

Low-calcium slag cement: A potential solution to promote circular economy in the management of copper mine tailings

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OUTLINE

- **INTRODUCTION**
- **RESEARCH APPROACH**
- **MATERIAL PROPERTIES**
- **SPECIMEN PREPARATION**
- **RESULTS & DISCUSSION**
- **CONCLUSIONS**

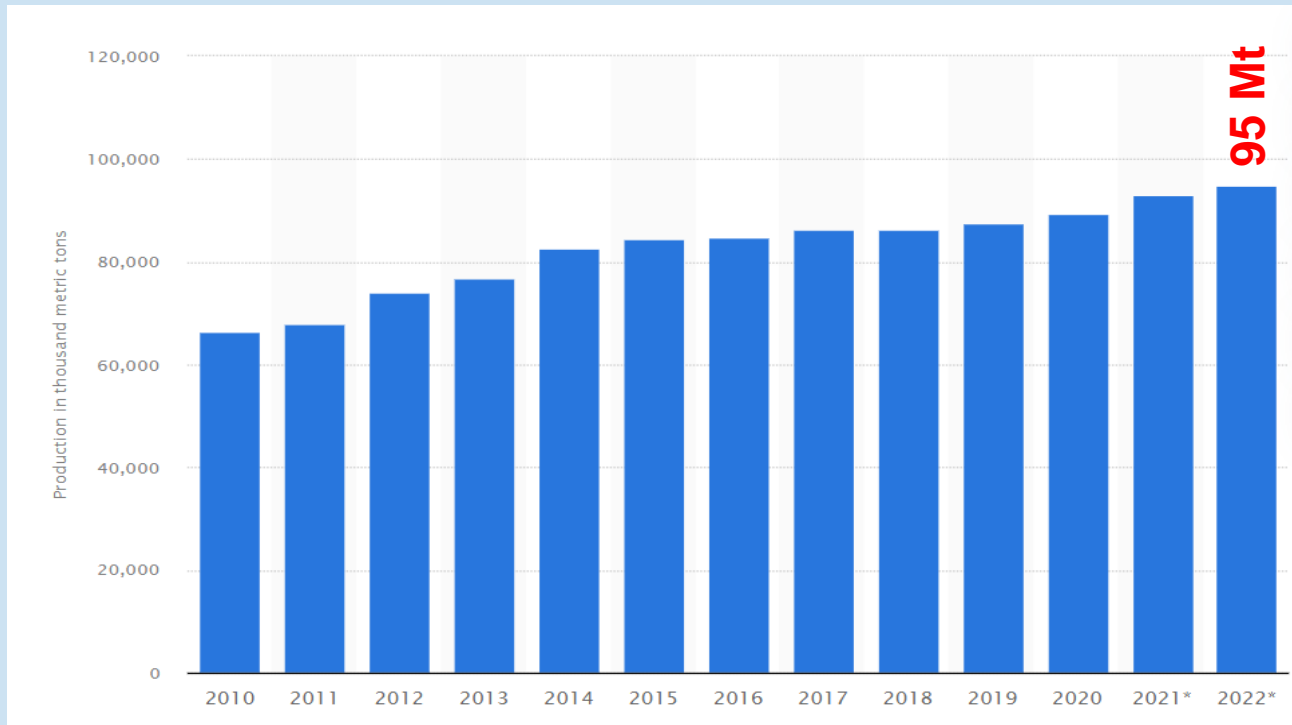
INTRODUCTION

Population growth and urban development have led to a significant increase in demand for ordinary Portland cement (OPC) in recent years (Celik et al. 2019)



INTRODUCTION

Production volume of Portland and masonry cement in the United States from 2010 to 2022



Graph taken from: <https://www.statista.com/statistics/219329/us-production-of-portland-and-masonry-cement/#:~:text=In%202022%2C%20an%20estimated%2095,produced%20in%20the%20United%20States.>

INTRODUCTION

1.5 ton raw
materials

1 ton OPC

1 ton CO₂

Cement industry is responsible
for **8%** of all CO₂

INTRODUCTION

Mining industry produces large amount
of mine **waste** every year

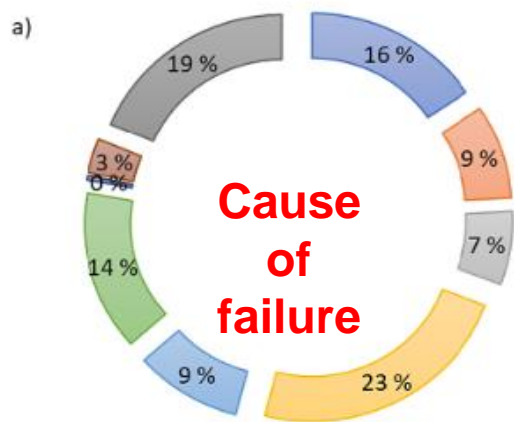
- 1.6 billion metric tons of mineral processing waste are produced each year in the United States.
- Copper smelting and refining facilities produce 2.5 million metric tons (MT) of smelter slag and 1.5 million MT of slag tailings per year.



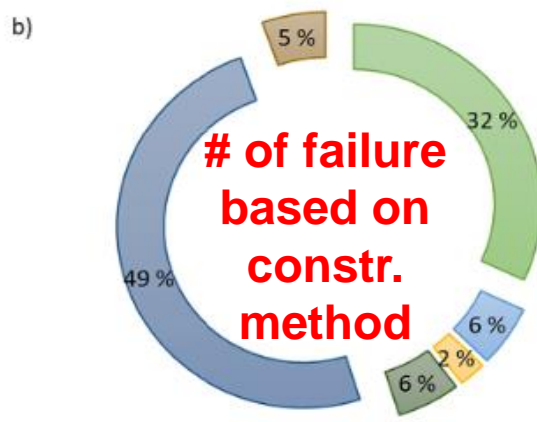
Image taken from <http://atcwilliams.com/projects/mt-rawdon-gold-mine>



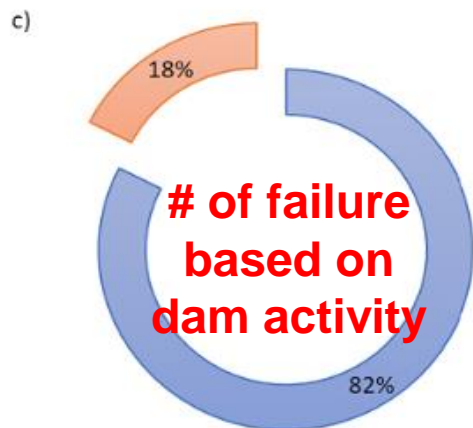
Image taken from <http://www.clui.org/ludb/site/sierrita-copper-mine>



■ SI ■ SE ■ FN ■ OT ■ ST ■ EQ ■ MS ■ ER ■ U



■ US ■ DS ■ CL ■ WR ■ U ■ Other



■ A ■ B



■ 0 ■ 1-10 ■ 11-50 ■ >50 ■ U

Released volume (M m3)

50
45
40
35
30
25
20
15
10
5
0

Number of the references to colour



Fig. 3. a) Reported causes of tailings dam failures: static failure (SI), seepage and internal erosion (SE), structural and foundation conditions (FN), overtopping (OT), structural inadequacies (ST), seismic instability (EQ), mine subsidence (MS), external erosion (ER), unknown (U); b) Reported number of failures by dam construction method: upstream (US), downstream (DS), centreline (CL), water retention (WR), unknown (U), other type of construction; c) Number of reported failures for active (A) and nonactive(B) tailings dams; d) Consequences in terms of categories of number of human losses.

INTRODUCTION



GROWING NUMBER OF REASONS TO LEAVE THIS APPROACH:



Reliable access to raw materials (cfr. EU raw materials strategy)



New technology allows for new manufacturing techniques & disruptive business models



New consumption patterns (user)/ conscious citizen



Cost reduction:
- energy & materials
- internalized external costs



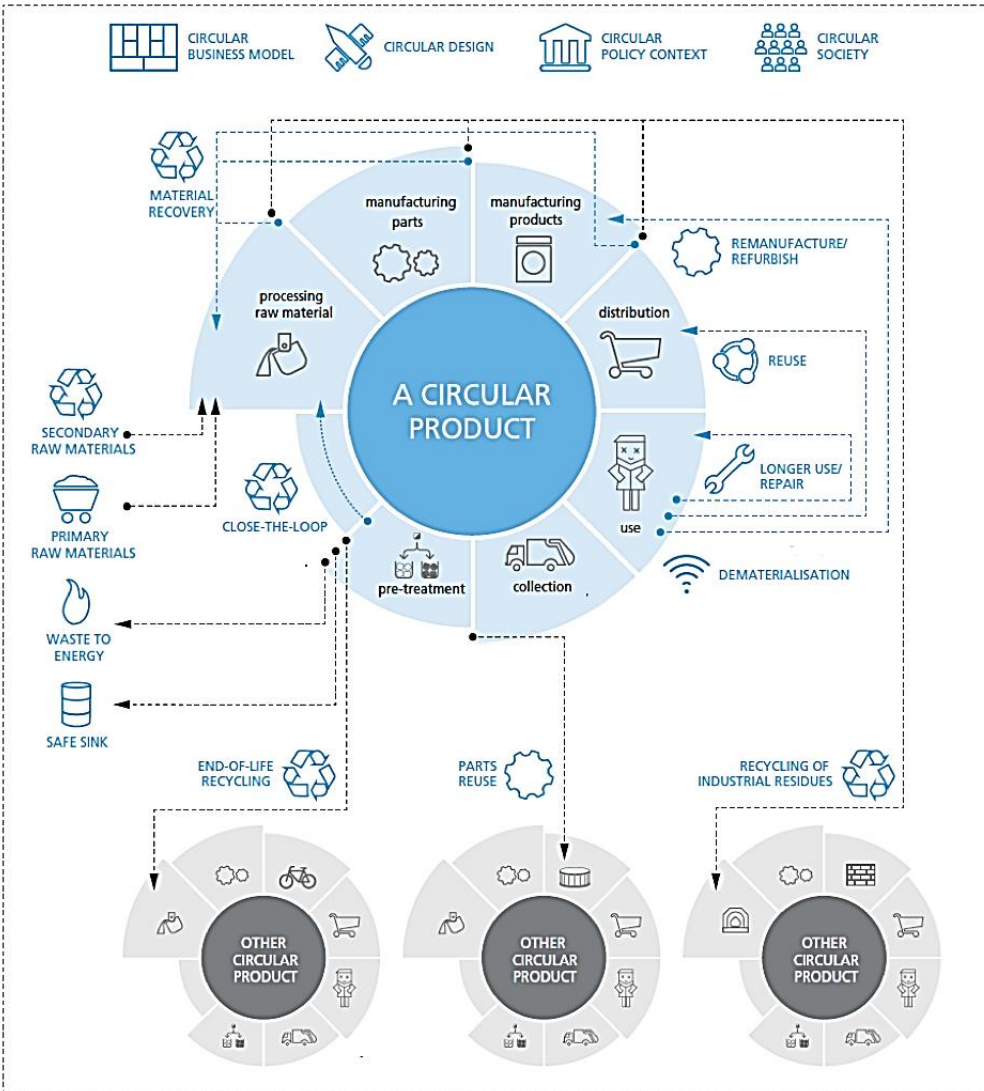
Environmental impact of mining, energy consumption, waste,...



