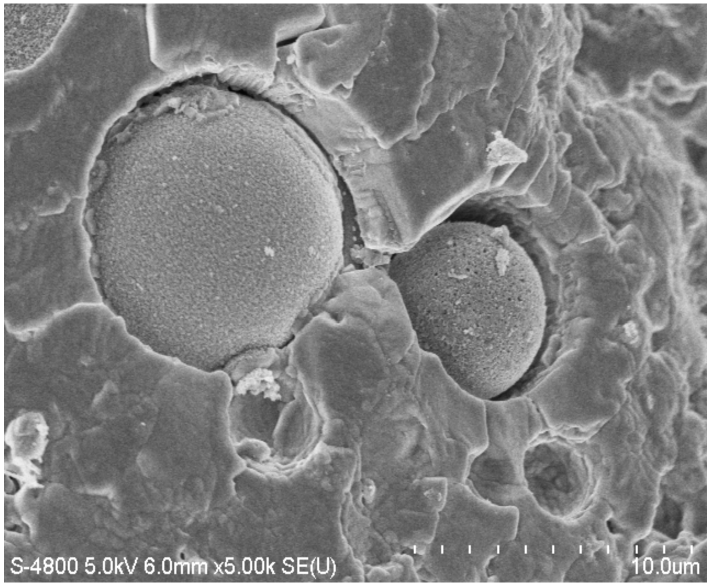


Particle Morphology

Fly Ash Before Activation

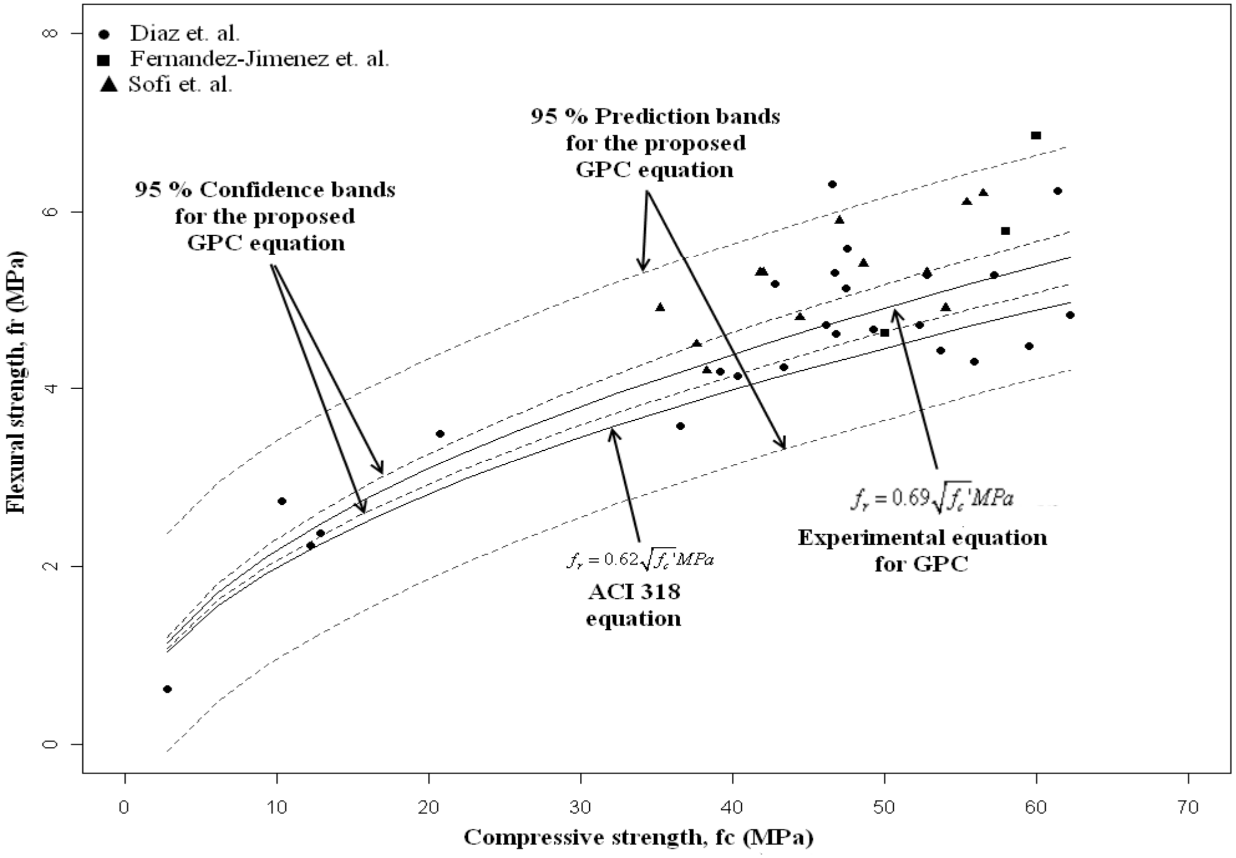


Fly Ash After Activation (Geopolymer)



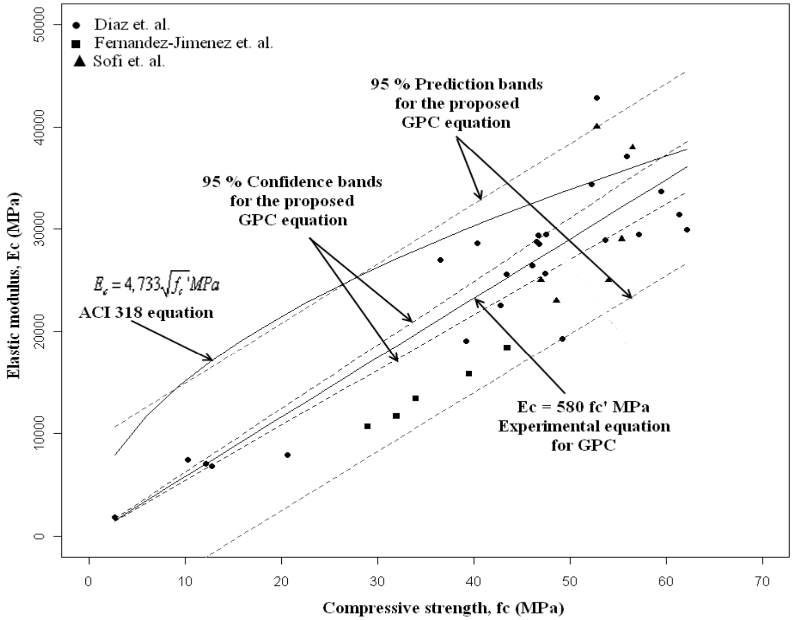
Correlations Within the Mechanical Properties

Flexural vs. Compressive Strength



Correlations Within the Mechanical Properties

Elastic Modulus vs. Compressive Strength



- The ACI equation:

  $$E_c = 4733\sqrt{f_c'}\ MPa$$

  was design for normal weight concrete (2300 kg/m^3)while the GPC samples ranged from 1890 to 2371 kg/m^3
- Therefore the density was included in the regression model:

