Application of Data Science Techniques to Estimate Soluble Alkali Contribution from Fly Ashes for Determination of Concrete Pore Solution Chemistry

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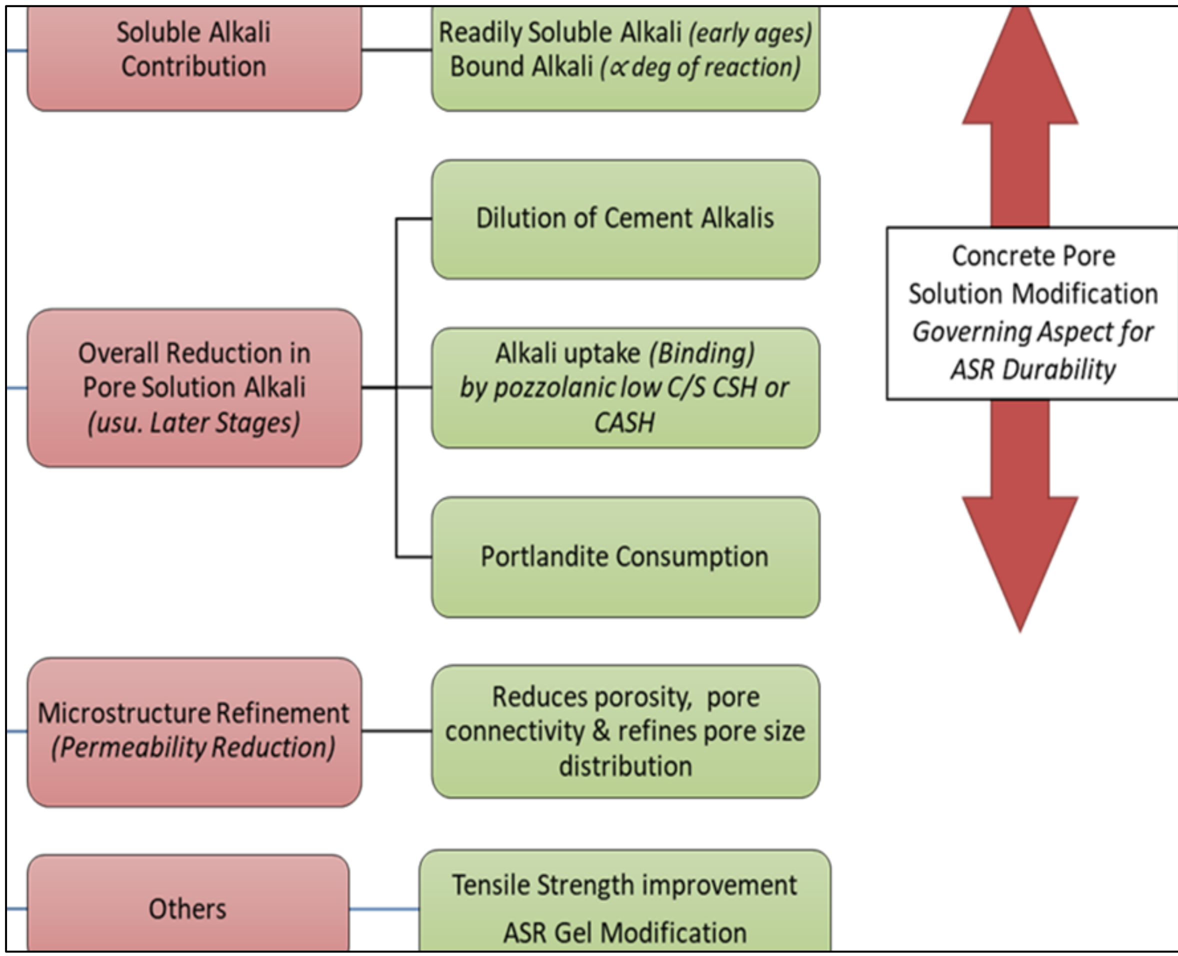
Concrete Durability & Alkali Silica Reaction Mitigation

- Fly Ash, a coal combustion product is most widely used SCM in North America
- Industry, National & State DOT Specifications rely on fly ash to reduce risk of deleterious reactions (ASR Control)
- achieve durable field performance of concrete structures in field.

Proposed Mechanisms for Improving Concrete Durability by Fly Ashes



Current Challenges: Fly Ash & Specifications

Decrease in Fly Ash Production

- ❑Rapid Rise of Natural gas
- ❑Emission Standards requirements for coal fired power plants
  - ➢*No New plants constructed after 2013*
  - ➢*Existing Plant Retirement*

Continuous Changes in Fly Ash Composition

- ❑Changes to Plant Operations *(to meet emission standards)*
- ❑Changes to Coal Burning Processes
- ❑Changing Coal Type being burnt

Decreasing Usage Rate of Fly Ash

- ❑Fly Ash not meeting "traditional" ASTM Specifications
  - ➢*80% of unused fly as disposed as landfill (Lack of Storage Options)*