Government wants you to (cfr. EU circular economy package)

Linear product chain (adapted from <https://www.coursera.org/learn/circular-economy>)

INTRODU



Circular product chain (adapted from <https://www.coursera.org/learn/circular-economy>)

INTRODUCTION

Economy

- Promoting the use of tailings as construction material

Ecology

- Unique stabilization technology called *Geopolymerization*

What is geopolymerization?

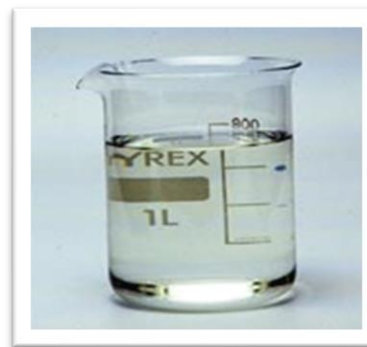
INTRODUCTION



Material rich in silica and alumina



Alkaline reagent

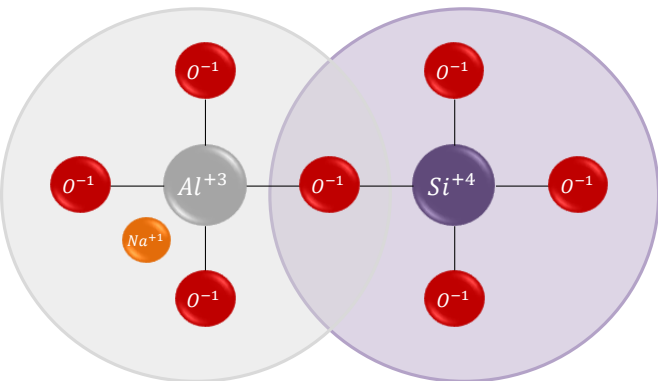


Water



Geopolymer paste

Geopolymerization process transforms aluminosilicate materials through chemical reaction with an alkali solution into a useful product called geopolymer



INTRODUCTION



Geopolymerization

- Abundant raw material resources
- Rapid development of mechanical strength
- Immobilization of toxic and hazardous materials
- Significant reduction of energy consumption and greenhouse gas emissions

INTRODUCTION

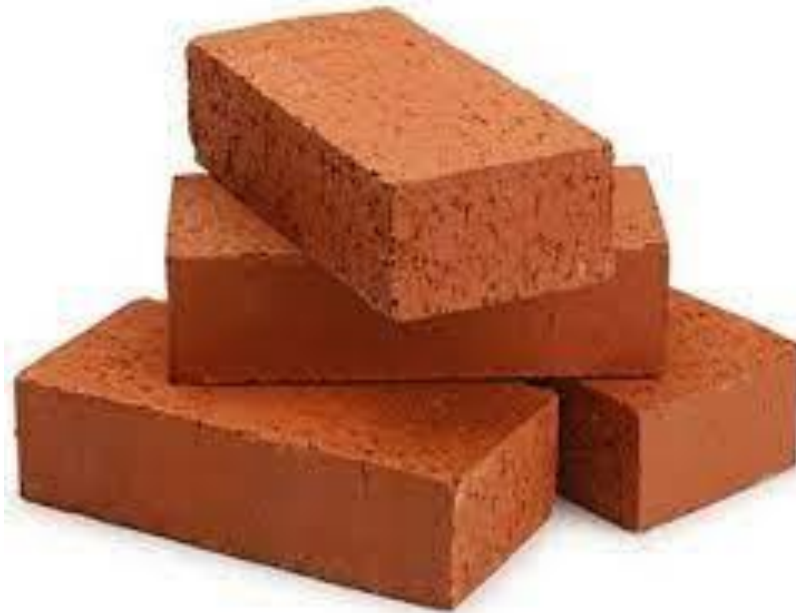


Photo taken from: <https://civiltoday.com/civil-engineering-materials/brick/69-characteristics-and-qualities-of-good-bricks-for-construction>

INTRODUCTION

- Bricks have been widely used as a major construction and building material for a long time.
- Conventional production methods have several disadvantages:
 - ✓ *mining operations are energy intensive, destroy the landscape, and produce large amount of waste.*
 - ✓ *High temperature kiln firing consumes huge amount of energy, and releases large quantity of CO₂ to the atmosphere.*
 - ✓ *Natural resources like clay is limited worldwide which needs to be protected.*



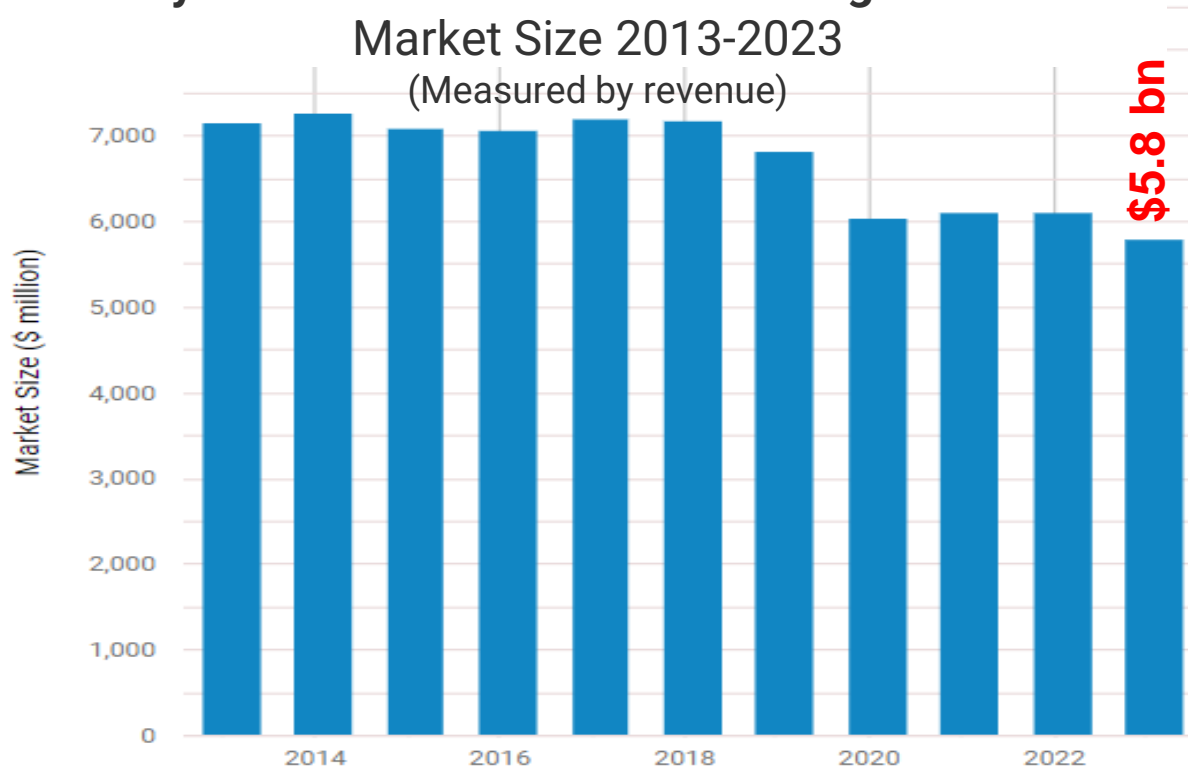
Photo taken from <https://ceramics.org/ceramic-tech-today/construction/the-many-types-of-bricks>



Photo taken from <https://www.quora.com/What-is-the-standard-size-of-Indian-brick>

INTRODUCTION

Clay Brick & Product Manufacturing in the US: Market Size 2013-2023 (Measured by revenue)



Plot taken from: <https://www.ibisworld.com/industry-statistics/market-size/clay-brick-product-manufacturing-united-states/#:~:text=The%20market%20size%2C%20measured%20by,is%20%245.8bn%20in%202023.>

INTRODUCTION

Geopolymer based Bricks

ASTM specifications for different applications of bricks is:

- ✓ Min UCS: 20.7 MPa
- ✓ Max water absorption: 16%



RESEARCH APPROACH

Macro-Scale Study

Uniaxial Compression test

Water Absorption test

Wet-Dry Cycles test

Freeze-Thaw test

Leaching test

Micro/Nano-Scale Study

SEM imaging

EDS analysis

XRD characterization

XRF analysis

Production of geopolymer bricks

MATERIAL PROPERTIES

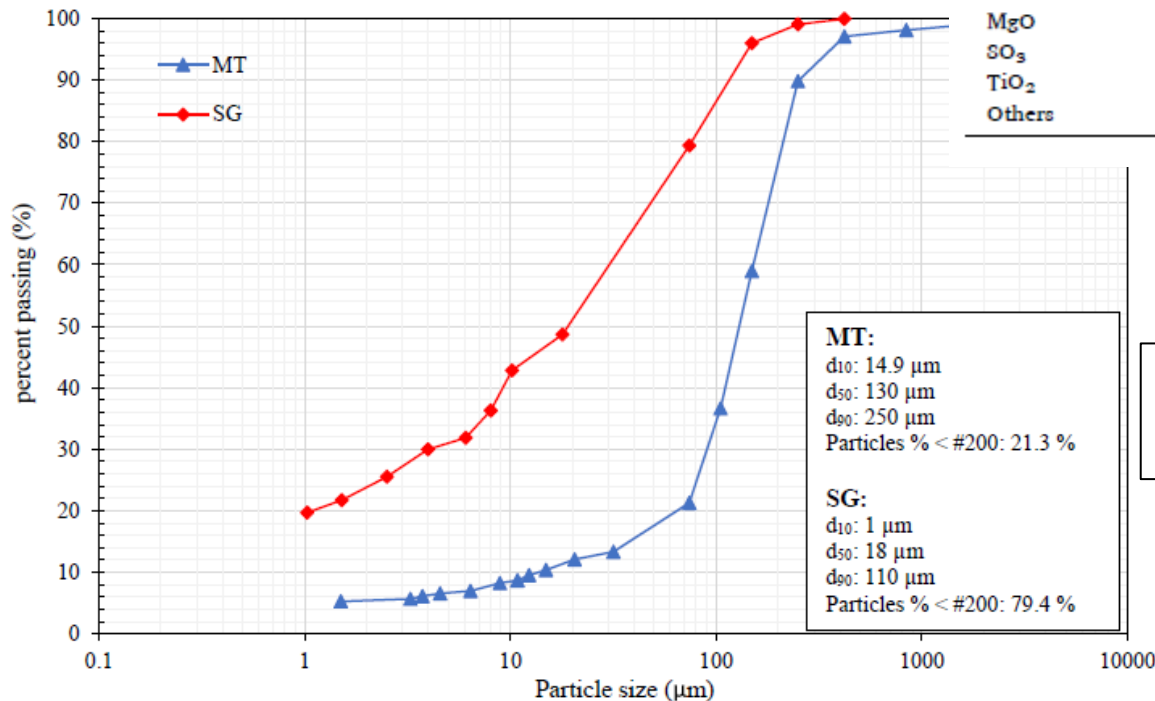
XRF analysis

Materials:

I. MT and SG

Chemical composition of MT and SG.

