A NEW KINETIC TYPE RAPID AGGREGATE ASR TEST METHOD

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Abstract

The current ASR test methods are largely empirical and yield test results that are applicable to a narrow band of conditions and doubts remain as to whether current tests used to assess ASR potential are realistic under field conditions. There is a strong need for a rapid and reliable ASR test method, which can predict ASR potential matching with field level of alkalinity and temperature. A volumetric expansion measuring device (VEMD) was developed as a fast and reliable aggregate ASR testing method at TTI. VEMD measures solution volume change over time in aggregate-solution tests where as-received aggregates were tested at varying levels of alkalinity and temperatures. A new ASR model was developed to calculate rate of reaction and activation energy. Activation energy was considered as a measure of aggregate reactivity. An apparent relationship between alkalinity and reactivity parameter was observed and modeled, which can be the basis to determine the threshold alkalinity of an aggregate.

Keywords: Aggregate, Solution chemistry, Alkali silica reaction, Volume expansion, Activation energy

1. INTRODUCTION

Since the ASR-related problems were first identified in the early 1940s, extensive research worldwide has been carried out on ASR over the past six decades. One of the main areas of research has recently addressed developing a quick and reliable test method to assess ASR potential of aggregate and concrete through a simulative type of approach. The main purpose of an ASR test method is to measure aggregate reactivity prior to their use in concrete structures. The most commonly used tests for assessing aggregate ASR potential are ASTM C 1260, ASTM C1567 and ASTM C 1293 [1,2,3]. The test conditions of ASTM C 1260 method (i.e., 1N NaOH and 80°C) are severe and the test results are unrelated to field performance. ASTM C 1293 is considered as the best index for field performance but at the same time, the length of the procedure (12 months) represents a major drawback.

2. RESEARCH SIGNIFICANCE

It is clear that there is a lack of a unified approach to address how different combinations of concrete materials may interact to affect ASR behavior and warrant a different approach for ASR testing. A fast and reliable testing protocol that can measure aggregate reactivity matching with field levels of alkalinity and temperature is needed. Experience with the current tests has clearly indicated that the expansion history rather than a single value of expansion can serve as effective criteria to assess ASR potential.

3. APPROACH FOR TEST PROTOCOL DEVELOPMENTS

ASR is a kinetic type chemical reaction where some initial conditions related to alkalinity, aggregate reactivity, moisture, and temperature conditions that must be met to initiate ASR. Therefore, kinetic type

model can be applied to derive fundamental alkali silica reactivity parameter. ASR activation energy (E_a) can serve as a single chemical material parameter to represent this kinetic type combined effects and can be used as a measure of alkali silica reactivity of aggregate. In the past, researchers have investigated the use of a kinetic type ASR model for either the prediction of mortar bar expansion [4] or for better interpretation of the existing test methods [5]. A simple chemical test by simulating aggregate-pore solution reaction that exists in concrete and measuring solid/solution volume change over time will be appropriate to determine rate of reaction and ASR activation energy (E_a).

A volumetric expansion measuring device (VEMD) was developed at Texas Transportation Institute [6, 7, 8], which simulates aggregate – pore solution reaction that exits in concrete and measures free volume change due to ASR over time. This test was performed with as-received aggregates, within a short period of time, and based on the direct measurement of volume change due to ASR.

A kinetic-type model (Equation 1) was used to model measured non-linear type expansion data over time. By fitting the model (Equation 1) to measured expansion data over time, the characteristics parameters (i.e., ε_0, β, t_0, ϱ) are calculated.

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_0} . e^{(\frac{\rho}{t-t_0})^{\beta}}$$

(1)

ε_0 = ASR ultimate volume change, β = Rate constant, t_0 = Initial time of ASR expansion (hr), P = Time corresponding to a volume change ($\varepsilon_0 / \varepsilon$)

The β values at multiple temperatures (minimum 3 temperatures) are then determined and activation energy is calculated by plotting $\ln(\beta)$ versus $(1/T)$. Based on rate theory [9], the slope of the linear regression is equal to $(-E_a/R)$ where R is the universal gas constant and E_a is the activation energy. For ASR, E_a is considered as the minimum energy required initiating ASR taking into account the combined effect of alkalinity, temperature and time. The concept of ASR activation energy was introduced as a representative single parameter of alkali silica reactivity of minerals and aggregates earlier [7]. Monitoring soak solution chemistry and microstructural characterization of the reacted aggregate are considered as supporting tools. A combined approach of this type is considered as the most fundamental approach to develop a new test method.