Increase in Supply "alternative" fly ash varieties

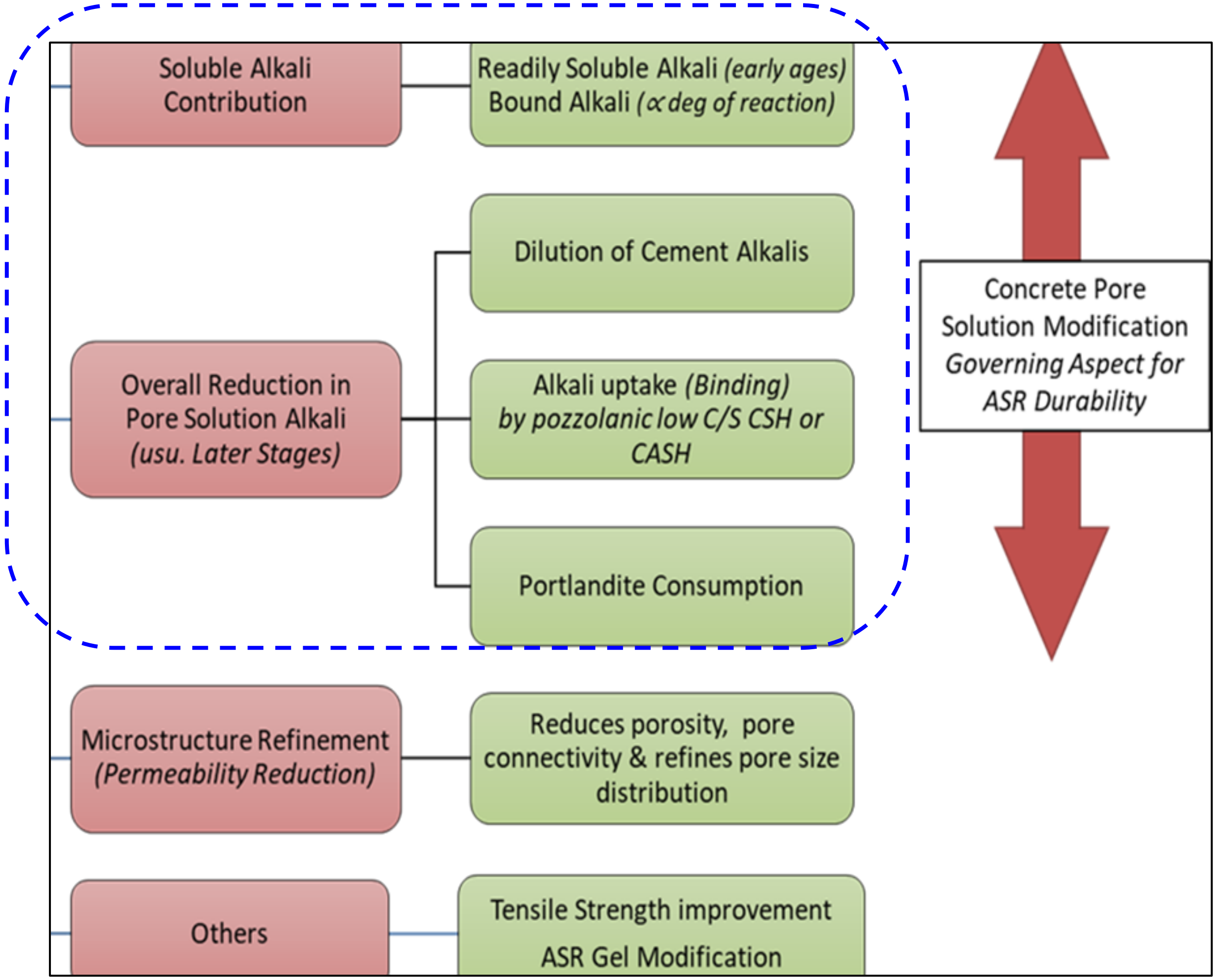
- Blended Coal Ash
- Blended Fly As
- Beneficiated Fly Ash
- Ponded Fly Ash
- Remediated Fly Ash

Decreasing Availability

- "quality", "traditional" or "production" fly ash varieties (Class C & F)
- Fly Ash meeting ASTM Specifications

Concrete Durability & Alkali Silica Reaction Mitigation

Proposed Mechanisms for Improving Concrete Durability by Fly Ashes



Direct influence of modifying pore solution

Theory of Concrete Pore Solution

Objective: Develop innovative model to estimate pore solution chemistry of concrete mixes.

Chemical Screening Tool (CST) for Rapid Prediction of Optimum Fly Ash Dosage for ASR Mitigation
(Saraswatula et al., 2022; Mukhopadhyay et al., 2023)

Pore Solution Chemistry

- ↑ Soluble Alkali → ↑ pore sol conc
- ↑ Alkali binding → ↓ pore sol conc

\+ **Total Soluble Alkali**

− **Alkali Binding**

Readily Soluble Alkali (Early Ages) ↔ **CEM > C FA > F FA**

Bound Alkali (released ∝ degree of reaction) ↔ **CEM > SF > C FA > F FA**

SiO2/CaO Ratio of Ingredient (composition) ↔ **SF > F FA > C FA > CEM**

Degree of reaction ↔ **CEM > SF > C FA > F FA**

Total Soluble Alkali
CEM (~ 75%) > SF (~70-75%) > C FA (50-60%) > F FA (30-50%)

↓ Ca/Si of CSH → ↑ alkali binding
SF > F FA > C FA > CEM

› TTI Model-2: Prediction of pore solution concentration (PSC) of binary and ternary concrete mixes containing fly ashes (FA) & silica fume (SF) at long-term hydration ages.

