The Use of Reaction Kinetics in Classifying Alkali Silica Reactivity Potential of Aggregates

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Abstract: The Australian Standard accelerated mortar bar test (AMBT) method, AS 1141.60.1, adopts the expansion limits at two exposure periods to classify the alkali silica reactivity (ASR) of aggregate. This was a first step toward the use of 'reaction kinetics' or 'rate of reaction' to detect and classify alkali silica reactivity. The AS 1141.60.2 concrete prism test (CPT), on the other hand, uses a single expansion limit at one year to classify ASR. This paper examines the validity of the use of reaction kinetics, evaluated from the AMBT expansion data, to gauge and classify the reactivity. This may enable a better quantification of the degrees of reactivity and a more fundamental approach to ASR mitigation.

Keywords: Accelerated mortar bar test (AMBT), concrete prism test (CPT), reaction kinetics.

1. Introduction

Alkali Silica Reactivity (ASR) is an internal reaction that can lead to deterioration of concrete. While only a small proportion of concrete suffers from deterioration due to ASR, its effects can lead to a significant reduction in service life of affected structures. Consequently, much effort has been expended in developing test methods to evaluate ASR reaction potential.
International accelerated mortar bar (NBRI method, ASTM C1260 and CSA A23.2-25A methods) and concrete prism test methods (ASTM C1293, CSA Test method A23.2-14A) have been used in Australia, together with derived test methods adopted by various statutory authorities such as RTA T363 Rapid Mortar Bar Test and Vic Roads RC376.04 Concrete Prism Test. These test methods were joined in 2014 by two new standard test methods published by Standards Australia CE-012 Aggregate and Rock for Engineering Purposes committee:

AS 1141.60.1:2014 Potential alkali-silica reactivity - Accelerated mortar bar method (AMBT) and
AS 1141.60.2:2014 Potential alkali-silica reactivity - Concrete prism method (CPT).

AS 1141.60.1 accelerated mortar bar method (AMBT) adopts the expansion limits at two exposure periods to classify the alkali silica reactivity (ASR) of aggregate, while AS 1141.60.2 concrete prism test (CPT), on the other hand, uses a single expansion limit at one year to classify ASR.

However, alkali silica reaction is a phenomenon occurring over time. These test methods do not address the issue of how much time is likely to pass before deleterious expansion occurs. Johnston, Stokes and Surdahl (2000) [2] attempted to develop a kinetic based model for better interpreting results from the ASTM C1260 mortar bar test. A literature search resulted in the selection of the Kolmogorov-Avrami-Mehl-Johnson (KAMJ) model, which describes nucleation and growth transformation reaction kinetics. A number of tests were done at various ages using extremely reactive sand and fitted into the KAMJ model. The conclusion from the research in this paper was that a kinetic based model can provide a means of interpreting the results of ASTM C1260 independent of the 14 day result.

A further study was undertaken by Johnston, Stokes, Fournier and Surdahl (2004) [3] to try to correlate the rates of reaction determined by the KAMJ model to the onset of cracking of concrete in service and large slabs and blocks stored externally. The study concluded that using the kinetic approach of the KAMJ model allows for a significant improvement in the reliability in predicting the reactivity of aggregates. Results from the study indicate that the same equation is applicable to laboratory test ASTM C1260 and slab and block concrete specimens exposed outdoors and in predicting the time to onset cracking of concrete pavements, all of which support its suitability as a model.
This paper examines the validity of the use of reaction kinetics, evaluated from both the AS 1141.60.1 (AMBT) and AS 1141.60.2 (CPT) expansion data, to gauge and classify the reactivity. This may enable a better quantification of the degrees of reactivity and a more fundamental approach to ASR mitigation.

2. Value of AMBT & CPT

Rocker, Mohammadi, Sirivivatnanon and South (2015) [1] reviewed international data on AMBT and CPT tests, as well as field performance of large concrete blocks.
It was found that the AMBT was a good indicator of reactivity of some aggregates. In many cases, however, the results from the AMBT disagreed with those from the CPT and the outdoor simulated field tests. In general, reactivity diagnosed by CPT was found to correlate well with reactivity in field exposure.
This mirrors the experience of Boral Construction Materials testing over many years and the requirements of some authorities that, where an aggregate is classified as reactive by AMBT, it be tested using the CPT. This often results in a non-reactive result.
While there is no agreed hierarchy of the two test methods, experience and current practice suggests the CPT has a closer correlation to reactivity in field exposure.