4. EXPERIMENTAL PROGRAM

Four aggregates with different types of reactive silica and varying range of reactivity were tested. The nature of reactive component(s), mineralogy, ASTM C 1260 expansion data and others for these aggregates are summarized in Table 1. The design factors and levels for aggregate testing are presented in Table 2.

4.1 Test methods and measurement

The VEMD (Figure 1) consists of a pot, a teflon-coated brass lid, a hollow tower, and a steel float. The pot and tower are made of stainless steel whereas the lid is made of naval brass. At the top of the tower, a casing is installed to ensure proper alignment of the linear variable differential transducer (LVDT) and the float. The LVDT used is the SCHAEVITZ Model 1000 HCA, which has a maximum range of 2 inches. The LVDT is placed with an O-ring located at the bottom of the casing and secured with six set screws through the side of the casing. A thermocouple with compressing fitting is inserted through the side of the pot to measure the temperature of the solution.

VEMDs are filled up with as-received aggregate (approx. 8-9 lbs) and alkaline solution of different concentrations [e.g., 1N, 0.5N, 0.25N NaOH $\pm$ Ca(OH)$_2$] and tested at different temperatures (e.g., 60, 70 and 80°C) inside an oven according to the experimental design in Table 2. The aggregate sample size was approximately 80 percent by volume of the dilatometer pot. A constant aggregate/solution volume ratio and gradation was used for all the aggregate testing in Table 2. The test procedure consisted of four steps, i.e., (i) aggregate (oven dry) saturation in selected alkaline solution (12-14 hours) at room temperature, (ii) vacuuming (aggregate + solution) under vibration (2-3 hours) – primarily removes air bubbles from solution, (iii) Placing dilatometer inside oven and heat the dilatometer to the selected target temperature (3-4 hours) - LVDT reading at stable target temperature represents the reference (initial) LVDT reading for calculating ASR displacement, (iv) LVDT movement due to ASR (~ 96 hours) - all LVDT readings after temperature stabilization (step 3) minus the reference LVDT reading in step 3 represents displacement (ΔH) due to ASR over time. Solution volume changes as the chemical reaction between aggregate and alkaline solution progresses, which make the float to move. As the float moves inside the tower, the stainless steel rod attached with the float also moves inside the LVDT and electrical signals are generated (Figure 1). Therefore, the physical phenomenon (i.e., movement of the rod) is converted into a measurable electrical signal. All LVDT and thermocouples signals are amplified through the use of signal conditioners and then transferred though a USB cable to a workstation where a program in LabVIEW was developed to display, analyze, and store the generated data (Figure 1). ΔH over time multiplied by surface area of the VEMD tower represents volume change of solution due to ASR over time. Volume changes of solution divided by total aggregate volume multiplied by 100 represents percent volume change of solution over time.

5. TEST RESULTS AND DISCUSSION

5.1 Activation energy

For each aggregate, 18 test runs were conducted. It involved 6 aggregate-solution tests (2 tests at each alkalinity with total 3 levels of alkalinity) at each temperature with total three levels of temperatures. Eight VEMD simultaneously run inside an oven for 5 days. The approximate total time to complete all 18 test runs is 21 days without any interruption.

The four aggregates were tested using the VEMD according to the experimental design in Table 2 and ASR free volume change over time was measured. Using the modeling approach previously outlined, the four modeled parameters (i.e., ε_0, β, t_0, ϱ) characteristics of the measured volume change over time along with activation energy were determined at different levels of temperature for each aggregate. A computer program on MATLAB called "EXPANSION 2008" was developed based on NEWTON numerical approach to calculate the above four modeled parameters and activation energy where expansion over time is the main input. The modeled parameters and activation energy for all the tested aggregates are listed in Table 3 along with solution chemistry data (discussed next). Figure 2 shows the measured and calculated volume change over time at three different temperatures (60, 70, and 80°C) and activation energy as an example.

The following main observations on activation energy can be postulated from Table 3

a) NMR shows lowest energy and PRG shows highest energy at any level of alkalinity. SuG shows energy values in between NMR and PRG. A high R^2 value (i.e., 0.95-0.99) between ln(β) vs. 1/T plot (calculation of activation energy) was invariably observed for the all aggregates, which indicates that the new proposed kinetic model is a very effective approach to derive rate constants from VEMD measured expansion data.

b) It can be seen from the results that an apparent relationship exists between the alkalinity of test solution and E_a of the aggregate, i.e., E_a decreases as the alkalinity of solution increases. This possibly suggests that the energy barrier to initiate ASR become low at high alkalinity or high at low

alkalinity. An attempt has been made to model the relationship between E_a and alkalinity, which is presented later.

