Calcined Clays of Lower Kaolinite Content and Their Use as Pozzolanic Materials

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Background

- Metakaolin obtained by calcination of high-quality kaolinite– expensive
- Ongoing research on using lower-purity kaolinite-containing clays
- FDOT had an interest in exploring the possibility of using locally-available clays as pozzolanic material in concrete
- Preliminary investigation objectives:
  - Identification and characterization of lower-purity kaolinite clay sources in Central Florida
  - Assessment of pozzolanic activity of the calcined clays through compressive strength measurements

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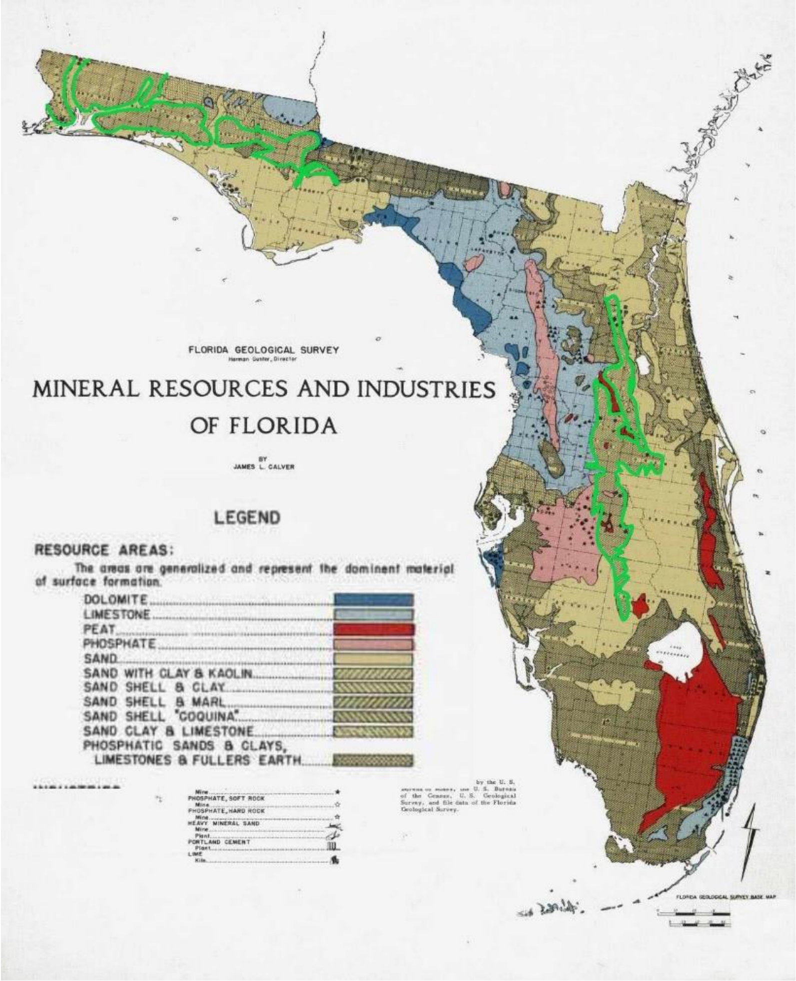
Identification of Clay Sources in Florida

- Integrated Habitat Network (IHN) used to identify potential clay sampling locations http://geodata.dep.state.fl.us
  - Locations predominantly both active and inactive mining sites
  - No specific information on clay mineralogy



http://floridafisheriesscience.blogspot.com/2013/08/whats-in-lake-exploring-floridas.html

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Material Sampling

- 9 locations selected in Central Florida (A through I)
  - Currently mined for sand or road base material
- 20 field samples
- Multiple samples were obtained from several location based on color variation

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Preliminary Characterization

- All samples dried in the laboratory at 110^{o}C until constant mass
- Sieved through 45 µm to separate the clay fraction for preliminary x-ray diffraction (XRD) investigation
- Collected scans were compared visually to identify samples with variable mineralogy

↓

- 10 samples selected for further study

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ASTM C618 Requirements

- Calcined clays – Class N natural pozzolans
- Chemical Requirements:
  - $SiO_2+Al_2O_3+Fe_2O_3 \geq 70.0\%$
  - $SO_3 \leq 4.0\%$
  - Moisture content ≤ 3.0%
  - Loss on ignition (LOI) ≤ 10.0%

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ASTM C618 Requirements

- Physical Requirements:
  - Amount retained on 45 µm sieve (wet-sieved) ≤ 34%
  - Strength activity index:
    - At 7 days ≥ 75% of control
    - At 28 days ≥ 75% of control
  - Water requirement ≤ 115 % of control
  - Soundness: autoclave length change ≤ 0.8%

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Detailed Investigation of Selected Samples

- Sand content determination – wet-sieved through 45 μm sieve
- Retained = sand fraction
- Passing = clay fraction
- Sand content 65-80%
- Clay content 20-35%

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Clay Fraction Characterization

- Elemental oxide composition
  - X-ray fluorescence (XRF)
- Mineralogical analysis
  - Fourier transform infrared spectroscopy (FTIR)
  - X-ray diffraction (XRD)
  - Thermogravimetric analysis (TGA)

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Elemental Oxide Composition

Clay ID	A1	B1	B2	B3	B4	C	D1	E	F	G
SiO_2	46.0	42.5	43.3	37.1	41.1	34.1	38.5	43.7	42.6	43.8
Al_2O_3	37.7	35.9	34.3	33.1	33.3	33.1	31.3	30.1	34.9	32.5
Fe_2O_3	0.9	1.6	3.0	10.2	5.4	6.6	8.9	6.5	4.6	5.5
CaO	<.01	0.05	<.01	0.02	0.17	1.1	0.12	0.37	<.01	<.01
MgO	0.16	0.39	0.24	0.34	0.33	0.29	0.49	0.28	0.21	0.22
SO_3	<.01	<.01	<.01	<.01	<.01	0.06	<.01	0.02	<.01	<.01
L.O.I (950˚C)	14.2	16.1	15.1	16.5	15.6	16.3	16.6	15.7	15.4	14.4
Total	99.5	99.2	99.2	100.0	99.1	99.23	99.1	98.9	99.3	99.2
Na_2O_{eq}	0.21	0.15	0.16	0.15	0.15	0.38	0.2	0.14	0.1	0.22
$SiO_2+Al_2O_3+Fe_2O_3$	85.6	80.0	80.6	80.4	79.8	73.8	78.7	80.3	82.1	81.8