2.1 Aggregate classification based on AMBT

The non-mandatory appendix in ASTM C1260 provides guidance to the interpretation of test results with the following expansion limits: 14-day expansions of less than 0.10% to be indicative of "innocuous" behavior whereas 14-day expansions of more than 0.20% are indicative of "potentially deleterious" expansion. Aggregates with 14-day expansions between 0.10 and 0.20% are known to be innocuous and deleterious in filed performance, and supplemental information in the form of petrographic examination or identification of alkali reaction products in specimens after tests, or field service record can be used in the assessment of the performance

Table 2.1 Comparison of ASTM and AS Mortar bar expansion limits

ASTM C1260		**AS 1141.60.1**		
Interpretation	**14 days**	**Classification**	**10 days**	**21 days**
Innocuous	< 0.10*%	Non-reactive	-	< 0.10*%
"uncertain"	0.10*-0.20%	Slowly reactive	< 0.10*%	0.10*% to <0.30%
Potential deleterious	≥ 0.20*%	Reactive	≥ 0.10*% -	- ≥ 0.30%

*The value of the lower limit for natural fine aggregate is 0.15%

The AS 1141.60.1 classified aggregates with 21-day expansion below a lower limit of 0.10% to be non-reactive, and those with 10-day expansion equal or greater than the lower limit of 0.10% or 21-day expansion equal or greater than the upper limit of 0.30% to be reactive. For aggregates with 10-day expansion below the lower limit of 0.10% but 21-day expansion equal to or exceeding the lower limit of 0.10% but not exceeding the upper limit of 0.3% to be a "slowly reactive" aggregate. Note that the lower limit applicable to natural sand is 0.15%.

2.2 Aggregate classification based on CPT

The ASTM C1293 tests the expansion of concrete with a cement content of 420 ± 10 kg/m^3 and a dry mass of coarse aggregate per unit volume of concrete equal to 0.70 ± 0.02 of its dry-rodded bulk density with a water to cementitious material ratio (w/cm) of 0.42 to 0.45 by mass. The cement has a total alkali content of 1.25% of Na_2O equivalent by mass of cement. Specimens are placed in a container stored in a 38.0 ± 2 °C. The non-mandatory appendix states that an aggregate might reasonably be classified as potentially deleteriously reactive if the average expansion of three concrete specimens is equal to or greater than 0.04% at one year (CSA A23.2-27A-00 Table 1). It also suggests that it is reasonable to conclude that the amount of pozzolan or slag used in combination with an aggregate is a least the minimum needed to prevent excessive expansion in field concrete if the average expansion is less that 0.04% at two years (CSA A23.2-28A-02).

The AS 1141.60.2 uses essentially the same concrete mix proportion and test method as the ASTM C1293 but classifies an aggregate with a prism expansion of less than 0.03% at 52 weeks as "non-reactive" and an aggregate with a prism expansion equal to or greater than 0.03% at 52 weeks as "potentially reactive". The lower expansion limit is considered more conservative as it was adopted from the RMS T364 which tests concrete with a higher adjusted cement alkali of 1.38% Na_2O equivalent.

2.3 Aggregate classification based on reaction kinetics

The current standard methods adopted by Australia in determining ASR involve the collection of information regarding whether or not deleterious expansion occurs and should be expected for the concrete in service. This process and the information gathered fails to address the time frame; that is the amount of time that passes until significant damage might occur in the concrete in question. For this reason it is desirable to develop a model and method that explores the correlation between rates of reaction, and the development of cracking in concretes in service. By implementing a kinetic-based method for interpreting AMBT or CPT test data not only can relative potential for ASR be evaluated and determined by the existing laboratory tests, but more information regarding the time frame in which damage occurs in field concrete may also be obtained and determined from these same tests.