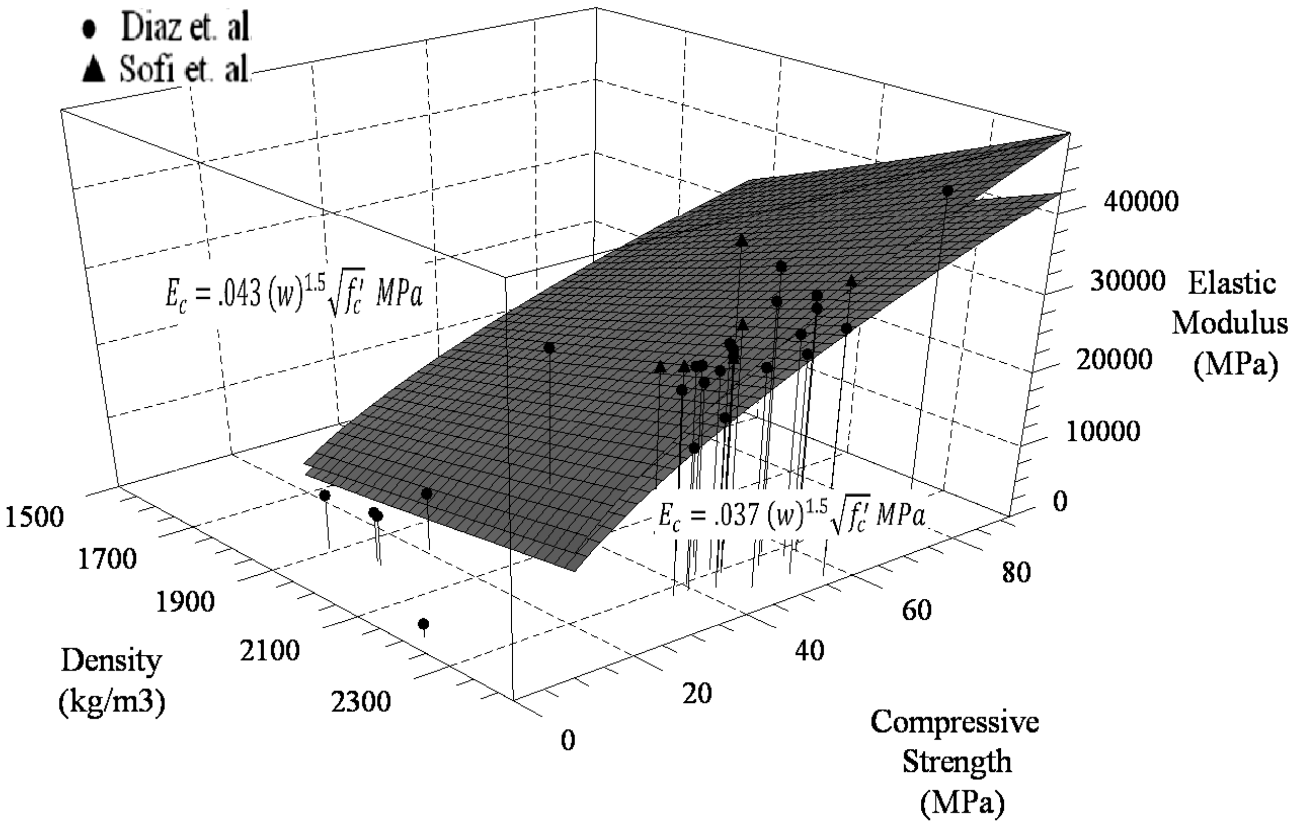
  $$E_c = .037\,(w)^{1.5}\sqrt{f_c'}\ MPa$$

- Compared to ACI equation:

  $$E_c = .043\,(w)^{1.5}\sqrt{f_c'}\ MPa$$

Correlations Within the Mechanical Properties

Elastic Modulus vs. Compressive Strength & Density



Engineering fly ash-based geopolymer concrete

Development of a Prediction Model

FLY ASH VARIABLES:

- Reactive Silica
- Reactive Alumina
- Reactive Calcium
- Loss on Ignition
- Fineness
- Specific Surface Area

GPC RESPONSE:

