A study of the ASR of an aggregate with high chert content by means of ultra-accelerated mortar bar test and pore fluid analysis

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**Various studies have indicated that the use of some ultra-accelerated mortar bar expansion test methods for assessing the alkali-silica reactivity of concrete aggregates (particularly those using 1 M NaOH solution at 80 ºC) can give rise to misleading results causing certain types of aggregates to be inappropriately accepted. This is the case if the aggregates contain more than 2 % by mass of reactive constituents, in the form of porous chert or flint and chalcedony. To date, no explanations have been given for this anomaly. This paper deals with a study aimed at investigating this anomaly. A sample of crushed sea gravel, dredged from the southeast coastal waters of England, containing 12.5 % of reactive constituents, was used for the study. Fractions of the crushed sea gravel amounting to 0, 25, 50, 75 and 100 % of the total aggregate fraction and corresponding to 0, 3.1, 6.3, 9.4 and 12.5 % reactive constituents, were incorporated in mortar bars, which were subsequently subjected to RILEM ultra-accelerated mortar bar expansion test.
At the end of the test, the bars were examined by means of concrete petrography to establish whether or not attack due to ASR had taken place. The study was designed in this way in order to examine whether or not North Sea gravel from the southeast coastal waters of England exhibits a pessimum effect.**

Key words: alkali-silica reaction, North Sea gravel, chert, mortar bars, pessimum, pore fluid

1 Introduction

1.1 Background

In June 2000, CUR Technical Committee VC 62: “Alkali-silica reaction in concrete” [1] was set up to review CUR Recommendation 38: *“Measures to prevent damage due to alkali-silica reaction in concrete”* [2]. The task of the technical committee was completed in 2002 after publication of CUR Recommendation 89 [3]. The purpose of this review was to update the existing recommendation in the light of new developments on the subject of alkali-silica reaction (ASR), since the promulgation

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of that recommendation in 1994. Two of the central issues were concerned with the alkali-silica reactivity of gravel dredged from the North Sea and the method by which its potential reactivity in concrete could be suitably assessed. North Sea sand and gravel, dredged from the southeast coastal waters of England contain considerable amounts of cherts and flints (up to about 80 % by volume), which have been found in practice to be potentially reactive with regard to alkali-silica reaction, especially the porous particles [4-6]. Laboratory work by Nixon and others [7, 8] using river sand and gravel in which the predominant rock type was chert/flint in combination with a non-reactive limestone showed that maximum expansion of the concrete tested occurred when a specific proportion of the chert/flint aggregate was present. Negligible expansions occurred at higher dosages of the chert/flint aggregate. According to Nixon et al. [7], the specific proportion at which maximum expansion occurs, the so-called pessimum occurs in real concrete structures with all kinds of reactive materials. In the United Kingdom, many of the worst cases of ASR damage have occurred in concrete made with sand containing flint or chert in combination with limestone or granite as coarse aggregate. In contrast, in the southeast of England, there has been extensive use of concrete prepared with sand and gravel dredged from the North Sea with no reported cases of damage due to ASR. North Sea-dredged sands and gravels are increasingly used for producing concrete in the Netherlands and as such raises questions concerning their potential threat to the durability of concrete structures with regard to ASR.

Two of the several questions that are raised are concerned with the following aspects:

1. *Pessimum effect:* that is, whether or not aggregates dredged from the North Sea, especially, gravel dredged from the southeast coastal waters of England exhibits a pessimum effect in the ultra-accelerated mortar bar test (UAMBT).
2. *Alkali-silica reactivity:* why the UAMBT, using 1 M NaOH solution at 80 oC is not effective in assessing the potential alkali-silica reactivity of aggregates containing high contents of chert or flint, such as this North Sea-dredged gravel.