2.3.1 The Kolmogorov-Avrami-Mehl-Johnson (KAMJ) model

The study performed by Johnston et. al. (2000, p. 142)[2] was conducted to determine an appropriate model to represent ASR expansion in the C1260 test. The Kolmogorov-Avrami-Mehl-Johnson (KAMJ) model which describes nucleation and growth transformation reaction kinetics was selected as potentially applicable and has the following form:[2]

$$\alpha = 1 + \alpha_0 - e^{-k(t-t_0)^M} \qquad (1)$$

$$\alpha = \alpha_0 + (1 - \alpha_0)(1 - e^{-k(t-t_0)^M}) \qquad (2)$$

Johnston et. al. (2000, p. 142-144)[2] explains the equations:
α_0 is the degree of reaction at time t_0 when nucleation and growth become dominant, and k is a rate constant which combines the effects of nucleation, multidimensional growth, the geometry of reaction products, and diffusion. For expansion, α is the degree of reaction and α_∞ cannot exceed 1.
For the study, ASTM C1260 tests were conducted using extremely reactive sand from South Dakota, and length measurements taken at 3, 7, 11, 14, 17, 21, 25, and 28 days with data being fit into the above equations. A value of three days was selected for t_0 with the corresponding expansion value used for α_0. The fit was determined with linear regression using:[2]

$$\ln \ln \left(\frac{1}{1 + \alpha_0 - \alpha} \right) \text{ vs. } \ln (t - t_0) \qquad (3)$$

The table 2.2 below taken from Johnston et. al. (2000, p. 145)[2] shows the expansion values and kinetic parameters for the different test conditions.

Table 2.2: ASTM results with different base concentrations[2]

ASTM results with different base concentrations.

Time (days)	ASTM C 1260 Percent Expansion (NaOH Normality)					
	0.5	0.6	0.7	0.8	0.9	1.0
3	0.017	0.026	0.036	0.045	0.055	0.065
7	0.025	0.041	0.087	0.122	0.156	0.196
11	0.043	0.102	0.182	0.240	0.248	0.290
14	0.071	0.162	0.248	0.303	0.303	0.336
17	0.100	0.207	0.297	0.347	0.368	0.373
21	0.129	0.256	0.343	0.391	0.384	0.430
25	0.160	0.301	0.390	0.432	0.420	0.467
28	0.174	0.324	0.407	0.454	0.464	0.488
ln*k*	−7.1320	−6.2530	−4.4130	−3.7460	−3.3430	−2.9550
M	1.715	1.694	1.179	1.001	0.850	0.743
R^2	0.989	0.960	0.971	0.965	0.983	0.996

Where ln k is the intercept and M is the slope of the regression line, the figure below is a plot of M versus ln k. Figure 2.1 shows a uniform response with respect to the exponential and rate components of the kinetic parameters.

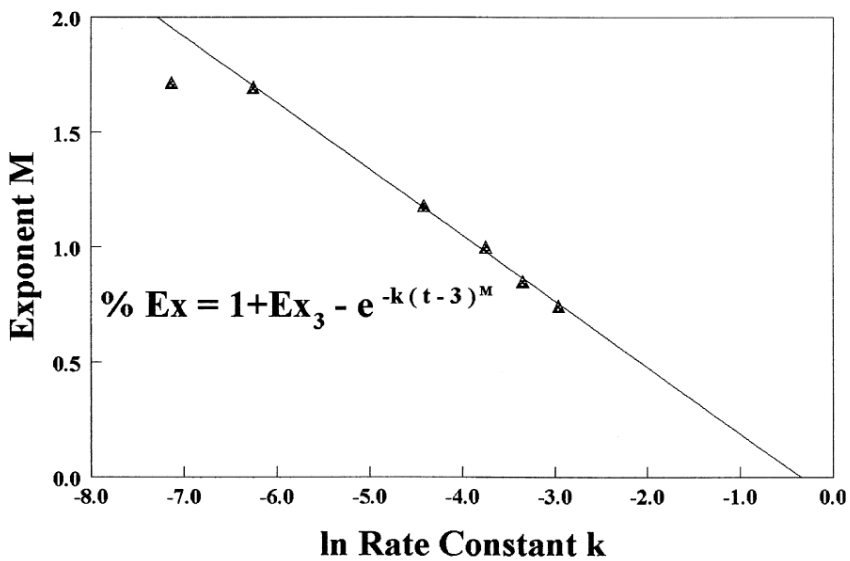

Figure 2.1: Exponent versus ln rate constant: ASTM C1260 at different concentrations. [2]