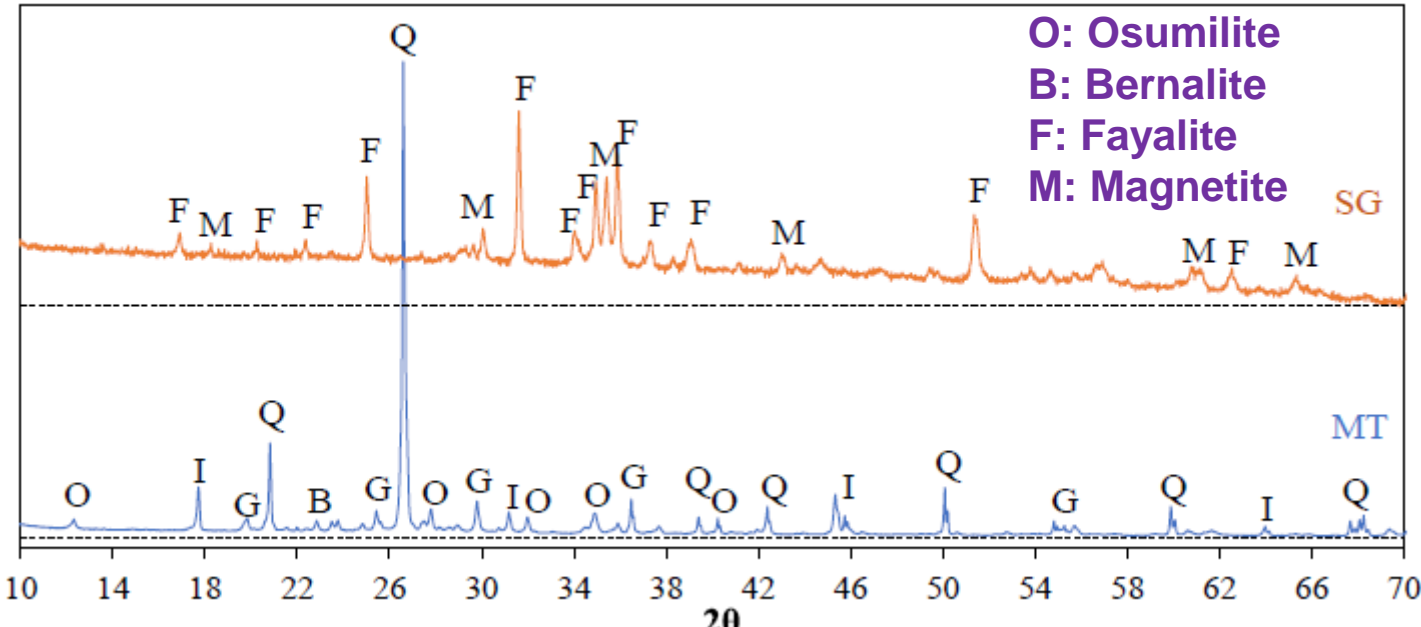
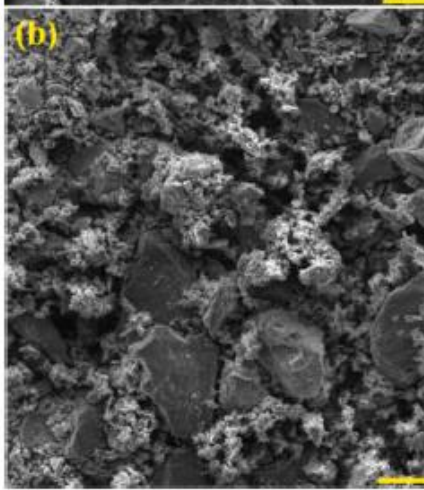
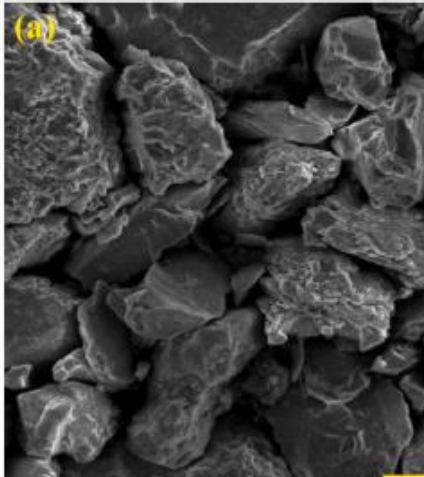
Chemical compound	Percentage by weight (%)	
	MT	SG
SiO ₂	61.2	32.9
Al ₂ O ₃	24.6	2.43
K ₂ O	5.38	
Fe ₂ O ₃	4.35	37.5
Fe ₃ O ₄		5.48
CaO	0.18	2.13
MgO	1.48	-
SO ₃	1.23	1.56
TiO ₂	0.83	-
Others	0.75	18.0



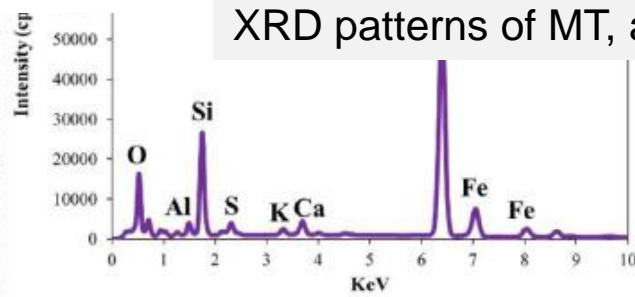
Sieve and hydrometer analysis

MATERIAL PROPERTIES

Q: Quartz
 I: Illite
 G: Grossite
 O: Osumilite
 B: Bernalite
 F: Fayalite
 M: Magnetite
 SG

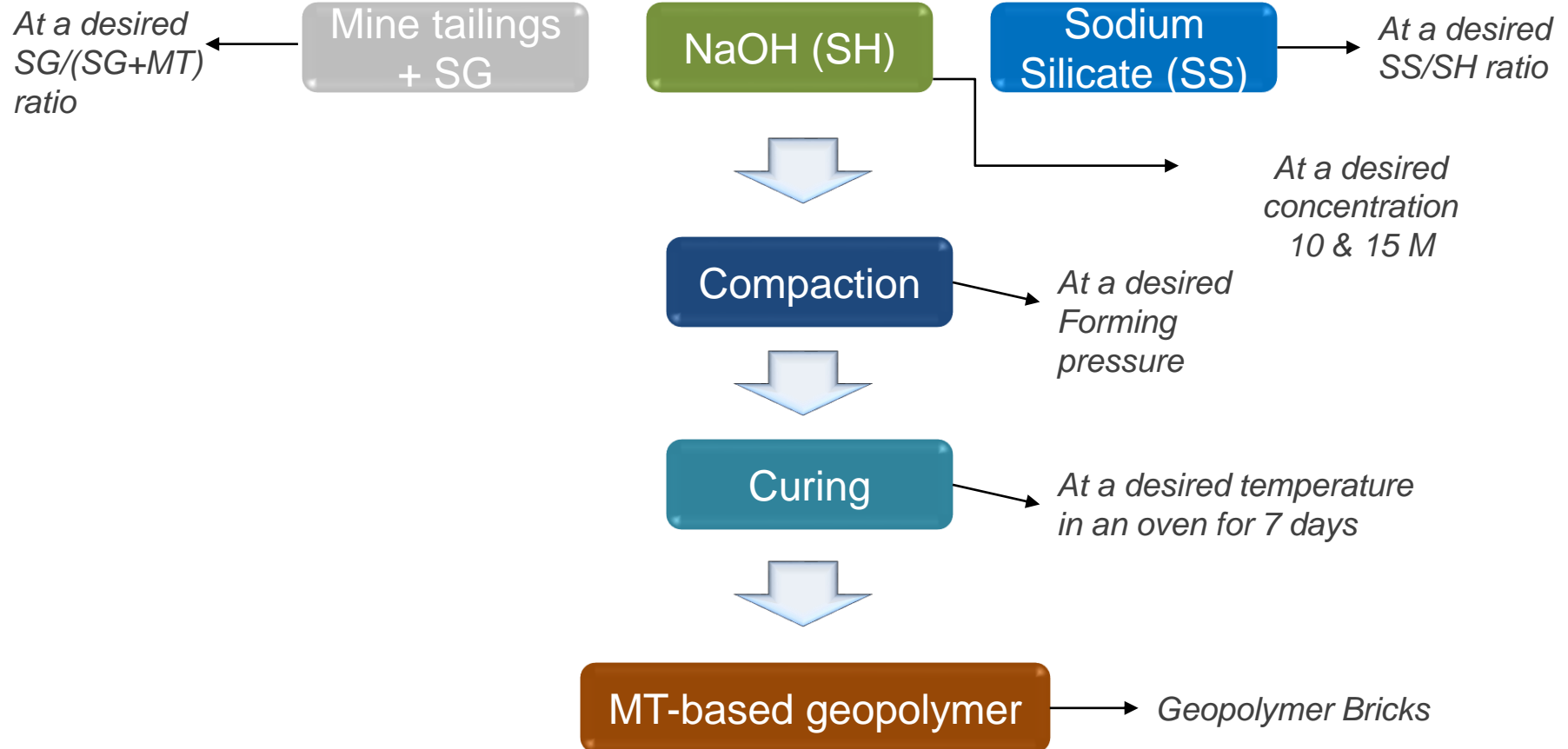


XRD patterns of MT, and SG powders



SEM micrographs: (a) MT, and (b) SG powders

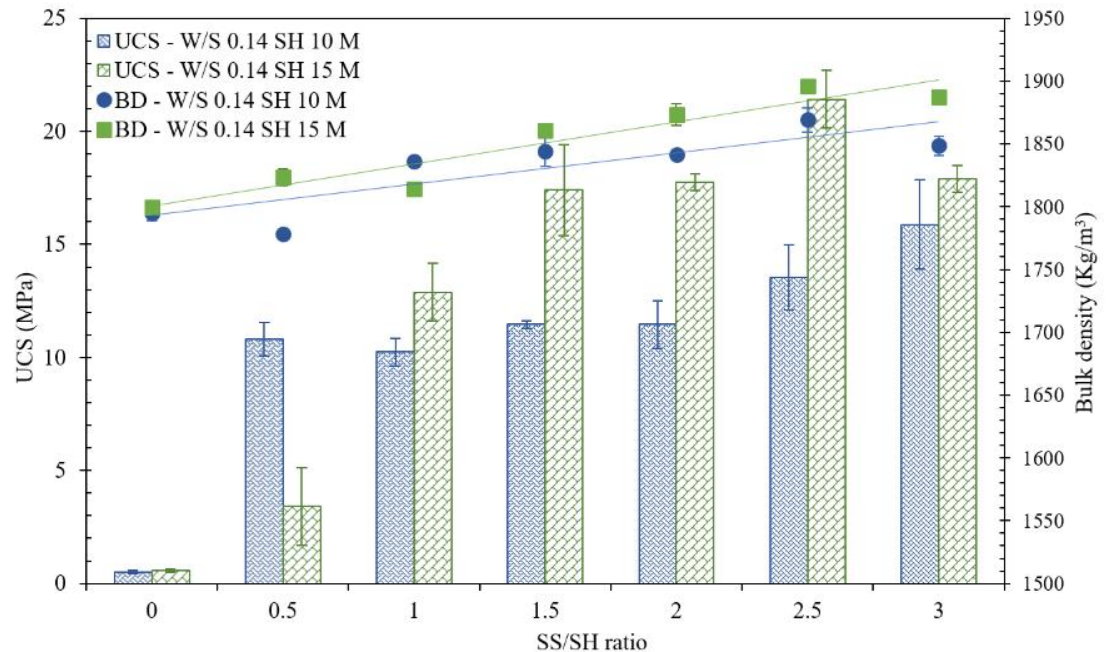
SPECIMEN PREPARATION



RESULTS AND DISCUSSION

The effect of NaOH molarity and SS/SH ratio

- ✓ Increasing the NaOH molarity results in higher UCS and bulk density
- ✓ UCS and bulk density are increased by increasing the SS/SH ratio





