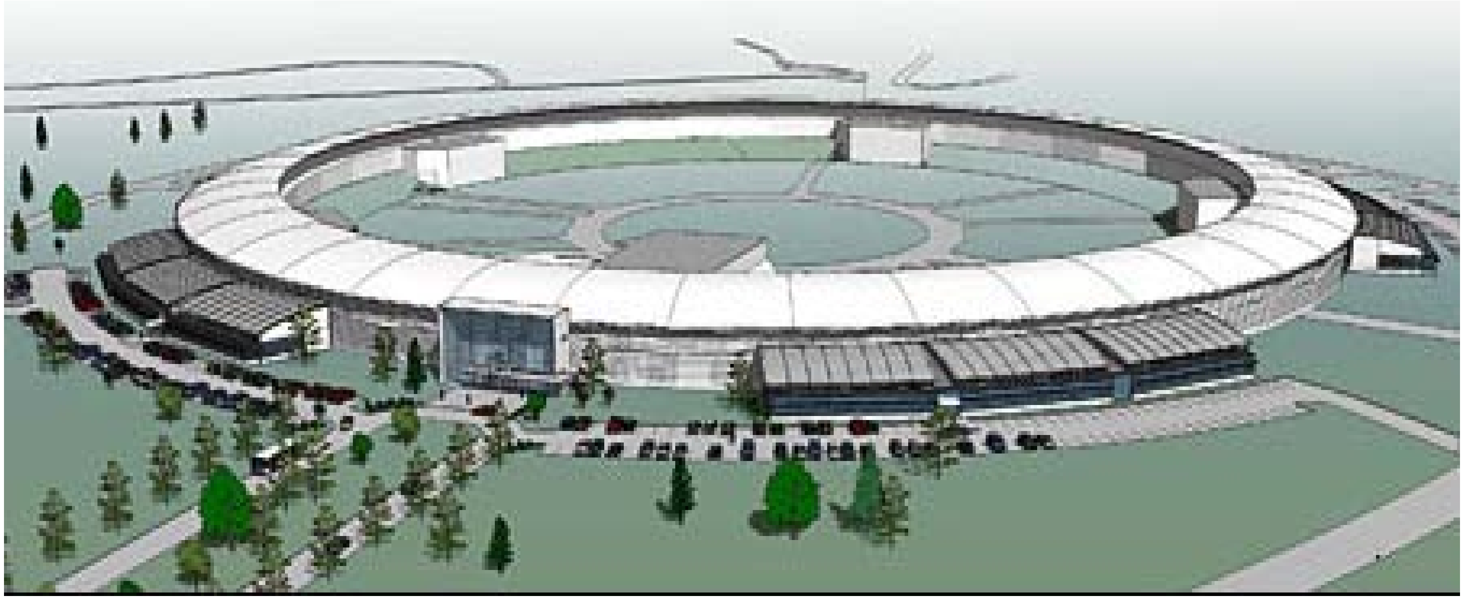

BNL National Synchrotron Light Source II

# Geopolymer Sealing Materials

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# Relevance/Impact of Research



**Objectives**: Develop and characterize field-applicable geopolymer temporary sealing materials in the laboratory and to transfer this developed material technology to geothermal drilling service companies as collaborators for field validation tests.

**Impact**: Since geopolymer made with industrial by-products is characterized as cost-effective, acid-resistant, set-controlling, and refractory cementitious materials, if success, the impact will include;

- Reduction of total costs of sealing and drilling operation including the drilling rig and crew cost of "waiting on sealing's set" and raw material cost.
- New science and technology regarding self-degradable cementitious materials.
- High potential as thermal shock-resistant EGS well casing cement without self degradation.
- Mitigation of environmental impact by eliminating Ordinary Portland Cement (OPC), which emits 1 ton $CO_2$ gas during its 1 ton production.