$SiO_2+Al_2O_3+Fe_2O_3$ and SO_3 contents meet ASTM C618

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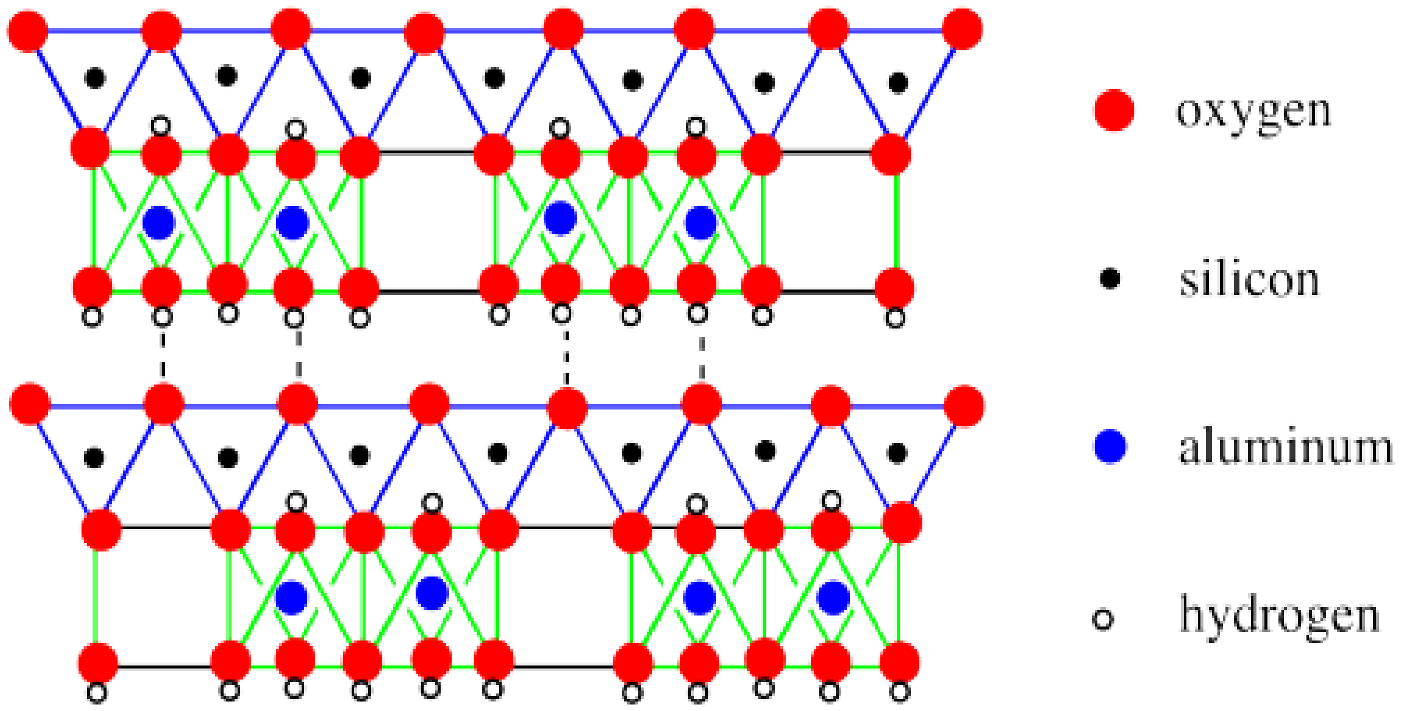
Mineralogical Analysis

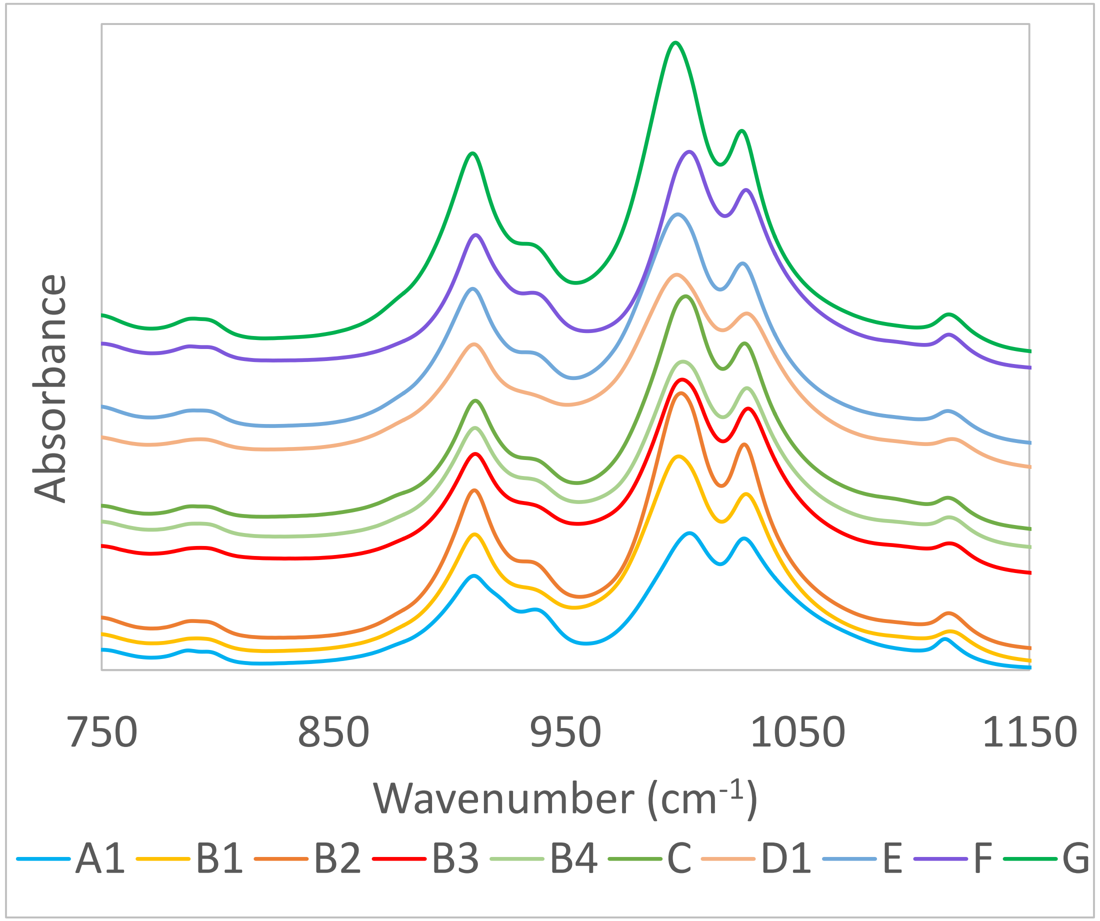
Challenges in accurate assessment of clay fraction mineralogy:

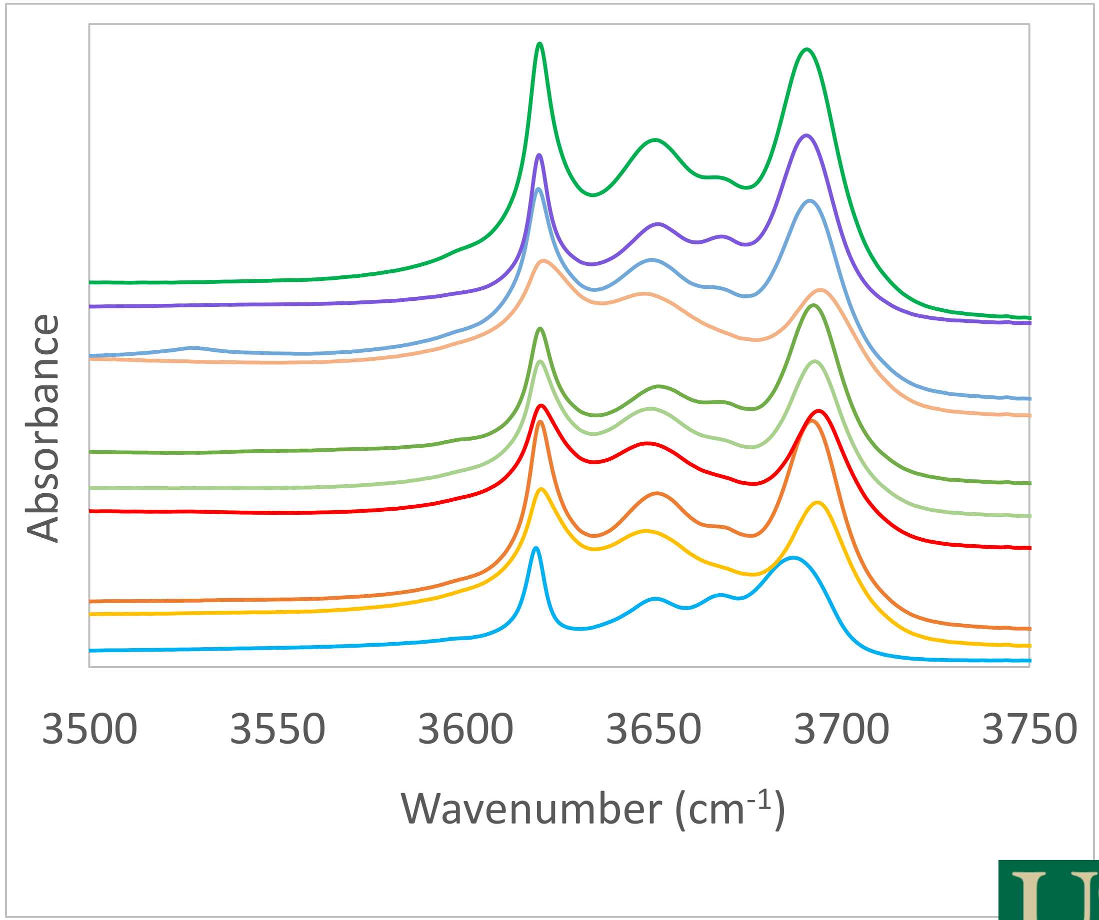
- Isomorphous substitutions
- Varying degree of disorder