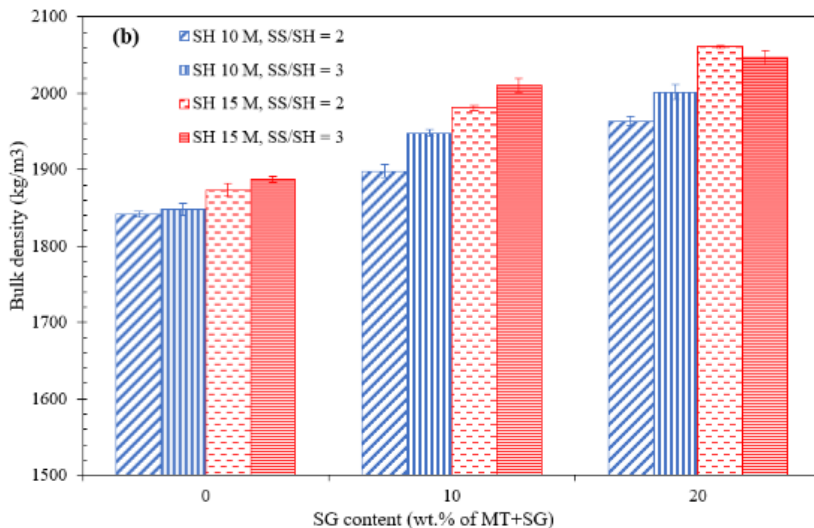
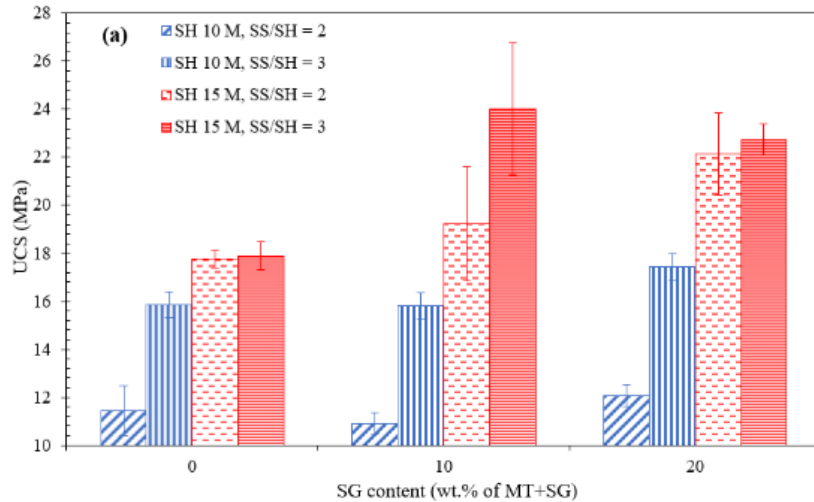
SG 0 wt.%



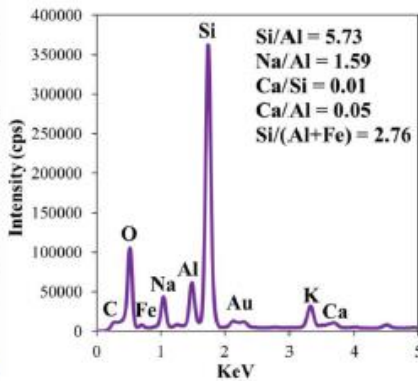
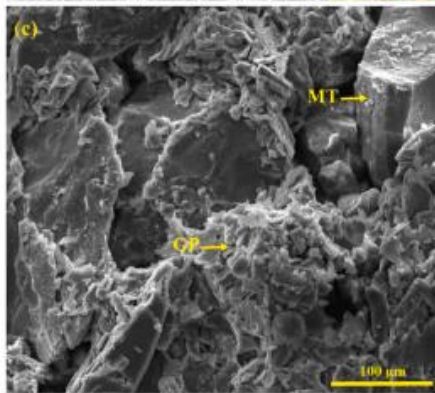
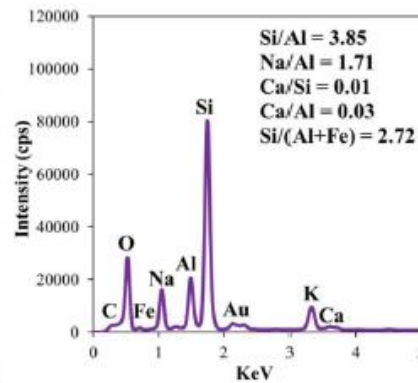
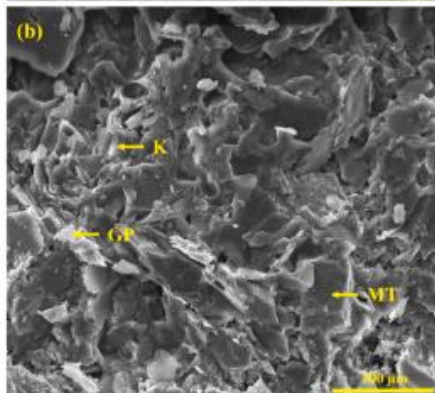
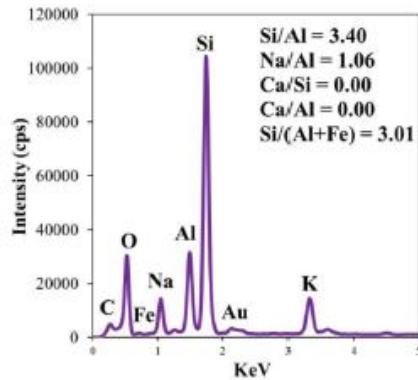
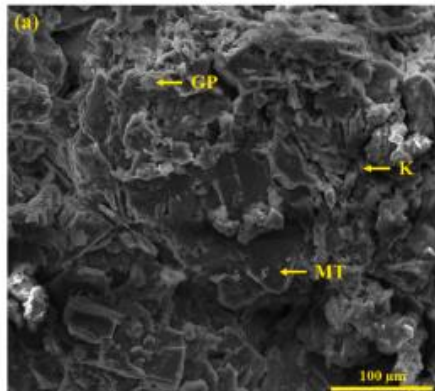
SG 10 wt.%

RESULTS AND DISCUSSION

The effect of SG content



- ✓ Higher SG content improves the geopolymerization and increases the bulk density
- ✓ 10 wt.% SG is selected for the rest of study

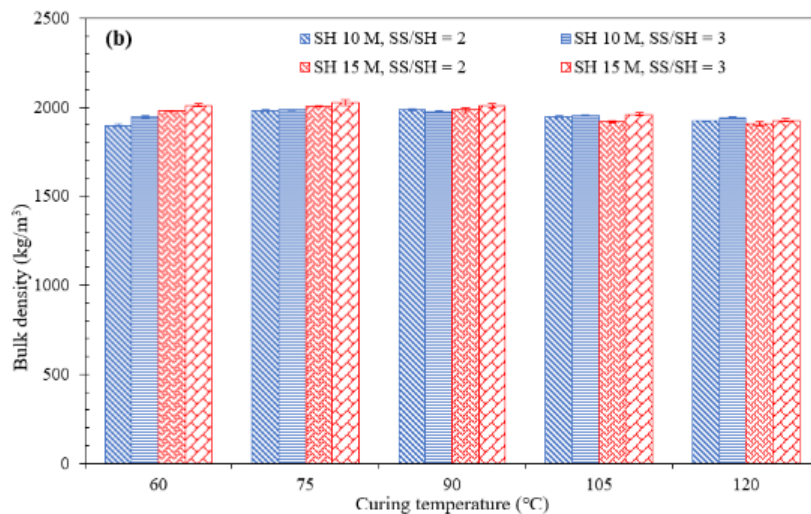
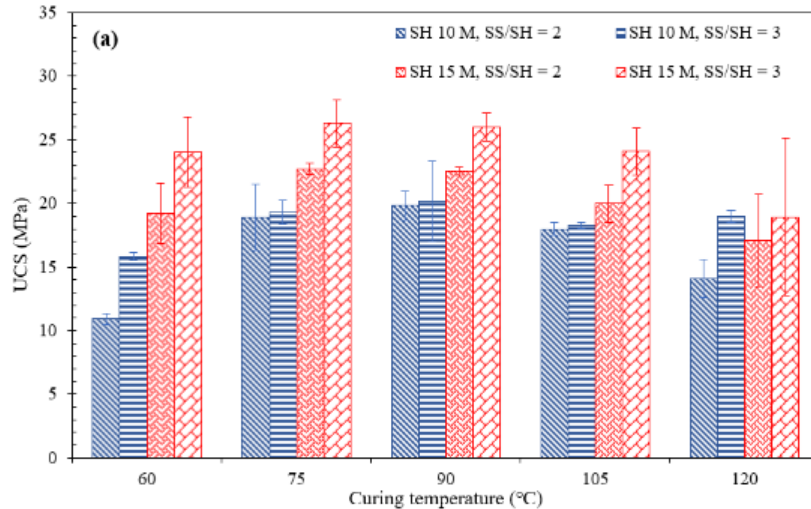


SEM micrographs and EDX analysis results of geopolymer specimens at different SG contents and with the same W/S = 0.14, 10 MPa forming pressure, 10 M NaOH, SS/SH = 2, and curing temperature of 60 °C for 7 days: **(a) 0 wt% SG**; **(b) 10 wt% SG**; and **(c) 20 wt% SG**. GP = geopolymer gel, MT = mine tailings, and K = alkali-silica gel.