# Scientific/Technical Approach

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- In 2003-2006, BNL developed a new-type of cost-effective acid-resistant casing cements through *alkali activation reaction* of sodium silicate. The developed cements were applicable to highly concentrated $H_2S$ environments (pH <2.0) encountered in the upper regions between 0.1 to 5 Km of wells at temperatures of up to 200ºC.
- Cements for reducing raw material cost were formulated using recycled industrial wastes such as granulated blast *slag* from steel manufactures and *fly ash* from coal combustion plants.
- Cements were associated with *$Na_2O$-$CaO$-$Al_2O_3$-$SiO_2$-$MgO$ system*, *$NaAlSi_2O_6.H_2O$ (Zeolitic Analcium)* and $x$$Na_2O$-$y$$Al_2O_3$-$z$$SiO_2$system (Geopolymer).

**Advantages of Sodium Silicate-activated Cements Compared with Conventional OPC-based Well Cements:**

1. Acid and $CO_2$ resistance
2. Simple setting control without retarders
3. Heat and thermal shock resistance attributed to refractory cementitious properties
4. Cost effectiveness
5. Green material
6. Environmental mitigation

## Milestones

| | FY2009 | FY2010 | | | | FY2011 | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 4Q | 1Q | 2Q | 3Q | 4Q | 1Q | 2Q | 3Q | 4Q |
| **Phase I. Material development and characterization** | | | | | | | | | |
| Task 1. Establish the basic formulation of temporary sealing materials | | | | 90%* | | | | | |
| Task 2. Characterization | | | | | 20%* | | | | |
| Task 3. Develop expandable and swelling sealers | | | | | | | 5%* | | |
| Task 4. Develop self-degradable sealers | | | | | | | | 10%* | |
| Task 5. Report | | | | | | | | | |
| **Phase II. Technology transfer to geothermal industries** | | | | | | | | | |

* Percent completion

**Budget:** FY09 $347,000. FY10 $232,000.

**Partners:** Halliburton (cost-share partner), AltraRock Energy Corporation (cost-share partner), Sandia National Laboratory (collaborator)

**Material Criteria**

- One dry component product
- Plastic viscosity, 20 to 70 cp at 300 r.p.m
- Maintenance of pumpability for at least 1 hour at 85° C
- Compressive strength >200 psi
- Be self-degradable by injection with water at a certain pressure
- Expandable and swelling properties; >10% of total volume of sealer
- Be compatible to drilling fluid and mud
- Excellent permeability through porous structures, corresponding to its applicability to soil stabilizing grout
- Bond strength to rock surfaces > 50 psi
- Anti-filtration properties
- Low material cost which is equal or less to that of conventional OPC-based well cements
- Potential for use as well casing cement without self-degradation

# Scientific/Technical Approach

- Formulation:
  -Slag(S)/Class C fly ash (C) blending system;
  -Slag(S)/Class F fly ash (F) blending system;
  -Class C fly ash (C)/Class F fly ash (F) blending system.

- Initial setting time measurement:
  -ASTM C 191-92; by Vicat needle at 85° C.

- Sample preparation for compressive strength test:
  -200° C autoclave for 5 hours;
  -200° C autoclave for 5 hours + 250° C heat for 24 hours;
  -200° C autoclave for 5 hours + 300° C heat for 24 hours.