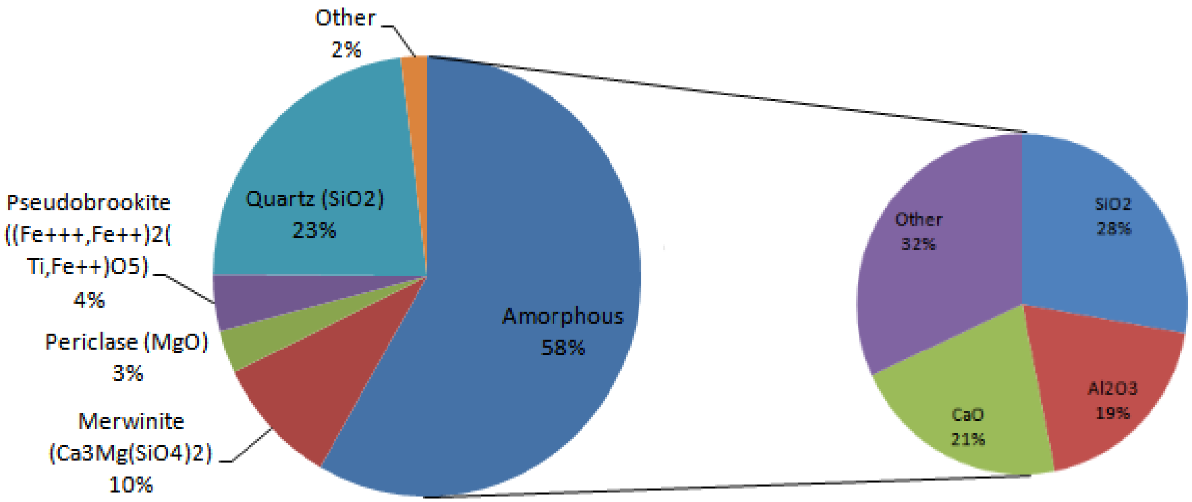
- Compressive Strength

Development of a Prediction Model

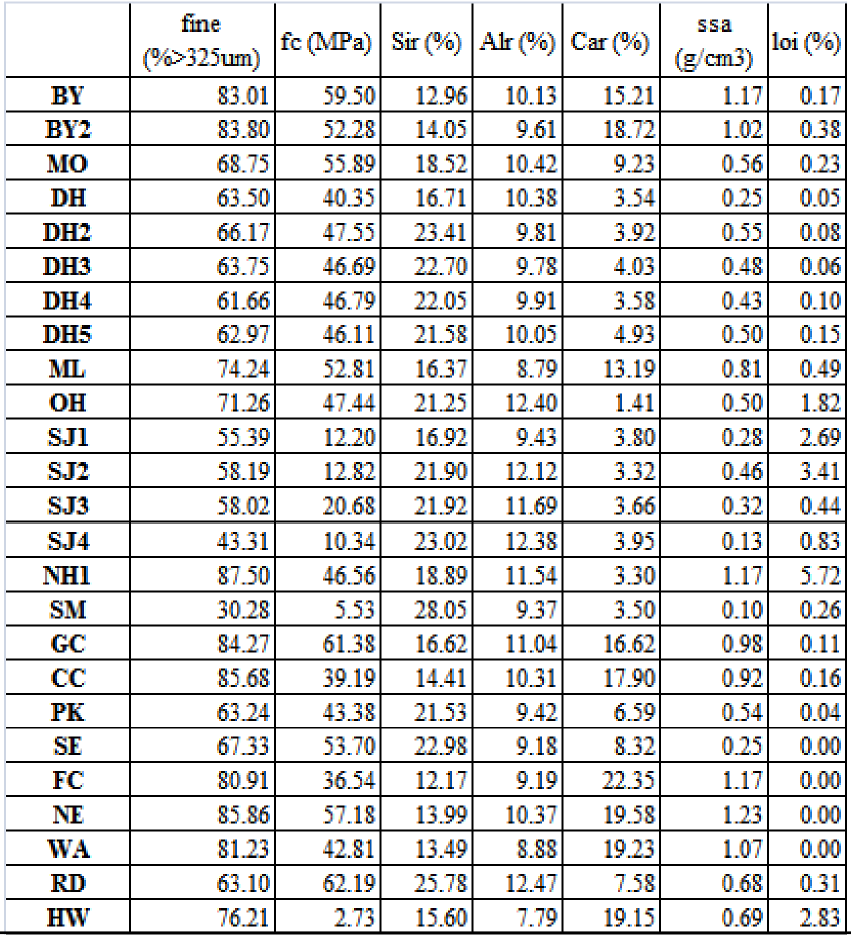
Introduction of Silica, Alumina and Calcium Content to the Model