5.2 Test Solution Chemistry

The pH and cations (Na^+, Ca^{2+}) concentration of the test solution before and after each test was measured using a pH meter (Fisher Scientific Accumet Excel XL25 pH meter) and flame spectrophotometer respectively. The drop in pH is expressed in terms of % reduction of OH^- ions using mathematical equation which relates pH and OH^- concentration. Reduction of Na^+ was determined based on initial and final Na^+ concentrations. Reduction of Na^+ and OH^- along with ultimate volume change and E_a are presented in Table 3.

The following are the observations on the relationship between E_a, modeled parameters and solution chemistry based on Table 3:

a) The lower the energy the higher is the reactivity. NMR shows lowest energy and highest ASTM C 1260 14 days expansion (highest reactivity) whereas PRG shows highest energy and lowest C 1260 14 days expansion (lowest reactivity). The intermediate level of reactivity of SuG is supported by both medium range E_a and ASTM C 1260 14 days expansion. Therefore, aggregate reactivity ranking based on activation energy matches well with the reactivity ranking based on ASTM C 1260 for the studied aggregates.

b) Aggregate with high reactivity (e.g., NMR) shows higher % reduction of Na^+ and OH^- and higher ultimate volume change than those at aggregate with low reactivity (e.g., PRG)

c) Percent reduction of Na^+ and OH^- increases with the increase of both temperature and alkalinity.

Therefore, the changes of soak solution chemistry supports the activation energy based reactivity and ultimate volume change measurement by VEMD.

5.3 Microstructures

The selective specimens were examined by SEM-EDS to identify the reaction products. For a highly reactive aggregate (e.g., NMR, opal) the presence of in-situ type reaction products were observed (Figure 3a). Figure 3b shows the presence of layer type reaction product on a reacted opal particle surface. The presence of mainly Si with considerable amount of Na was evident from EDS analysis. For a slowly reactive aggregate, the presence of surface etching, cracking was observed with no obvious presence of gel within 4-5 days of testing period.

Aggregates are in general heterogeneous material that is often composed of different mineral phases, i.e., reactive phases (one or more phases) and non-reactive phases (crystalline minerals). Therefore, it is better to call the calculated energy as compound activation energy. It shouldn't be confused with classical activation energy of pure phase in chemistry.

6 APPARENT RELATIONSHIP BETWEEN ACTIVATION ENERGY AND ALKALINITY

An apparent relationship between compound activation energy (E_a) and concentration (e.g., alkalinity) is evident from the results of the studied aggregates (Table 3). The higher the alkalinity the lower is the E_a. An attempt was made to establish a mathematical relationship between E_a and alkalinity. The following model was used to establish a relationship between E_a and alkalinity:

$$E_a = E_{a_0} + \frac{C_1}{C^n} \tag{2}$$

Where, E_a = Activation energy (KJ/mol), E_{ao} = Activation energy – threshold (KJ/mol), C_1 = Activation energy curvature coefficient (KJ/(mol)$^{1-n}$, N = Activation energy curvature exponent, C = Alkalinity (mol)

The results are presented in Figure 4 for the three aggregates. As shown from the plot, as alkalinity increases, the E_a decreases for all the three aggregates. A good fit between the measured and predicted E_a values is manifested and this demonstrates the applicability of the proposed model. The existence of a characteristic threshold alkalinity for each aggregate is manifested from this plot. For example, the threshold alkalinity for Platt Gravel is relatively higher than NMR and SuG. Maintaining a low level of total alkalinity in concrete is a very stringent condition for both NMR and SuG. However, as E_a of SuG is slightly higher than NMR, the tolerance level of alkali for SuG will be more than NMR. The common approaches to maintain a low level of pore solution alkalinity are (i) use of low alkali cement, (ii) use of good quality fly ash with low content of alkalis, and (iii) ensuring minimum contribution of additional alkalis from external source(s). A reactive aggregate can practically behave as non-reactive or very slow reactive provided the alkalinity can be maintained below the threshold level of alkalinity. The validation of this apparent relationship through large number of aggregate testing is highly needed in order to utilize this kind of relationship.

A threshold alkali concentration is a characteristic for each reactive phase below which the reaction does not occur [13, 14]. It seems threshold alkali concentration seems to vary for different aggregates. Therefore, assigning a common total concrete bulk alkali (e.g., 4lb/cubic yard) irrespective of aggregate reactivity may not provide enough protection.