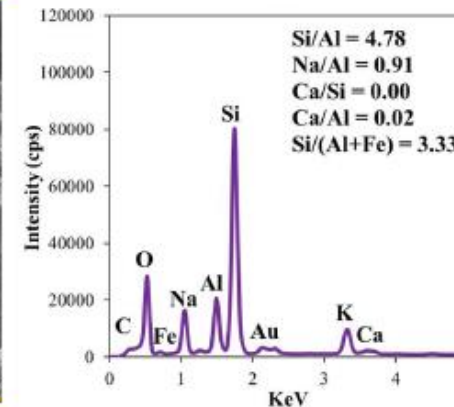
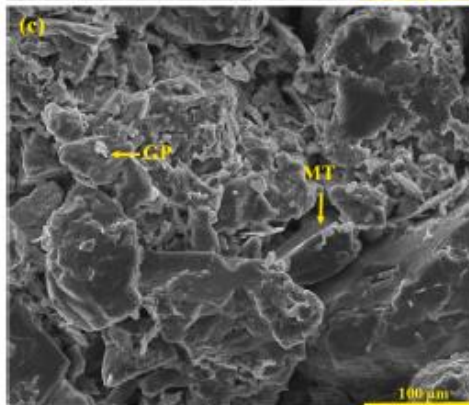
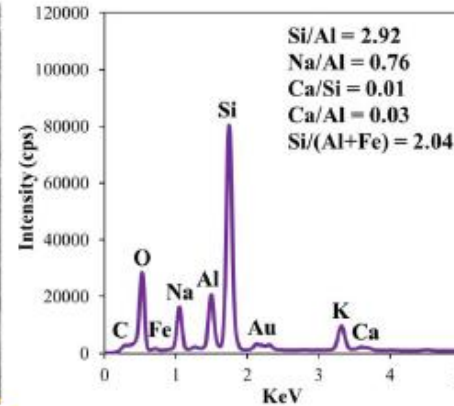
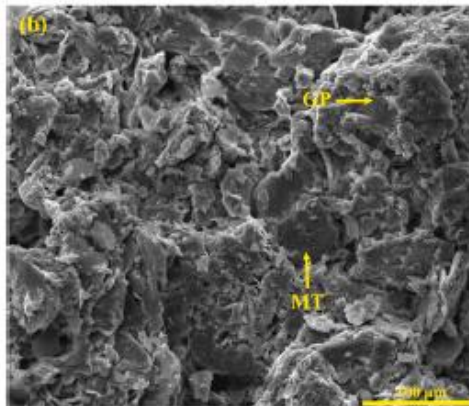
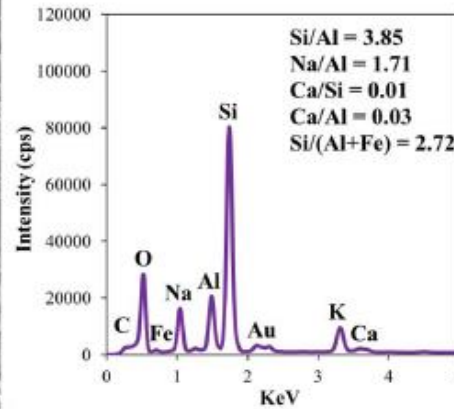
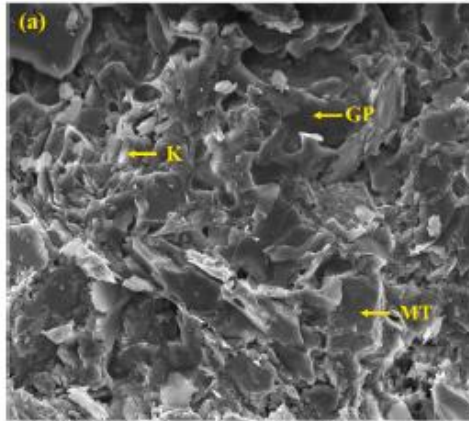
- ✓ At higher SG content, more geopolymer gels can be seen and the material also becomes more compact and denser.
- ✓ Si/(Al+Fe) ratio is favorable at higher SG content.

RESULTS AND DISCUSSION

The effect of curing temperature



- ✓ UCS increases with curing temperature up to 90 °C and then decreases
- ✓ higher curing temperature accelerates the dissolution of silica and alumina and then the polycondensation
- ✓ Bulk density slightly increases with curing temperature up to 90 °C and then decreases



SEM micrographs and EDX analysis results of geopolymer specimens at different curing temperatures and with the same 10 wt% SG, W/S = 0.14, 10 MPa FP, 10 M NaOH, SS/SH = 2, curing time of 7 days: **(a) 60 °C**; **(b) 90 °C**; and **(c) 120 °C**. GP = geopolymer gel, MT = mine tailings, and K = alkali-silica gel.

- ✓ At higher curing temperatures (> 120 °C), the dissolution of Al and Fe from the MT and SG was hindered due to the quick formation of geopolymer gels
- ✓ Water evaporation results in higher porosity

