



INVESTIGATION INTO THE EFFECTS OF METAKAOLIN AS A CEMENT REPLACEMENT MATERIAL IN ASR REACTIVE CONCRETE.

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ABSTRACT

As a result of previous promising results from the use of metakaolin as a cement replacement material for the suppression of the alkali-silica reaction, the BRE has undertaken a large scale test programme to identify the cement replacement levels at which it becomes effective using different reactive natural aggregates.

Concrete prisms have been produced using three known UK reactive aggregates at alkali levels varying between 2.74 and 5.005 kg/m³ Na₂Oeq. Cement replacement by metakaolin was undertaken at 0, 5, 7.5, 10 and 15 % by weight. Expansion testing was undertaken at 38°C and 20°C at 100 % RH. Additional to these, concrete prisms were also tested at 38°C in 2 M NaCl and in inter-tidal marine conditions. Larger scale (300 mm² x 500 mm) concrete blocks have also been produced for external exposure testing using equivalent concrete mixes produced with 0 and 10 % metakaolin replacement levels. The early 100% RH 38°C and 20°C expansion test results suggest the use of a 10 % replacement of the cement with metakaolin can avoid the development of ASR in all the various concrete mixes produced. Early results (26months) from the external exposure tests confirm this view. However, a level of more than 10% appears to be necessary when using the most reactive aggregate in a high alkali concrete immersed in salt solution at 38°C.

Keywords: Alkali-silica reaction, prevention, reactive natural aggregates, metakaolin, concrete prism tests.

INTRODUCTION

For the development of deleterious alkali-silica reaction (ASR) to occur three constituents must be found in adequate quantities. These three components are a reactive form of silica, usually as a constituent of the aggregate, a source of alkali metal ions, primarily derived from the cement pore solution and moisture. If any one of these three occurs only to a limited extent or is depleted over time, deleterious ASR will not occur or will stop with time.

Over recent years various techniques have been employed to suppress the development of deleterious ASR by the avoidance of, or reductions in, the use of these various constituents of the reaction. One well proven technique for reducing the alkalinity of a concrete is the use of pozzolanic materials such as pulverised fuel ash (Pfa), ground granulated blast furnace slag (ggbs), microsilica, natural volcanic ashes and now, metakaolin. These pozzolans consume the alkaline Ca(OH)_2 [Portlandite] constituent of the hydrated cement paste to varying degrees, and reduce the overall alkalinity of the concrete. In many cases this has been sufficient to significantly reduce or even stop, deleterious ASR expansion occurring, assuming an adequate amount of pozzolan has been added as a cement replacement material. The pozzolans consume the Ca(OH)_2 to generate further cementitious hydrate material [Gehlenite and Tobermorite], (Turrizani, 1964) thereby increasing the strength and quality of the concrete concerned.

Metakaolin is a highly reactive pozzolan derived from the high temperature (700 to 800°C) calcining of pure kaolin clay. This pure kaolin clay is initially derived from decomposition of feldspar in granite. The calcined end product is ground to a fine powder, (90% less than 10µms in diameter). The metakaolin formed has a highly disorganised structure making its reactivity with Ca(OH)_2 very rapid (Ryle, 1999). The Chapelle test, which measures Ca(OH)_2 reactivity has shown it to be substantially more pozzolanic than many of the other regularly used cement replacement materials. Table 1 gives details of results of the Chapelle test reported by Largent (1978).

TABLE 1: Reactivity of Pozzolans using the Chapelle Test

Pozzolan type	Pozzolan reactivity measured as mg of Ca(OH)_2 consumed per g of pozzolan
Ground granulated blast furnace slag	40
Microsilica	427
Pulverised fuel ash	875
Metakaolin	1050

It is well documented that the use of metakaolin reduces permeability of a concrete by refining the pore structure and improves the adhesion of cement paste to aggregate bond, a good example being by Larbi and Bijen (1992). It also has generally beneficial effects on strength development and other durability related properties such as chloride ingress and sulphate attack, (Page and Coleman, 1994). As shown above, when added to a concrete it also removes the Ca(OH)_2 , reduces alkalinity, and potentially reduces a concrete's alkali silica reactivity. Larbi (1991) has shown that Ca(OH)_2 was virtually eliminated from a cement paste containing 20% replacement of the cement by metakaolin. Because of its high

reactivity and ease of dispersion, it can be used at high replacement levels, up to 25% of the OPC, if required.