7 REPEATABILITY

Activation energy based intra-laboratory (within the laboratory) comparison was made in order to verify the repeatability. Activation energy based COV% was within 7 for the tested aggregates, which indicates that the results are highly repeatable.

8 CONCLUSIONS

The main findings of this study are summarized below:

a) VEMD based test method was developed to determine ASR Activation energy (E_a) of aggregate. Activation energy was found to be a very effective parameter to determine aggregate alkali silica reactivity. The E_a of ASR could be a potential screening parameter to categorize aggregates based on their reactivity.

b) The COV% within 7 indicates highly repeatable results.

c) The relationship between E_a and alkalinity can be used as a means to adjust the laboratory measured E_a with respect to field level of alkalinity and characterize the threshold alkali requirements of aggregate.

d) VEMD method has the merits to be considered as a rapid and reliable ASR test method and have the potential to overcome the shortcomings of the current test methods.

9. WORK UNDER PROGRESS AND POTENTIAL FUTURE SCOPE

The research work that research team is currently pursuing is listed below along with some relevant future work:

1. Testing aggregates passed / failed by ASTM C 1260 but failed/passed by ASTM C 1293 and verify whether VEMD methods identify those aggregates correctly

2. Conducting a large number of aggregate testing and develop an aggregate classification system with well defined range of activation energy.

3. Implementation through round-robin aggregate testing – a COV of ≤ 12% was obtained based on limited aggregate testing between two laboratories.

4. Develop a combined materials approach–a combined materials approach i.e., combining laboratory measured aggregate and concrete material properties through performance based modeling. Based on aggregate testing (aggregate-solution tests) and limited concrete testing (concrete-solution tests), a combined materials approach to assign threshold alkalinity of concrete mix has been developed. Further work on refinement of the calibration procedure using field exposed concrete along with repeatability testing using a variety of coarse aggregates are recommended in order to validate this combined approach.

Work for items 1-3 are in progress through TxDOT projects. After successful completion of the current TxDOT projects, the research team is highly anticipating research project to pursue items 4.

10   REFERENCES

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Aggregate Information	New Mexico Rhyolite (NMR)	Platt River Gravel (PRG)	Sudbury Gravel (SuG)	Spratt Limestone (SL)
Source	Las Placitas Gravel Pit, New Mexico	Nebraska	Sudbury area of Ontario, Canada	Spratt quarry in Ontario, Canada
Rock type / mineralogy	Rhyolite acid volcanic rock	Sandy Gravel composed of mainly quartz	Calcareous gravel with siliceous impurity	calcite with small amount of dolomite, minor siliceous component as impurity
Reactive component (s)	Acid volcanic glass [10]	Strained quartz	microcrystalline quartz [11]	Microscopic chalcedony, and black chert (3-4%) [12]
ASTM C 1260 14D Exp%	1.3	0.28	0.30	0.38

TABLE 1: Reactive components, mineralogy, and other relevant aggregate data.

NMR, SL and SuG are coarse aggregates; PRG is finer than conventional coarse aggregate and slightly coarser than sand (ASTM C 33)

TABLE 2: Factors and levels for aggregate testing.

Factors	No. of levels	Level description
Aggregate type	4	New Mexico Rhyolite (NMR), Platt River Gravel (PRG), Spratt Limestone (SL), Sudbury Gravel (SuG)
Temperature	3	60, 70 and 80°C
Solution normality	3	0.25, 0.5, and 1N NaOH with $Ca(OH)_2$

			ASR Modeled Parameters		Activation Energy	Solution Chemistry		ASTM C 1260, 14D
Aggr. Type	Alkalinity (NaOH)	T (°C)	β	Ultimate volume change (%)	E_a (KJ/mol)	Reduction of Na$^+$ (%)	Reduction of (OH)$^-$ (%)	Exp (%)
NMR	1NH + CH	60	1.90	0.103	10.72	32	86.16	1.3
		70	2.13	0.113		39	86.35	
		80	2.36	0.119		43	87.78	
	0.5NH + CH	60	1.82	0.070	18.09	24	58.22	
		70	2.14	0.102		33	62.59	
		80	2.64	0.107		37	68.16	
	0.25NH +CH	60	0.87	0.042	34.28	13	21.66	
		70	1.23	0.054		15	24.14	
		80	1.75	0.063		20	38.06	
PRG	1NH + CH	60	1.37	0.030	46.46	7	48.71	0.28
		70	2.03	0.036		14	58.60	
		80	3.55	0.053		16	67.34	
	0.5NH + CH	60	1.13	0.022	56.68	6	59.73	
		70	2.10	0.027		10	54.71	
		80	3.60	0.045		13	59.54	
SuG	1NH + CH	60	1.67	0.025	35.49	22	49.77	0.30
		70	2.10	0.034		25	53.33	
		80	3.47	0.059		28	67.86	
	0.5 NH + CH	60	1.44	0.020	38.42	12	64.27	
		70	2.07	0.036		16	64.19	
		80	3.17	0.057		23	66.96	