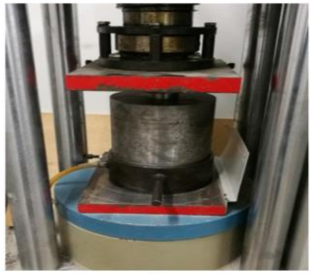
$$Na^{+}\left(\frac{mol}{L}\right)=\frac{\sum_{i}^{n}\frac{\left(2m_{f,i}^{(Na_2O)}\cdot\frac{M_i}{M_{cm}}\cdot f_i\right)}{mm_{Na_2O}}}{\left[\left(\frac{w}{cm}-\sum_{i}^{n}k_i\alpha_i\right)+\left(\sum R_d\cdot m_{CSH}\right)\right]}$$

- Total alkali dissolution
- fi → ratio of soluble to total alkali
  - Cement, Fly Ashes & SF → 75% (

- Alkali Binding
- Rd → distribution ratio of alkali in hydration product (Hong, et al., 1996)
- m_{csh} → mass and stochiometric composition of CSH from hydration reactions

Current Approaches to Determine Long Term Pore Solution Chemistry

ACCURACY - RELIABILITY - COMPLEXITY



(b)

Extraction
1. Contingent on applied pressure
2. Early ages ~7 days
3. No standardized procedure
4. Difficult for SCMs esp. SF

Parameter		**NIST Model** *(Bentz et al., 2007)*	***NIST + ASTM C 311*** *(Mukhopadhyay et al., 2019)*	**GEMS Thermodynamic Modelling** *(Lothenbach., 2008)*
Overall Approach		Empirical	Empirical	Thermodynamic model
Soluble Alkali from Ingredients	Cement & Silica Fume	75% of Bulk Alkali	75% of Bulk Alkali	Alkali dissolution based on degree of reaction *QXRD/ TGA/ SEM analysis*
	Fly Ash (FA)		***= Available Alkali (AA, ASTM C 311)***	
Alkali Binding		✓ Silica Fume × Fly ashes	✓ Silica Fume *(NIST Model)* × Fly ashes	✓ In Built CSHQ model
Comments		• Rapid approach • *High error & Low reliability for Fly Ash mixes*	• Rapid approach • **Improved accounting of soluble alkali from Fly Ashes** • *AA ~ total soluble alkalis from FA* • *Consideration of alkali binding is important* • ***ASTM C 311 discontinued??***	• Accurate & Reliable • *Reliability → accuracy in quantifying minerology & degree of reaction inputs* • *Complex and not suited for rapid implementation*

Significance of Available Alkali test (Currently, ASTM C 311)

- The Available Alkali test dates back to the 1940's , developed at the US Bureau of Reclamation (Moran and Gilliland 1950; Mielenz 1967).
- The test procedure **was created to measure the rate of release of alkali from pozzolans.**
  - eventually adopted by ASTM (ASTM C 311) to **estimate the amount of alkali in pozzolans that was "available" for contributing to ASR**
- Current C 311 -> 5g SCM + 2.5 g $Ca(OH)_2$ + 10 ml water → 38±2°C for 28 days → Measure Na &K (ppm)
- Typical drawbacks of this test procedure well documented:
  - Test takes too long to complete ; Poor agreement between labs ; Calibration standards do not match test samples ; Alkali release continues past the 28-day curing period *(Lee, 1996)*
- Major Criticism:
  - **Lack of Correlation with ASTM C 1567 Mortar Bar Expansion Measurements**
  - "The available alkali content of the fly ash generally did not produce the best correlations to measured expansions; this was especially true if one was allowed to change fly ash replacement level" (*Source: Schlorholtz, S. M. (2015). Alkali Content of Fly Ash – Measuring and Testing Strategies for Compliance)*

