# Cast Stone Waste Form – Development & Optimization

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Pacific Northwest National Laboratory

EM Waste Processing Technical Exchange

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# Cast Stone

- CH2M Hill, Inc
- Ingredients
  - Portland Cement type I, II
  - Fly Ash Class F
  - Blast Furnace Slag
- Getters Tested
  - Bone char, bone ash, bone black, synthetic apatites, iron ($Fe^0$) powder, Fe- phosphate, silver (Ag)-zeolite, tin (Sn[II])-apatite
- Wastes
  - Basin 43 Waste – LERF
  - Low-Activity Waste (LAW) Simulant loading 8.2–24.2% wt
  - Iodine (I)-rich caustic waste - Hanford

# Starting Materials

| Ingredient | DRF2 (wt %) |
|---|---|
| Portland Cement Type I, II | 8 |
| Fly Ash Class F | 45 |
| Blast Furnace Slag, Grade 120 | 47 |

| Chemical Analysis (wt %) | Cement | Fly ash | Slag |
|---|---|---|---|
| $SiO_2$ | 20.2 | 49.0 | 32.4 |
| $Al_2O_3$ | 4.8 | 16.1 | 12.2 |
| $Fe_2O_3$ | 3.4 | 6.2 | 0.9 |
| CaO | 64.0 | 14.1 | 43.4 |
| $Na_2O$ ) | 0.5 | 4.24 | 0.88 |
| $K_2O$ ) | - | - | - |
| MgO | 0.8 | 4.6 | 4.9 |
| $CaCO_3$ | 3.2 | - | - |
| $SO_3$ | 2.7 | 0.8 | 4.9 |
| $C_3S$ | 62.22 | - | - |
| $C_2S$ | 10.98 | - | - |
| $C_3A$ | 6.96 | - | - |
| $C_4AF$ | 9.00 | - | - |
| Specific Gravity ($kg/m^3$) | 3.15 | 2.58 | 2.89 |
| Specific Surface area ($m^2/g$) | 1.05 | - | 0.515 |
| Average Particle Size (μm) | 19 | 41 | 17 |
| Color | Grey | Light brown | white |

[1] For cement, usually equivalent $Na_2O$ content is used for representation of alkali contents in cement. Equivalent $Na_2O$ content can be calculated using $Na_2O$ content + 0.658 × $K_2O$ content.
[2] $K_2O$ content is not specified from the manufacturer because it is already included in equivalent $Na_2O$ content.

# Simulant Compositions

| Element (mole/liter) | S1 Caustic Scrubber Median | S2 Statistical – Cluster 1 3/16/2038 | S3 Statistical – Cluster 2 05/28/2024 | S4 Caustic Scrubber /10% of SBS Blend | Phase 1 Simulant | Target Russell et al. (2006) |
|---|---|---|---|---|---|---|
| Na | 1 | 1 | 1 | 1 | 2.0 | 2.0 |
| $Al(OH)_3$ | 9.39E-02 | 1.14E-01 | 9.22E-02 | 4.24E-02 | 0.23 | 0.011 |
| Si | 1.88E-03 | 2.04E-03 | 7.74E-04 | 1.39E-02 | - | - |
| K | 5.82E-04 | 6.51E-04 | 2.18E-03 | 2.87E-02 | - | - |
| $NH_4^+$ (total) | --- | --- | --- | 4.41E-01 | - | - |
| $OH^-$ | 3.98E-01 | 3.98E-01 | 3.98E-01 | 1.02E-08 | 1.2 | 0.094 |
| $NO_3^-$ | 3.28E-01 | 1.90E-01 | 3.97E-01 | 1.13E+00 | 0.69 | 0.018 |
| $CO_3^{-2}$ | 2.28E-02 | 4.66E-02 | 3.94E-02 | 1.04E-02 | 1.5E-6 | 0.96 |
| $Cl^-$ | 2.25E-02 | 2.17E-02 | 2.91E-02 | 1.04E-02 | - | - |
| $NO_2^-$ | 1.20E-02 | 1.05E-02 | 3.83E-02 | 4.31E-02 | - | - |
| $PO_4^{-3}$ | 6.87E-03 | 4.85E-03 | 6.03E-03 | 5.10E-03 | 1.7E-2 | - |
| $SO_4^{-2}$ | 4.41E-03 | 5.81E-03 | 5.14E-03 | 4.36E-02 | 9.7E-3 | - |
| $F^-$ | 5.57E-04 | 3.75E-04 | 4.42E-04 | 1.02E-08 | - | - |

# Simulant Test Matrix

| Nominal Sodium Concentration | S1 Median | S2 Cluster 1 | S3 Cluster 2 | S4 Caustic Scrubber / SBS Condensate Blend |
|---|---|---|---|---|
| 2 M | X | X | X | X |
| 4 M | X | | | |
| 6 M | X | | | |
| 8 M | X | | | |
| 10 M | X | | | |

# Simulant Preparation

| | Simulants | | |
|---|---|---|---|
| Add Order | S1 | S2 | S3 |
| 1 | Sodium meta silicate | Sodium meta silicate | Sodium meta silicate |
| 2 | Potassium nitrate | Potassium nitrate | Potassium nitrate |
| 3 | Sodium nitrate | Sodium nitrate | Sodium nitrate |
| 4 | Silver nitrate | Silver nitrate | Silver nitrate |
| 5 | Sodium monohydrogen orthoarsenate | Sodium monohydrogen orthoarsenate | Sodium monohydrogen orthoarsenate |
| 6 | Cadmium nitrate tetrahydrate | Cadmium nitrate tetrahydrate | Cadmium nitrate tetrahydrate |
| 7 | Mercury (II) nitrate | Mercury (II) nitrate | Mercury (II) nitrate |
| 8 | Lead nitrate | Lead nitrate | Lead nitrate |
| 9 | Sodium carbonate | Sodium carbonate | Sodium bicarbonate |
| 10 | Sodium chloride | Sodium chloride | Sodium chloride |
| 11 | sodium nitrite | sodium nitrite | sodium nitrite |
| 12 | Sodium dihydrogen orthophosphate | Sodium orthophosphate | Sodium dihydrogen orthophosphate |
| 13 | Sodium sulfate | Sodium sulfate | Sodium sulfate |
| 14 | Sodium fluoride | Sodium fluoride | Sodium fluoride |
| 15 | Sodium dichromate | Sodium dichromate | Sodium dichromate |
| 16 | Sodium iodide | Sodium iodide | Sodium iodide |
| 17 | Sodium perrhenate | Sodium hydroxide | Sodium perrhenate |
| 18 | Sodium hydroxide | Sodium perrhenate | Sodium hydroxide |
| 19 | Sodium oxalate | Sodium oxalate | Oxalic Acid |
| 20 | Gibbsite | Gibbsite | Sodium oxalate |
| 21 | Technetium in potassium hydroxide | Technetium in potassium hydroxide | Gibbsite |
| 22 | | | Technetium in potassium hydroxide |

| Add Order | S4 |
|---|---|
| 1 | Sodium meta silicate |
| 2 | Potassium nitrate |
| 3 | Ammonium nitrate |
| 4 | Sodium nitrate |
| 5 | Silver nitrate |
| 6 | Sodium monohydrogen orthoarsenate |
| 7 | Cadmium nitrate tetrahydrate |
| 8 | Mercury (II) nitrate |
| 9 | Lead nitrate |
| 10 | Ammonium carbonate |
| 11 | Sodium chloride |
| 12 | sodium nitrite |
| 13 | Sodium orthophosphate |
| 14 | Ammonium sulfate |
| 15 | Sodium dichromate |
| 16 | Sodium iodide |
| 17 | Sodium perrhenate |
| 18 | Sodium oxalate |
| 19 | Gibbsite |
| 20 | Technetium in ammonium hydroxide |

| Simulant | Specific Gravity |
|---|---|
| S1-2M | 1.08 |
| S1-4M | 1.17 |
| S1-6M | 1.27 |
| S1-8M | 1.34 |
| S1-10M | 1.40 |
| S2-2M | 1.09 |
| S3-2M | 1.11 |
| S4-2M | 1.13 |