In the 1960's several major dams were constructed in the Amazon basin using a blend of local calcined kaolin and Portland cement. The only aggregates available were shown to be alkali reactive. Andriolo and Sgarboza (1986) claimed that the use of the metakaolin had prevented deleterious ASR expansion developing, a claim also made by several other researchers. Previous investigations have shown that the presence of some metakaolin as a cement replacement material significantly reduces the potential development of deleterious ASR. As previously mentioned, this is accomplished, firstly, by reducing the reservoir of soluble Ca^{2+} and OH^- ions, (even though metakaolin may contain a higher concentration of alkali metal ions than does OPC, see Table 3), but also by retarding the migration of water through the concrete. Importantly, there is no need to remove all the $\text{Ca}(\text{OH})_2$ in order to prevent expansion. When metakaolin reacts with $\text{Ca}(\text{OH})_2$, only insoluble crystals of 'CSH' and 'CASH' are formed. This is important because other pozzolans can give undesirable products.

Jones et al. (1992) showed that deleterious ASR was avoided by a 10% replacement of the cement by metakaolin, within a potentially reactive concrete mix, even when placed in severe environmental conditions. This provides such concrete with a high resistance to ASR induced expansion, even in highly saline conditions, without associated reductions in the pore solution pH which, remained above 12.5. They also observed that a 15% replacement of the cement by metakaolin removes all the free $\text{Ca}(\text{OH})_2$. The absence of the $\text{Ca}(\text{OH})_2$ from the cement paste removes one of the components of a chemical process by which extra alkalis can be made available to the alkali-silica reaction in the presence of sodium chloride (Sibbick and Page, 1996). Jones states that although minimum metakaolin replacement levels required to prevent deleterious expansion are not yet known, experience suggests a level of 10% replacement would be sufficient, when reactive concretes were tested at 100% relative humidity (RH). Establishing robust evidence for this figure is major objective of this investigation.

MIX DESIGN

The level of metakaolin as a cement replacement material needed to avoid the development of deleterious ASR has been investigated primarily using a range of reactive aggregates, in concrete mixes of differing cement and alkali content with different levels of metakaolin cement replacement. Expansion testing using prisms of dimensions 200 x 75 x 75mm was undertaken in accordance with the relevant British standard (DD 218, 1995). This expansion testing was carried out in a number of different environments:

- i) At $38^\circ\text{C} \pm 2$ in 100% relative humidity,
- ii) At $38^\circ\text{C} \pm 2$ totally immersed in 2M NaCl which was not replenished over the test period, expansion measuring being undertaken at the same temperature,
- iii) At $20^\circ\text{C} \pm 2$ in 100% relative humidity,
- iv) Immersed in the inter-tidal zone at the BRE marine exposure site, Shoeburyness, Essex.

The concrete expansion prisms with expansion reference studs on their ends were made using three well-documented reactive aggregates, (Table 2), in the various mix designs

summarised in Tables 4 to 7. The two cements used had medium and high alkali contents with the metakaolin also containing a modest amount of alkali, Table 3. Larger prisms of dimensions 500 x 300mm², with the 0 and 10% metakaolin cement replacement mixes as highlighted in Table 1, were also placed in ponds created by rainwater, externally at the BRE site, Fig 1.

TABLE 2: Reactive Aggregates used within the Test Concretes.

Aggregate name	Aggregate Pessimism	Alkali threshold	Reference
Dry Rigg siltstone	~100%	3.5 kg/m ³ Na ₂ Oeq	Sibbick & Page, 1992
Thames Valley sand	~12%	5.2 kg/m ³ Na ₂ Oeq	Thomas & Blackwell, 1996
Bally Barnes greywacke	~100%	4.5 kg/m ³ Na ₂ Oeq	Blackwell et al., 1996



Fig. 1: BRE external exposure site for 500x300x300 mm concrete blocks.