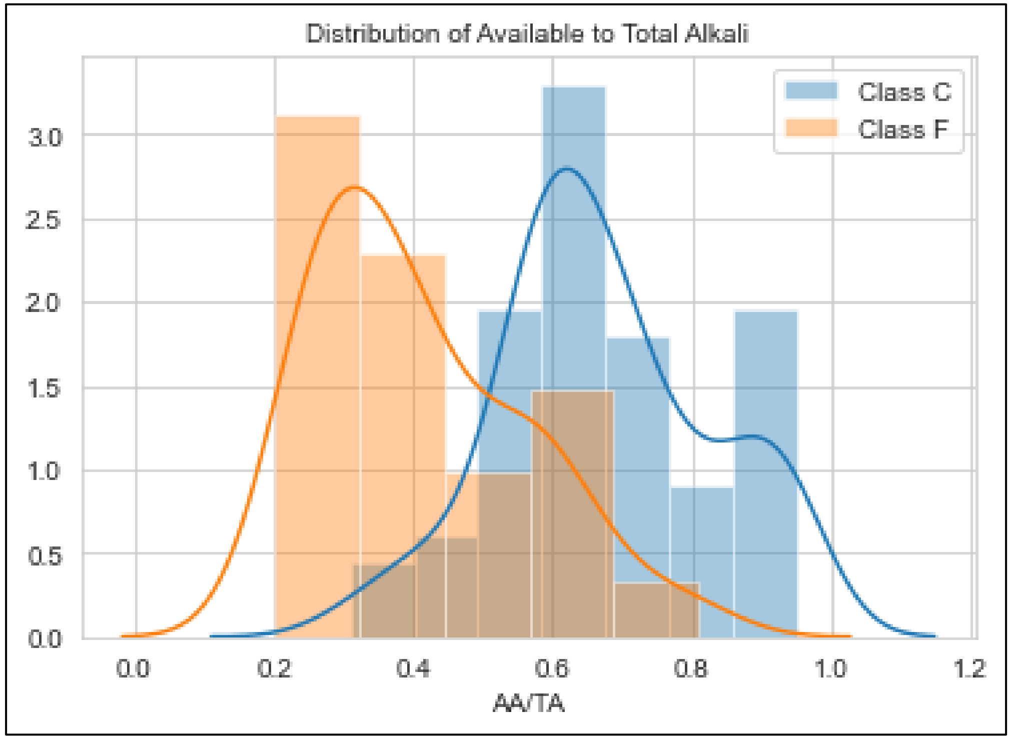
Summary of Data used for Machine Learning Model Development

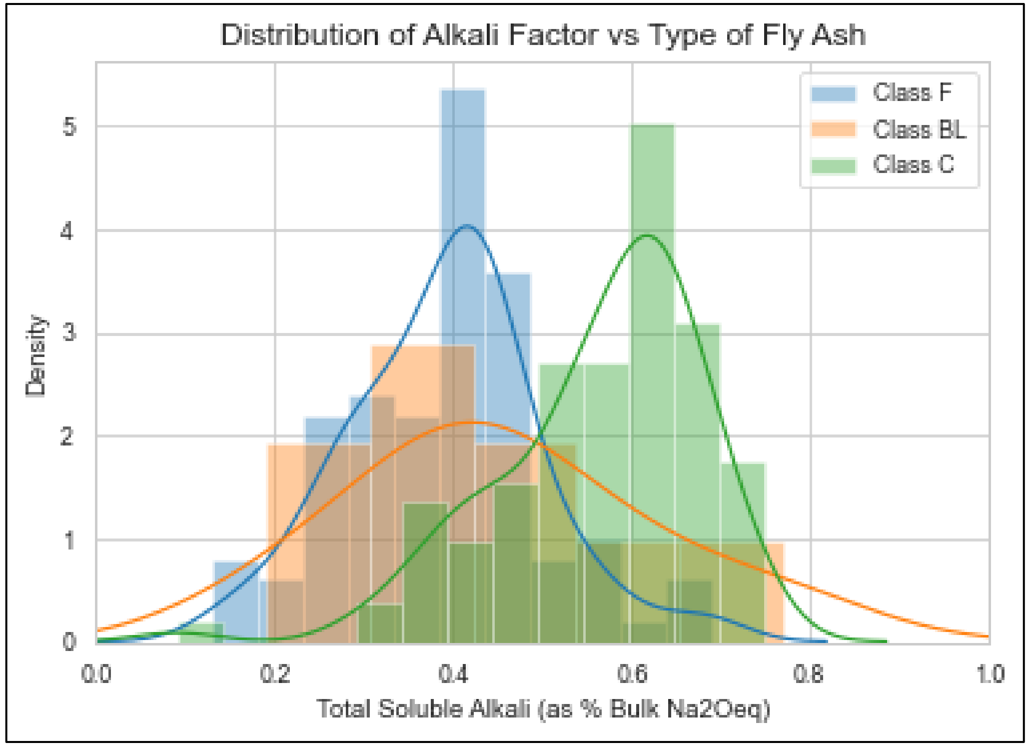
Dataset (Summary)	**Bulk Oxide Composition**	**X-Ray Diffraction (QXRD)**	**Soluble Alkali Measurements**		**Pore Solution Extraction Data**	**Supplemental data on FA reactivity**	**#**
		Amorphous Content, Crystalline Content & Reactive Crystalline %	Water Soluble Alkali ASTM C 114	Available Alkali ASTM C 311	Na & K Concentration *(1 to 180 days extraction measurements)*	TGA, XRD, Isothermal calorimetry, others.	
Set- 1	✓	×	×	×	✓	✓	200
Set - 2	✓	×	✓	✓	×	×	36
Set- 3	✓	✓	×	✓	×	✓	194
Set -5	✓	✓	×	×	×	✓	57
Set -4	✓	✓	×	×	×	×	74
Set – 5*	✓	✓	✓	✓	✓	✓	53