TABLE 3: ASR Modeled aggregate parameters, E_a and solution chemistry changes as a function of alkalinity and temperature.
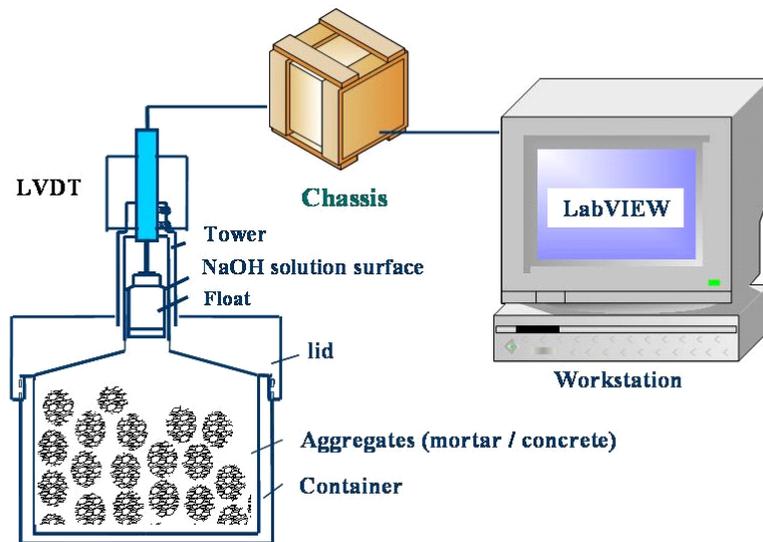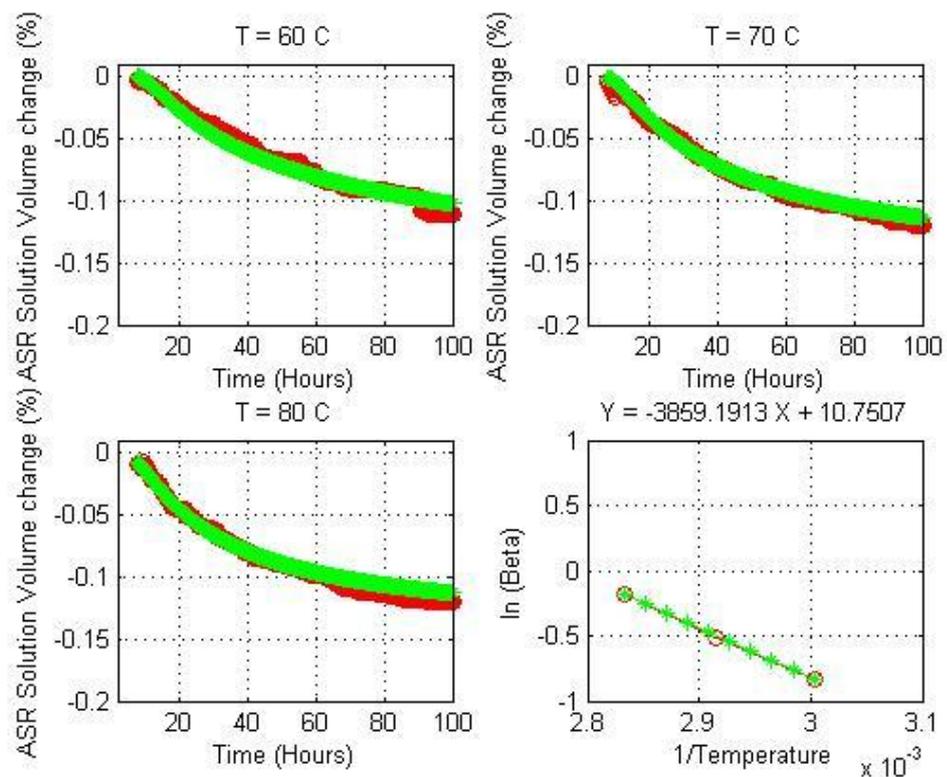
FIGURE 1: VEMD test setup.