In the case of the siltstone and greywacke, the fine aggregate in the concrete was a known non-reactive limestone (Cheddar), and for the Thames Valley sand containing concrete prism mixes, the coarse and the residual fine aggregate, (other than the 12% of the total aggregate comprising Thames Valley sand), was also composed of the same non reactive Cheddar limestone. After 24 hours the concrete prisms were demoulded, labelled and cured for a further 28 days at room temperature wrapped in damp sacking, underneath plastic sheeting. After this period of curing the concrete prisms were measured, weighed and wrapped in polythene with a small volume of water (100ml), before being placed in a sealed plastic container above water, giving a relative humidity of approximately 100%. The concrete prisms were then placed in temperature controlled rooms at 38°C and 20°C, the 38°C prisms being removed from this temperature 24 hours prior to measuring. Selected concrete prisms were also placed, unwrapped, in 2M NaCl solution within sealed plastic containers at 38°C. Importantly the salt solution was not replaced during the testing and all the measuring in this environment was carried out at 38°C.

TABLE 3: Chemical Analysis of Cement and Metakaolin

Cement Ref. & No.	%Na ₂ O by weight	% K ₂ O by weight	% Na ₂ Oeq by weight
985 'standard' cement	0.112	0.755	0.609
991 'High alkali' cement	0.260	0.980	0.910
986' Metastar 500' Mk	0.240	0.620	0.648

The use of these two cements at mix content levels of between 350 to 550 kg/m³ gave a range of alkali contents to the concretes of 2.740 to 5.005 kg/m³ Na₂Oeq, Tables 4 to 6. The water to cementitious material ratio ranged between 0.38 and 0.60 and the aggregate to cementitious material ratio ranged between 3.06 and 5.40 depending on the mix design criteria as given in Tables 4 to 8. Expansion measurements and weights, which were taken at various points during the next 700 days, are the basis of this paper. Expansion figure in shown in bold indicate a significant level of expansion. However, this expansion testing is on-going (200 weeks +) and more advanced results will be reported at a later date.

EXPANSION TEST RESULTS

Samples tested at 38°C and 100% RH.

The expansion test results are summarised in Tables 4 to 6 and Figures 2 to 6. Similar testing using the Bally Barnes greywacke is continuing, and the early results are reaffirming the main findings of this paper. It is, however, possible to establish from the Dry Rigg siltstone and Thames valley sand concrete expansion results that a level of 10% replacement of the cement by metakaolin has stopped deleterious expansion in all the various concrete mixes produced, Figures 2 and 3. Deleterious expansion is normally equated with the first signs of visible microcracking on the surface of a concrete prism and an expansion in excess of 0.05%. In most circumstances a 7.5% level of cement replacement by metakaolin also appears to be sufficient to stop deleterious ASR. However, the results of the extremely high alkali (5.0 kg/m³ Na₂Oeq) concretes show a total expansion of 0.05% is obtained after around 620 days with 7.5% replacement, Figure 2. The Thames Valley sand concrete mixes all presently appear non-reactive when tested at 38°C and 100% RH, regardless of the level of metakaolin replacement used and so the data is not shown. This is probably due to the initial alkali contents of these concretes, which were at best borderline, with regard to the alkali threshold for Thames Valley sand concretes, (Thomas and Blackwell, 1996). This has occurred due to the lower than anticipated alkali content of the high alkali reference cement (No. 991), see Table 2. However, testing is continuing to confirm the non-reactive nature of such concrete mixes.

TABLE 4: Total Expansion Figures for DR Siltstone (High Reactivity Aggregate) Mixes at 700 days. Tested at 38°C and 100% RH. 100% Reactive Coarse Aggregate, inert Fine Limestone Aggregate.

Cement content (kg/m ³)	Cement Ref. No.	OPC derived alkali in kg/m ³ equiv.	Expansion figure (%). Mix design based on weight percentage metakaolin replacement of cement.				
			0%	5%	7.5%	10%	15%
550	991	5.0	0.178	0.153	0.064	0.022	-0.004
450	991	4.1	0.114	0.097	0.036	0.022	0.006
550	985	3.4	0.071	0.031	0.009	-0.011	-0.017
350	991	3.2	0.000	0.006	0.015	0.000	0.012
450	985	2.7	-0.012	-0.010	-0.007	-0.014	-0.015

TABLE 5: Total Expansion Figures for DR siltstone (High Reactivity Aggregate) Mixes at 595 to 667 days. Tested at 38°C Totally Immersed in 2M NaCl. 100% Reactive Coarse Aggregate.