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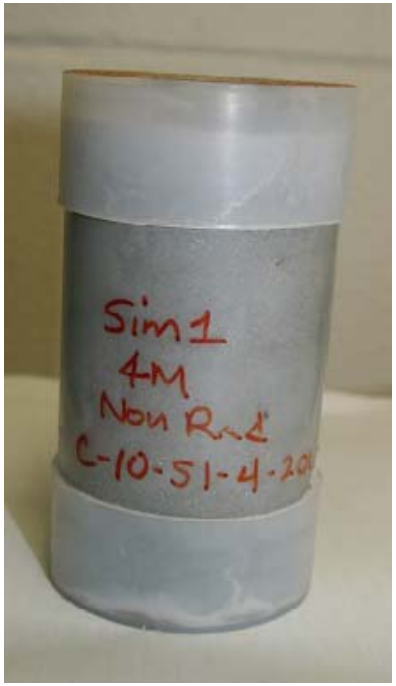
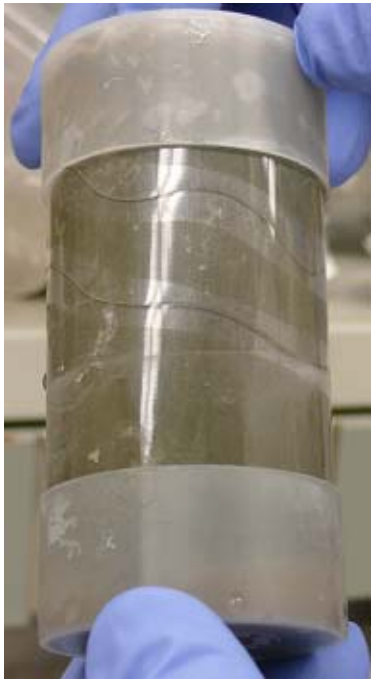
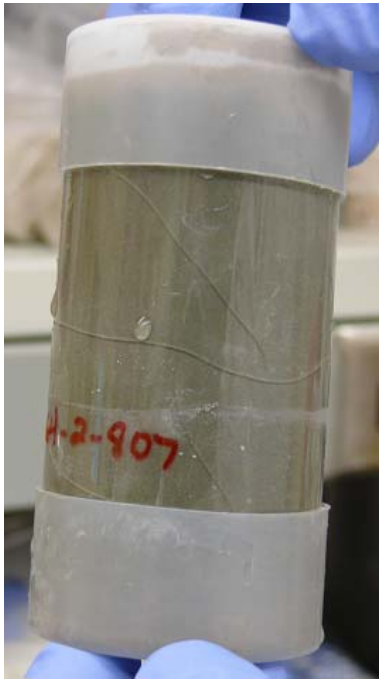
# Monolith Preparation







- Cracking of the plastic molds (fully sealed) in the case of simulant S4 is potentially due to stress generated by ammonia release observed during sample preparation.
- Ammonia is in the simulant and is most likely released due to high pH of the pore water in the cement. Exact mechanism of ammonia release is not known.

# Monolith Preparation

- 50 mm (in diameter) ×100 mm (in length) cylindrical specimens were prepared.
- Temperature was measured at the center position of the cylindrical specimen.
- Target cementitious binder to simulant solution ratio is 1g to 0.389 ml.



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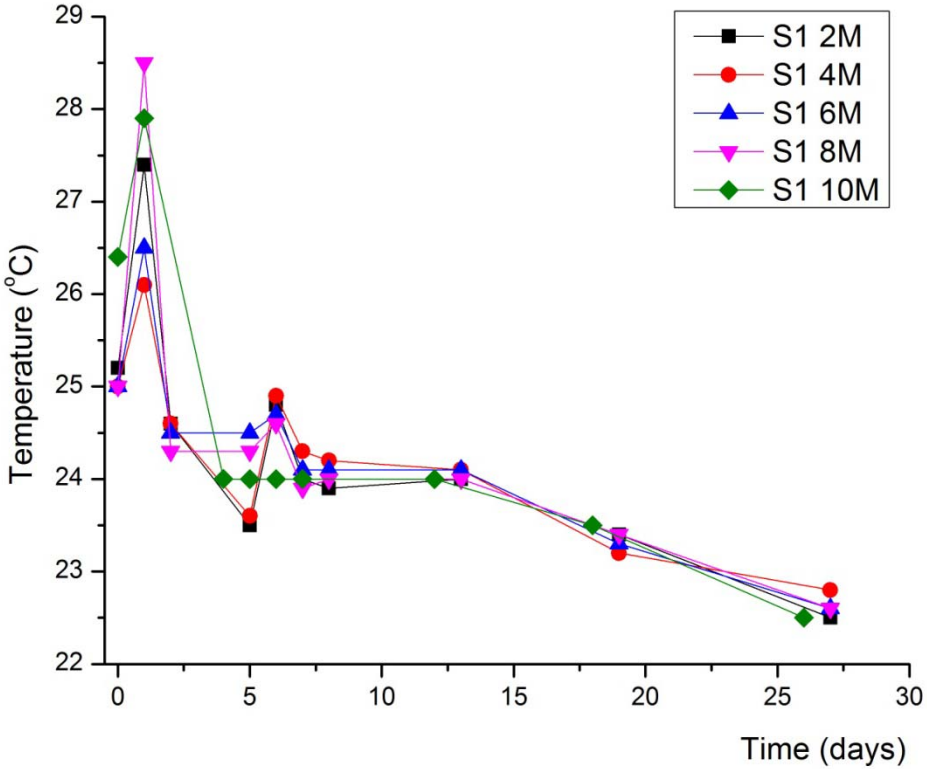
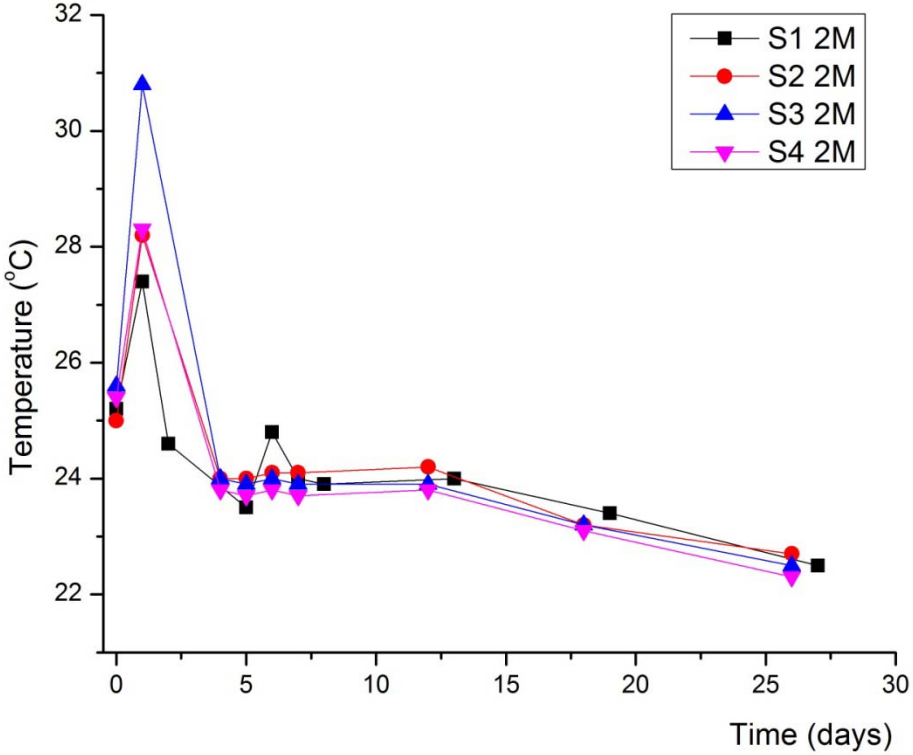
# Sample Temperatures