https://employees.csbsju.edu/cschaller/Principles%20Chem/network/NWalumina.htm

Infrared Spectroscopy





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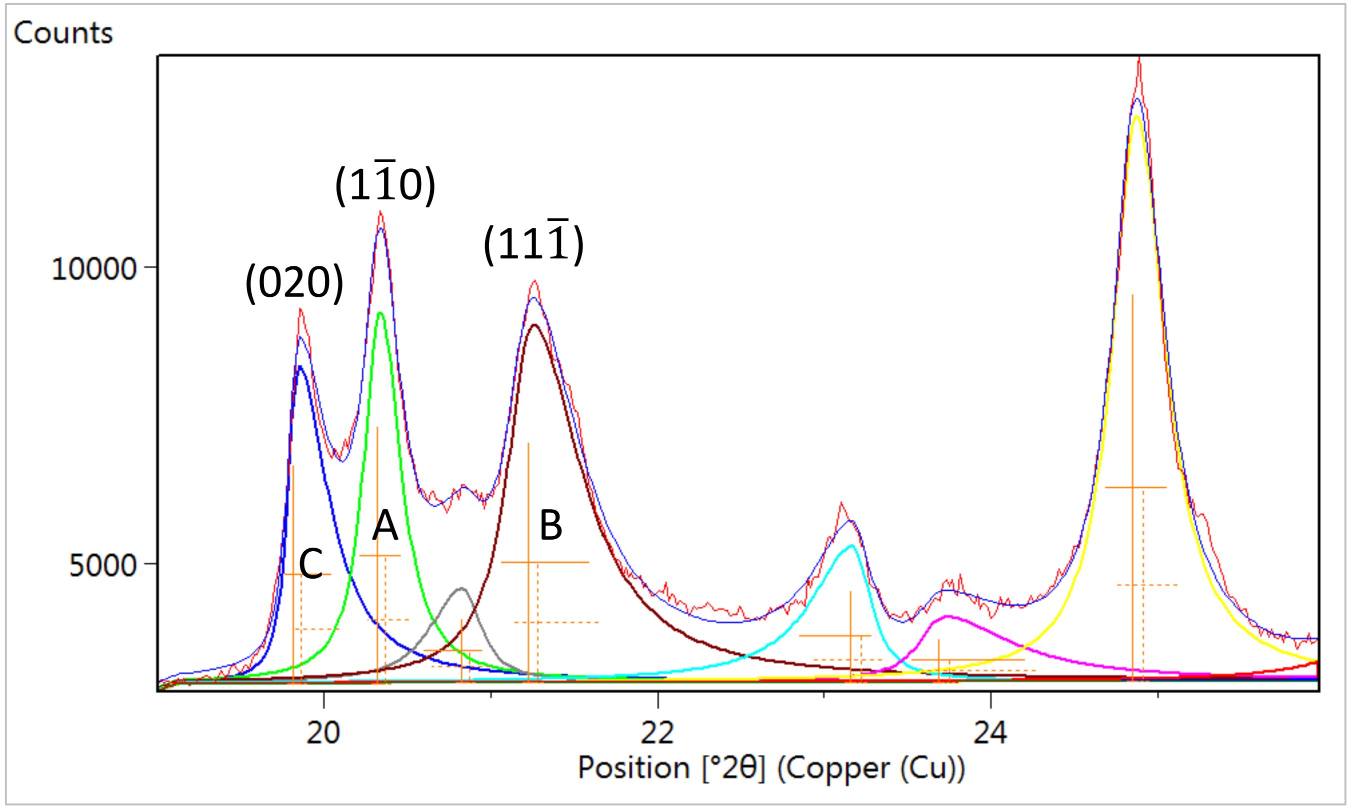
Varying Degree of Disorder

- Aparicio-Galan-Ferrell index (AGFI):



$$AGFI = \frac{I_A + I_B}{2I_C}$$

Amount of defects	AGFI
Low	1.25 - 1.60
Medium	0.90 - 1.25
High	< 0.90

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Varying Degree of Disorder

Clay ID	A1	B1	B2	B3	B4	C	D1	E	F	G
AGFI	1.1	0.5	0.7	0.6	0.8	0.8	0.5	1.1	1.1	0.9
Defect "density"	medium	high	high	high	high	high	high	medium	medium	medium

- No low-defect (high crystallinity) kaolinites
- Medium-defect – 4 samples
- High-defect (low crystallinity) – 6 samples

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Rietveld Refinement

- In this study, it was observed that fitting can be significantly improved by considering the kaolin group minerals as a superposition of kaolinite, nacrite and dickite structures
- Ideal kaolinite formula: $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
- The modified chemical formula ($(Al_2O_3)_{(1-x)}(Fe_2O_3)_x \cdot 2SiO_2 \cdot 2H_2O$) was used in the refinement where *x* was the Fe-Al substitution parameter
- In kaolinite structure Al^{3+} can be substituted by Fe^{3+}, Mg^{2+}, Ti^{4+}, and V^{3+}
- Only Fe^{3+} substitution was considered based on XRF

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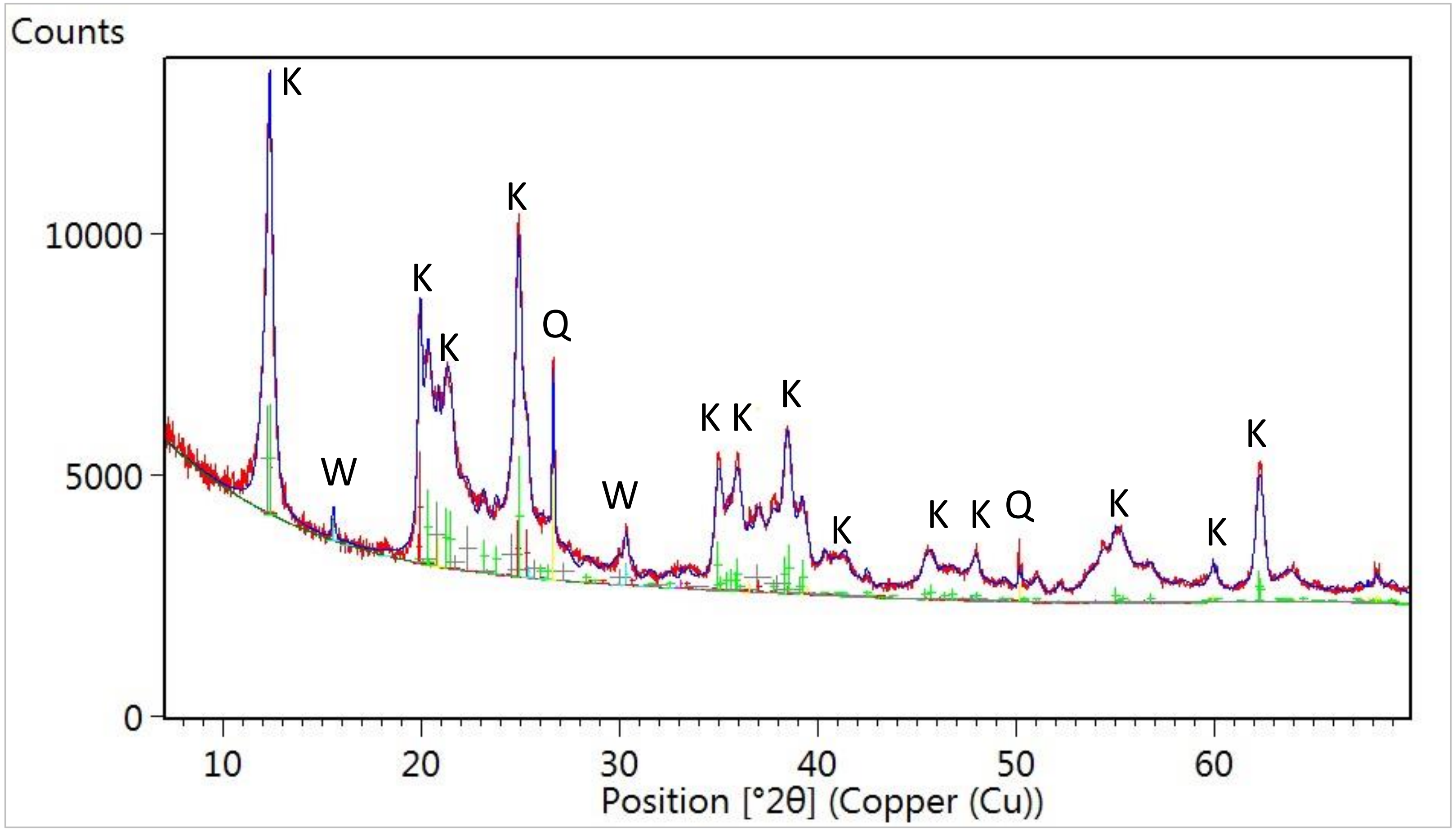
Sample Rietveld Refinement



