RAPID CHEMICAL METHOD FOR DETERMINATION OF AGGREGATE ALKALI SILICA REACTIVITY

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Alkali Silica Reaction (ASR)

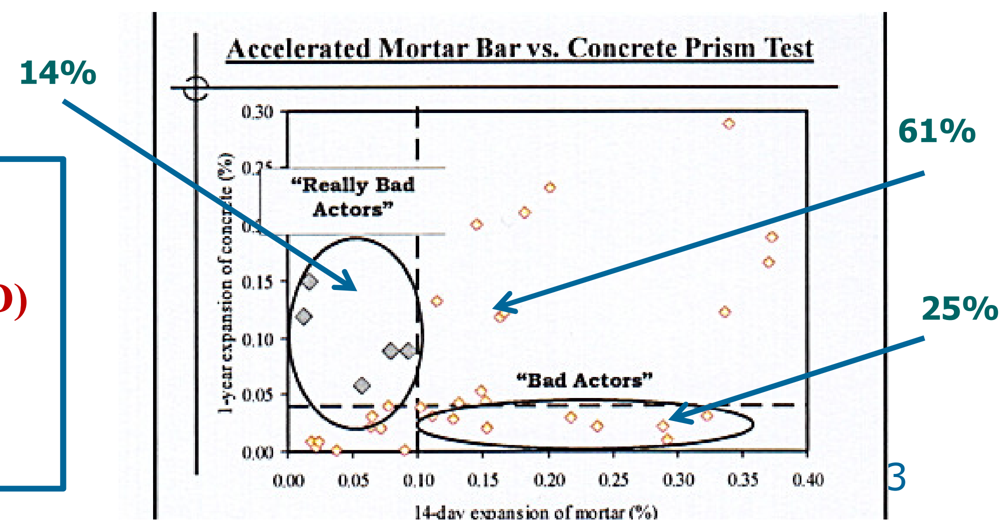
- A deleterious chemical reaction between hydroxyl (OH^-) ions associated with alkalis (Na_2O and K_2O) in cement and other sources and certain reactive silica in coarse or fine aggregates produces **ASR gel**

- When ASR gel **absorbs moisture**, it **expands**, and eventually produces cracks in aggregate particles as well as in the cement paste in concrete.

The Need of a Rapid and Reliable ASR Test Method

	Effect of cement Alkalis	Rapid	Reliable	False positives (passed by 1260 but failed by 1293)	False negatives (failed by 1260 but passed by 1293)
C 1260 (Accelerated mortar bar) 1N NaOH, 80 degC)	No	Yes (14D)	Yes (???) Severe test conditions	increasing	More
C 1293 (Concrete Prism)	No	No (1-2 yrs)	Yes (??) Leaching (20-35%)		
Exposure block	Yes	NO	Yes		

- ❖ Current Approach heavily depends on - AMBT based and prescriptive mix design
  - ❖ 3.5 lbs/yd3, 25% Fly Ash, 0.08% (14D) ASTM C 1567 - ASR still occurs
- ❖ Threshold alkalinity is either not possible or reliable



Objectives

- A fast and reliable test method that can measure aggregate reactivity
  - At various alkali loadings.
  - Matching with field levels of alkalinity and temperature
- A test method of this type will be used as an alternative to ASTM C 1260.
- Provide effective ways of tailoring ASR mix-design options to the level of protection needed.
  - This will ensure valuable resource conservation and avoid paying for premium ASR protection when only minor protection is needed.

Research Projects: Acknowledgements

Texas Department of Transportation (TxDOT)

- **Project 0-6656 - ASR Testing: A New Approach to Aggregate Classification and Mix Design verification, (Sep, 10 – August, 13)**

<u>**Research Team**</u>

- **Anol Mukhopadhyay – Research Supervisor**
- **Kai-Wei Liu (Victor) – Graduate Student**
- **Dan Zollinger**

Innovative Pavement Research Foundation (IPRF)

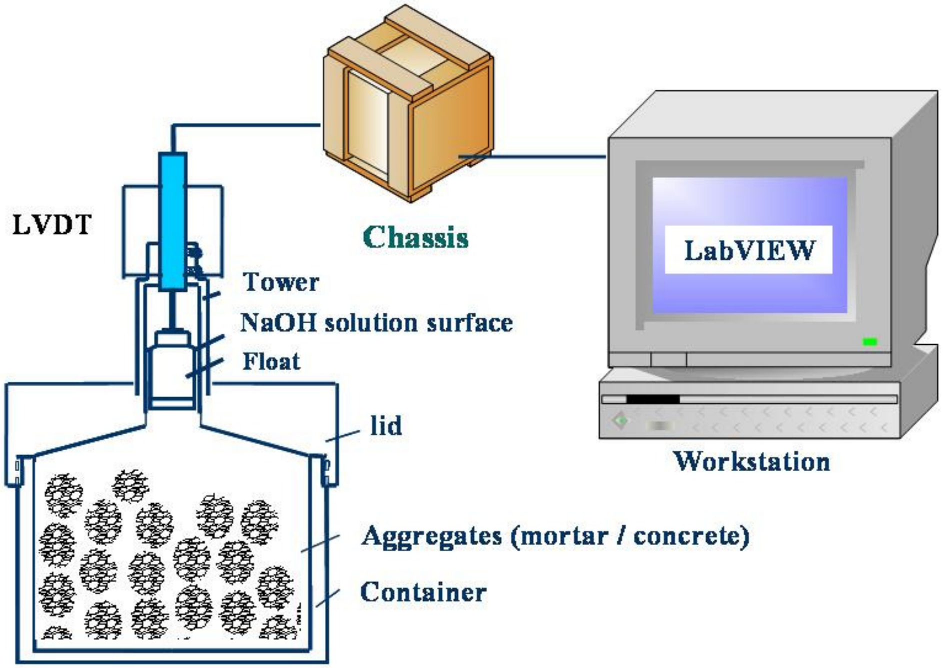
- **Mitigation of ASR in Concrete – Combined Materials test Procedure (01-G-002-03-2, 05-08)**

<u>**Research Team**</u>

- **Texas A&M University (Dan Zollinger, Anol Mukhopadhyay)**
- **University New Hampshire (David Gress)**
- **University of Toronto (Doug Hooton)**

(http://www.iprf.org/products/IPRF-03-2-Final%20Report-12.7.09.pdf)