- No significant temperature rise was observed.

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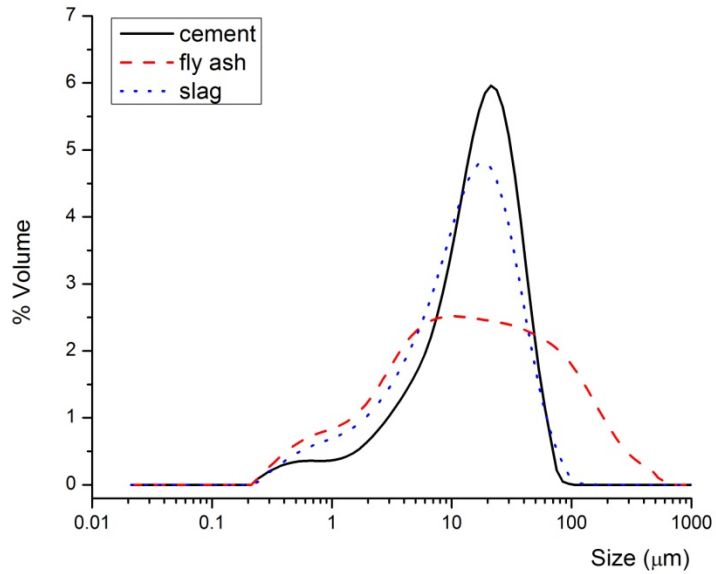
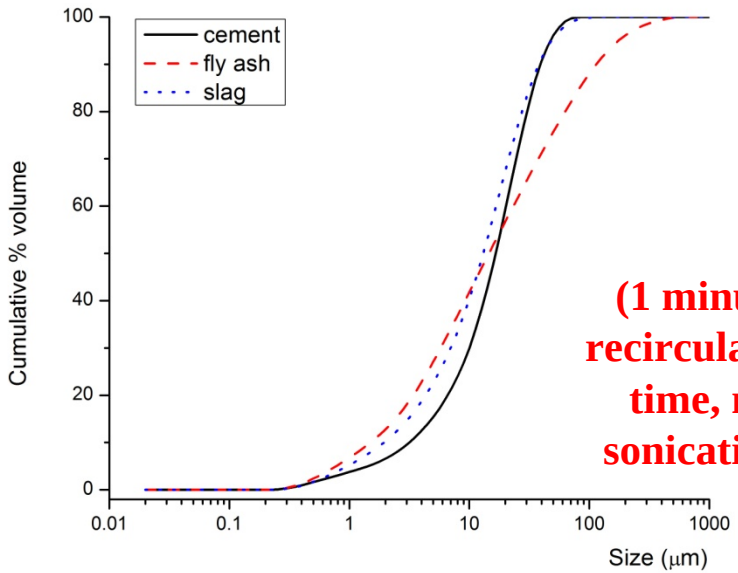
# Characterization and Analytical

- Particle size distribution
- X-ray diffraction (XRD)
- Scanning electron microscopy (SEM)/energy dispersive spectrometer (EDS)
- Strength
- Specific surface area and pore size and distribution
- Leachability testing
  - EPA methods 1313, 1315, and 1316
- Rheology (in progress)
- Advanced characterization (in progress)
  - Ultrasonic wave reflection
  - Impedance spectroscopy

# Particle Size Distribution




**(1 minute recirculation time, no sonication)**

- The average particle size of cement and slag are 19 μm and 17 μm, respectively. Cement and slag have similar PSDs because they have been ground in a mill by the supplier.
- Fly ash has a broader particle size distribution with an average particle size of 43 μm. Fly ash is used in the as -received condition.

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# Phases in Cementitious Materials

- C-S-H (or C-A-S-H): amorphous calcium (alumino) silicate hydrate
- CH: calcium hydroxide (portlandite)
- Ettringite: calcium aluminum sulfate hydrate

$$C_6A\overline{S}_3H_{32}$$

- AFm: typically called monosulfoaluminate, other types of anions can enter into AFm structure, resulting in changes in x-ray diffraction angle,

$$C_4A\overline{S}H_{12}$$

- Anions can be also adsorbed to C-S-H.