K = kaolin
W = waylandite
Q = quartz

Mineralogical Phase Content

	A1	B1	B2	B3	B4	C	D1	E	F	G
Kaolin (wt.%)	89.7	87.4	86.6	79.2	84.9	69.2	76.9	71.3	90.2	85.6
Fe substitution *x*	0.0	0.0	0.05	0.2	0.08	0.0	0.1	0.08	0.07	0.08
Muscovite (wt.%)	0.5									
Waylandite (wt.%)			0.2	0.5	0.7	1.6	0.5	0.1	0.1	0.5
Hematite (wt.%)			0.2	0.3	0.2	0.1	0.3	0.4	0.7	1.0
Gibbsite (wt.%)						1.7		3.6		
Quartz (wt.%)	0.5	0.3	2.1	1.6	1.9	0.8	2.6	10.9	1.2	4.0
Amorphous/ unidentified (wt.%)	8.0	12.0	10.9	18.4	12.2	26.5	19.7	13.7	7.8	8.9

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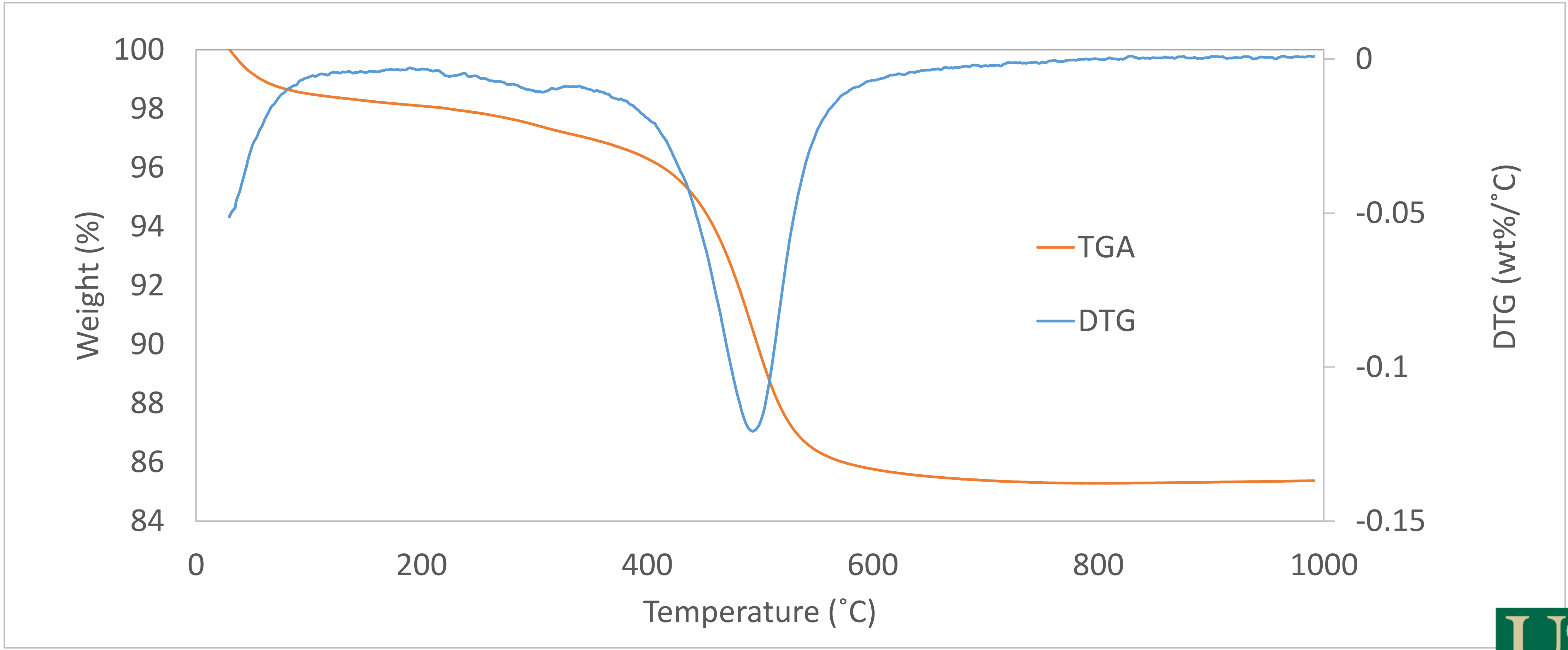
Thermogravimetric Analysis



Thermogravimetric Analysis

- Kaolinite content calculation from TGA:

$$m_K = m_{loss} \frac{M_K}{2M_{H_2O}}$$

- where m_K is the mass of kaolin, m_{loss} is the TGA mass loss over a temperature interval using the tangential method, M_K is the molecular mass of kaolin (258.13 g/mol), M_{H_2O} is the molecular mass of water (18.0 g/mol) and the constant 2 corresponds to the 2 moles of water in the kaolin formula($Al_2Si_2O_5(OH)_4$)