## Geopolymer Synthesis at temperature, ranging from 60°C to 250°C

**Step 1. Dissolution of $Al_2O_3$-/$SiO_2$-enriched reactants in alkali medium**

$$-(NaO.SiO_2-)_n- \longrightarrow xNa^+ + yH_3SiO_4^- + zOH^-$$

sodium silicate

$$3Al_2O_3.2SiO_2 + zOH^- \longrightarrow xAl(OH)_4^- + yH_3SiO_4^-$$

mullite in fly ash

**Step 2. Reaction between these dissociated ionic species**

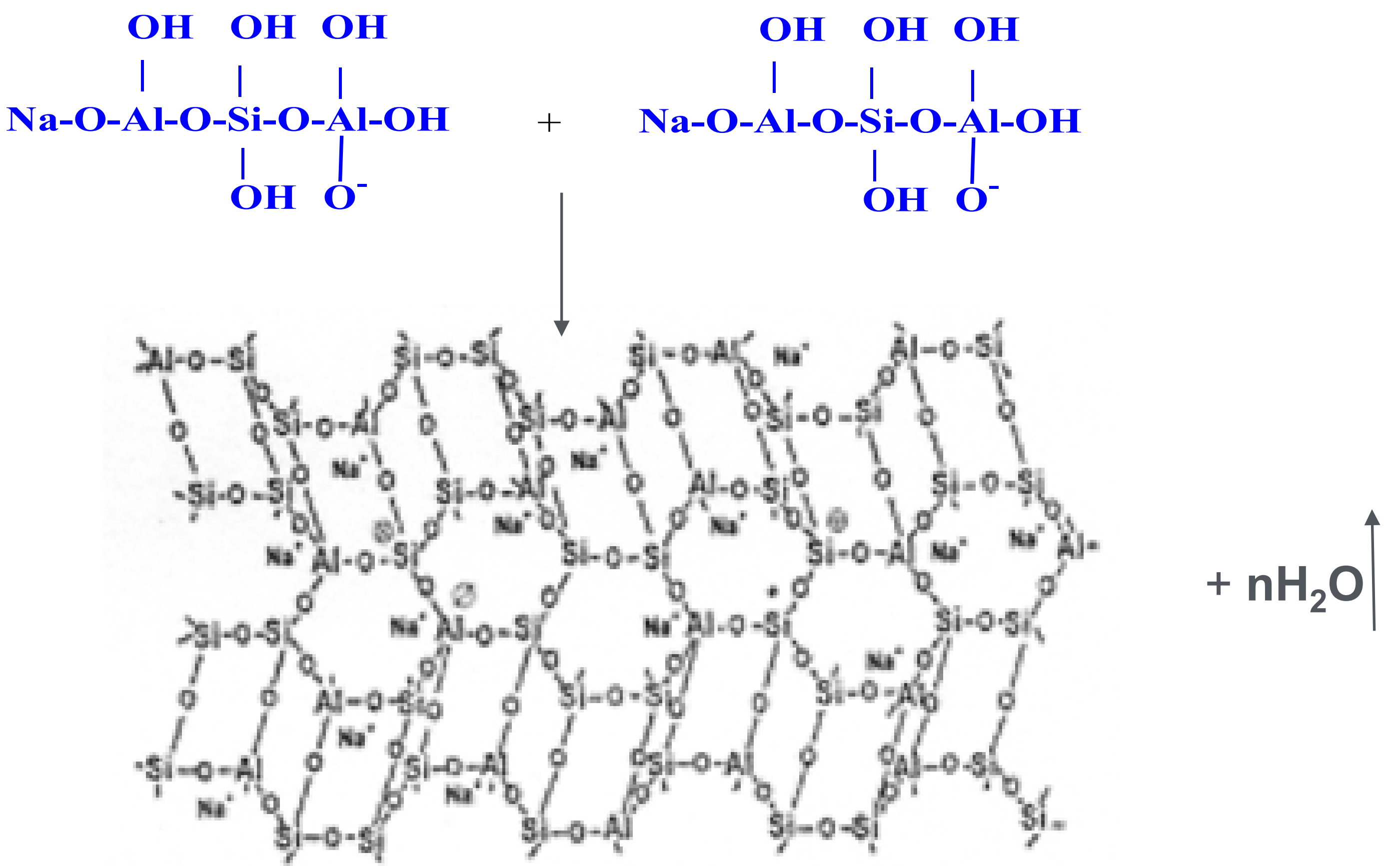
$$Na^+ + H_3SiO_4^- + 2Al(OH)_4^- \longrightarrow Na\text{-}O\text{-}Al(OH)\text{-}O\text{-}Si(OH)(OH)\text{-}O\text{-}Al(OH)(O^-)\text{-}OH + 3H_2O$$