RESULTS AND DISCUSSION

The effect of water content and forming pressure

✓ The effect of water content on the UCS is complex

Lower W/S



Lower Na+



Lower UCS

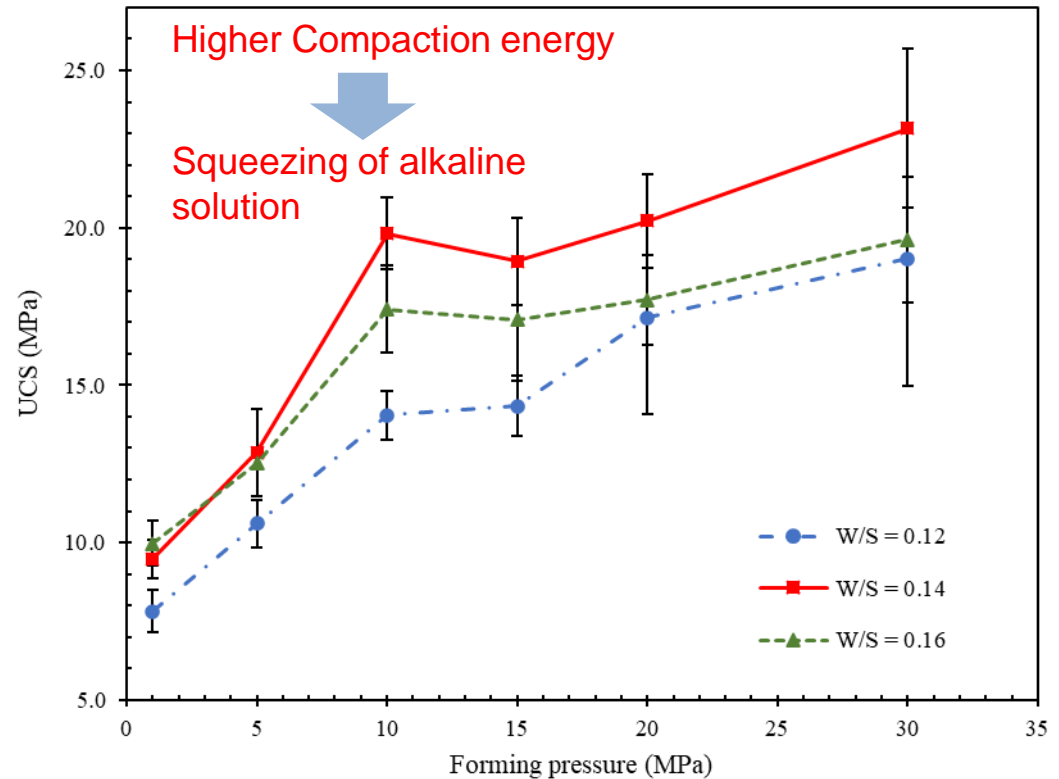
Higher W/S

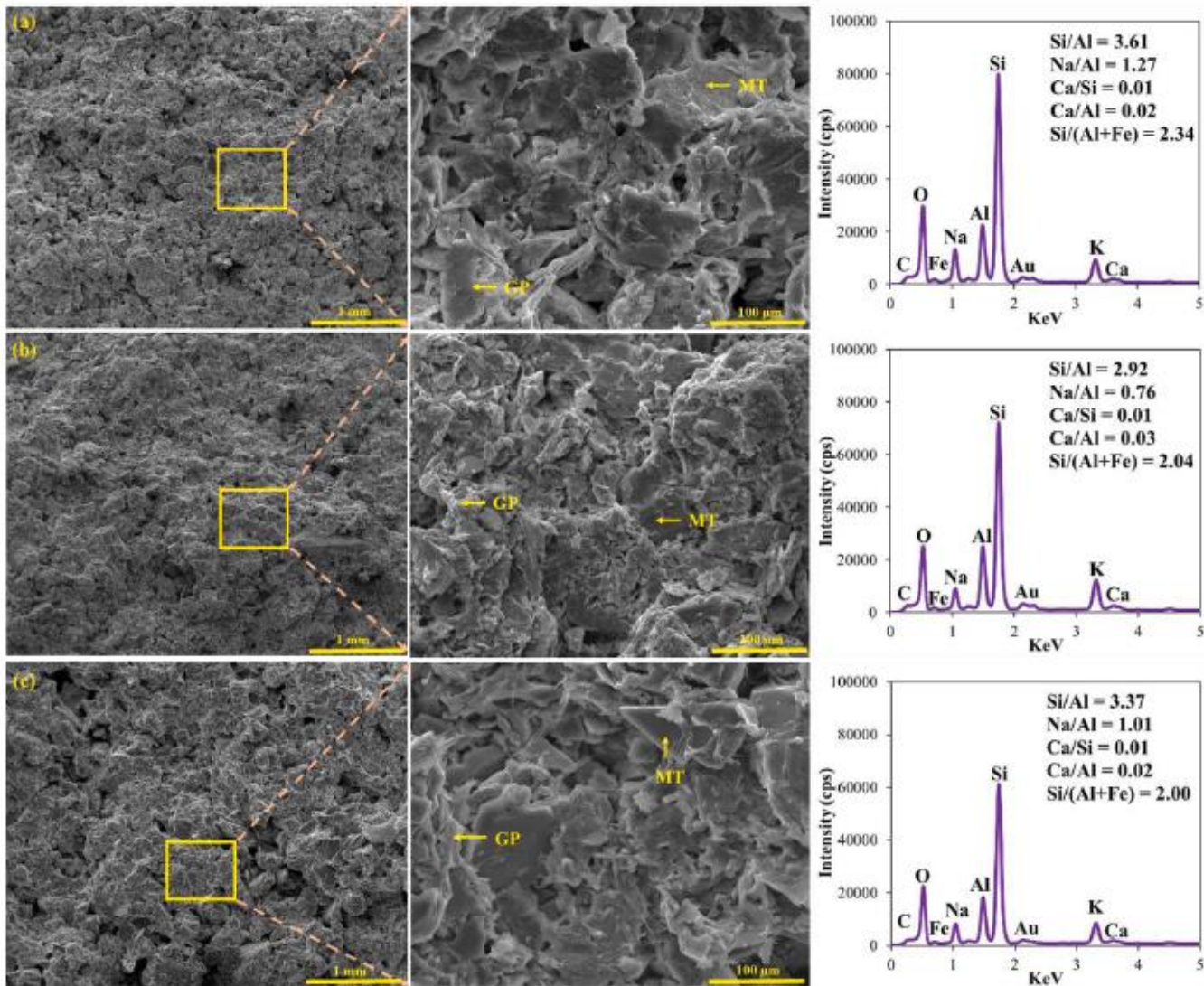


Higher Na/Al & Na/Si



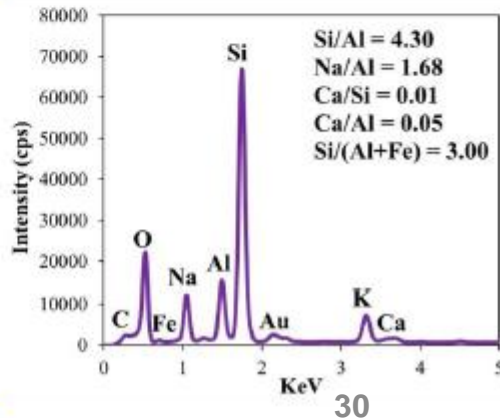
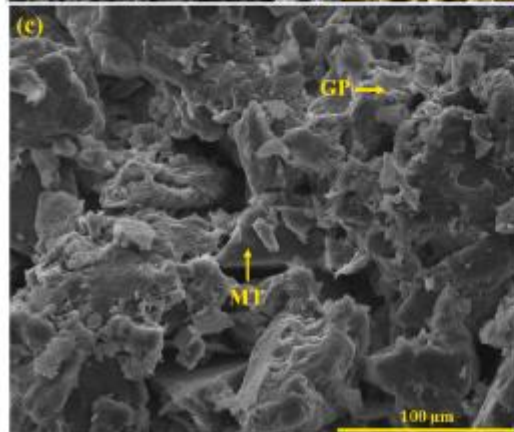
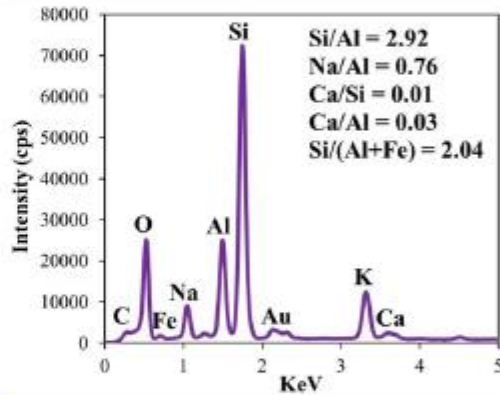
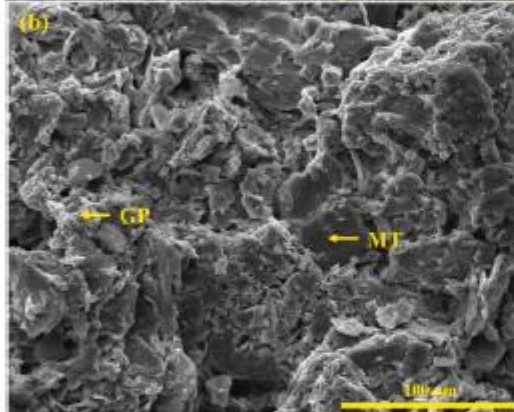
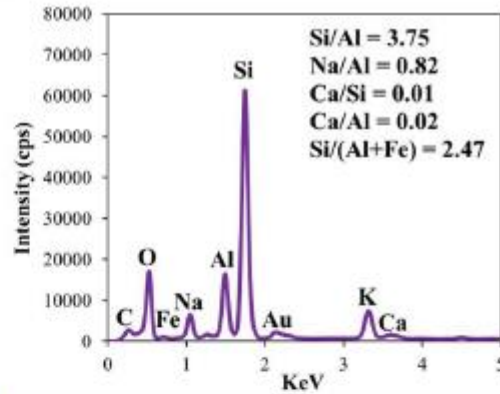
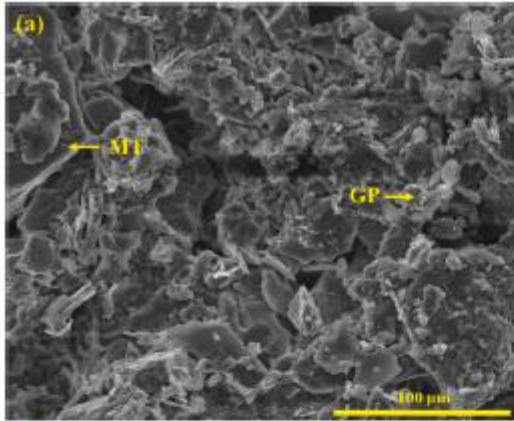
Higher UCS





- ✓ Higher forming pressure results in more compact and denser microstructure.
- ✓ Higher forming pressure results in smaller voids and slower evaporation of the alkaline solution from the geopolymer specimen and thus more dissolution of Al and Fe.

SEM micrographs and EDX analysis results of geopolymer specimens at different forming pressures (FPs) and with the same W/S = 0.14, 10 wt% SG, 10 M NaOH, SS/SH = 2, and curing temperature of 90 °C for 7 days: **(a) FP = 1 MPa**; **(b) FP = 10 MPa**; and **(c) FP = 20 MPa**. GP = geopolymer gel, MT = mine tailings.



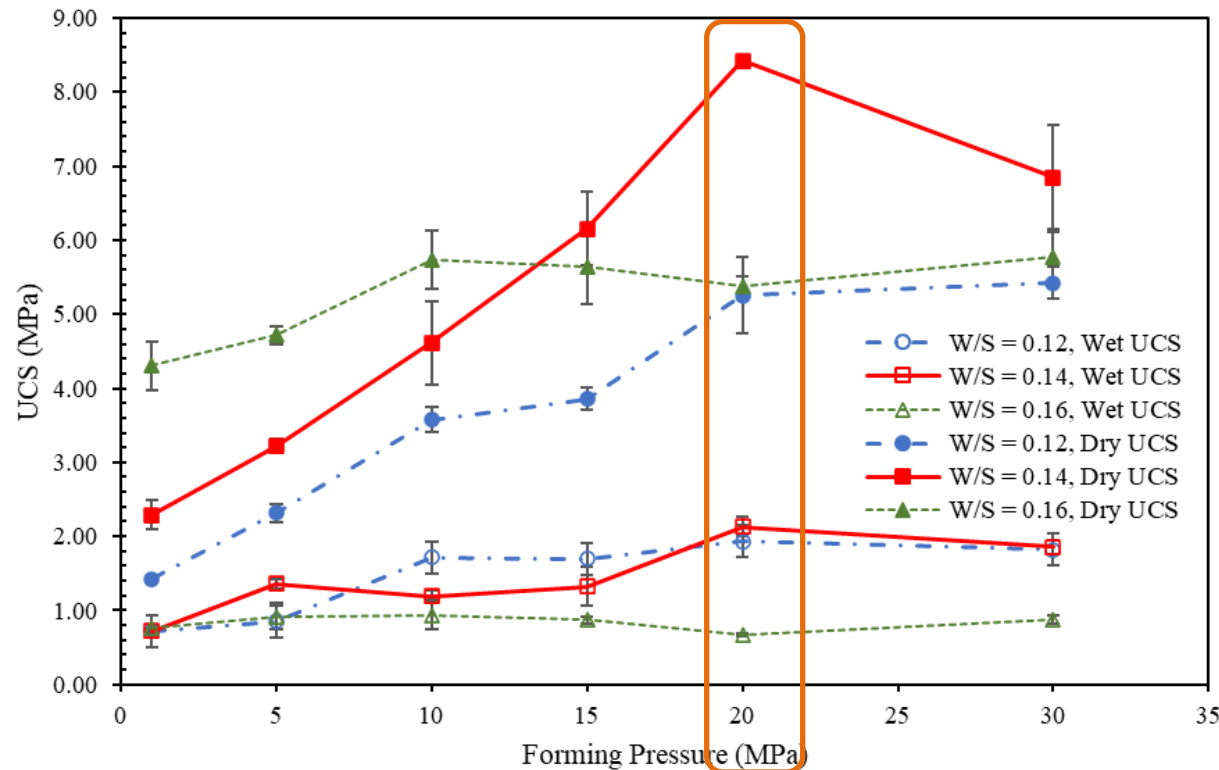
SEM micrographs and EDX analysis results of geopolymer specimens at different W/S ratios and with the same 10 MPa forming pressure (FP), 10 wt% SG, 10 M NaOH, SS/SH = 2, and a curing temperature of 90 °C for 7 days: **(a) W/S = 0.12**; **(b) W/S = 0.14**; and **(c) W/S = 0.16**. GP = geopolymer gel, MT = mine tailings.

- ✓ Higher W/S ratio results in higher NaOH availability
- ✓ Too high a W/S ratio results in higher porosity

RESULTS AND DISCUSSION

- ✓ Water absorption is below 13.13%
- ✓ Increasing the forming pressure results in lower water absorption
- ✓ **20 MPa** was selected as the optimum forming pressure