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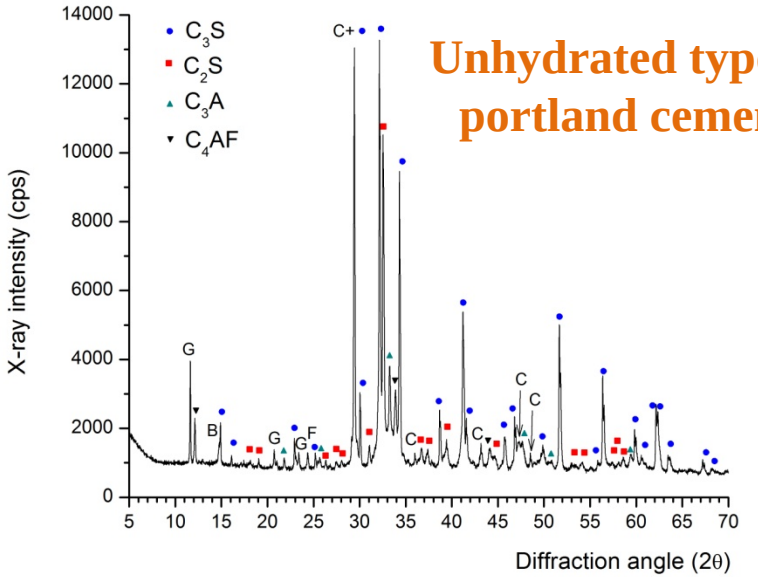
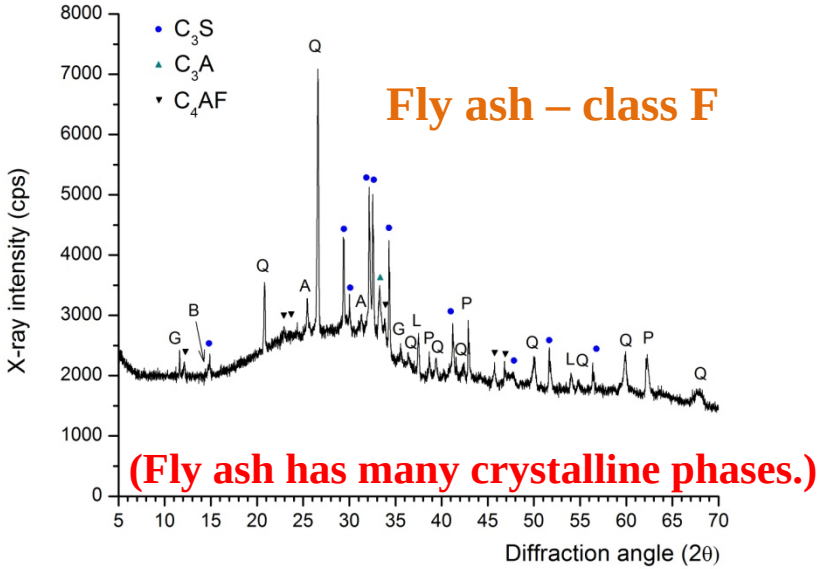
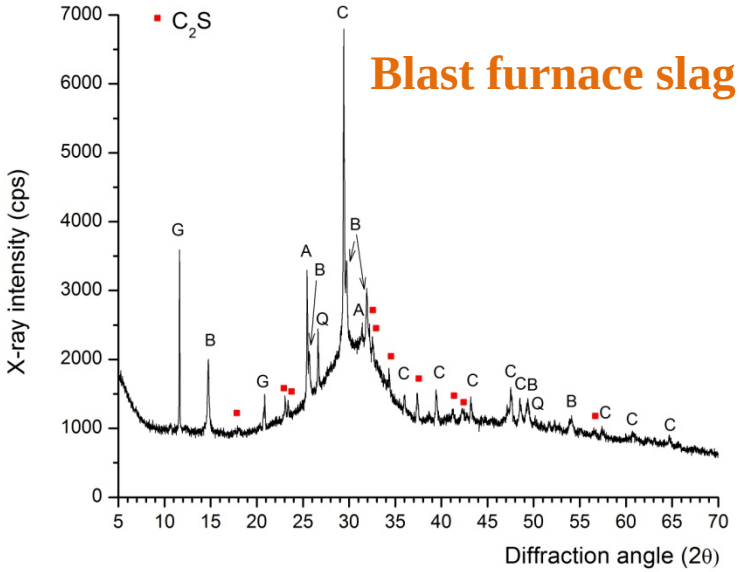
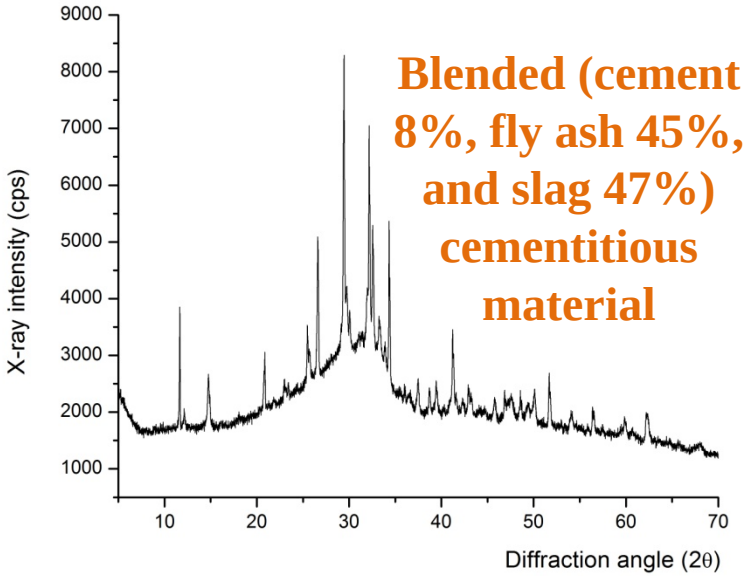
# XRD of Starting and Blended Materials




(Slag contains calcium sulfate polymorphs.)

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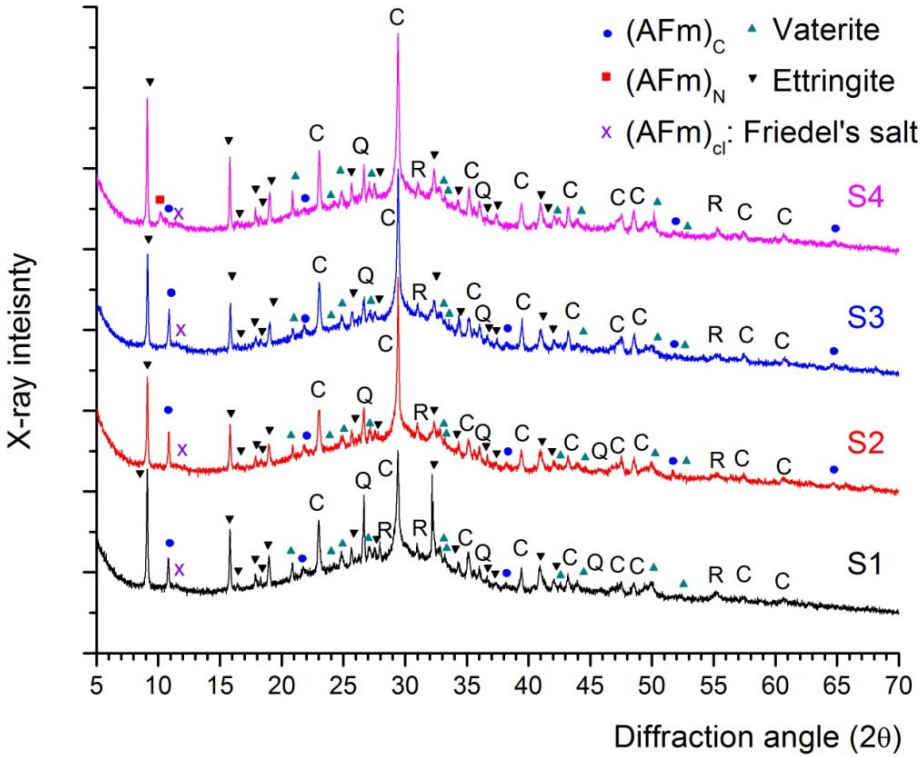
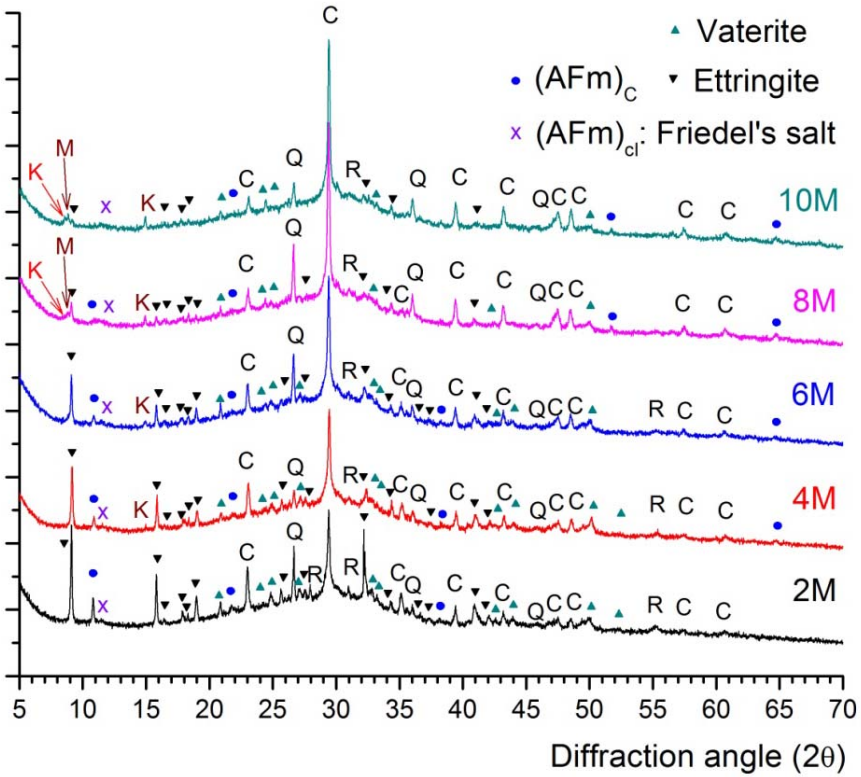
# XRD of Hydrated Cast Stone