Pre-geoplymer

$$Na^+ + yH_3SiO_4^- + Al(OH)_4^- \longrightarrow NaAlSi_2O_6.H_2O$$

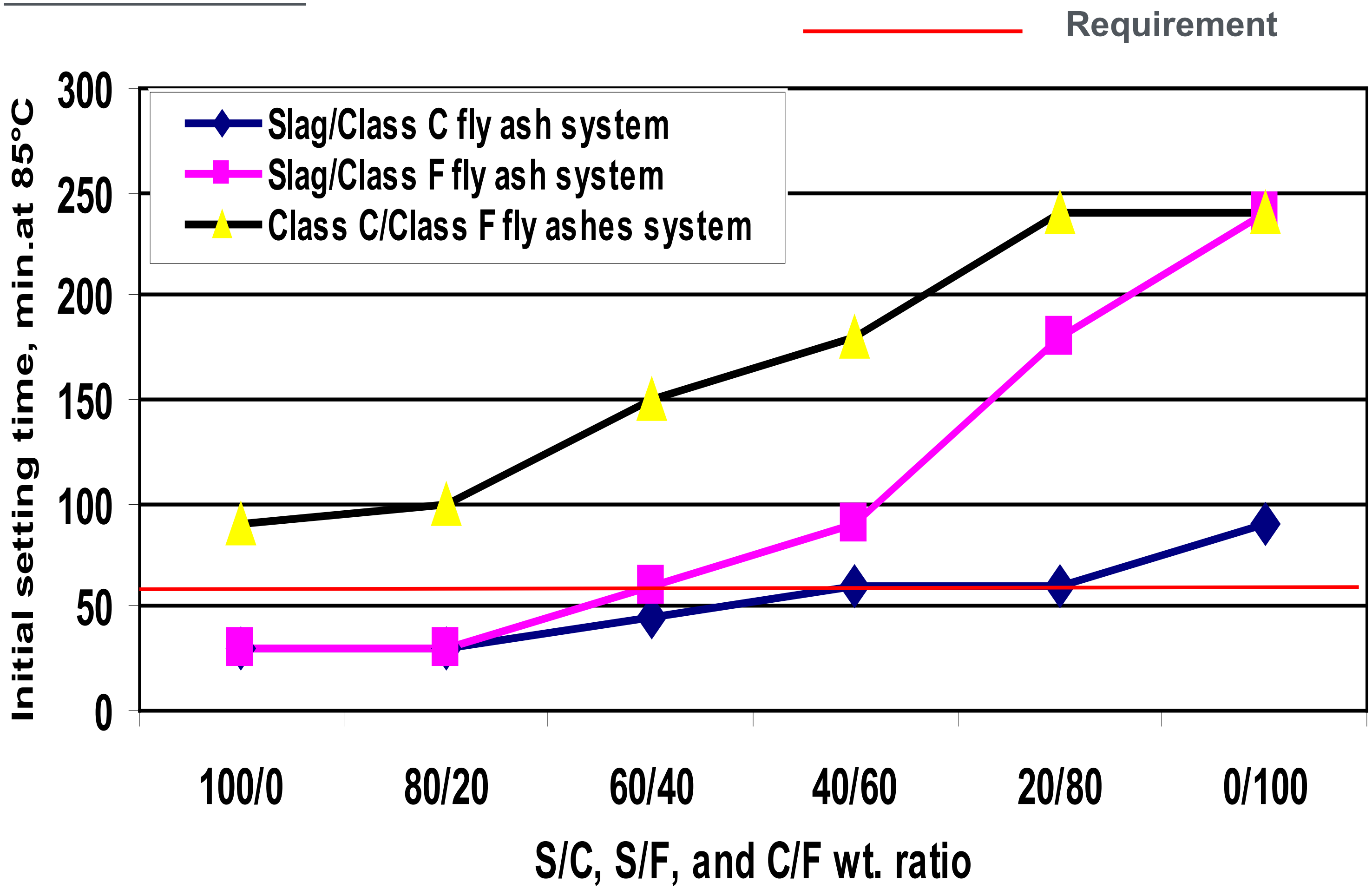