ASR Testing by VCMD and Measurement of Activation Energy

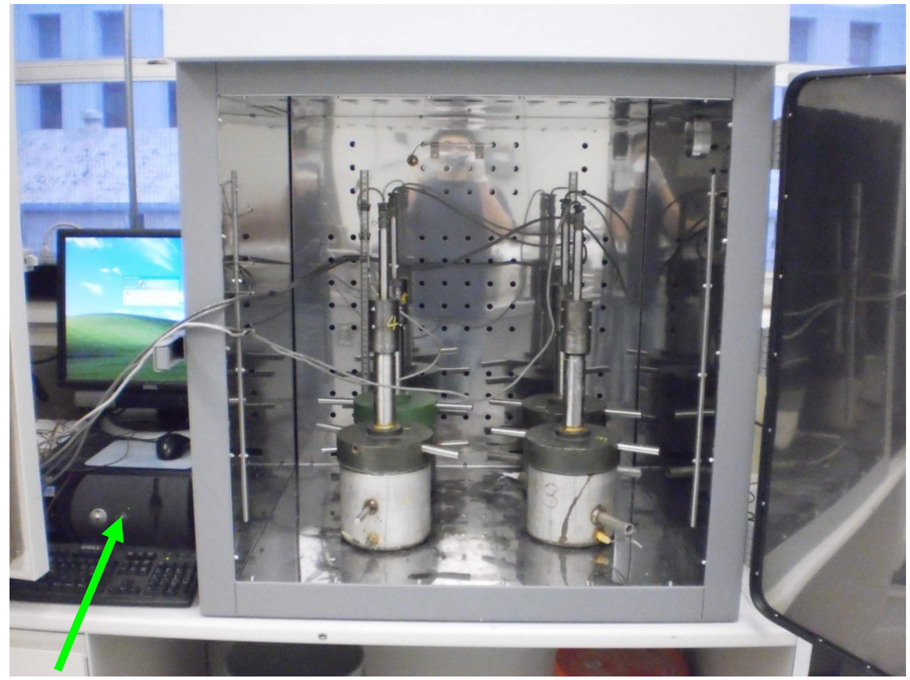


- Chemical test: simulate the aggregate-pore solution reaction
- No aggregate crushing (testing as-received aggregate)
- Fixed aggregate gradation
- Constant aggregate / solution volume ratio
- Short testing period: ~ 4-5 days

VEMD Testing Inside Oven

Oven 1

Data Acquisition System



Oven 2

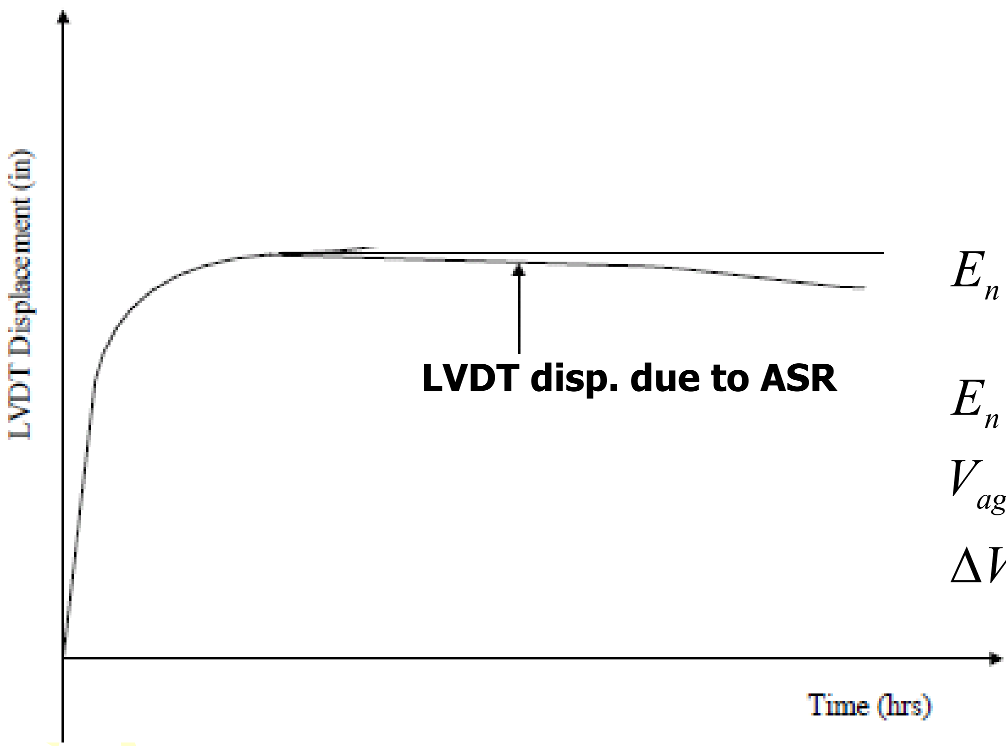
Aggregate	Alkalinity	Temperature
1	2, i.e., (i) 1N NaOH (NH) + CH, (ii) 0.5N NH + CH, and (iii) 0.25NH+CH	3 (60, 70, and 80 degC)
➢ Total 18 test runs - 3 temperatures, 2 alkalinities, and 3 replicas, ➢ Limited tests @ 0.25N NH+CH ➢ 9 VEMDs run simultaneously at one T		

VEMD: Sample Preparation and Procedure

Saturation

1. Aggregate immersed in alkaline solution – kept overnight at RT
2. Vacuum saturation with mild vibration for ~ 2 hours at room T followed by 45 min. at target T
3. Ensures saturation near completion.

- **Place the VEMDs inside an oven and start heating to reach the target T (60, 70, 80°C)**
- **LVDT displacement due to ASR for 90 to 94 hours (~ 4 days) at target T**



$$E_n(\%) = \frac{\Delta V_{ASR}}{V_{aggr.}} \times 100$$

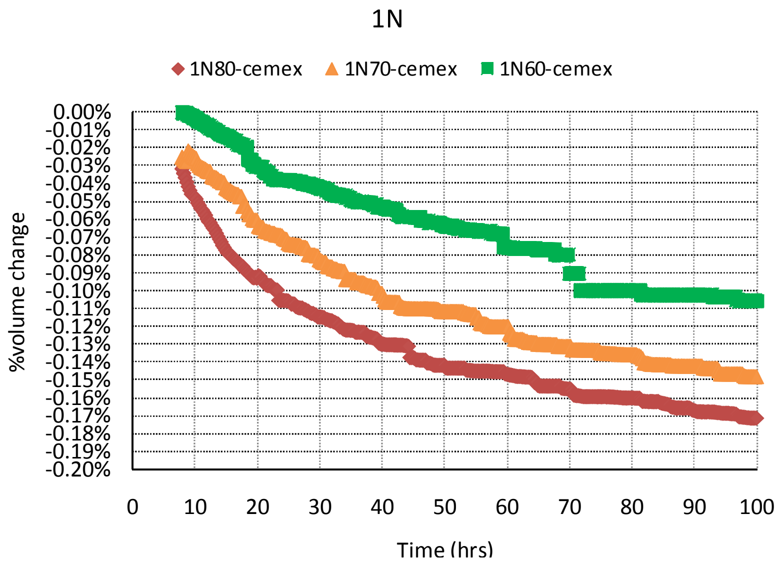
$$E_n(\%) = volume\ change\ at\ n\ hours$$