Thermogravimetric Analysis

- Kaolinite content adjusted for the Fe substitution:

$$m_K(x) = m_K \left[1 + x \frac{M_{Fe_2O_3} - M_{Al_2O_3}}{M_K}\right]$$

- where $M_{Fe_2O_3} = 159.69$ g/mol and $M_{Al_2O_3} = 101.96$ g/mol are the molecular weights of iron and aluminum oxides respectively and *x* was the substitution parameter determined from XRD

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Kaolinite Content

Clay ID	Kaolinite Content (wt.%) (no substitution)	Corrected Kaolinite Content (wt%)	Difference in Kaolinite between XRD and TGA
A1	94.3	94.3	-4.6
B1	90.9	90.9	-3.5
B2	79.2	80.1	6.5
B3	75.5	78.9	0.3
B4	82.2	83.7	1.3
C	75.2	75.2	-5.9
D1	73.9	75.6	1.3
E	76.6	77.9	-6.6
F	86.2	87.5	2.7
G	79.8	81.4	4.4

Calcination

- Kaolinite is non-reactive
- Removal of the OH^- groups on heating transforms kaolinite to metakaolinite

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \xrightarrow{450-700°C} Al_2O_3{\cdot}2SiO_2 + 2H_2O\ (g)$$

$$\text{kaolinite} \xrightarrow{450-700°C} \text{metakaolinite + water vapor}$$

- Metakaolinite is amorphous while kaolinite is crystalline, so the transformation process can be followed by XRD

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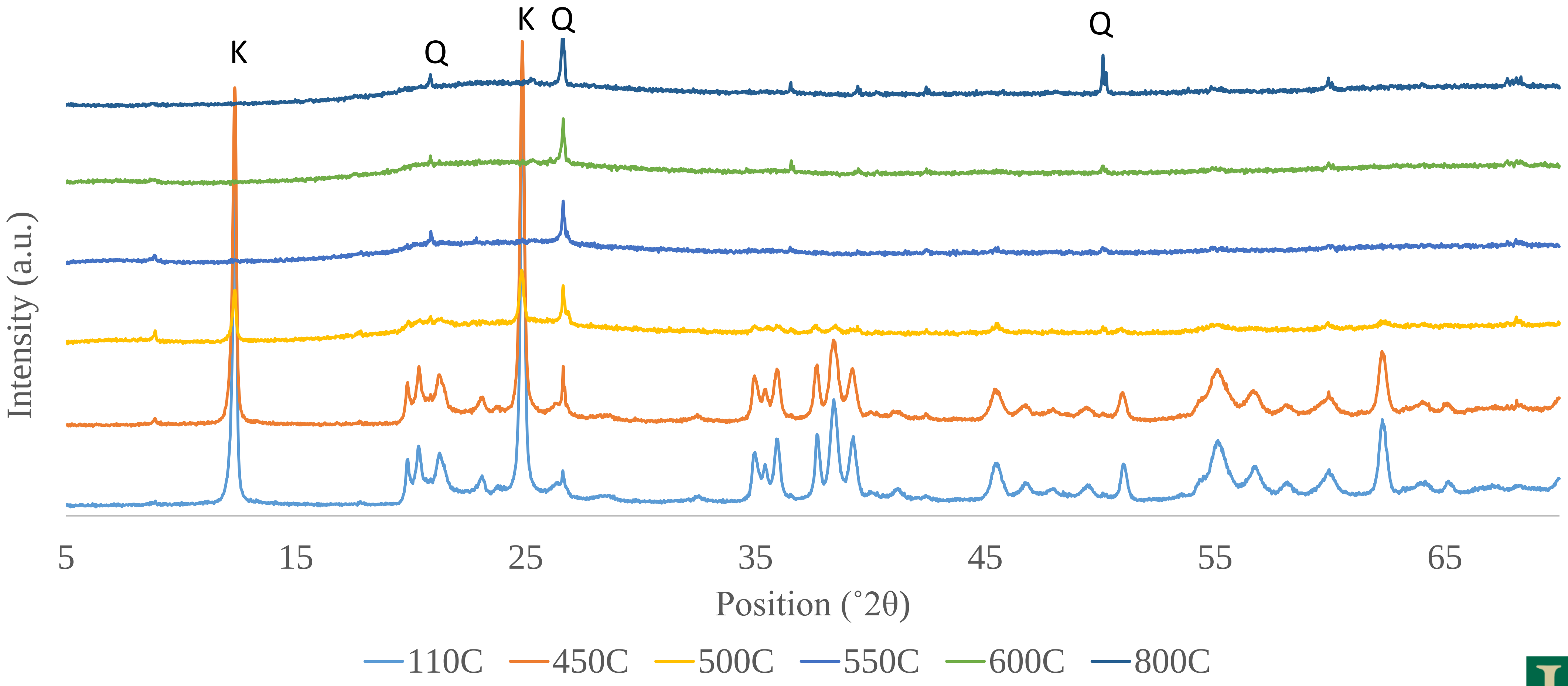
Selection of Calcination Temperature



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Compressive Strength

- Based on XRD, 600^{o}C was selected as the calcination temperature
- Samples obtained from the field were calcined at 600^{o}C for 1 h without separating the sand and clay fractions
- Mortar cubes prepared at 10% cement replacement with calcined clay and w/cm = 0.485
- The amount of calcined clay was calculated using the sand/clay fractions determined from wet sieve analysis
- Ottawa sand was then adjusted to account for the sand coming from the calcined material