The results of Johnston et. al. (2000)[2] conclude that an application of a kinetic model based on the KAMJ equation provides a means of interpreting the results of ASTM C1260 independent of expansion values obtained at 14 days. The use of a kinetic plot of slope M, and intercept, ln k, obtained from a least-squares fit to the logarithmically transformed kinetic equation differentiates between reactive aggregates having ln k > -6, and innocuous aggregates with ln k < -6.

2.3.2 Analysis of Australian Data

Existing test data on 56 Australian aggregates tested for ASR in accordance with procedures detailed in AS1141.60.1 and AS1141.60.2 Table 2.3 below is an extract from that data.

Table 2.3: ASR classification results based on AMBT and CPT to Test Methods 1141.60.1 and 1140.60.2

		Aggregate Reactivity Classification		AMBT Expansion	
Identifier	**Aggregate type**	**(AS1141.60.1)**	**(AS1141.60.2)**	**% Expansion (14 days)**	**% Expansion (28 days)**
A1	Olivine Basalt	Non- Reactive	Non- Reactive	0.020	0.049
A2	Basalt	Non- Reactive	Not completed	0.013	0.035
A3	Basalt	Non- Reactive	Non- Reactive	0.030	0.056
A5	Pyroxene Andesite	Reactive	Non- Reactive	0.403	0.739
A6	Latite	Non- Reactive	Non- Reactive	0.012	0.055
A7	CRG	Reactive	Non- Reactive	0.230	0.462
A8	Rhyodacite Porphyry	Reactive	Reactive	0.318	0.533
A9	Hornfels	Slowly Reactive	Non- Reactive	0.081	0.217
A10	Limestone	Non- Reactive	Non- Reactive	0.008	0.011

The complete set of results for AMBT is plotted in Figure 2.2 showing expansion vs time for the AMBT test data. Also plotted are indicator lines at 0.1% and 0.3% as per the classification criteria of aggregates expansion based on AS11411.60.1.

Kinetic parameters were then calculated at 14 days and 28 days and analysed using the KAMJ model to establish any correlation between test results and a kinetic based method of interpretation. This is shown in table 2.4 below.

Table 2.4: Kinetic Parameters based on AMBT (1141.60.1)

		Kinetic Parameters							
Identifier	**Aggregate type**	$\ln k_{14}$	k_{14}	M_{14}	R^2_{14}	$\ln k_{28}$	k_{28}	M_{28}	R^2_{28}
A1	Olivine Basalt	-6.6494	0.001295	0.935	0.948	-7.0670	0.000853	1.165	0.969
A2	Basalt	-5.7956	0.003041	0.321	0.695	-7.1331	0.000798	1.084	0.852
A3	Basalt	-6.2066	0.002016	1.012	0.994	-6.1822	0.002066	1.001	0.995
A5	Pyroxene Andesite	-6.2644	0.001903	2.367	0.986	-5.2587	0.005202	1.805	0.959
A6	Latite	-7.7286	0.000440	1.370	0.996	-8.2360	0.000265	1.661	0.988
A7	CRG	-5.0423	0.006459	1.548	0.993	-4.6093	0.009958	1.304	0.987
A8	Rhyodacite Porphyry	-3.7765	0.022903	1.151	0.991	-3.5206	0.029582	1.008	0.990
A9	Hornfels	-6.5472	0.001434	1.702	1.000	-6.2498	0.001931	1.538	0.994
A10	Limestone	-9.2881	0.000093	1.534	1.000	-8.2226	0.000269	1.008	0.920