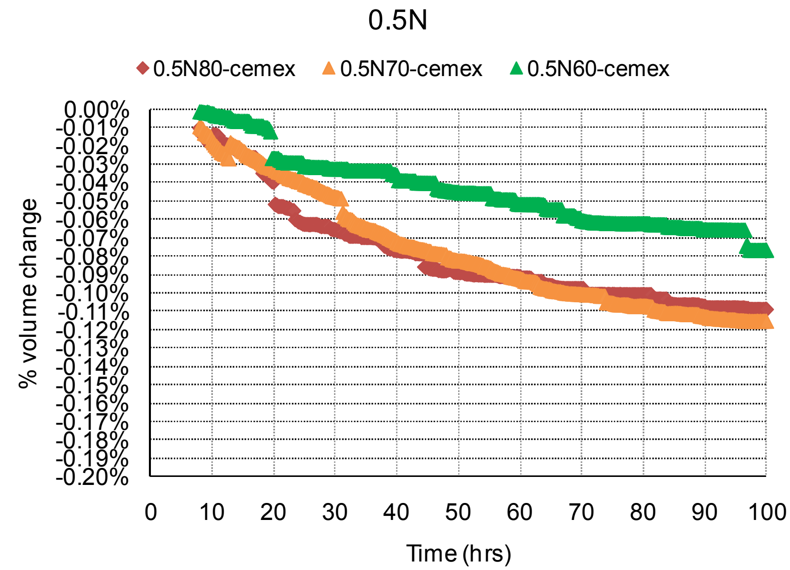
$$V_{aggr.} = initial\ volume\ of\ aggrs.$$

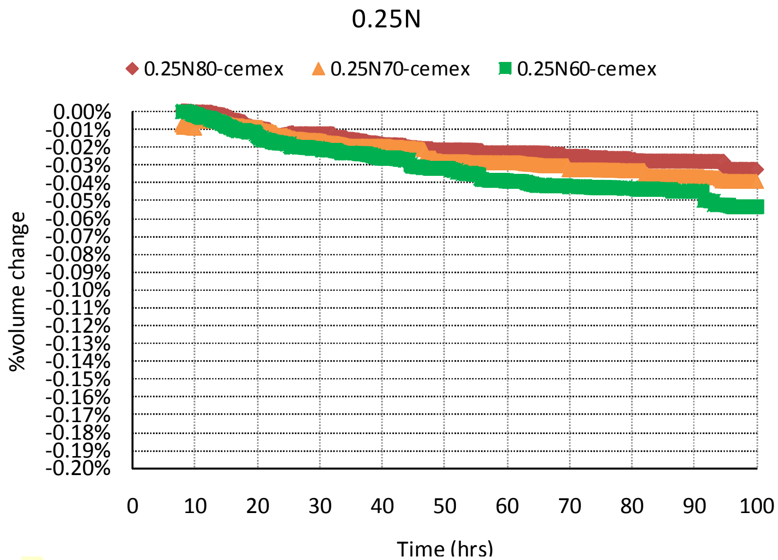
$$\Delta V_{ASR} = volume\ change\ of\ aggr.\ at\ n\ hours$$

Solution Volume Change in VEMD

Highly reactive FA at 3 temperatures







Important Observations: Aggregate-Solution Test

- ❖ VEMD measures net solution volume contraction over time
  - ❖ Pure non-porous glass ball experiments – proof of concept
  - ❖ Support from literatures (Geiker and Kundsen, 1985)
    - ❖ Fine aggregate-alkaline solution (10N NaOH solution) at 50°C in closed system set up
    - ❖ measured chemical shrinkage (CS) over time - the higher the CS the more reactive the aggregate is.

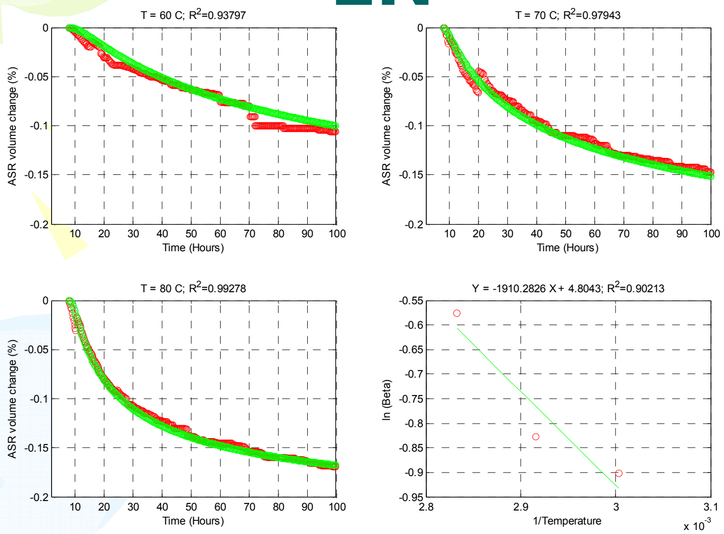
Equipment Calibration

- Testing with water or alkaline solution at any of the selected temperatures (e.g., preferably at 80°C)
  - to check smooth float movement and ensure that the device is leak-proof.

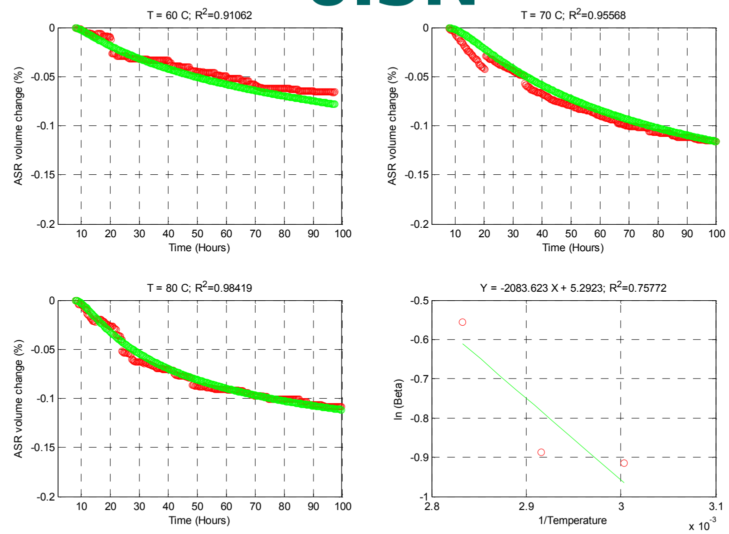
- A one-time calibration testing is recommended. However, it is necessary to repeat the calibration testing whenever there is a change in float and / or a repair in the device.