Na-Zeolite, Analcime

## Step 3. Self-polycondensation between pre-polymers

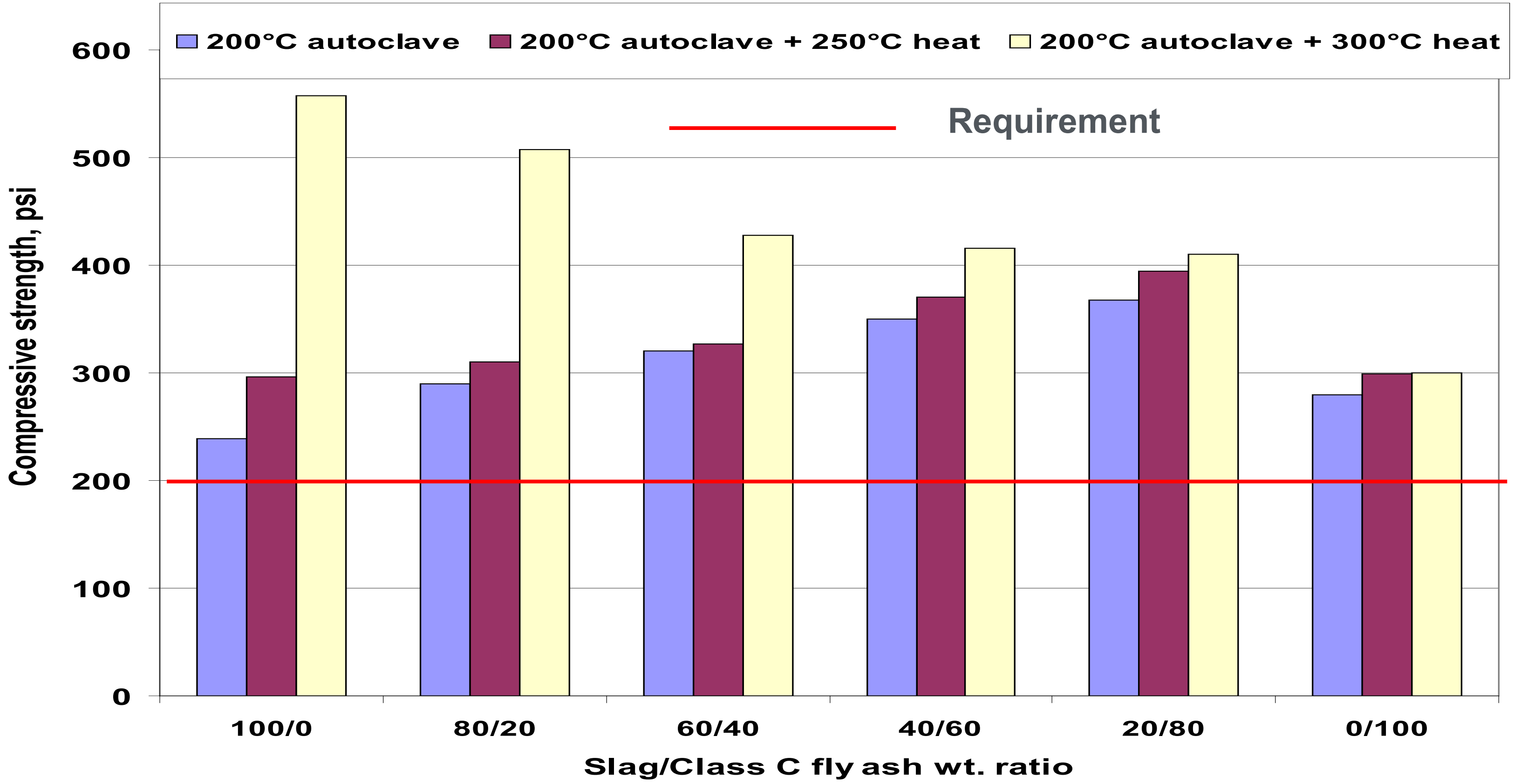



Geopolymer