Elemental Analysis

	BY
SiO2	37.77
Al2O3	19.13
SiO2/Al2O3	1.97
SiO2+Al2O3	56.90
CaO	22.45



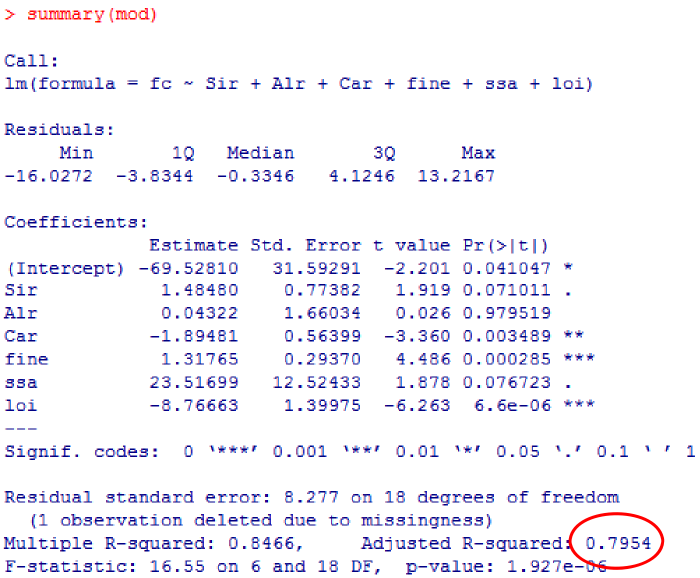
Development of a Prediction Model



	fine (%>325um)	fc (MPa)	Sir (%)	Alr (%)	Car (%)	ssa (g/cm3)	loi (%)
BY	83.01	59.50	12.96	10.13	15.21	1.17	0.17
BY2	83.80	52.28	14.05	9.61	18.72	1.02	0.38
MO	68.75	55.89	18.52	10.42	9.23	0.56	0.23
DH	63.50	40.35	16.71	10.38	3.54	0.25	0.05
DH2	66.17	47.55	23.41	9.81	3.92	0.55	0.08
DH3	63.75	46.69	22.70	9.78	4.03	0.48	0.06
DH4	61.66	46.79	22.05	9.91	3.58	0.43	0.10
DH5	62.97	46.11	21.58	10.05	4.93	0.50	0.15
ML	74.24	52.81	16.37	8.79	13.19	0.81	0.49
OH	71.26	47.44	21.25	12.40	1.41	0.50	1.82
SJ1	55.39	12.20	16.92	9.43	3.80	0.28	2.69
SJ2	58.19	12.82	21.90	12.12	3.32	0.46	3.41
SJ3	58.02	20.68	21.92	11.69	3.66	0.32	0.44
SJ4	43.31	10.34	23.02	12.38	3.95	0.13	0.83
NH1	87.50	46.56	18.89	11.54	3.30	1.17	5.72
SM	30.28	5.53	28.05	9.37	3.50	0.10	0.26
GC	84.27	61.38	16.62	11.04	16.62	0.98	0.11
CC	85.68	39.19	14.41	10.31	17.90	0.92	0.16
PK	63.24	43.38	21.53	9.42	6.59	0.54	0.04
SE	67.33	53.70	22.98	9.18	8.32	0.25	0.00
FC	80.91	36.54	12.17	9.19	22.35	1.17	0.00
NE	85.86	57.18	13.99	10.37	19.58	1.23	0.00
WA	81.23	42.81	13.49	8.88	19.23	1.07	0.00
RD	63.10	62.19	25.78	12.47	7.58	0.68	0.31
HW	76.21	2.73	15.60	7.79	19.15	0.69	2.83