**2M simulant solution – prepared and diluted with deionized water to make 26% concentration**




**S1 simulant solution – diluted from 2M to 10M with deionized water to make 26% concentration**

- Ettringite and AFm are the main hydrated phases.
- AFm contains various anions ($CO_3^{2-}$, $Cl^-$, $NO_3^{2-}$).
- Ettringite contains sulfate ($SO_4^{2-}$).

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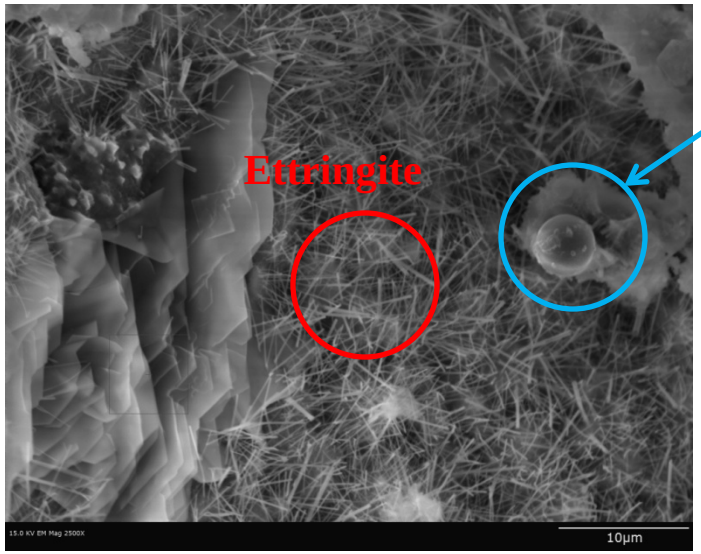
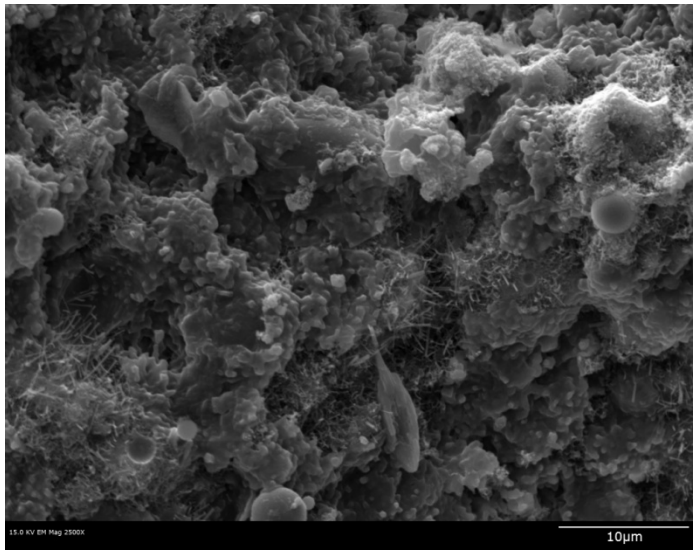
# Microstructure (continued)