Compound Activation Energy Calculation

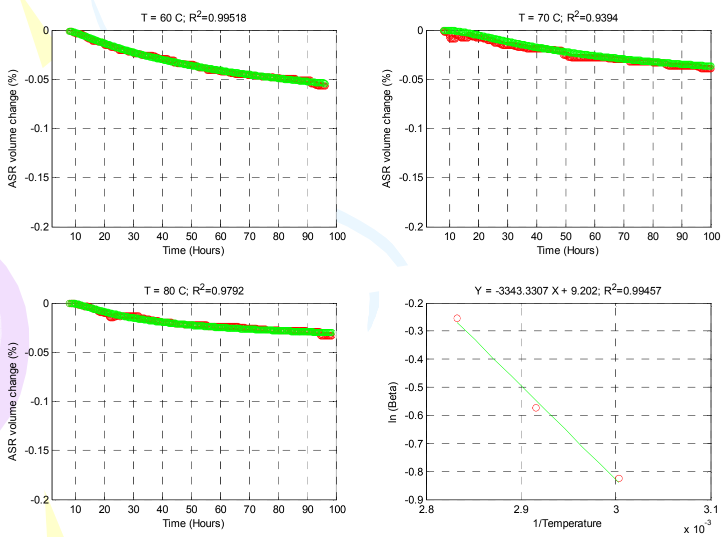
1N



0.5N



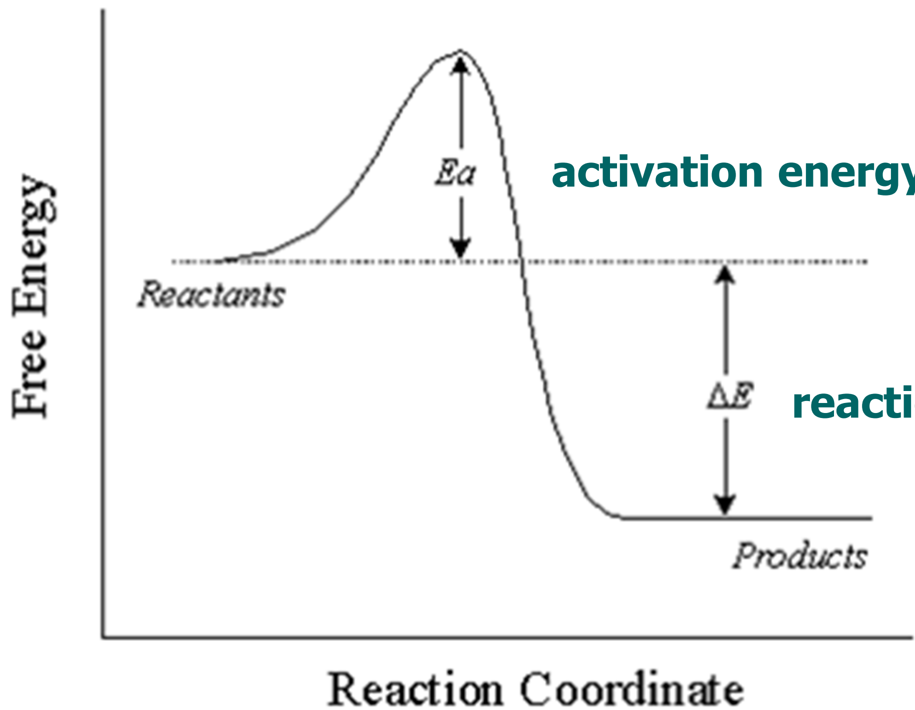
0.25N



$$\varepsilon = \varepsilon_0 e^{-\left(\frac{\rho}{t-t_0}\right)^{\beta}}$$

Normality	Ea
1N	15.88
0.5N	17.32
0.25N	27.80

Measuring Compound or Equivalent Activation Energy



activation energy

reaction energy

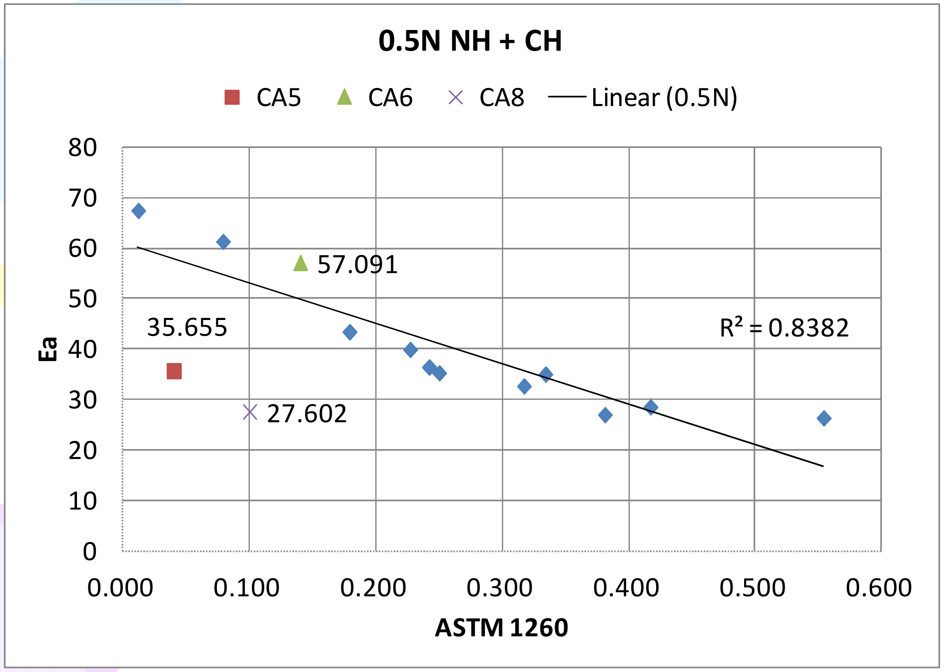
ASR reaction + product formation in VEMD