*Experimental TTI Laboratory

- **400+ data points collected from literature+ experimental work at TTI**
- Literature Compilation → **Spanning ~ 40 years (1980 – 2020)**
  - Covering different aspects of alkali dissolution, reactivity, minerology & pore solution – FA & FA Mixes
  - Fly Ash types – Class C , Class F , Blended Fly Ashes (Blended coal/blended ash)

Evaluation of Available Alkali Test (ASTM C 311)





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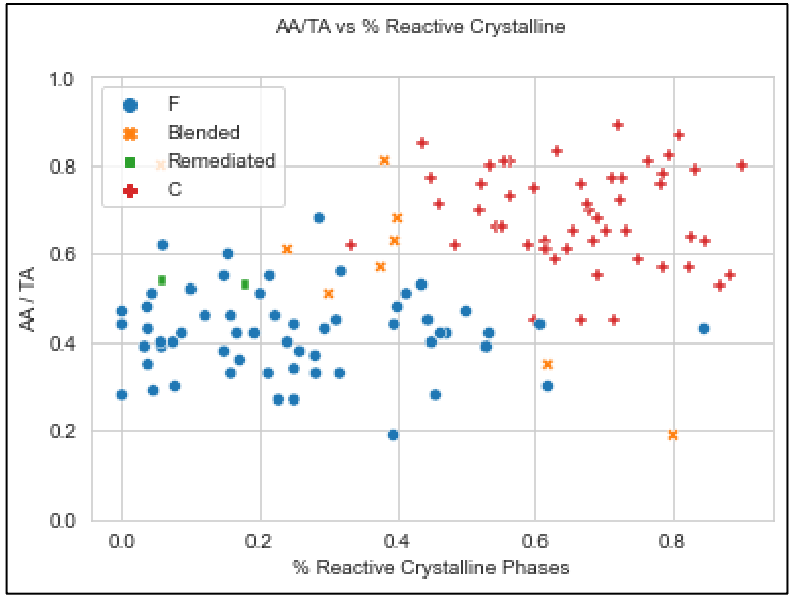
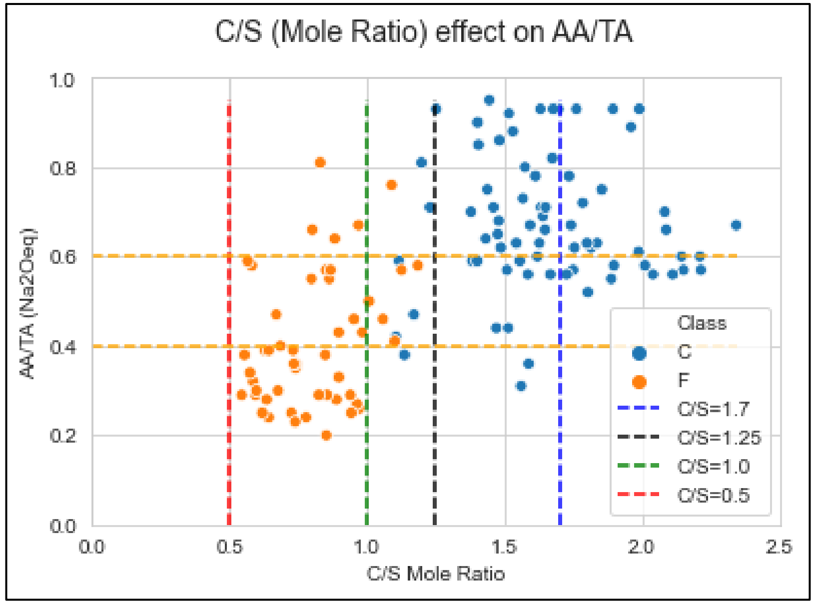
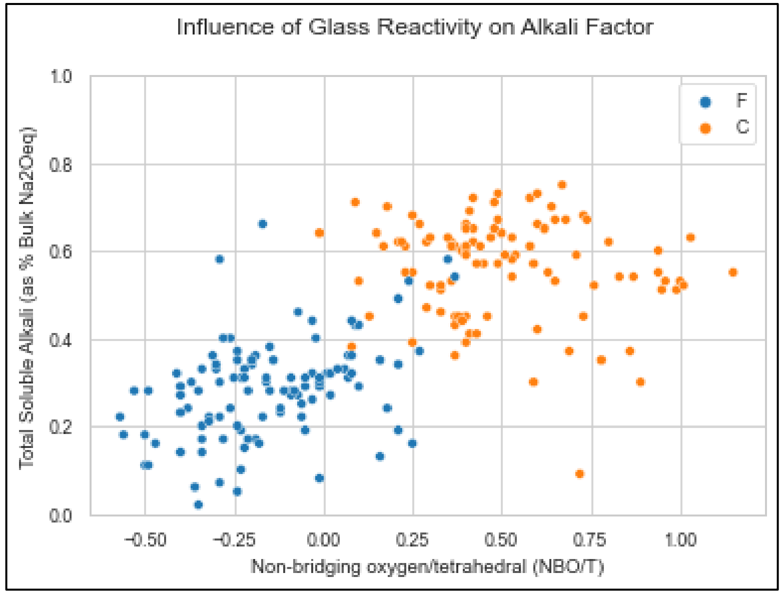