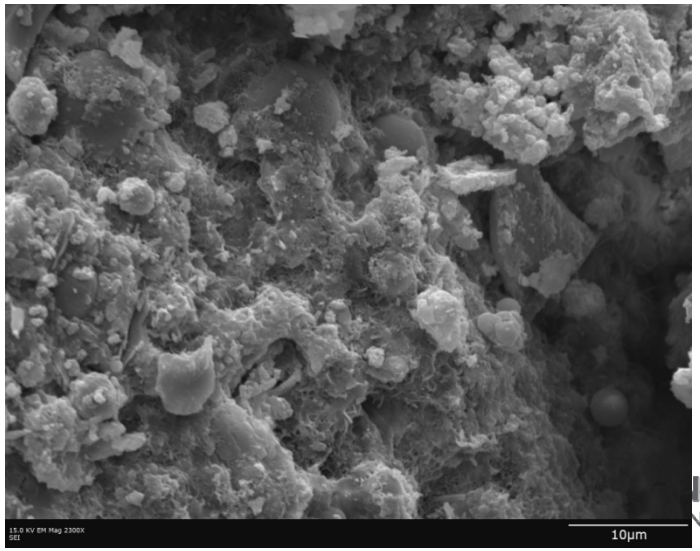
Simulant S1, 2M, 1500×




Simulant S2, 2M, 2500×




Simulant S3, 2M, 2500×

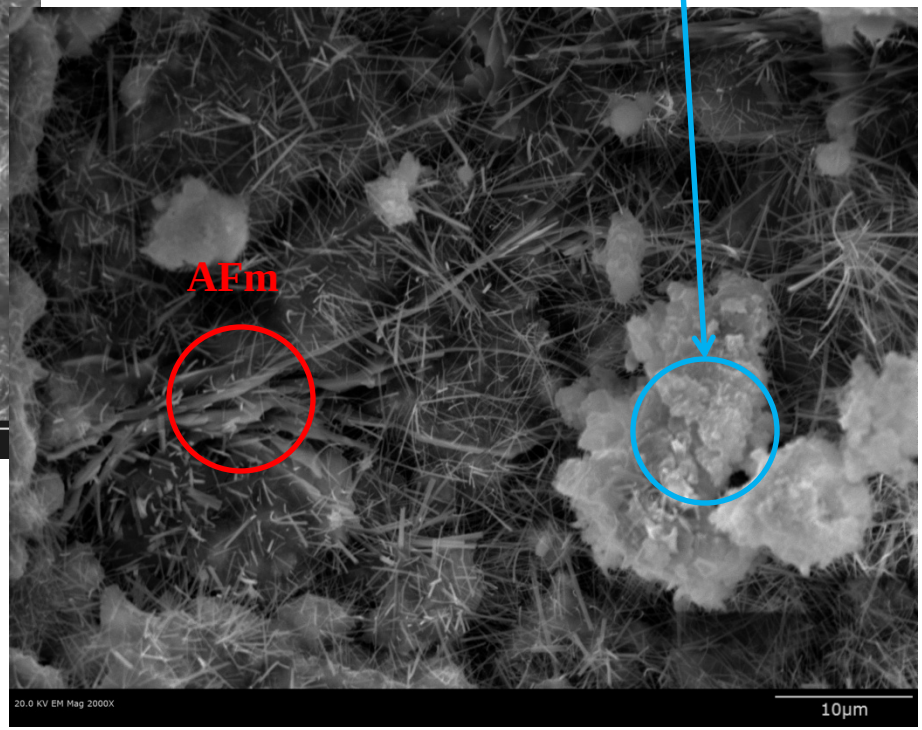



Simulant S4, 2M, 2300×

# Microstructure (continued)

Simulant S1, 2M, 1500×

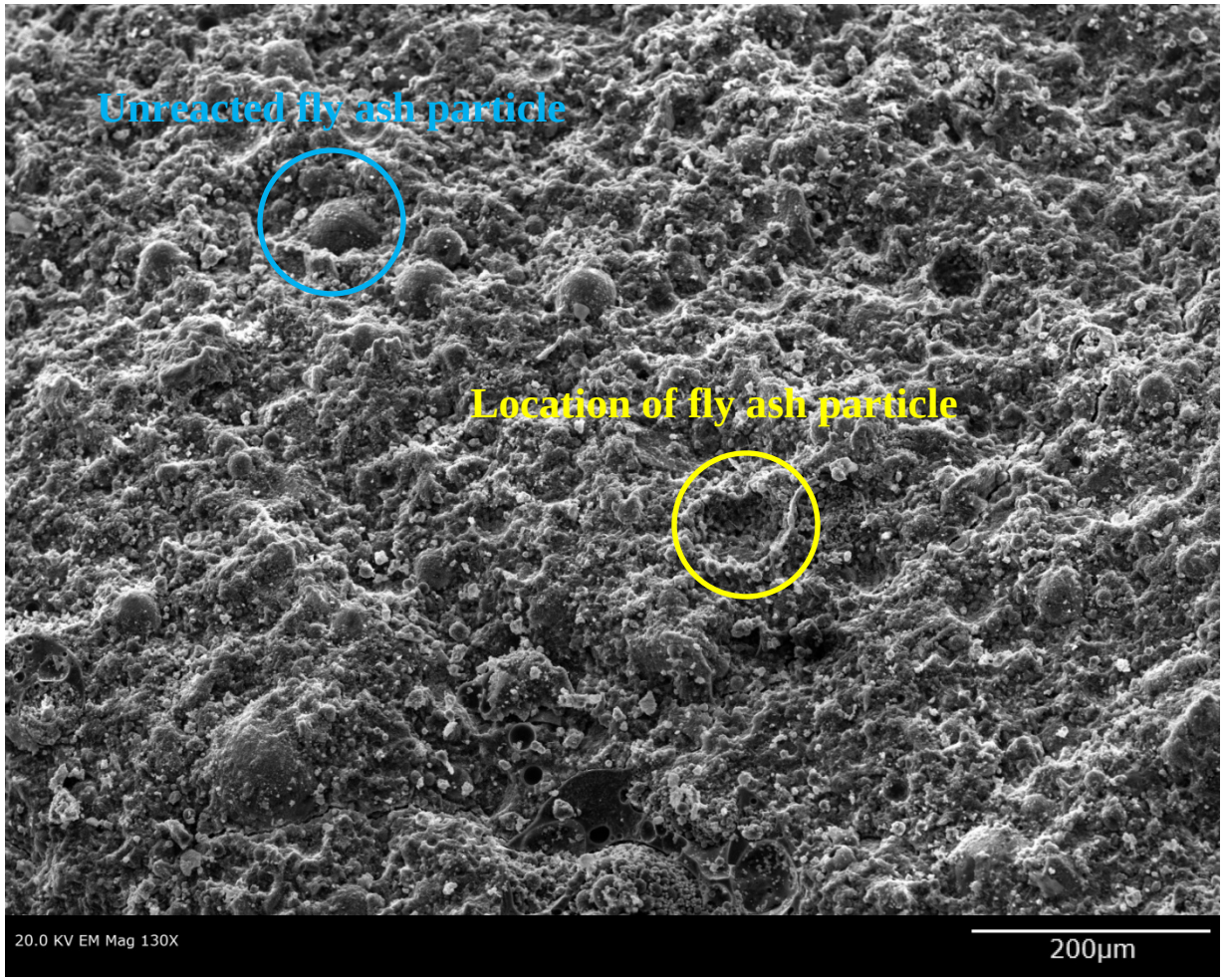
Calcium Aluminum Silicate Hydrate (C-A-S-H)?




Simulant S1, 4M, 2000×

- Microstructures of S1, S2, and S3 specimens are similar.
- Microstructure of S4 is slightly different.

# Microstructure




**SEM (secondary) image of specimen with simulant S1 6M solution at 130×**
**Note: All different specimens showed similar surface characteristic**

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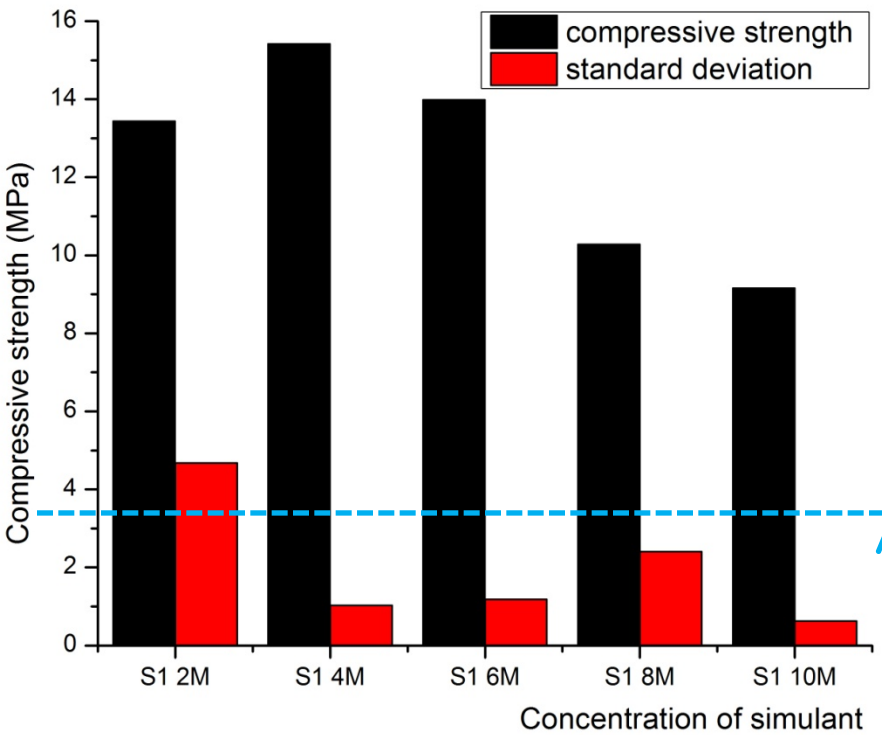
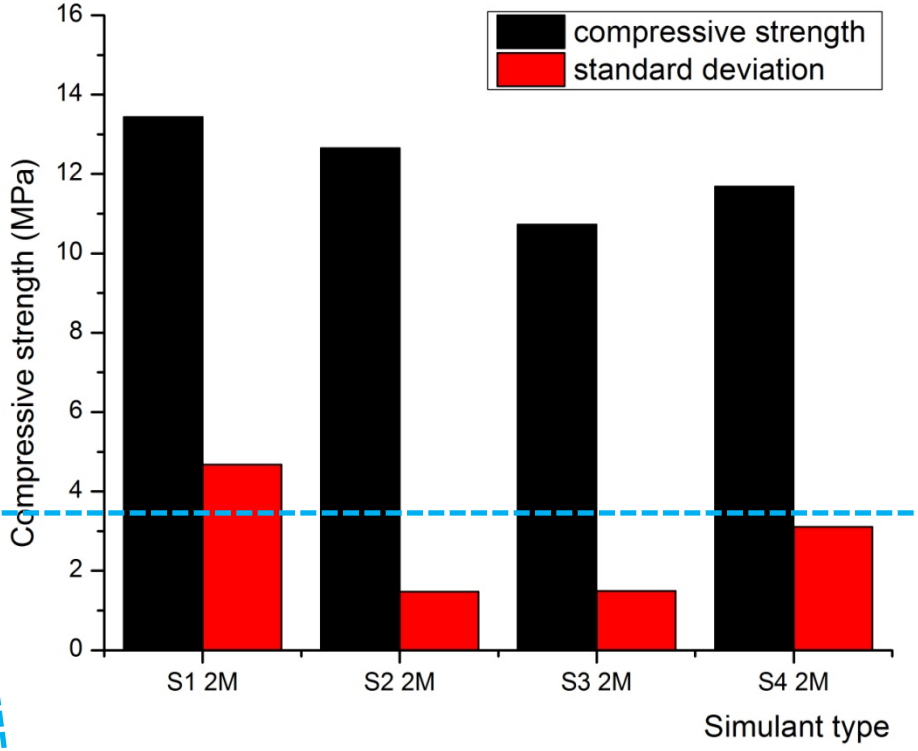
# Compressive Strength