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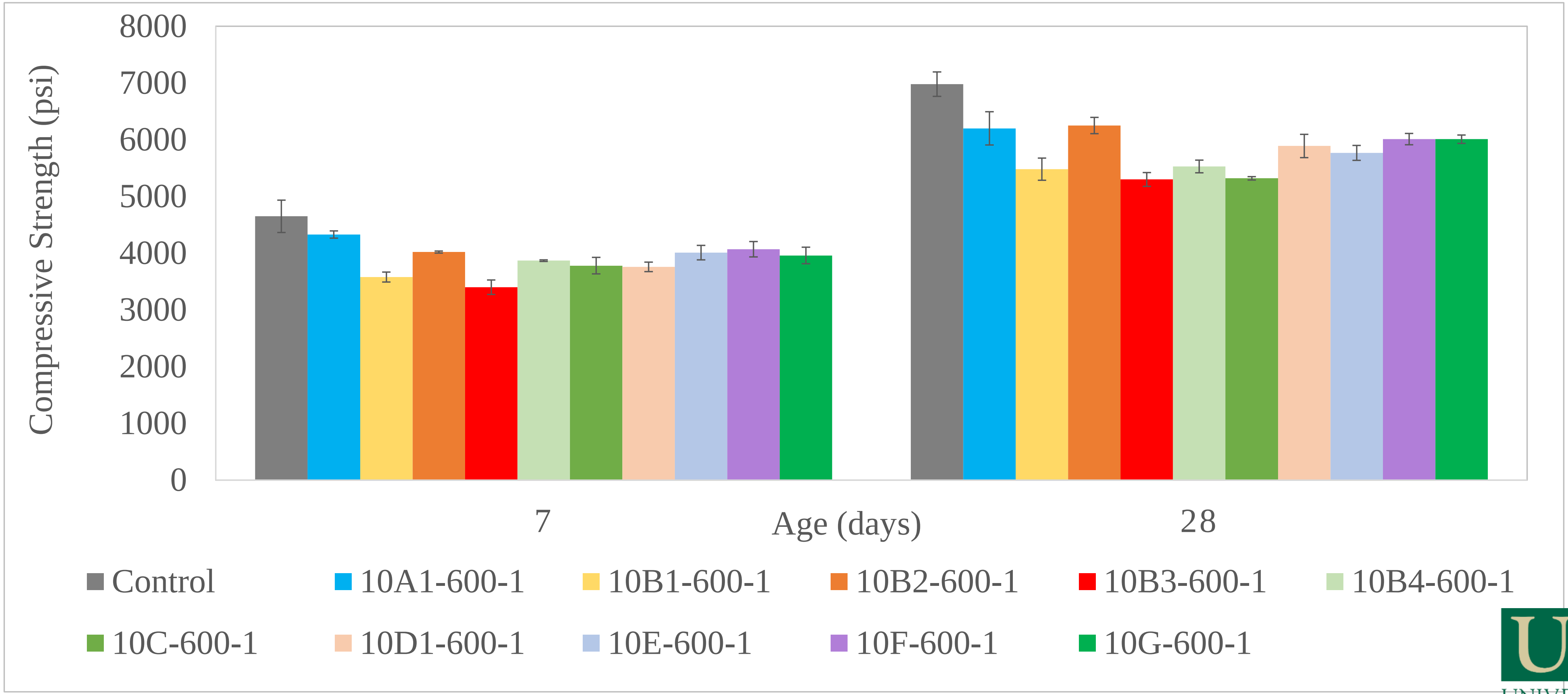
Compressive Strength of Mortar Cubes



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Strength Activity Indices

Mix ID	Strength Activity Index	
	7 days	28 days
10A1-600	93 %	89 %
10B1-600	77 %	79 %
10B2-600	86 %	90 %
10B3-600	73 %	76 %
10B4-600	83 %	79 %
10C-600	81 %	76 %
10D1-600	81 %	84 %
10E-600	86 %	83 %
10F-600	88 %	86 %

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Summary

- A number of potential kaolin sources were identified in Central Florida
- Moderately high kaolinite content in most of the clays
- Presence of large amount of sand
- Possible solutions: separating the sand before calcination, grinding or adjusting the sand in the mix design
- Adjusting the sand content produced compressive strengths within 76-90% of the Control

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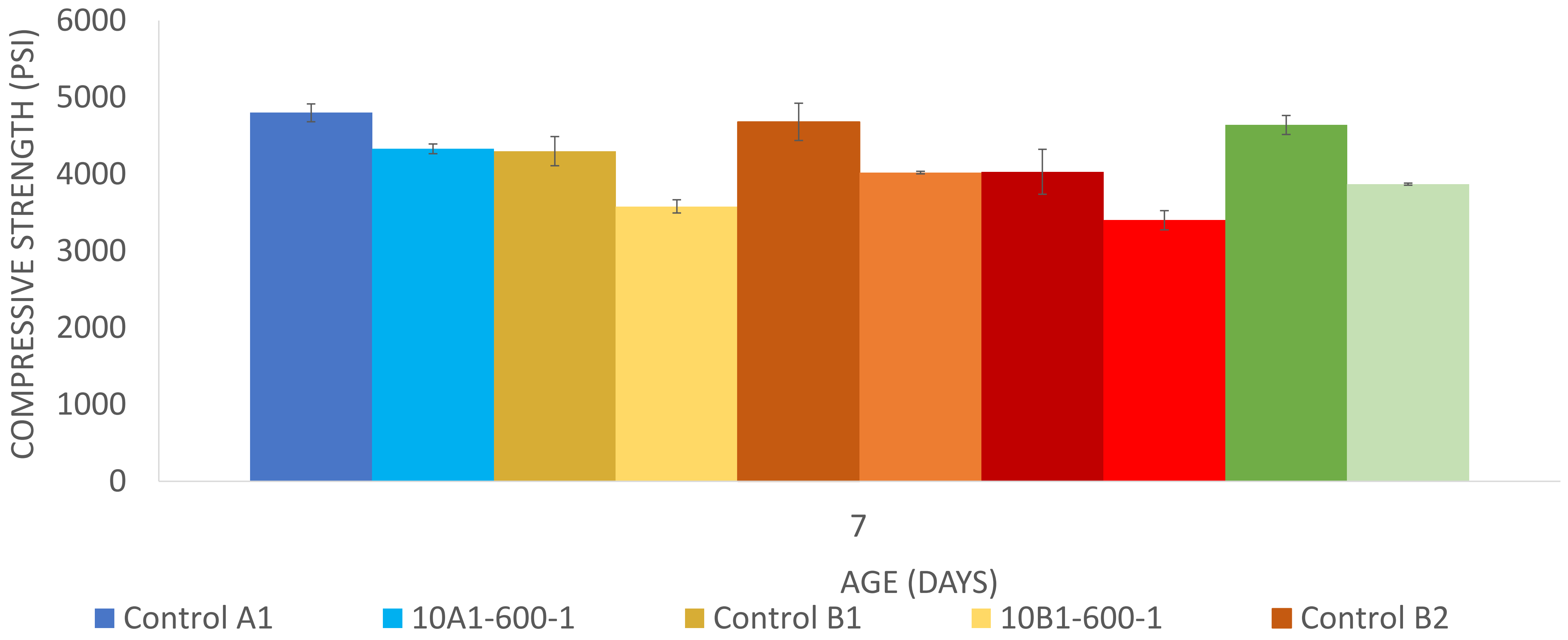
	A1	B1	B2	B3	B4	C	D1	E	F	G
Cement (g)	450	450	450	450	450	450	450	450	450	450
Ottawa sand (g)	1207	1271	1159	1224	1236	1176	1282	947	1213	1223
Calcined material (g)	217	153	266	200	188	248	142	477	211	201
Clay from calcined material (g)	50	50	50	50	50	50	50	50	50	50
Sand from calcined material (g)	167	103	216	150	138	198	92	427	161	151
Water (g)	242	242	242	242	242	242	242	242	242	242