Cement Hydration $C_3S + 2H = 0.5C_{1.7}S_1H_{1.5} + 0.5\,CH$

$C_2S + 3H = 0.5\,C_{1.7}S_1H_{1.5} + 1.5\,CH$

Fly Ash Hydration $1.5\,CH + S = C_{1.5}SH_{1.5}$

Silica Fume Hydration $S + 1.1\,CH + 2.8\,H = C_{1.1}SH_{3.9}$

Fan et al., 2015; Haha et al., 2010; Liao et al., 2019; Lothenbach et al., 2011; Ramanathan et al., 2019; Zeng et al., 2012)

Development of Innovate Model to Predict Concrete Pore Solution Chemistry

TTI Model-2 Research Approach

Experimental Study

- Available Alkali (AA) from Fly Ashes (*ASTM C 311)*
- QXRD Measurements
- GEMS Modelling

Machine Learning Model Development

- Bayesian ML Model to predict AA from FA
- 230 Data Points (1980-2019)
- 75%/25% train/test

Development of TTI Model-2

- Combined Effect of
  1. *Soluble Alkali from CEM & SF*
  2. *Available Alkali from FA*
  3. *Alkali Binding by pozz. CSH*

Validation Study

- Extraction Measurements
- GEMS Thermodynamic Modelling

Soon to be published

Machine Learning Model – Our Approach

Current Research: Bayesian Monte Carlo Markov Chain (MCMC) Modelling Approach

❑ Why Bayesian Approach ?

- ✓ Probabilistic Modelling
- ✓ Data is treated as random variables i.e. *true* distribution (kernel-density functions) opposed to point observations
- ✓ Uncertainty quantification into model parameters using Bayesian statistical inference.

❑ Why Markov Chain ?

- ✓ Pore Solution Concentration (dissolution)and extraction measurements → time dependent process
- ✓ State of a system at the current iteration step (t) is only dependent on the previous iteration step (t-1)

❑ *How are new samples generated?*

- ✓ *Markov Chain with adaptive No U turn sampling (NUTS) algorithm.*
- ✓ *Samples are generated from a "proposed" posterior distribution of model parameters*

❑ Monte Carlo Simulations

- ✓ 100,000 loop cycles based on 1000 sets of alkali concentration from the posterior distributions of the model parameters
- ✓ The model predictions were used to calculate 2.5th and 97.5th percentile values to obtain 95% prediction intervals.

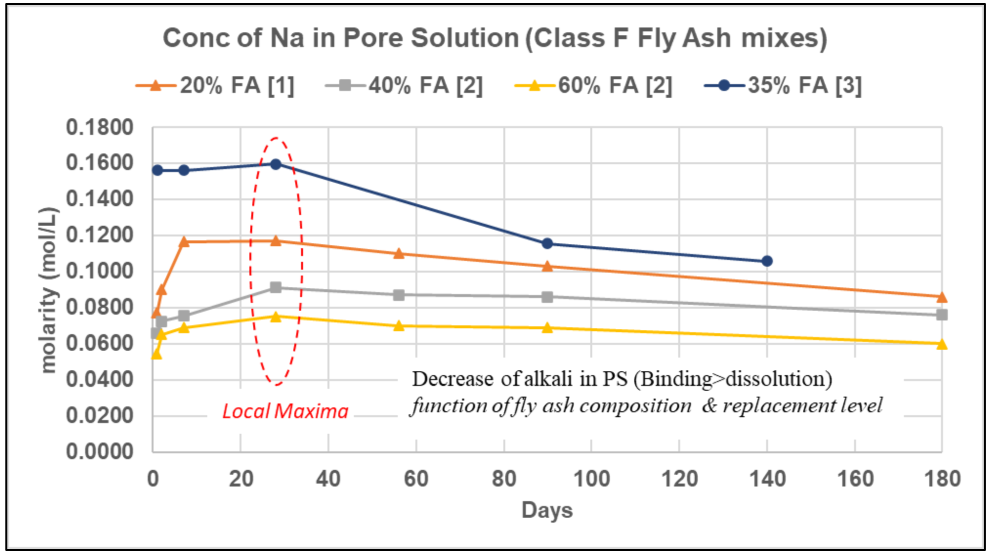
TTI Model Approach (Soluble Alkali Determination from Fly Ashes)

Three prior steps were used calibrate certain parameters used in ML model development.