FIGURE 2: Measured (red) and calculated (green) ASR solution volume change over time and activation
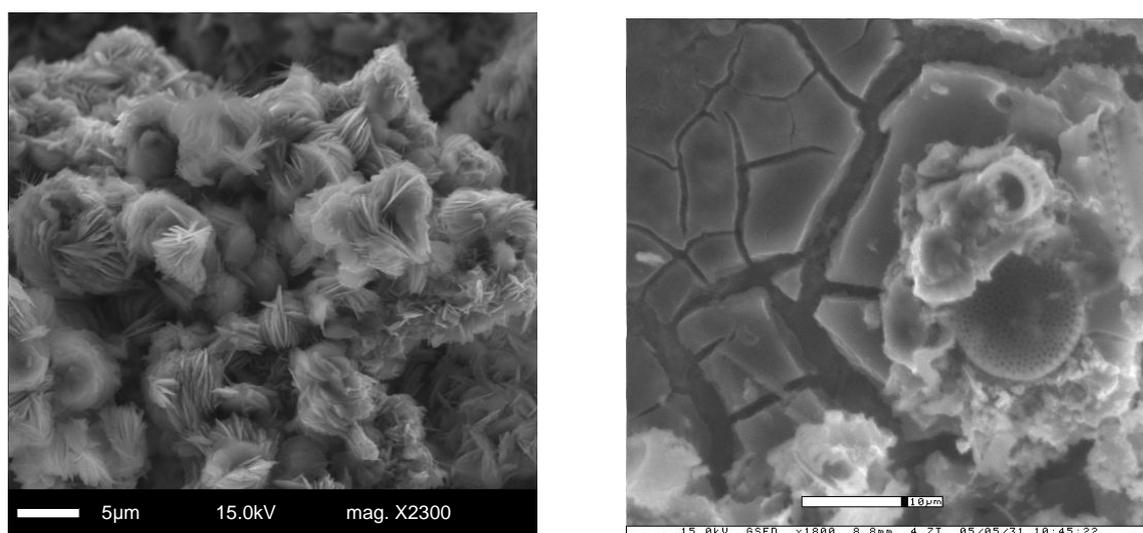energy calculation for PRG at 0.5N NaOH + Ca(OH)$_2$.

FIGURE 3 (a): Reaction products on a reacted NMR particle, 1N NaOH + CH, 72 hours, (b) reaction products
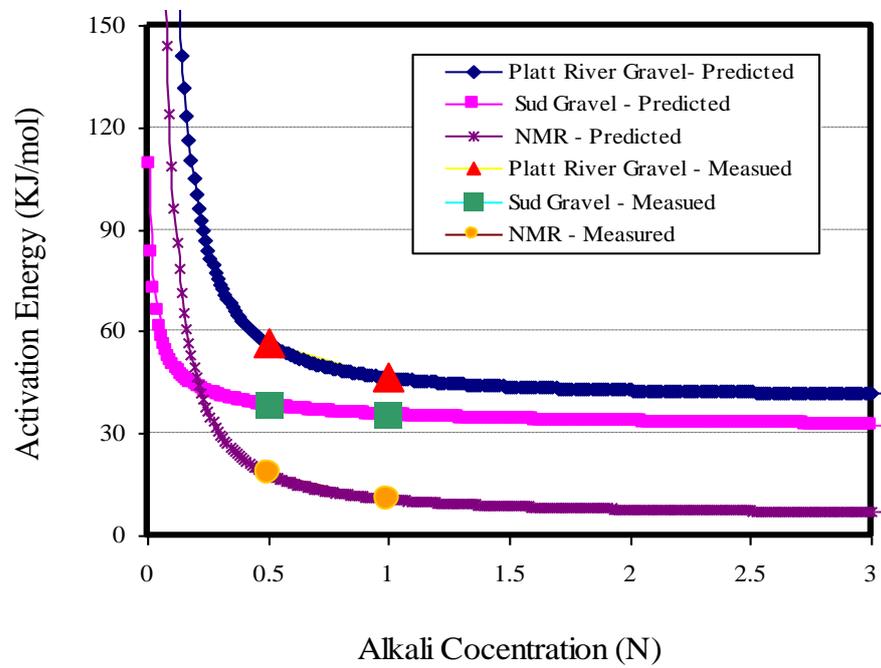on a reacted opal particle, 1N NaOH + CH, 72 hours.

FIGURE 4: Alkalinity versus activation energy for the studied three aggregates.