Cement content (kg/m ³)	Cement Ref. No.	OPC derived alkali in kg/m ³ equiv.	Expansion figure (%). Mix design based on weight percentage metakaolin replacement of cement.				
			0%	5%	7.5%	10%	15%
550	991	5.0	0.341	+	+	0.055	+
450	991	4.1	0.418	+	+	0.045	+
550	985	3.4	0.492	0.101	0.032	0.017	0.010
350	991	3.2	0.101	+	+	0.045	+
450	985	2.7	0.223	0.081	0.036	0.030	0.018

TABLE 6: Total Expansion Figures for Thames Valley sand (Moderate Reactivity Aggregate) Mixes at 577 to 648 days. Tested at 38°C Totally Immersed in 2M NaCl. 12% Reactive Fine Aggregate, Remaining Aggregate Inert Limestone.

Cement content (kg/m ³)	Cement Ref. No.	OPC derived alkali in kg/m ³ equiv.	Expansion figure (%). Mix design based on weight percentage metakaolin replacement of cement.				
			0%	5%	7.5%	10%	15%
550	991	5.0	0.297	+	+	0.037	+
450	991	4.1	0.031	+	+	0.040	+
550	985	3.4	0.019	0.023	+	0.025	0.025
350	991	3.2	0.033	+	+	0.033	+
450	985	2.7	0.029	0.034	+	0.021	0.030

+ - Mix not tested in this environment

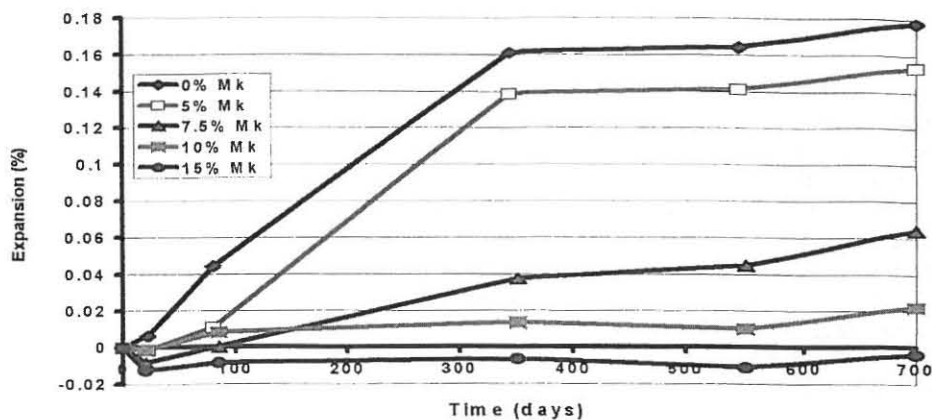


Fig. 2: Expansion (%) v time (DR 5.0 kg/m³ Na₂Oeq).

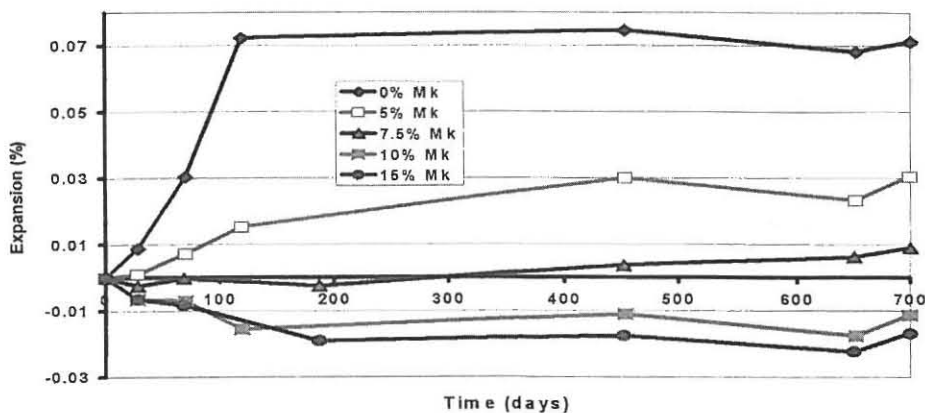


Fig. 3: Expansion (%) v time (DR 3.35 kg/m³ Na₂Oeq)