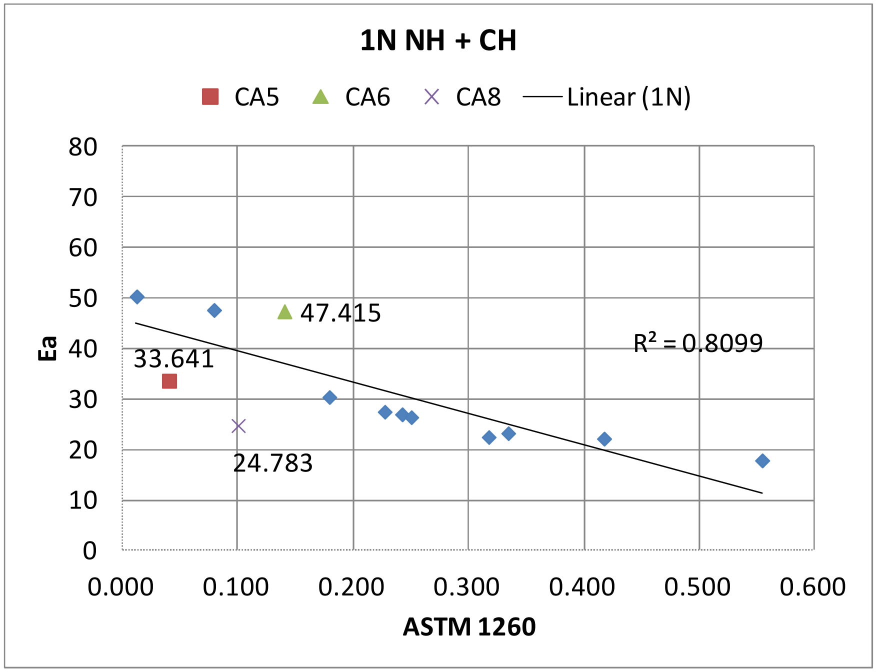
Summary of activation energy

Aggregate	1N	0.5N	0.25N	1260 value	1293 value	
Borosilicate Glass balls (6mm)	5.512	5.537 (0.5N) 5.528 (0.5N NH+0.4NKOH)				
NMR, CA		11.310		1.300		
FA1	17.857	26.322	31.826	0.554		
CA3	22.164	28.499		0.417	0.078	
FA2	22.485	32.640		0.317	0.058	
CA2	27.486	39.864		0.227	0.071	
CA5	30.409	43.365	64.630	0.179	0.149	
FA3	47.645	61.246		0.079	0.035	
CA4	50.344	67.293		0.012	0.027	
CA5	33.641	35.655		0.040	0.129	*Passed C1260, failed C1293*
CA6	47.415	57.091		0.140	0.02	*Passed C1293, failed C1260*
FA4	26.980	36.391		0.242	0.043	
CA7	26.437	35.244		0.250	0.047	
FA5	23.254	34.979		0.334	0.171	
CA8	24.783	27.602		0.100		*Passed C1260, failed C1293*
FA6		26.961		0.381	0.391	
FA7		Cannot measure		0.019		

Compound Activation Energy vs. ASTM C 1260 (14D expansion)

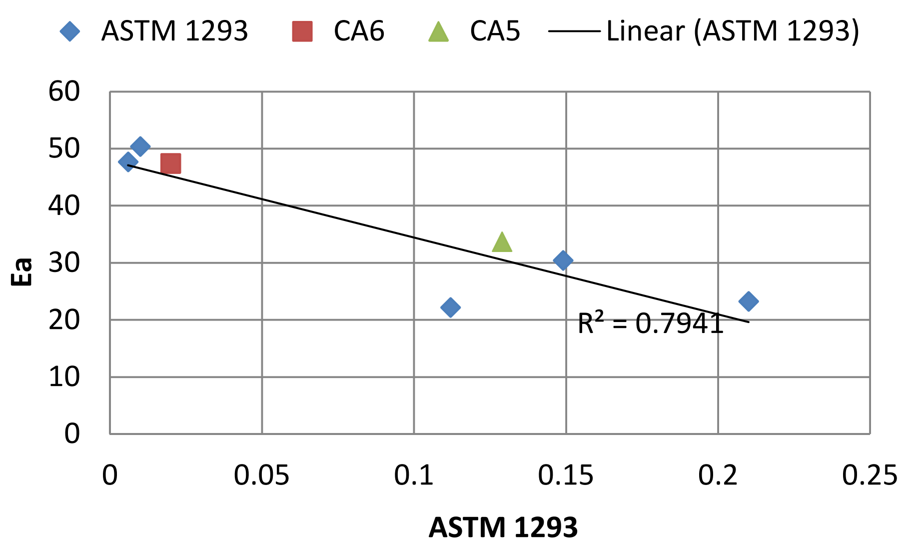
	ASTM 1260	ASTM 1293
CA5	0.04	0.129
CA6	0.14	0.02
CA8	0.10	NA

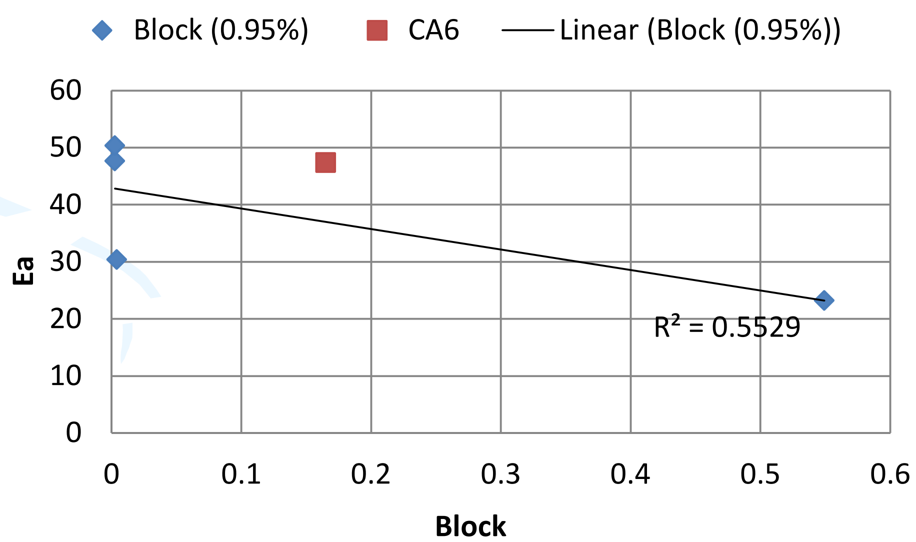




Activation Energy vs. ASTM C 1260 (14D expansion)

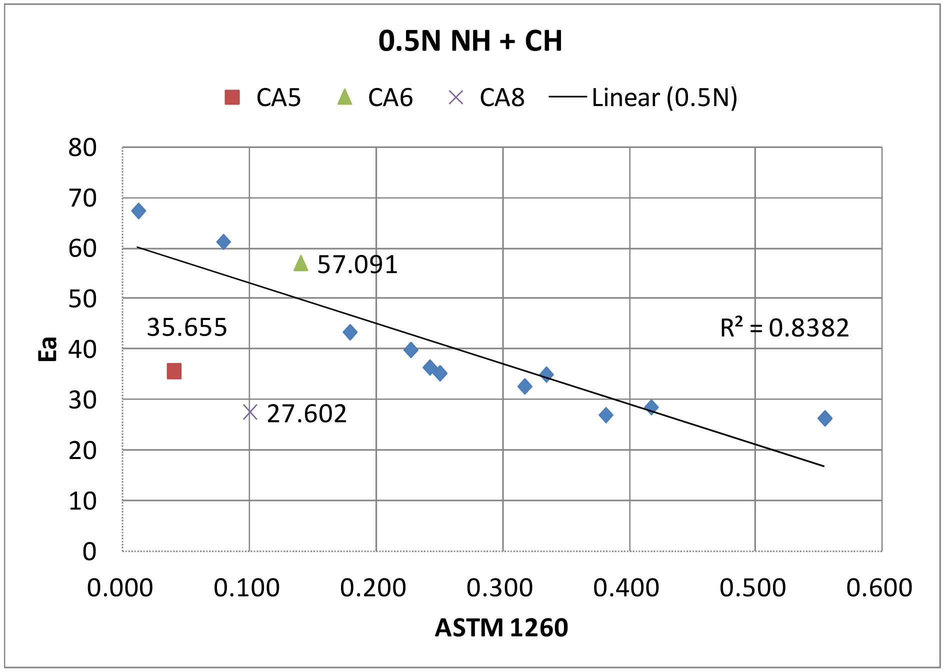
Compound Activation Energy vs. ASTM C 1293 / Block