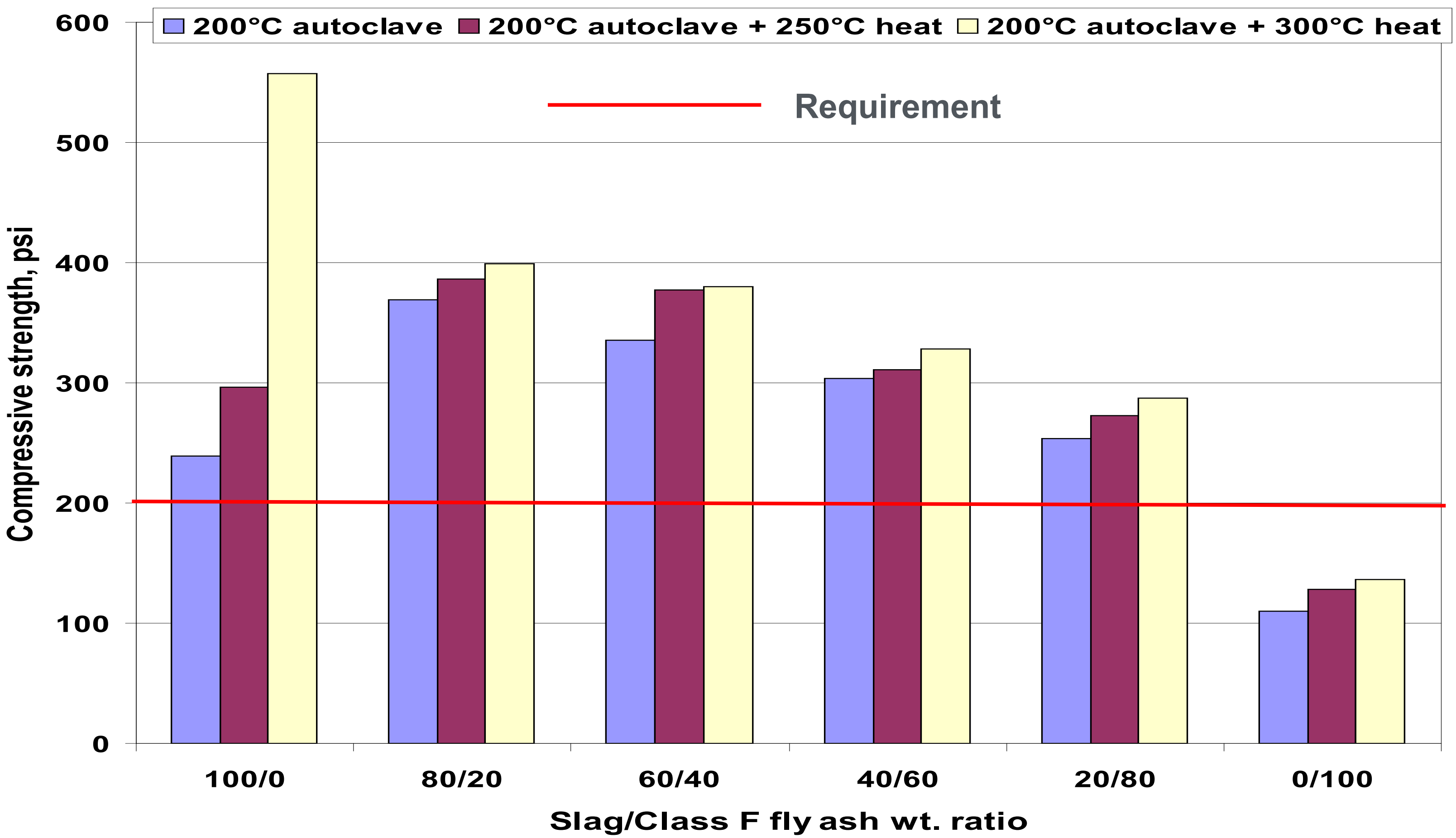
## Changes in Initial Setting Time as a Function of S/C, S/F, and C/F Ratio at 85° C