**Minimum strength requirement for Cast Stone (500 psi) = 3.45 MPa**

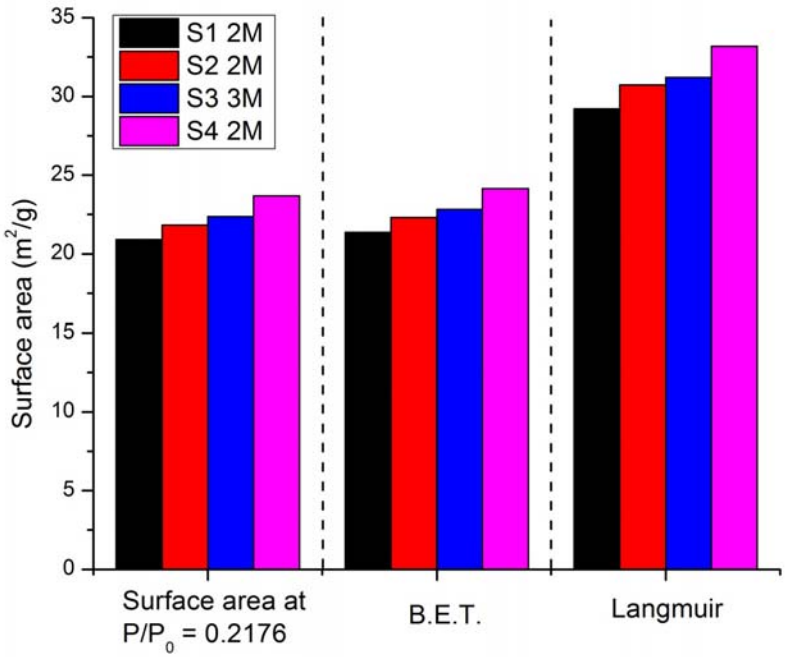
- Conventional compressive strength of concrete for structural purposes should exceed more than 25 MPa in 28 days. **Note the target strength or waste disposal is only 3.45 MPa.**

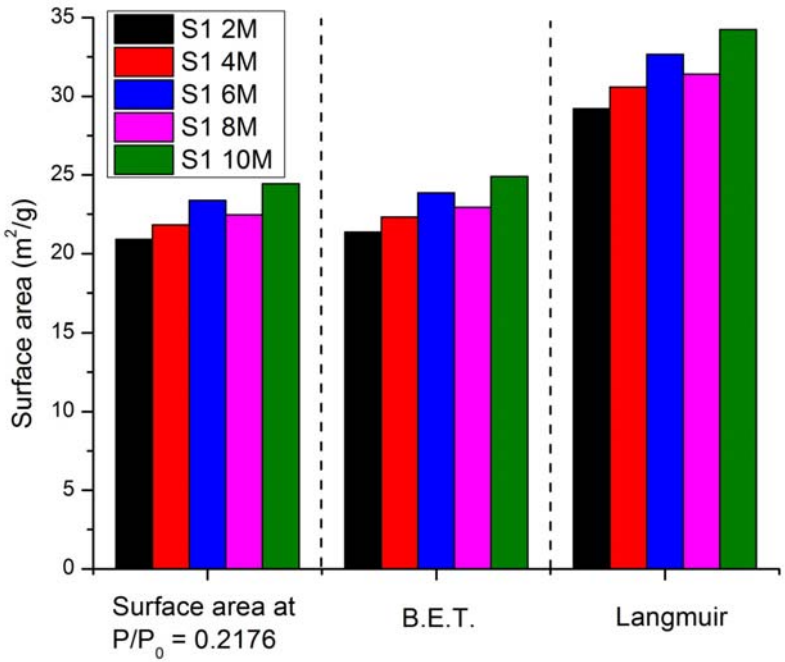
# Workability

| Sample | Increase in w/s | Increasing rate in w/s (%) | Strength (MPa) | Decreasing rate in strength (%) |
|---|---|---|---|---|
| S1-6M | 0.040706 | 10.2 | 13.98 | 9.7 |
| S1-8M | 0.056761 | 14.2 | 10.28 | 33.6 |
| S1-10M | 0.090543 | 22.6 | 9.17 | 40.8 |
| S4-2M | 0.004257 | 1.1 | 11.69 | 24.5 |

- The use of dispersing agent (superplasticizer) is not considered because sometimes abnormal stiffening occurs due to interaction between cementitious binder and superplasticizer.
- Decreasing rate in strength is calculated based on simulant S1 4M specimen that show the highest compressive strength.

# Specific Surface Area



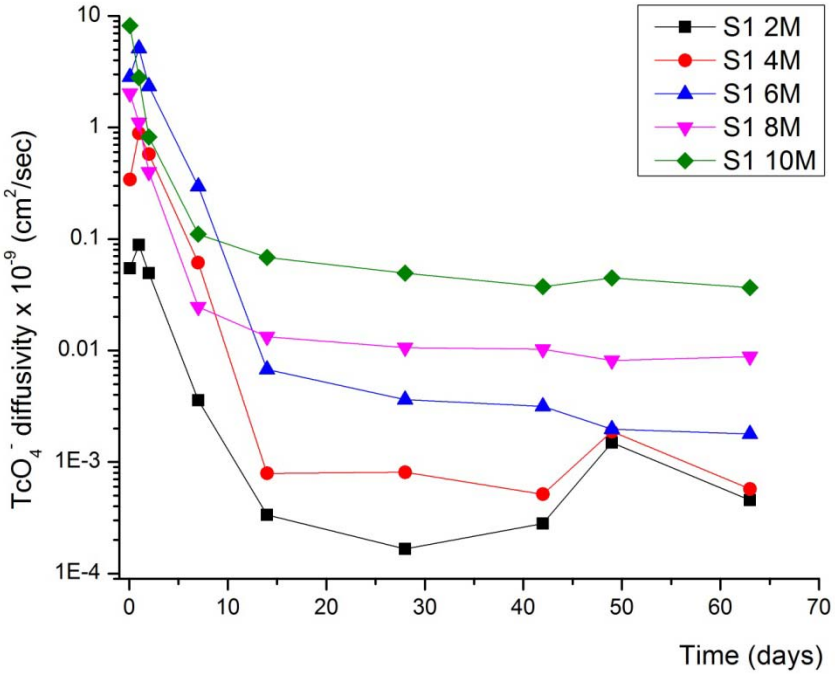

- There is no much difference in surface area between these samples.
- It is difficult to correlate surface area data to strength development and leachability.