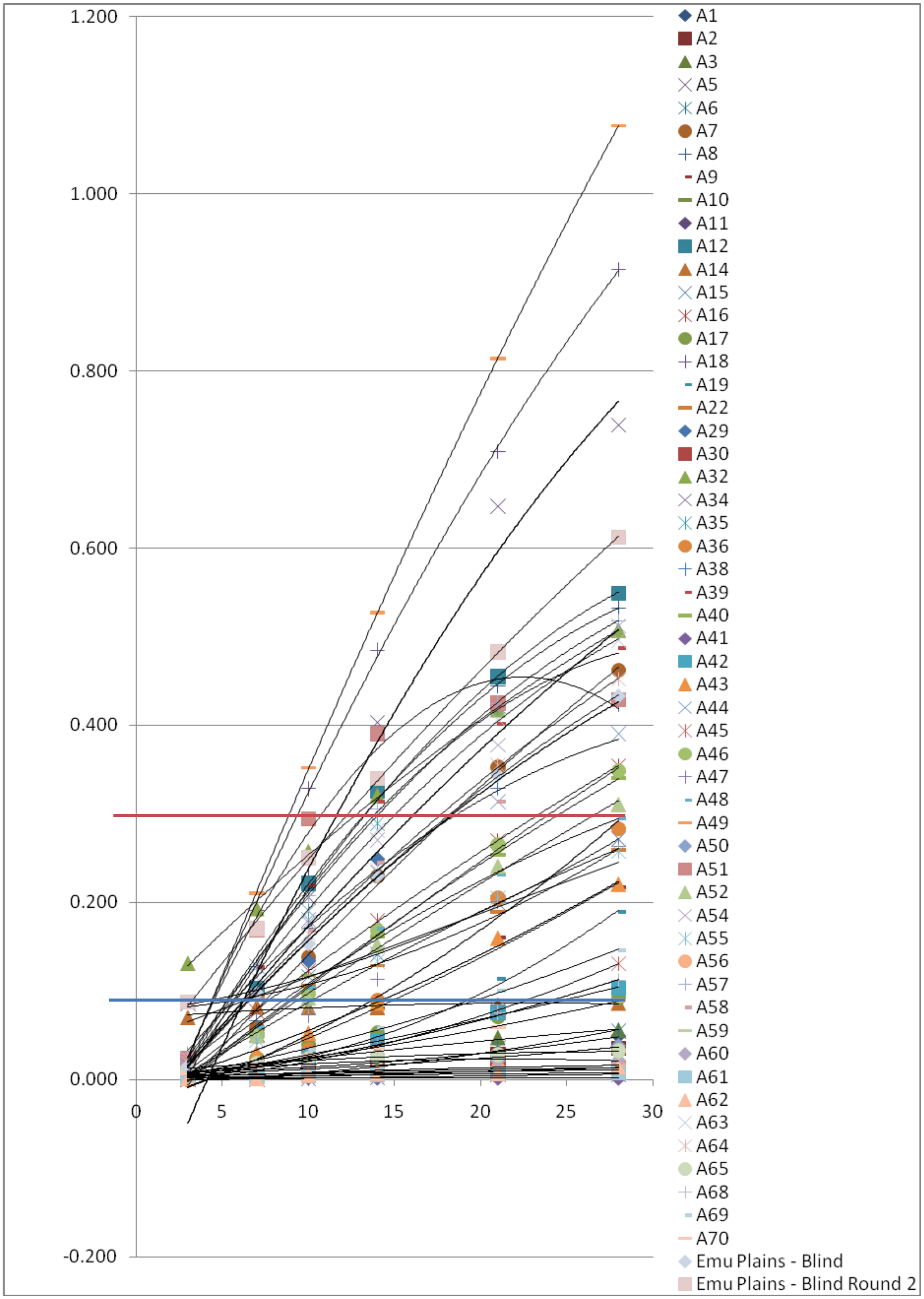

Figure 2.2: Plot of percent expansion vs time: AS1141.60.1 data

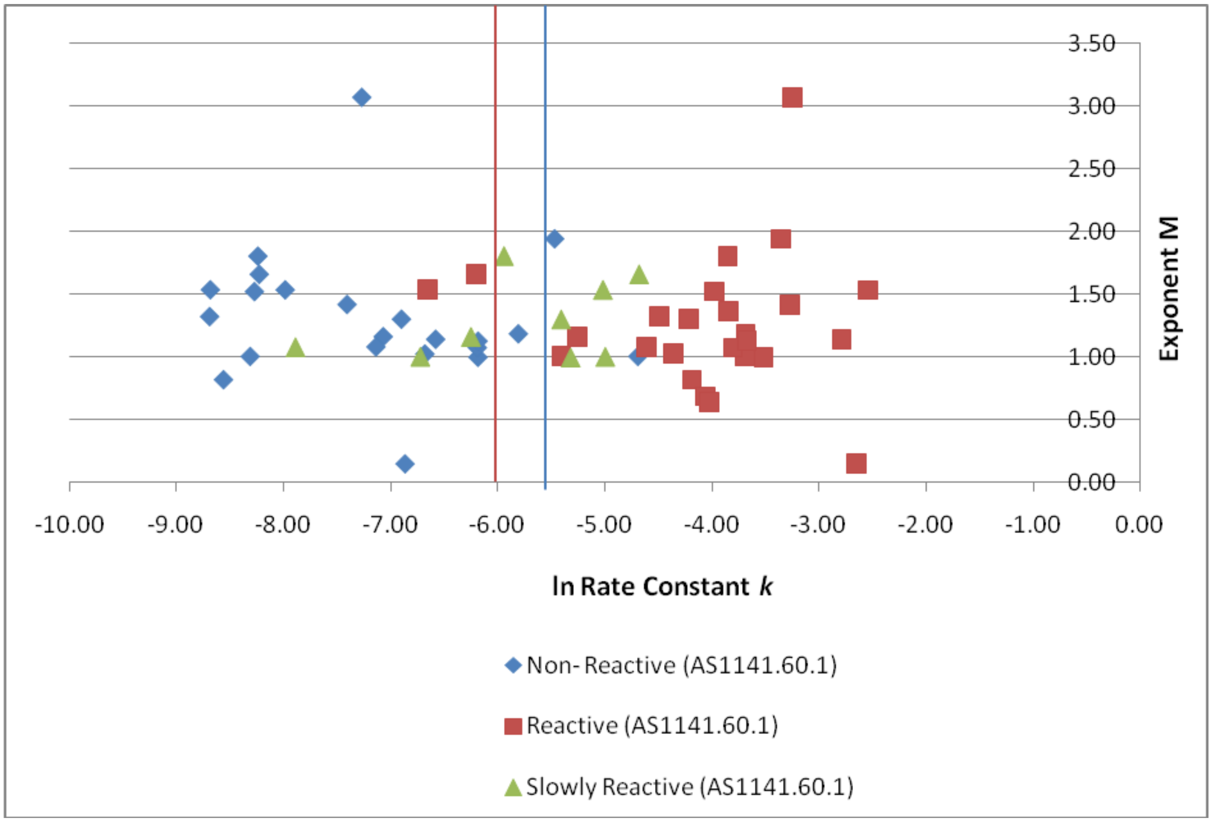

Figure 2.3: Reactivity plot based on AMBT (AS1141.60. 1 test data) – 28 days

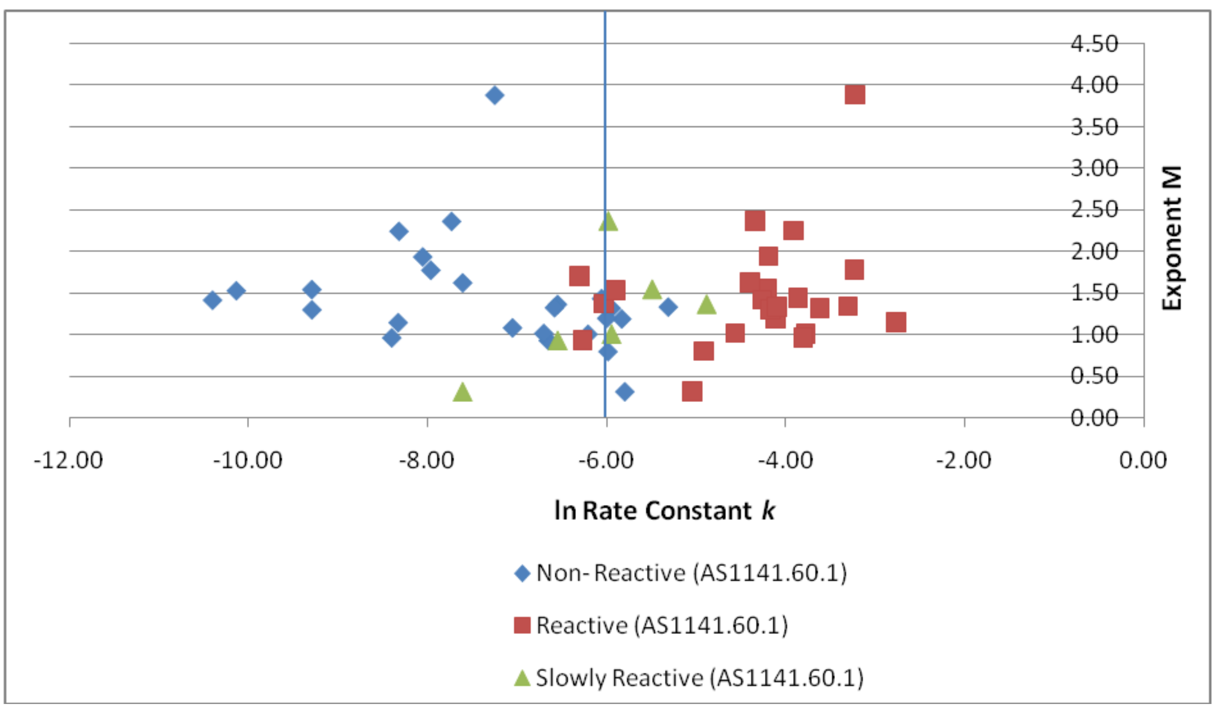

Figure 2.4: Reactivity plot based on AMBT (AS1141.60.1 test data) – 14 days

From figure 2.3 and 2.4 above, adopting the conservative value of ln *k* below which all aggregates are innocuous as -6 specified in Johnston et. al. (2000) results in a split in which most aggregates tested as non-reactive with AS1141.60.1 fall below, and those tested as reactive with AS1141.60.1 fall above. However, for both 14 and 28 days, there are some aggregates which tested as slowly reactive using AS1141.60.1 expansion criteria that are deemed to be innocuous based on the kinetic parameters, as well as some aggregate types which are reactive falling in the innocuous category of the graph and vice versa.