## Compressive Strength for Specimens Made with Various Slag/Class C Fly Ash Ratios Under Three Different Thermal Conditions



## Slag/Class F Fly Ash System



# Selected Formulations for Next Tasks

| System | Initial setting time, min. at 85° C | Phase composition | | Compressive strength, psi | | |
|---|---|---|---|---|---|---|
| | | Major | Minor | 200° C autoclave | 200° C autoclave + 250° C heat | 200° C autoclave + 300° C heat |
| 20%Slag/80% Class C | 80 | Hydrogarnet + boehmite | C-S-H + Ettringite + Brucite | 360 | 390 | 410 |
| 40%Slag/60% Class F | 90 | Geopolymer + Analcime (Na-zeolite) | C-S-H + Ettringite + Brucite | 304 | 311 | 328 |

# Accomplishments, Expected Outcomes and Progress



## Current Ongoing Work:

- Development of expandable and swellable additives contributing to10% increase in total volume of sealers

  -Use of alkali-swellable bentonite and smectite clay as well as foaming reagents

- Development of self-degradable sealers

  -Use of low heat temperature (>150° C) degradable biopolymer additives and fibers such as tertiary ester-linked biopolymers

**After 200° C autoclave + 250° C heat** → **After water-impregnation**

**7.8% Porosity** **48.9% Porosity**

# Project Management/Coordination

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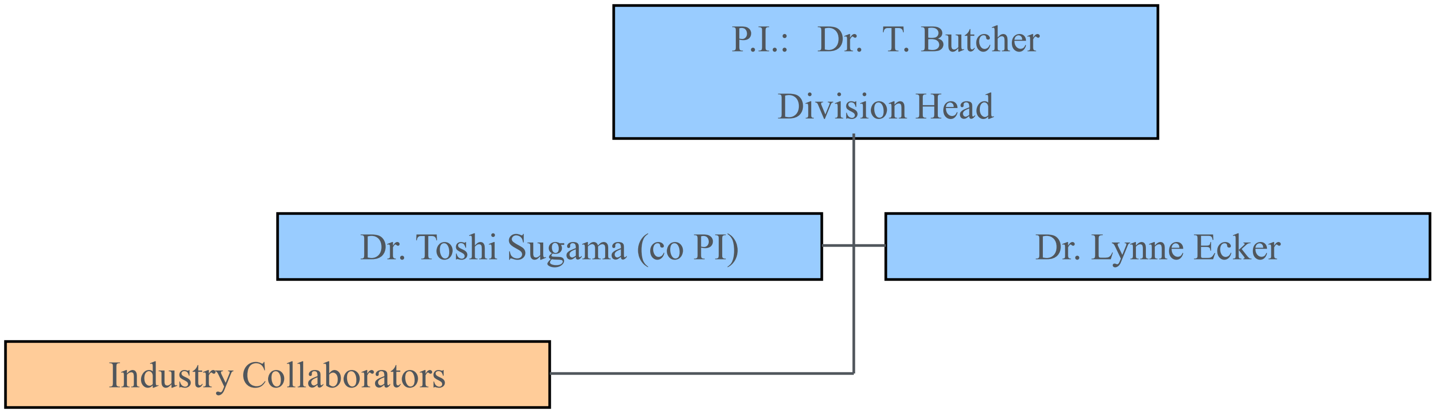


***Services – as needed***

- Laboratory Support
- Other BNL analytical tools
- Outside purchased services
- Outside Analytical Labs
- X-ray diffraction Lab and NSLS
- Students