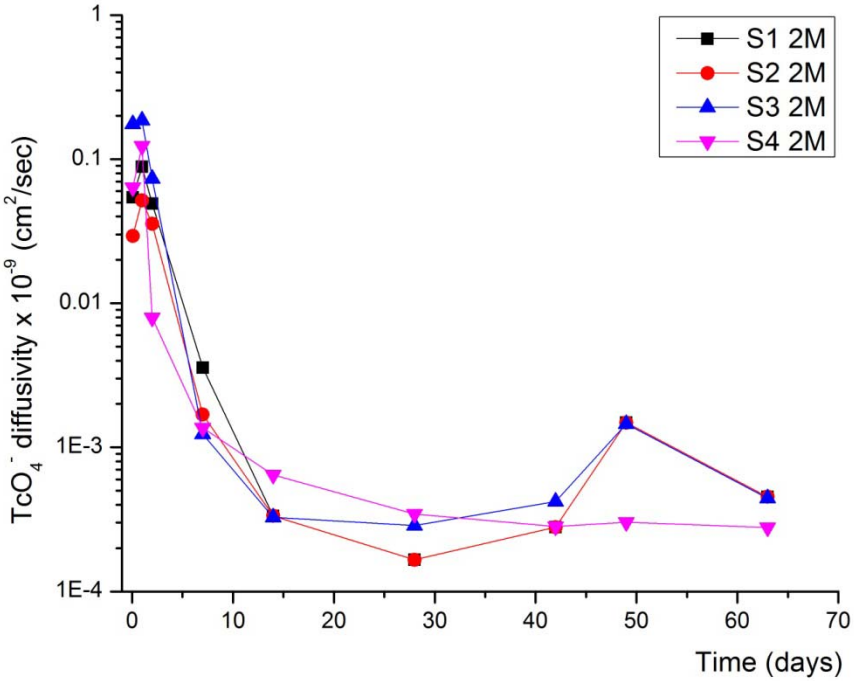
# Leachability Testing

| Cast stone | Specific surface area ($m^2/g$) of powder sample by $N_2$-BET | Average geometric surface area of monolith ($cm^2$) | Moisture content |
|---|---|---|---|
| S1-2M | 17.1±0.04 | 186.4 | 0.16 |
| S1-4M | 15.0±0.04 | 187.1 | 0.14 |
| S1-6M | 18.2±0.05 | 191.1 | 0.16 |
| S1-8M | 18.3±0.05 | 192.5 | 0.18 |
| S1-10M | 18.6±0.04 | 187.8 | 0.19 |
| S2-2M | 14.0±0.04 | 185.0 | 0.16 |
| S3-2M | 16.6±0.05 | 184.7 | 0.18 |
| S4-2M | 17.6±0.06 | 183.4 | 0.18 |

- Average of surface area is in similar range.

# Leachability Testing (continued)




- Technetium diffusivity is the highest during the first day, and it starts to decrease as a function of time.
- After 14 days, technetium diffusivity decreases significantly, showing almost no differences between specimens.

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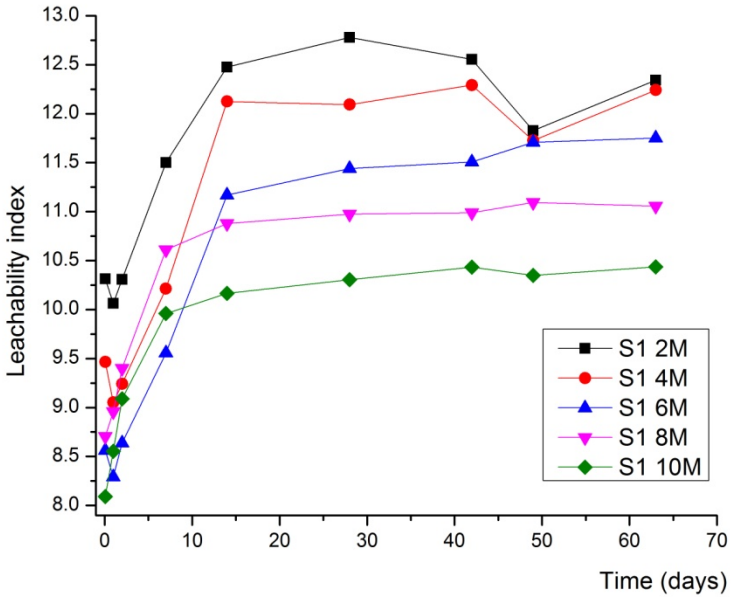
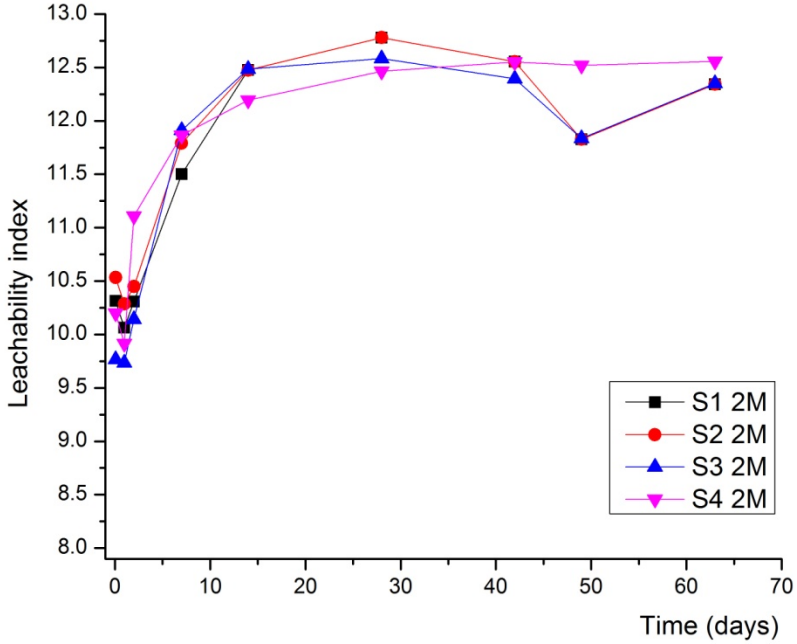
# Leachability Testing (continued)




- Average leachability index decreases as ionic strength increases.
- Leachability index in different simulants is very similar.

# Summary

- Preliminary strength along with leachability data demonstrates the promise of cast stone as a waste form.
- XRD and microstructure show similar hydration products in the cases of simulants 1 – 3.
- Simulant 4 samples show some differences compared to simulants 1-3. The strength of simulant 4 sample is a little lower but leachability is comparable. All our samples met the basic target strength (3.45 MPa).
- Workability and mixing criteria are critical for consistent performance and robust waste form.

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