When examining data points for aggregates with borderline results around ln k < -6 for 14 days (-6.5 < ln k < -5.5) there are 10 aggregates that fall into this area of the plot. Five (5) of these aggregates all have kinetic parameters that suggest the aggregates are non-reactive with correlating CPT classifications. While another 4 have border line reactive ln k values, -5.8976, -5.9465, -5.9832 and -5.8292 respectively, and are classed as non-reactive by the CPT expansion criteria. This suggests that the kinetic model using AMBT data, can give classification results consistent with the 12 month CPT test, but at 14 or 28 days. In our analysis the 14 and 28 day kinetic results gave comparable results with the 14 day results having slightly better agreement with the CPT classification.

3. Conclusions

Using a kinetic approach, such as the Kolmogorov-Avrami-Mehl-Johnson model, can provide the potential for decision making based not only on a single expansion value, but also the rate of expansion for various aggregates.

The results of this study show that the application of a kinetic model based on KAMJ provides a means of interpreting the results of AS1141.60.1 independent of expansion values obtained at both 14 and 28 days. Using this method aggregates examined with ln k < -6 are non-reactive or innocuous, whereas those with ln k > -6 are reactive.

The literature search by Rocker et al (2015) [1] and work by Ideker et al. (2012) [4] found that the reactivity diagnosed by CPT was found to correlate well with reactivity in field exposure. In our study, reactivity classifications from the kinetic method achieved close correlation to those from the CPT at both 14 and 28 days. This suggests that the kinetic approach offers potential to determine reactivity classifications consistent with those of CPT at 14 or 28 days, rather than the 12 months required by the CPT. It also has the potential to determine the rate of expansion of the alkali silica reaction, aiding in the evaluation of potential service life of a structure.

4. Acknowledgement

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5. References

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