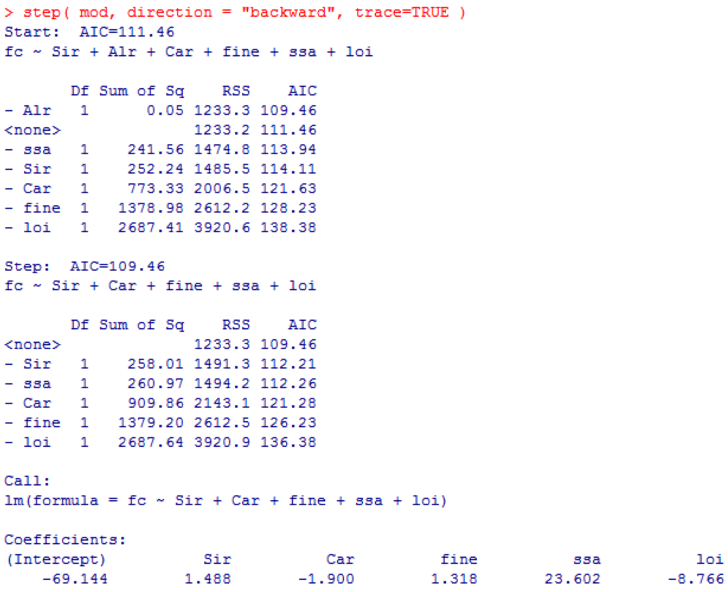
Development of a Prediction Model

Model with all possible variables



```
> summary(mod)

Call:
lm(formula = fc ~ Sir + Alr + Car + fine + ssa + loi)

Residuals:
     Min       1Q   Median       3Q      Max 
-16.0272  -3.8344  -0.3346   4.1246  13.2167 

Coefficients:
             Estimate Std. Error t value Pr(>|t|)    
(Intercept) -69.52810   31.59291  -2.201 0.041047 *  
Sir           1.48480    0.77382   1.919 0.071011 .  
Alr           0.04322    1.66034   0.026 0.979519    
Car          -1.89481    0.56399  -3.360 0.003489 ** 
fine          1.31765    0.29370   4.486 0.000285 ***
ssa          23.51699   12.52433   1.878 0.076723 .  
loi          -8.76663    1.39975  -6.263  6.6e-06 ***
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1 

Residual standard error: 8.277 on 18 degrees of freedom
  (1 observation deleted due to missingness)
Multiple R-squared: 0.8466,     Adjusted R-squared: 0.7954 
F-statistic: 16.55 on 6 and 18 DF,  p-value: 1.927e-06 
```

Stepwise regression



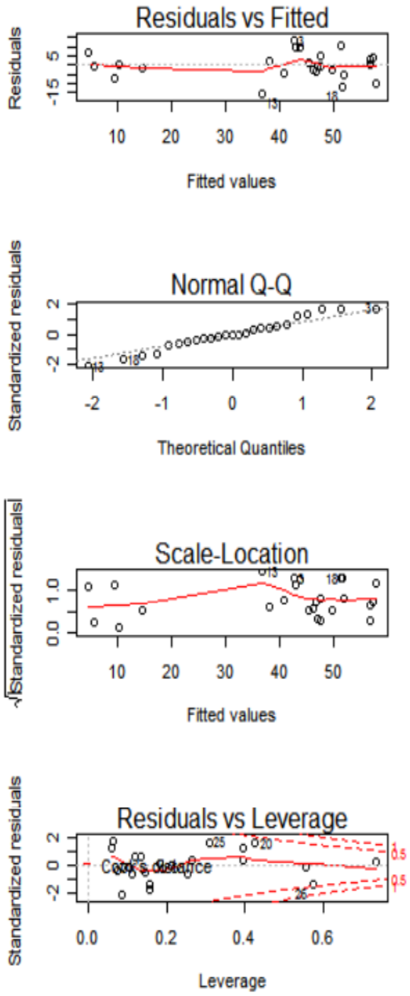
```
> step( mod, direction = "backward", trace=TRUE )
Start:  AIC=111.46
fc ~ Sir + Alr + Car + fine + ssa + loi

       Df Sum of Sq    RSS    AIC
- Alr   1      0.05 1233.3 109.46
<none>              1233.2 111.46
- ssa   1    241.56 1474.8 113.94
- Sir   1    252.24 1485.5 114.11
- Car   1    773.33 2006.5 121.63
- fine  1   1378.98 2612.2 128.23
- loi   1   2687.41 3920.6 138.38

Step:  AIC=109.46
fc ~ Sir + Car + fine + ssa + loi

       Df Sum of Sq    RSS    AIC
<none>              1233.3 109.46
- Sir   1    258.01 1491.3 112.21
- ssa   1    260.97 1494.2 112.26
- Car   1    909.86 2143.1 121.28
- fine  1   1379.20 2612.5 126.23
- loi   1   2687.64 3920.9 136.38

Call:
lm(formula = fc ~ Sir + Car + fine + ssa + loi)

Coefficients:
(Intercept)          Sir          Car         fine          ssa          loi  
    -69.144        1.488       -1.900        1.318       23.602       -8.766  
```