- Step 1: Water Soluble Alkali from Fly Ashes : Simplified Regression Based Model
- Step 2: Thermodynamic Modeling to estimate “total” soluble alkali contribution from ingredients into pore solution *(cross validation based on pore solution extraction data)*
- Step 3: Non-Linear Optimization to curve fit (time step process) the to alkali dissolution in pore solution and estimate fitting parameters (from step 2*)*

Challenges

- Literature extraction data is scarce (reliability & complexity)
- Soluble Alkali dissolution vs Pore Solution Concentration (PSC) vs age:
  - Soluble alkali increases with age
  - PSC increases up to 28 days but typically decreases beyond 28 days;



1 - Shaffer et al., 2003 ; 2 - Shaffer et al., 2006; 3 – Weerdt et al., 2013

Development of Innovate Model to Predict Concrete Pore Solution Chemistry

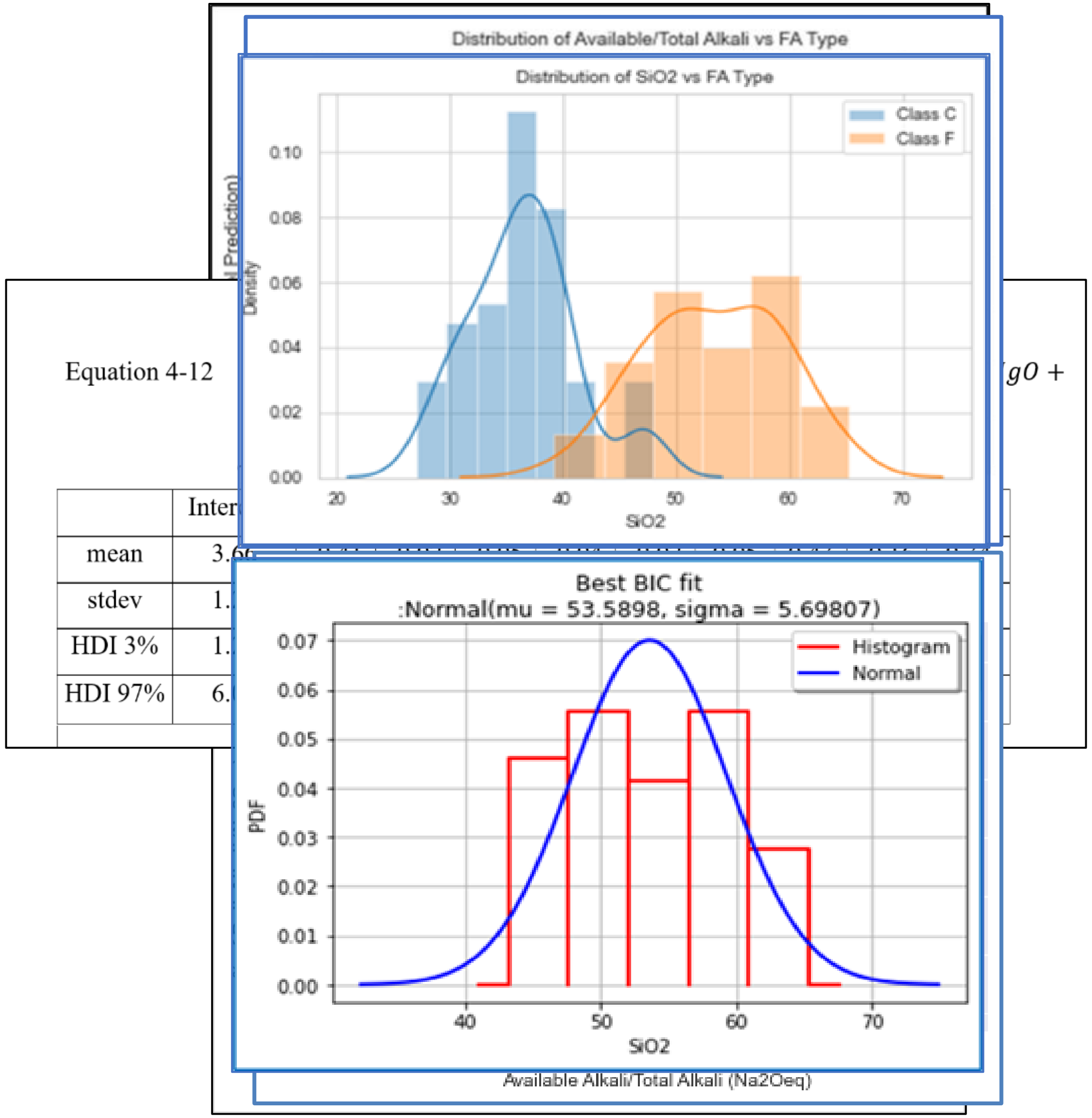
Major Findings & Results (TTI Model-2)

1. Machine learning (ML) model to predict available alkalis from fly ashes
   - *Bayesian Markov Chain Monte Carlo (MCMC)*

2. Results from ML Model

3. Validation study with experimental measurements
   - Overall, MAE → 9.2% ; Class F FA → 7.3%, Class C FA → 10.1%
   - *Available Alkali Test (1s) → 15-20% (Schlorholtz, 2015)*