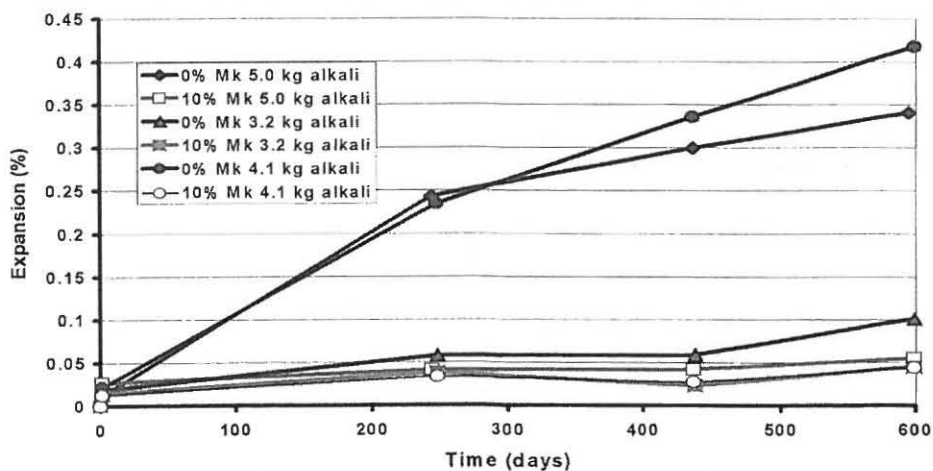


Fig. 4: DR siltstone at various alkali levels with 0 and 10% metakaolin replacement immersed in 2M NaCl at 38°C.

Salt immersed samples

The evidence from this work shows that the presence of the 2M NaCl solution has a considerable accentuating or even initiating effect on the deleterious expansions developed by the various Dry Rigg siltstone concretes containing no metakaolin replacement material, compared with the equivalent concretes immersed in 38°C and 100% RH. Moreover, the results to date indicate that a 10% level of cement replacement with metakaolin has avoided the development of deleterious ASR in all the concrete mixes tested with the exception of the high alkali Dry Rigg concrete mixes, even in the severe environmental conditions tested here, Figure 4. There is higher expansion developed by the concrete with an initial alkali content near the perceived alkali threshold for the Dry Rigg siltstone. ($3.5 \text{ kg/m}^3 \text{ Na}_2\text{Oeq}$) compared with the higher initial alkali mixes, Table 5. This is interesting and in line with previously reported findings, which suggested that an initial alkali content pessimum existed near each reactive aggregates alkali threshold for concrete mixes immersed in highly saline solutions, (Sibbick and Page, 1996). In the case of the high alkali ($5.0 \text{ kg/m}^3 \text{ Na}_2\text{Oeq}$) Thames Valley sand concrete mix immersed in the salt solution, it has clearly reacting vigorously, whilst the equivalent concrete with a 10% level of cement replacement by metakaolin, shows no significant expansion. The remaining Thames Valley sand concretes do not show evidence of any deleterious expansion either with, or without, the 10% level of cement replacement by metakaolin, Figure 5.

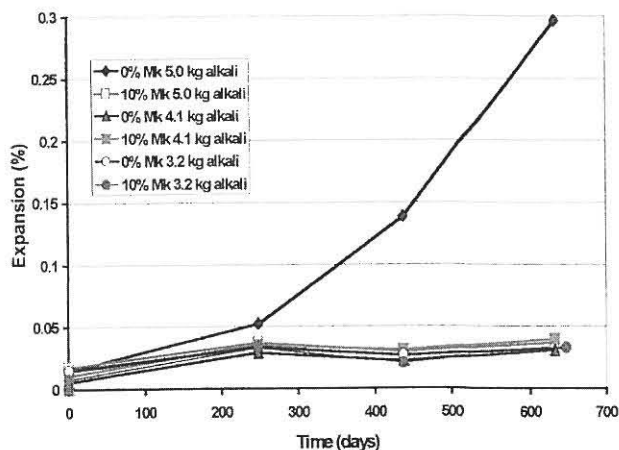


Fig. 5: Thames Valley sand mix at various alkali levels with 0 and 10% metakaolin replacement levels immersed in 2M NaCl at 38°C.