COMPRESSIVE STRENGTH (PSI)
6000
5000
4000
3000
2000
1000
0
7
AGE (DAYS)
Control A1
10A1-600-1
Control B1
10B1-600-1
Control B2

Strength Activity Index of Calcined Clay Mortars Compared to Their Respective Controls

Mix ID	Strength Activity Index at 7 days
10A1-600-1	90 %
10B1-600-1	83 %
10B2-600-1	86 %
10B3-600-1	84 %
10B4-600-1	83 %

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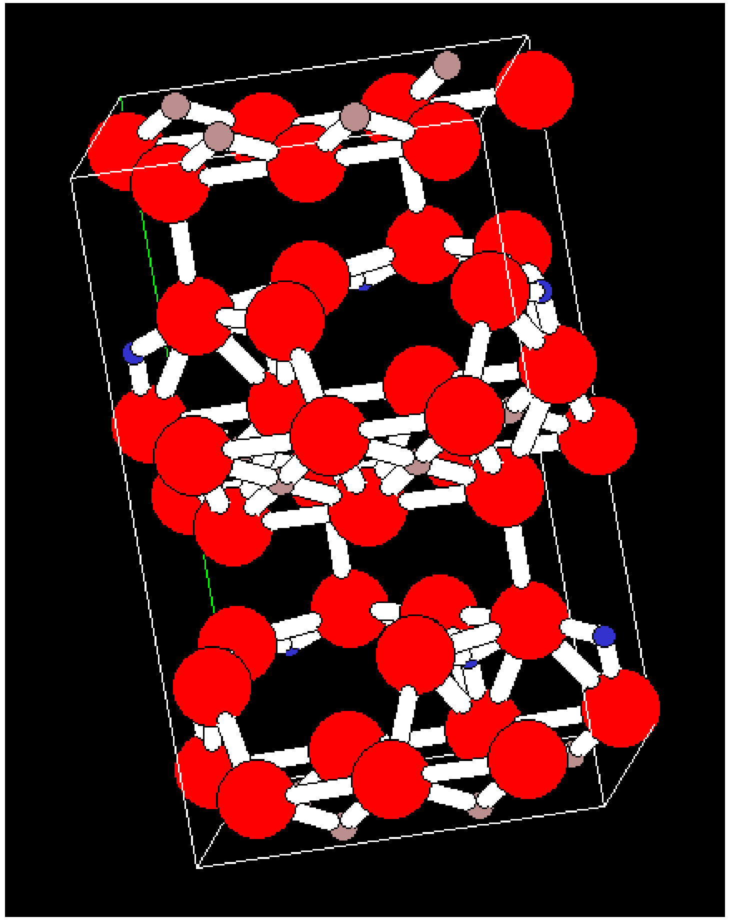
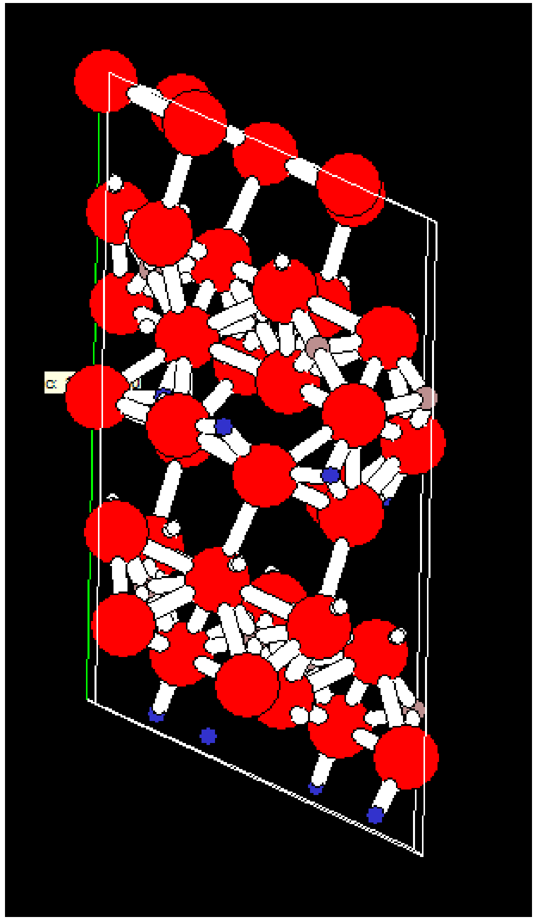
Amorphous Content of Calcined Samples

Sample ID	Amorphous content (wt%) after calcination at 600˚C	Amorphous content (wt%) after calcination at 800˚C
A1	99.9	99.8
B1	98.0	98.4
B2	96.3	96.8
B3	93.9	94.6
B4	95.7	94.9
C	97.4	97.5
D1	94.8	94.6
E	95.0	94.2
F	95.9	96.0
G	96.5	96.5

Kaolinite 2M



Nacrite



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