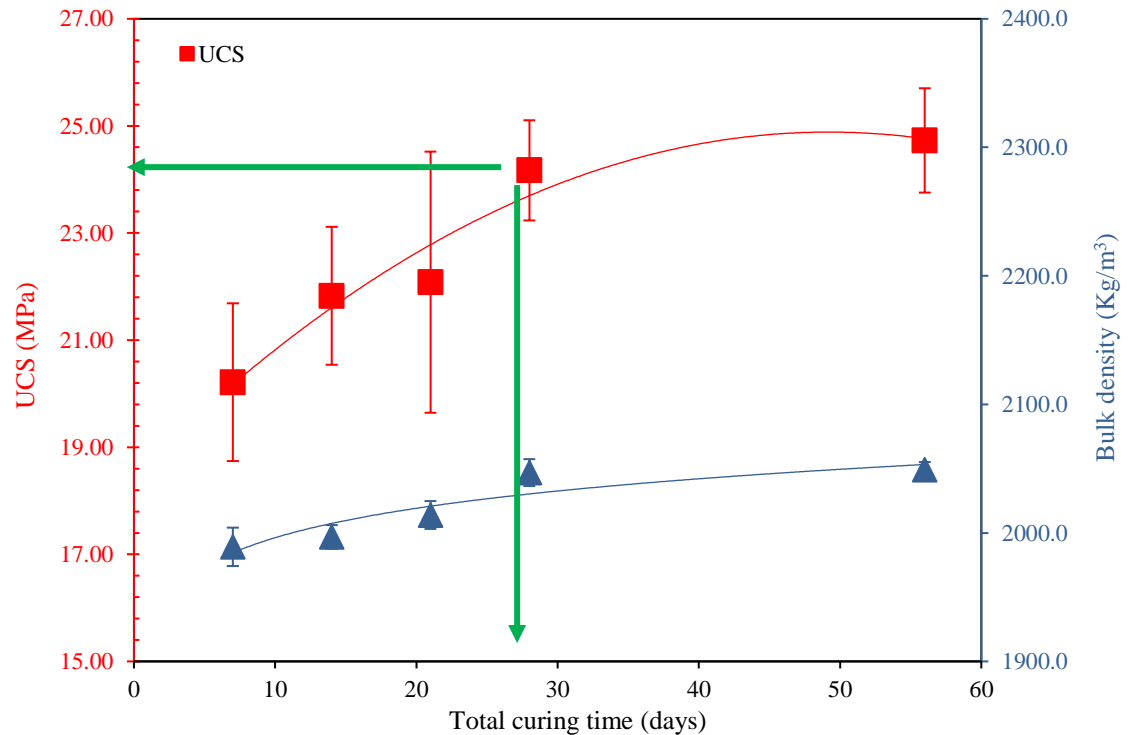
Water Absorption

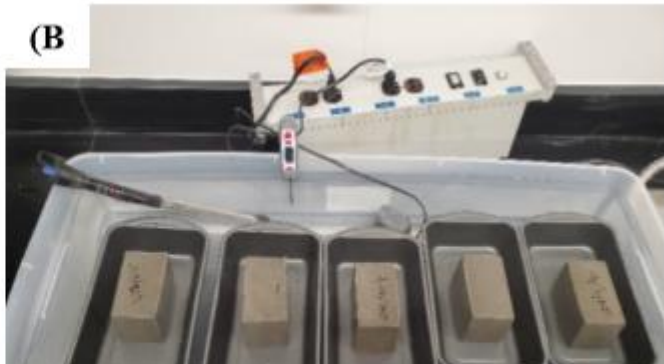


RESULTS AND DISCUSSION

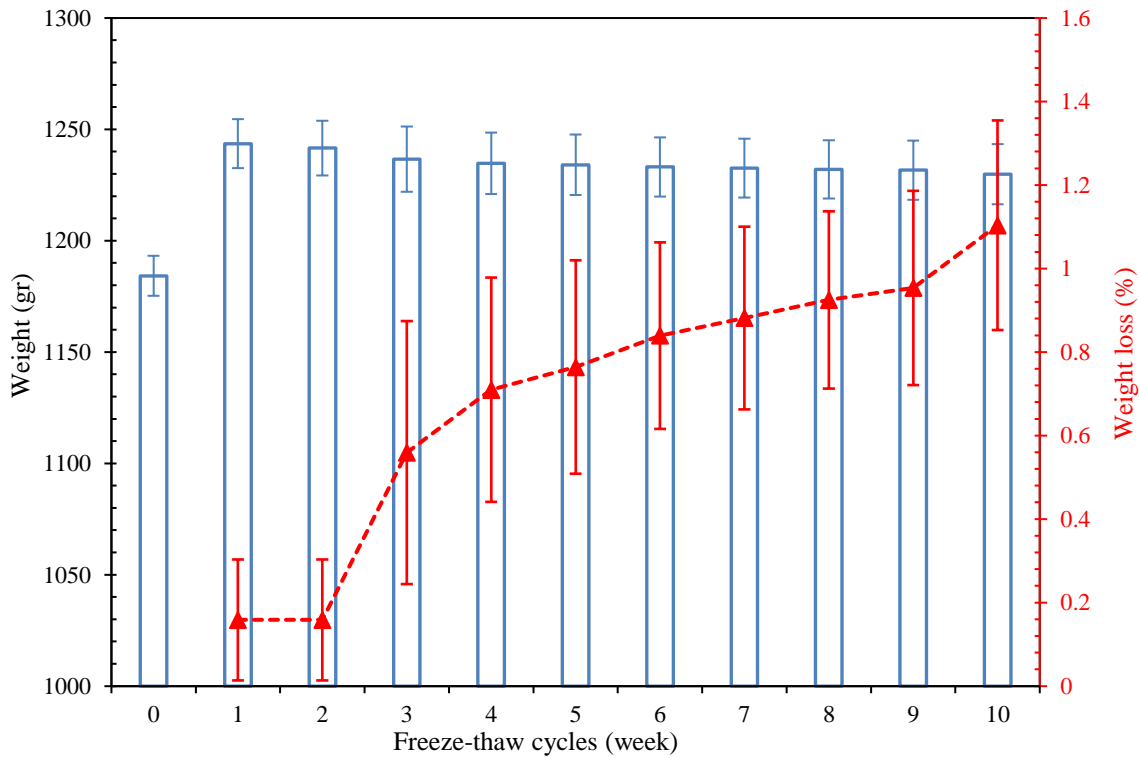
The effect of curing time

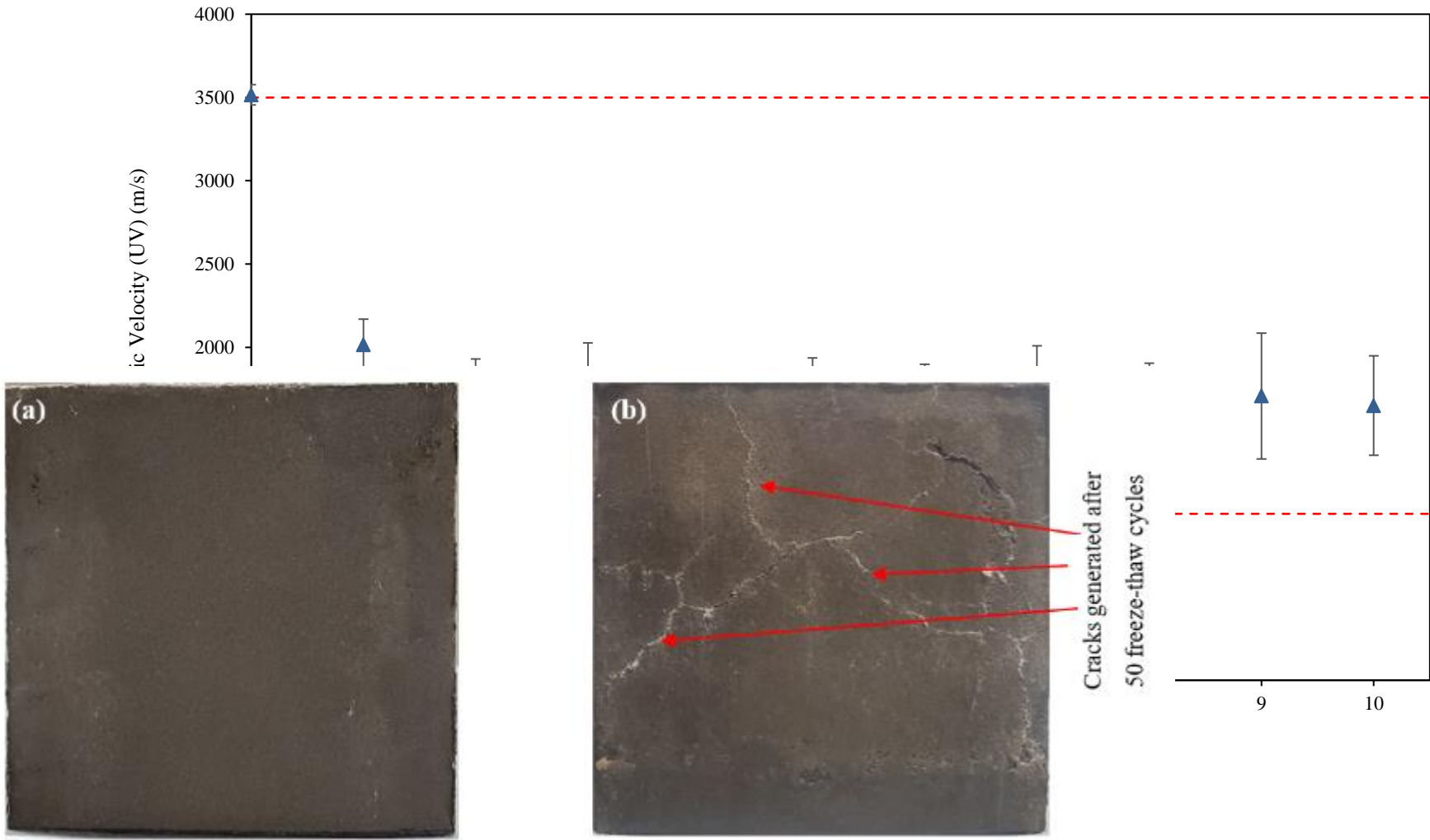
✓ UCS is increased significantly up to 28 days and then it is stabled





✓ Total weight loss is 1.1%.