Compound Activation Energy Based ASR Aggregate Classification

AE Range	Reactivity
< 30	4 (highly reactive)
30-45	3 (reactive)
45-60	2 (potential reactive)
> 60	1 (non-reactive)



ASTM C 1260	ASTM C 1293	Exposure Block / Field Performance	AE Range	AE - Based Reactivity
Pass	Pass	Good with no ASR	≥ 60	1
Fail	Fail	Poor	≤ 30	4
Pass	Fail	Poor	30 - 45	3, 4
Fail	Pass	Good	≥ 45	1, 2

Repeatability (COV%) Summary Based on all Aggregate Tests:

- Repeatability based on 3 rate constants from three batches of samples:

	COV. < 10%	COV. < 15%
1N + CH	85%	100%
0.5N + CH	92%	100%

Summary: Activation Energy Based Reactivity Prediction

- Measuring ASR E_a by VEMD method is considered as **a rapid and reliable method to predict aggregate ASR reactivity**
  - Can be used as an alternative to ASTM C 1260

No. of VEMDs	No of Oven	No. of Days	Activation Energy @ (0.5N NaOH + CH) solution
9	3	5	3 replicas
6	3	5	2 replicas
3	3	5	without replicas

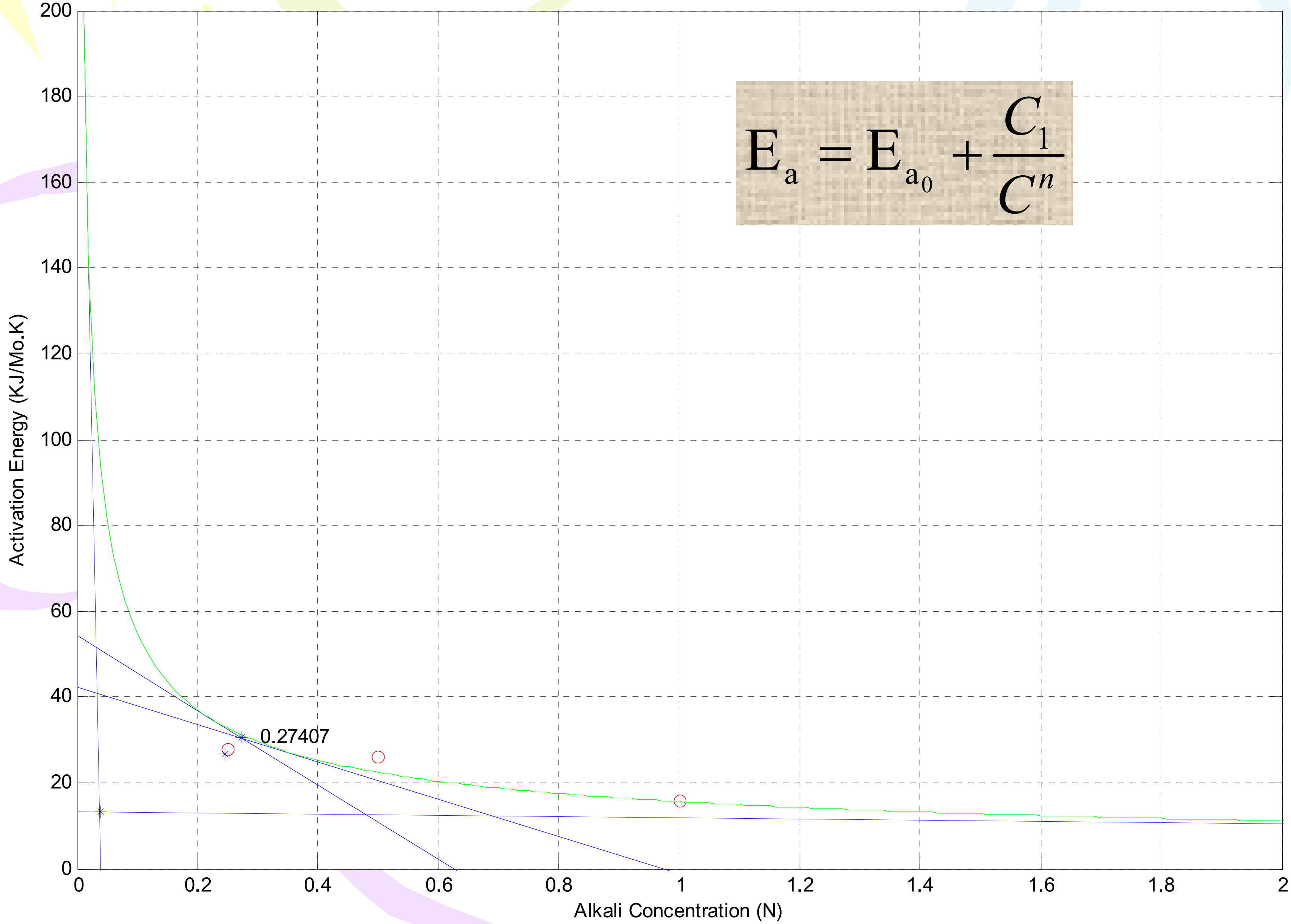
- ASR activation energy (E_a) can serve as a single chemical material parameter to represent alkali silica reactivity of aggregate – reduce the gap between Lab and field

Monitoring Soak Solution Chemistry changes and Microstructural Studies: Supporting Tools

- **Overall good support by solution chemistry**
  - **Ea vs. reduction in Na+, OH- relationship**
  - **Lower the Ea (high reactivity) higher is the consumption of Na+ and OH-**

- **Microstructural support**
  - **Type, distribution and amount of reactive constitutes in aggregates - petrography**
  - **Reaction products (gel like) were observed on the reacted aggregate surfaces – SEM-EDS**

Threshold Alkalinity from Aggregate-solution Tests



Threshold Alkalinity: Summary

Aggregate	THa Normality	1260	1293	Ea (0.5N)
CA3	0.37	0.417	0.078	28.499
FA1	0.27	0.554	-	26.322
CA1	0.52	0.179	0.149	43.365
FA2	0.47	0.317	0.058	32.640
CA2	0.5	0.227	0.071	39.864
CA7	0.46	0.250	0.047	35.244
FA4	0.46	0.242	0.043	36.391
FA5	0.46	0.334	0.171	34.979

ASR Testing: A New Approach of Aggregate Reactivity Prediction and Developing ASR Resistant Concrete Mix

Aggregate-solution Test

- Aggregate-solution test by volumetric expansion measuring device (VEMD) and determine **activation energy (E_a)**
- Determination of **threshold alkalinity (TH_A)** - Aggregate-solution tests @ multiple alkali levels

Formulation of ASR-resistant mix

- Select mix design controls and special protection measures depending on E_a, TH_A, and some consideration on ambient conditions