The evidence presented in Figure 6 which is for concretes containing Dry Rigg siltstone immersed in 2M NaCl solution, show that a 5% replacement of the cement by metakaolin is also insufficient to stop deleterious ASR expansion in such circumstances. The early results of the 20°C 100% RH expansion data indicate similar if,

presently, less well developed observations to those discussed above. This data along with other results from the samples exposed to inter-tidal saline conditions in the external environmental conditions, and results using the third aggregate type, (Bally Barnes greywacke) will be reported at a later stage. The early results (26 months) from the external environmental testing show some degree of visible surface microcracking and associated expansion is occurring on the Dry Rigg siltstone concretes of alkali levels 3.35 to $5.0 \text{ kg/m}^3 \text{ Na}_2\text{Oeq}$ with no cement replacement by metakaolin. All the other mixes presently remain sound.

FURTHER INVESTIGATIONS

As has been reported previously the use of metakaolin in concrete consumes the vast majority of the $\text{Ca}(\text{OH})_2$ within the cement paste thus leaving it unavailable to the ASR reaction. At a later stage in this investigation the concrete prisms will be examined by optical petrography to ascertain whether this reported loss of $\text{Ca}(\text{OH})_2$ can be detected visually and if variations observed can be attributed to variations in the content of metakaolin within the cement paste. It is also hoped to establish whether an associated reduction in the cement paste capillary porosity can be observed and if this has any effect on the form taken by the expansive microcrack networks as previously reported for ASR induced cracking occurring in similar concretes containing 25% cement replacement with

Pfa, (Sibbick and Page, 1995). Confirming the presence of cementitious hydrates such as Gehlenite and Tobermorite within the cement paste matrix, as reported by Turrizani (1964), will further confirm that the metakaolin is reacting with the Portlandite, $[\text{Ca}(\text{OH})_2]$, to produce a greater cementitious component and therefore, overall, better quality concrete.

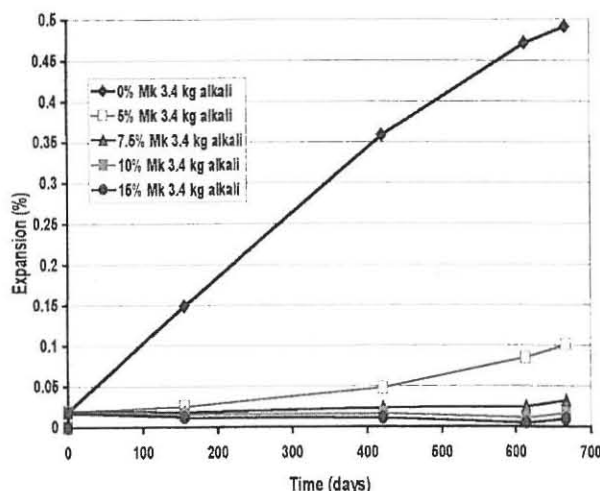


Fig. 6: DR siltstone Expansion (%) v time (3.4 kg/m³ Na₂Oeq) Immersed in 2M NaCl at 38°C.

CONCLUSIONS

1. Concrete expansion prisms, which have been tested at 38°C and 20°C in 100% relative humidity, using three reactive natural aggregates mixes at various alkali and cement replacement levels are indicating that a 10% level of cement replacement with metakaolin is sufficient to stop deleterious ASR, in all circumstances, when tested over a period of 24 months.
2. In most circumstances the replacement of 10 % of the cement with metakaolin has been shown to be adequate to avoid the development of deleterious ASR even in a highly saline environment (2M NaCl), tested at 38°C. The single exception to this result was observed for the high alkali/cement concrete containing the most highly reactivity aggregate (DR).
3. Evidence from the expansion test results suggests that a cement replacement rate of 7.5 % metakaolin is adequate, in virtually all cases, to avoid the development of deleterious ASR. It was only within the extremely high alkali/cement content mixes (550 kg/m³

cement) containing a highly reactive aggregate that such a level of cement replacement may not be suitable.

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