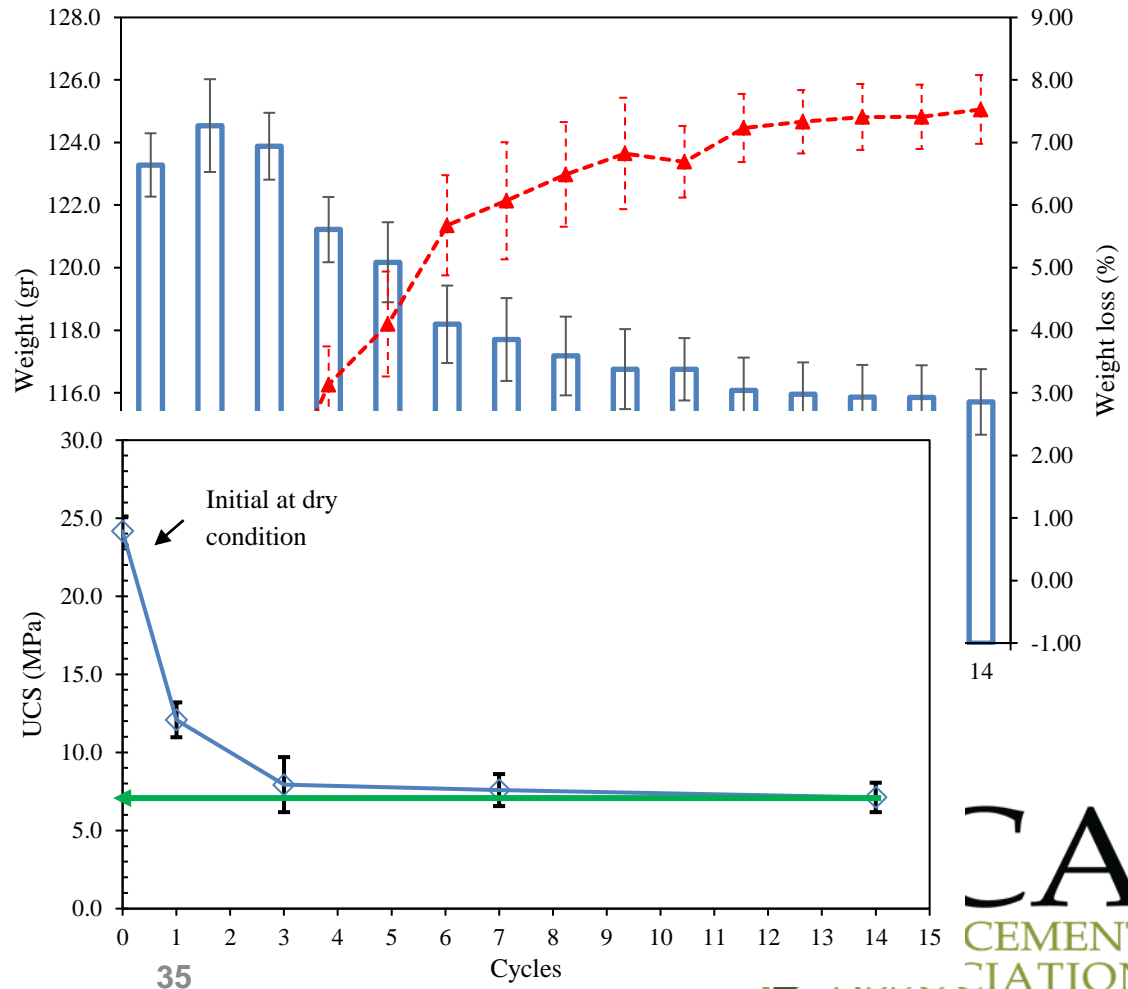


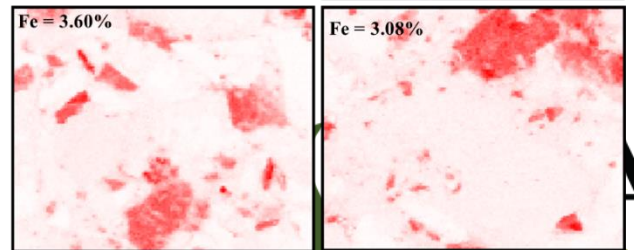
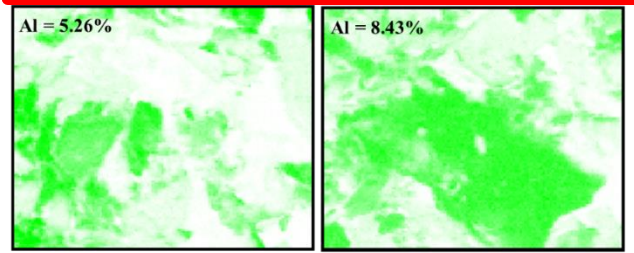
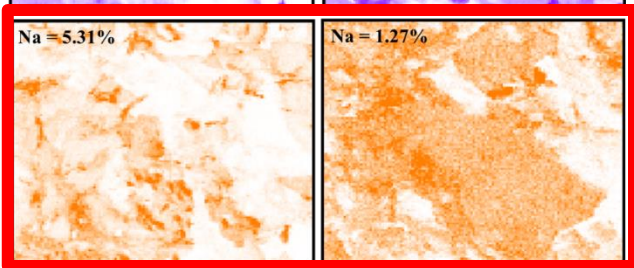
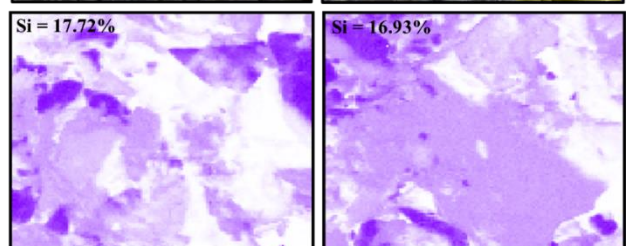
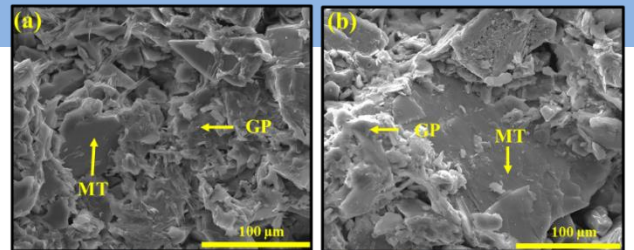
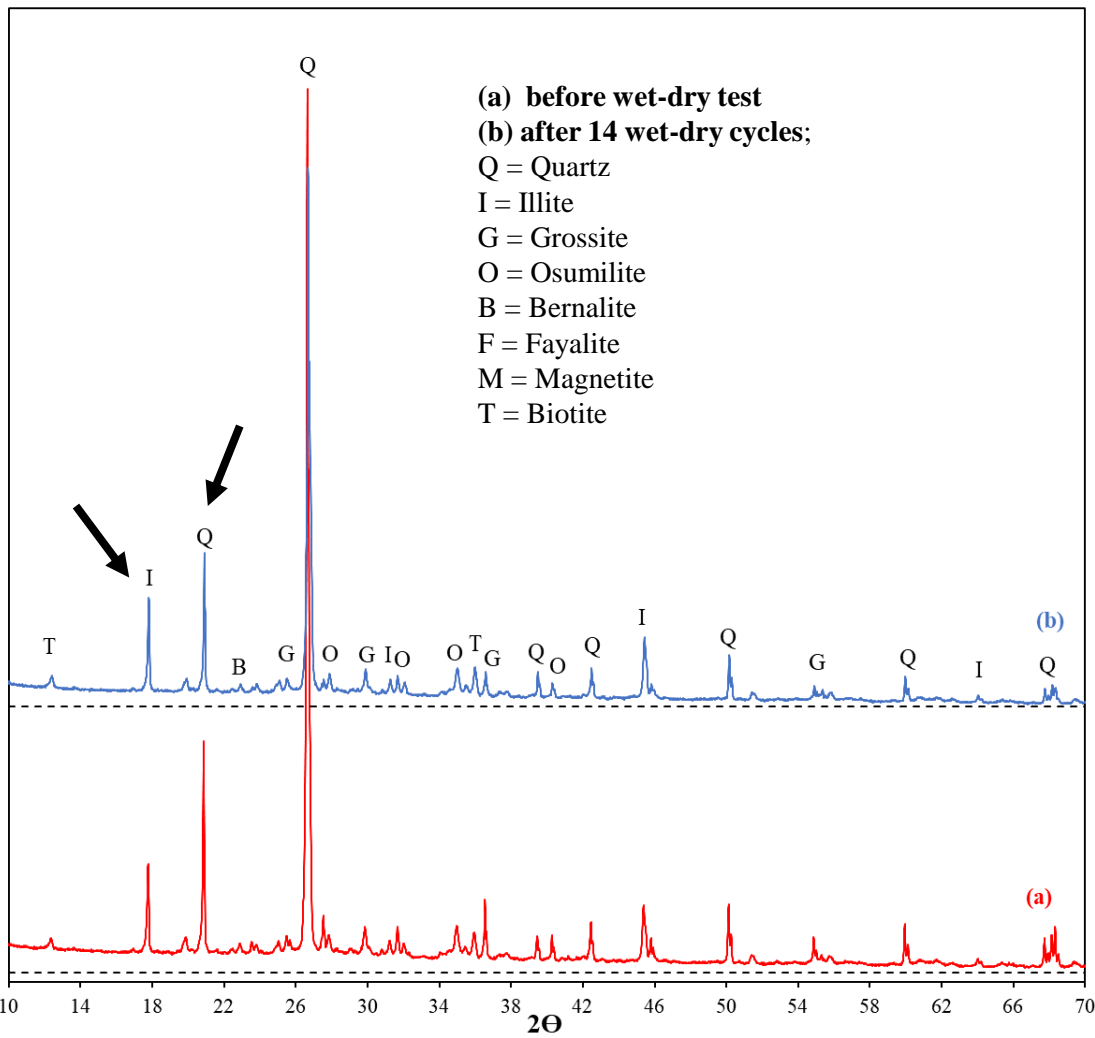
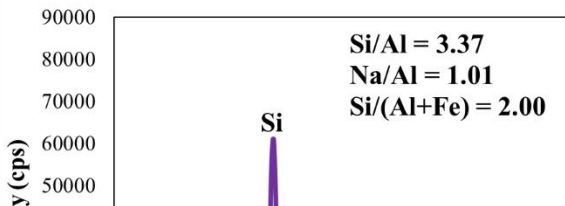
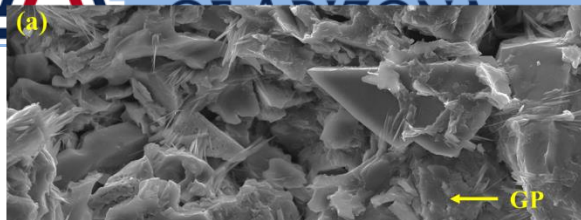


RESULTS AND DISCUSSION

- ✓ Total weight loss is 7.53%.
- ✓ The strength dropped from the initial 24.2 MPa to 7.12 MPa after 14 wet-dry cycles

Wet-dry cycles





RESULTS AND DISCUSSION

Leaching test (TCLP)

	pH	Na	Mg	Al	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Pb
MT+SG powder	4	39.69	12.79	5.64	122.1	42.16	0.0	2.39	94.09	0.21	0.19	56.30	24.48	0.0	0.01	0.0	0.04	0.07
	7	213.4	5.18	0.03	226.1	33.99	0.0	0.88	0.02	0.03	0.02	0.22	0.61	0.0	0.05	0.46	0.0	0.0
Geopolymer specimen	4	1149	0.12	0.51	26.0	2.1	0.0	0.0	1.8	0.0	0.0	0.5	0.3	3.5	0.1	13.0	0.0	0.0
	7	1202	0.07	0.02	29.2	1.6	0.0	0.0	0.2	0.0	0.0	0.1	0.0	5.3	0.2	14.9	0.0	0.0
EPA limit		NA	NA	NA	NA	NA	5.0	NA	NA	NA	5.0	NA	NA	5.0	1.0	NA	1.0	5.0
DIN		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.0-5.0	2.0-5.0	NA	NA	NA	NA	NA
Greek		NA	NA	2.0-10.0	NA	NA	NA	1.0-2.0	NA	NA	0.2-0.5	0.25-0.5	2.5-5.0	NA	NA	NA	NA	NA

■ ■ CONCLUSIONS



Using low-reactive copper MT and slag, geopolymer bricks were produced satisfying the ASTM requirements and at the same time stabilizing the hazardous elements.



Future Works

-  1 Life cycle and techno-economic analysis of the bricks



➤ **Published Research papers:**

1. **Nikvar-Hassani, A.**, Vashaghian, H., Hodges, R., & Zhang, L. (2022). Production of green bricks from low-reactive copper mine tailings: Chemical and mechanical aspects. *Construction and Building Materials*, 324, 126695. Doi: 10.1016/j.conbuildmat.2022.126695
2. **Nikvar-Hassani, A.**, Hodges, R., & Zhang, L. (2022). Production of green bricks from low-reactive copper mine tailings: Durability and environmental aspects. *Construction and Building Materials*, 337, 127571. Doi: 10.1016/j.conbuildmat.2022.127571
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