4. The ML model predictions → develop Bayesian linear regression equation for incorporation into excel based tool

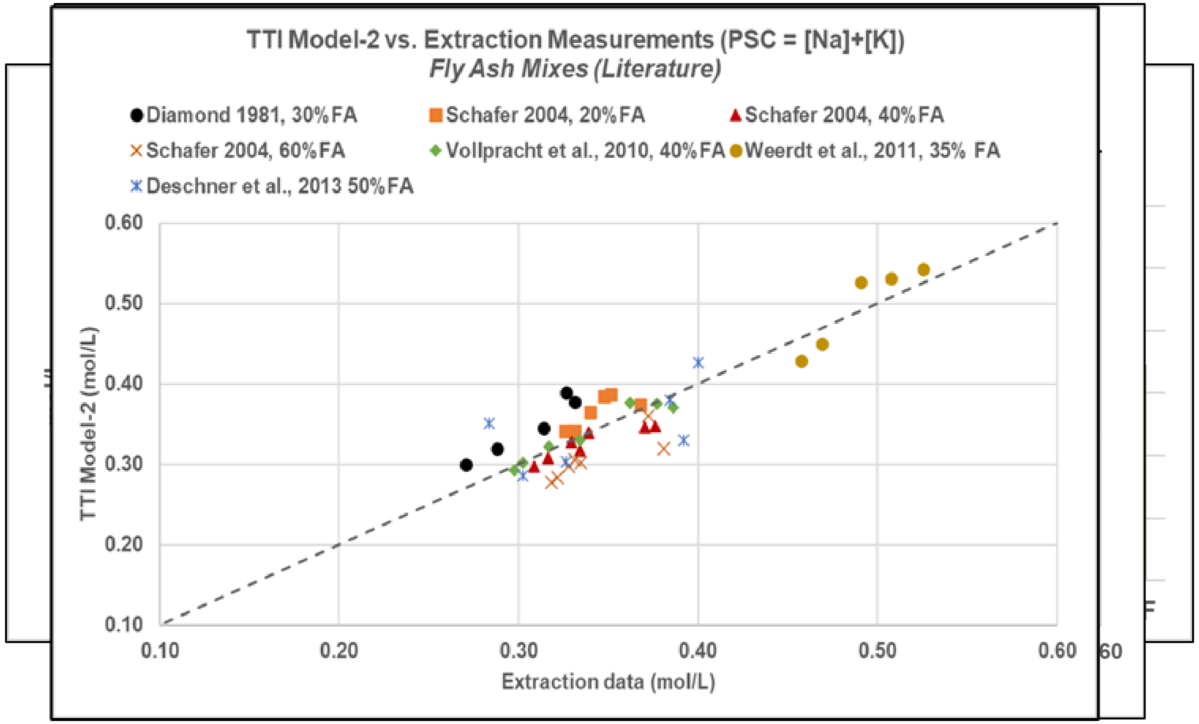


Major Findings & Results (TTI Model-2)

1. TTI Model-2 PSC predictions for binary & ternary mixes at long term hydration ages

2. TTI Model-2 PSC vs. GEMS Thermodynamic Model
   - Marginally higher for FA mixes (secondary hydration products); model R2~ 77-87%

3. TTI Model-2 PSC vs. Literature Extraction Measurements
   - Fly Ash Mixes → MAE ~ 7.8% - 11.7%



Publication under progress

Chapter 4: Development of Innovate Model to Predict Concrete Pore Solution Chemistry

ACCURACY - RELIABILITY - COMPLEXITY

Parameter		NIST Model	TTI Model-2	GEMS Thermodynamic Modelling
Model Approach to Predict Pore Solution		Empirical	**Mix of Empirical – Kinetic Model**	Thermodynamic model based on kinetics, dissolution and precipitation reactions
Soluble Alkali from Ingredients	Cement	75% of Bulk Alkali	75% of Bulk Alkali	Alkali Dissolution based on QXRD/ TGA/ SEM analysis
	Fly Ash	*Empirical:* 75% of Bulk Alkali	**Machine Learning Model for Soluble Alkali Estimation**	
Alkali Binding due to Fly Ash Incorporation *(& Methodology)*		X	**Stoichiometry; Parameters refined using *GEMS & Extraction Data***	✓ In Built CSHQ model
Model Sensitivity *PSC Prediction* ***At similar replacement level & bulk alkali % in Class C vs F Fly Ash***		Cannot Distinguish Class C & F Fly Ash Mixes	✓ Model Sensitive to Composition, minerology and Reactivity of fly ash	✓ Model Highly Sensitive to Composition & reaction kinetics of fly ash
Ease of Use & Reliability		Rapid estimating tool Low reliability for FA mixes	**Rapid estimating tool Easy to use Higher reliability for FA mixes** *(compared to NIST model)*	Accurate & High Reliability *but accuracy of model outputs is contingent on quantification of minerology & reactivity parameters*

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Saraswatula, P., **"Linking Pore Solution Chemistry of Concrete to ASR Potential Through Machine Learning as a Performance-Based Approach"**. Applications, Science, and Sustainability of Coal Ash (Ash atWork), Issue 2, 2020, American Coal Ash Association (ACAA)

THANK YOU

ANY QUESTIONS ?

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