Mix Adjustment / Verification

- Determine pore solution alkalinity (PSA) – pore solution extraction followed by AAS analysis
- PSA $< TH_A$ - mix should perform satisfactorily in the field with no ASR
- PSA $= TH_A$ - OK under mild ambient conditions
- PSA $> TH_A$ - Need further adjustment through mix design controls and special protection measures

Mix Design Validation

- Development of **VEMD based concrete cylinder test** (soak solution matching with pore solution and no leaching)

Guidelines to Formulate ASR Resistant Mixes

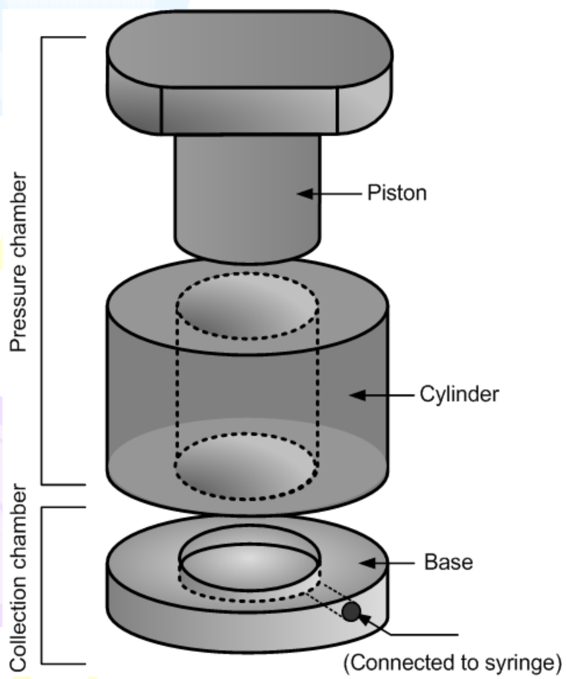
Aggr. Reactivity (E_a Based)	TH_A	Environmental Effects	Mix-Design Requirements (Protection Measures)	Special Protection Measures
High (5)	Low	High severity (i) High RH (high rainfall) (ii) High T (iii) Source of external alkalis - seawater-contaminated aggregate, or use of deicers	(i) Cement with low soluble $Na_2O_{eq.}$ - Na/K instead of Na_2O (ii) High amount (25-35%) of good quality fly ash (low alkali) (iii) Ternary blends instead of fly ash alone (e.g., fly ash + GGBS, fly ash + Metakaolin)	(i) HPC with low permeability (low w/c) (ii) Use of $LiNO_3$ (100% or more) (iii) Aggregate blend / light weight aggregate
High (5)	Low	Low severity Areas with (i) low rainfall, (ii) low temperature, and (iii) no source of external alkalis	Same as above	$LiNO_3$ (Low dosage)

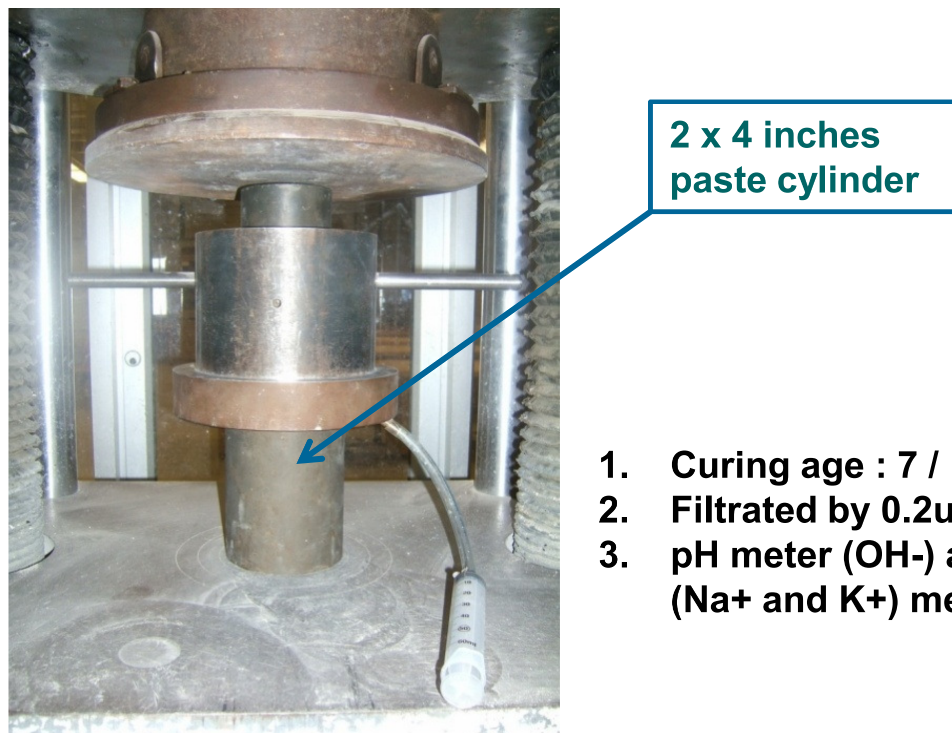
Formulation of ASR Resistant Mixes

Aggr. Reactivity (E_a Based)	TH_A	Environmental Effects	Mix-Design Requirements (Protection Measures)	Special Protection Measures
Low (2)	High	High	Maintain total alkali below TH_A (i) cement with low to intermediate soluble alkali (ii) Fly-ash with alkali lower than or similar to cement soluble alkali (some Class C ash can be used).	HPC with low permeability (low w/c)
Low (2)	High	Low	Maintain total available alkali ≤ TH_A (i) Cement with relatively high soluble alkali level can be used (ii) Fly ash with relatively high soluble alkali (Class C ash) can be used provided fly-ash alkali does not exceed cement alkali	NO Need

Mix Adjustment / Verification

- Determine pore solution alkalinity (PSA) – pore solution extraction technique
  - PSA < TH_A - mix should perform satisfactorily in the field with no ASR
  - PSA = TH_A - OK under mild ambient conditions
  - PSA > TH_A - Need further adjustment through mix design controls and special protection measures