Development of a Prediction Model

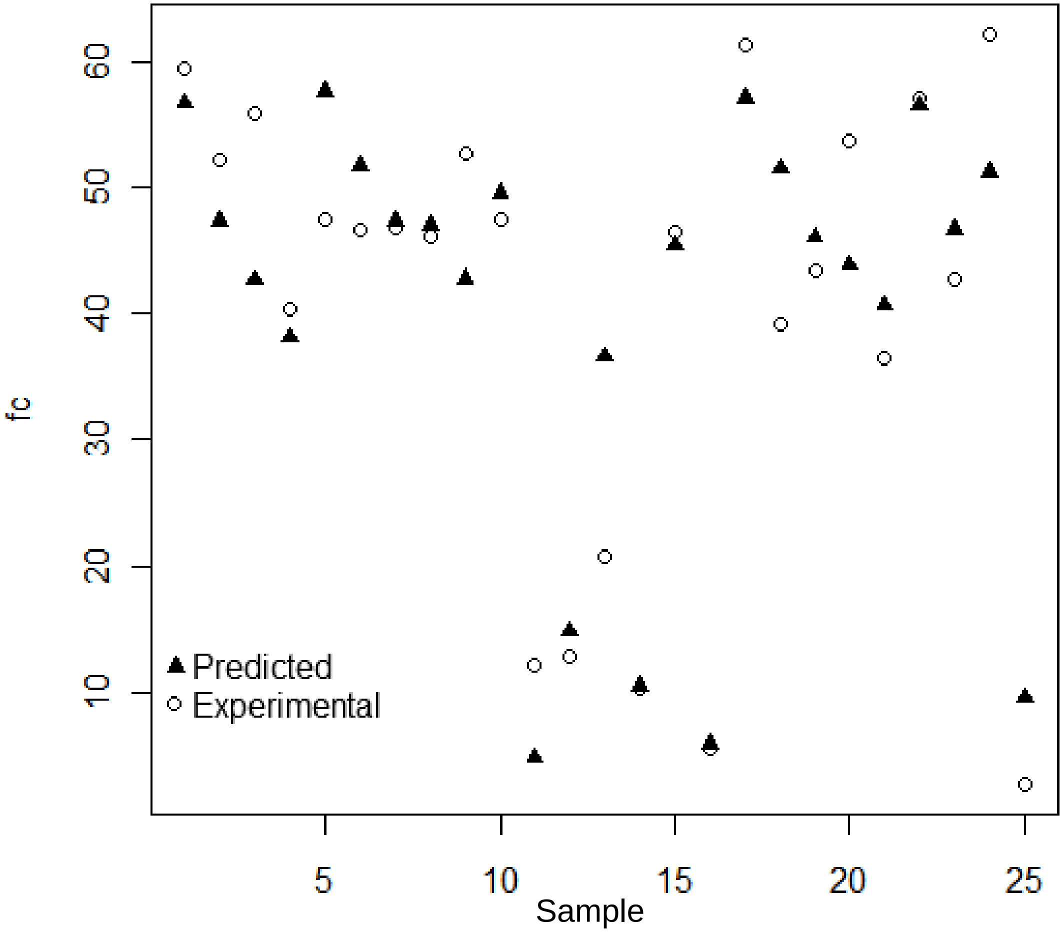
2nd model (Al not included)

```
> summary(mod2)

Call:
lm(formula = fc ~ Sir + Car + fine + ssa + loi)

Residuals:
     Min       1Q   Median       3Q      Max
-15.9767  -3.8599  -0.3816   4.1766  13.2318

Coefficients:
            Estimate Std. Error t value Pr(>|t|)
(Intercept) -69.1443    27.1972  -2.542 0.019880 *
Sir           1.4876     0.7461   1.994 0.060736 .
Car          -1.9004     0.5076  -3.744 0.001375 **
fine          1.3177     0.2859   4.610 0.000191 ***
ssa          23.6018    11.7707   2.005 0.059407 .
loi          -8.7661     1.3623  -6.435 3.61e-06 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 8.057 on 19 degrees of freedom
  (1 observation deleted due to missingness)
Multiple R-squared: 0.8466,     Adjusted R-squared: 0.8062
F-statistic: 20.96 on 5 and 19 DF,  p-value: 3.912e-07
```

```
> vif(mod2)
     Sir      Car     fine      ssa      loi
3.905245 4.559125 5.963463 6.399555 1.371505
```



Model Adequacy



Conclusions

- Geopolymer concrete possesses a very similar mechanical behavior to that of ordinary Portland cement concrete.
- Similar or in some cases the same equations given in the ACI building code can be used for the design of GPC structures.
- A model to predict the mechanical properties of GPC based on characteristics inherent to the fly ash is put forward.
- The model is based on the fly ash variables:

  SiO2, CaO, Loss on ignition, fineness & SSA