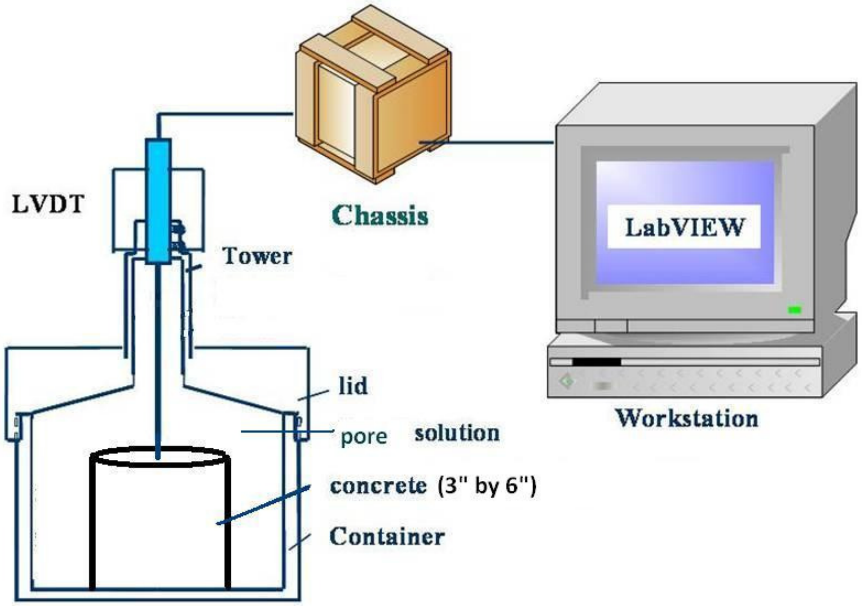


1. Curing age : 7 / 14 days
2. Filtrated by 0.2um filter
3. pH meter (OH-) and AAS (Na+ and K+) measurement

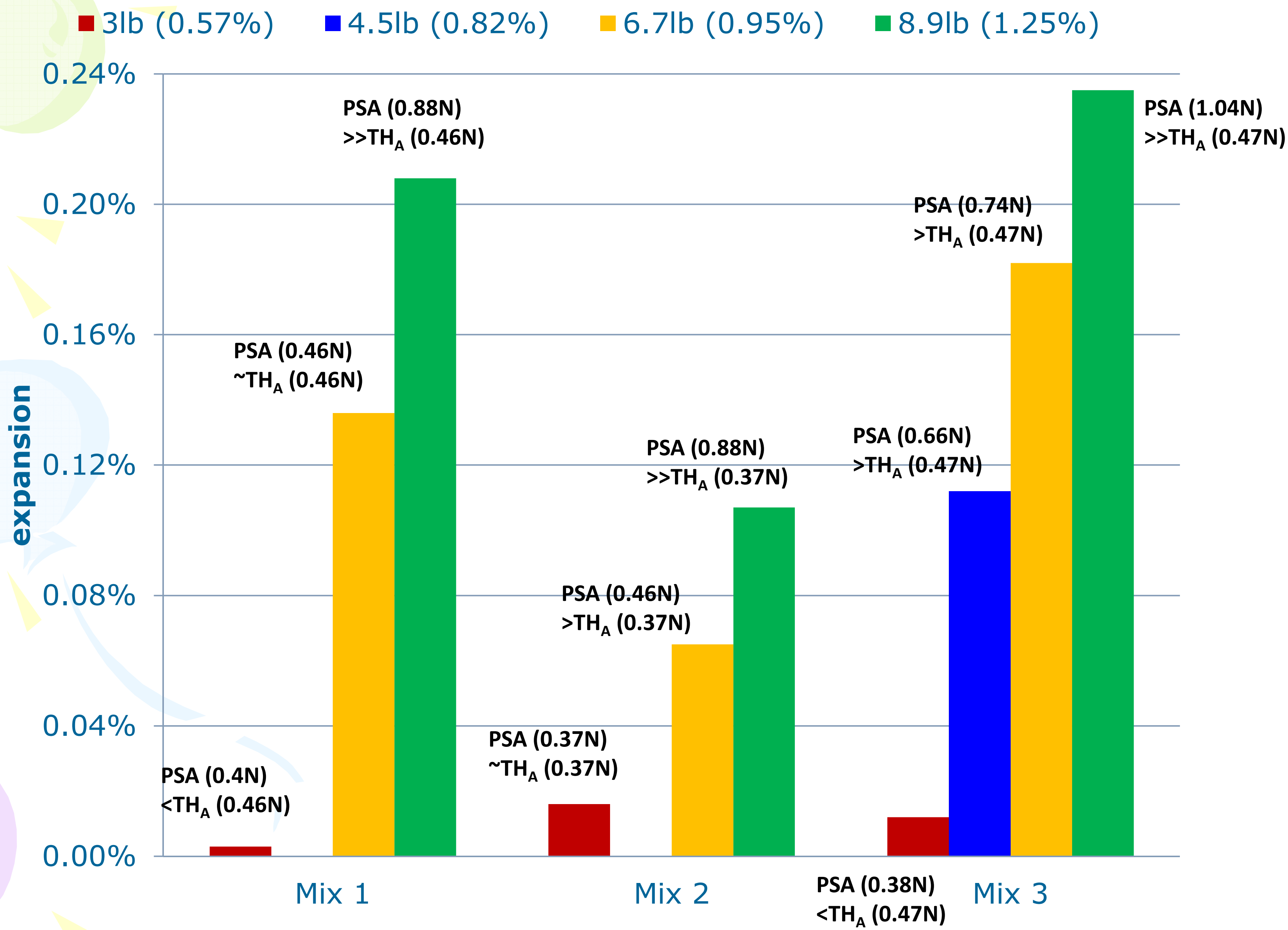
Mix Design Validation: Accelerated Concrete Cylinder Testing (ACCT)

1. Concrete cylinder (3 x 6 inches)
2. Curing (7 days) @ 100% RH and RT
3. Testing @ varying levels alkalinity
4. Place a concrete cylinder inside a VEMD with the soak solution chemistry matches with pore solution chemistry (no leaching)
5. Place the VEMD inside an oven and test @ 60˚C
6. Testing duration: ~ 28 days

No leaching



Automatic Data Collection



Pore solution vs. THa

Advantages of the VEMD Method

- A rapid (4-5 days) and reliable test method to determine aggregate reactivity
- As the reactivity prediction is based on measuring a fundamental kinematic material property (activation energy), it reduce the gap between lab and field
- Allows testing aggregate pits/stockpiles in periodic interval to address source variability as a part of quality control program

Economic Benefits

- **Categorize aggregates (belong to false +ve and -ve) consistently based on their Ea-based reactivity**
  - **Facilitates the use of locally available materials (promotes sustainability)**

- **Ensure valuable resource conservation and avoid paying for premium ASR protection when only minor protection is needed.**

- **Making long lasting durable concrete which reduces the repair and maintenance cost.**

Publications

Proposed New ASTM Test Method

Standard Test Method for Determination of Composite Activation Energy of Aggregates Due to Alkali-Silica Reaction (Chemical Method)

Recent Publications:

1. Liu, K. W., and A. Mukhopadhyay. Alkali-Silica Reaction in a Form of Chemical Shrinkage. *Journal of Civil Engineering and Architecture*, Vol. 2, 2014, pp. 235-244.
2. Liu, K. W., and A. Mukhopadhyay. A kinetic-Based ASR Aggregate Classification. Journal of Construction and Building Materials, Vol. 68, 2014, pp. 525-534.
3. Anal K. Mukhopadhyay, and Kai-Wei Liu, “ASR Testing: A New Approach to Aggregate Classification and Mix Design Verification”, Research Report FHWA/TX-14/0-6656-1, Texas Transportation Institute, The Texas A&M University System, College Station, Texas, April 2014.

Thank You

What Question Do You Have?