1.2 Pessiumum behaviour

According to Hobbs [9], with some faster forms of reactive siliceous constituents such as opal and porous chert or flint, there is a particular proportion of reactive material in an aggregate, which leads to maximum or peak expansion called the *pessimum content*. Such a reactive aggregate exhibits such behaviour, it is said to exhibit a pessimum behaviour or pessimum effect. Above or below the pessimum content, the expansion decreases. Figure 1 is an illustration of the pessimum behaviour of an aggregate in which opaline silica is the reacting constituent.

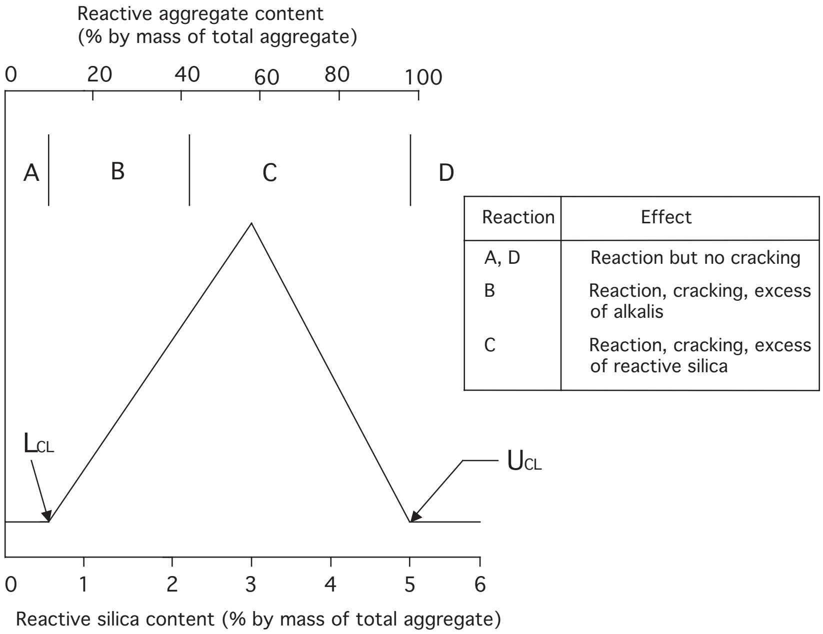


Figure 1 Pessimum behaviour: water-cement and aggregate-cement ratios 0.4 and 2.75 respectively, alkali content is 6 kg/m^3. LCL and UCL are the lower and upper critical limits respectively of the pessimum effect [9].

According to Shayan [10], the reason for the pessimum effect in the standard mortar bar expansion test is that, for a given level of alkali content, expansion of mortar bars increases with an increase in the amount of the reactive aggregate up to a point, the *'pessimum proportion'*, beyond which there is not sufficient alkali available for the formation of expansive gel. At reactive aggregate contents much larger than the pessimum proportion, the alkali content becomes so low or so diluted in the aggregate, that very little or no expansion occurs.

From the above definition, it is clear that the pessimum behaviour of an aggregate is characterised by two limits: the *upper critical limit and the lower critical limit*, within which damage due to alkali-silica reaction occurs [9]. The lower critical limit is usually established by the amount of reactive constituents present in the aggregate. If the amount of reactive constituents present in the aggregate is lower than the *lower critical limit*, the quantity of gel formed from the alkali-silica reaction will be so small that it will not able to swell enough (on absorption of water) to cause damage to the mortar or concrete, even if all the reactive constituents undergo complete reaction. In that case, there is an excess of alkalies relative to the reactive silica.

On the other hand, the *upper* critical limit is determined by the amount of alkalies in the concrete. If there is excess of reactive constituents present in the aggregate, above the *upper* critical limit, there are not enough alkalies at a given time to react with the excess silica in the reactive aggregate. In that case, the quantity of gel formed is so small that it is not able to swell enough, on absorption of water, to cause damage to the concrete. Moreover, it is believed that part of the gel is formed at an early stage of hydration of the cement when the concrete is still in the plastic phase. The other part is believed to form at a later stage, but diffusely spread throughout the concrete and thus making it ineffective in causing damage to the concrete by swelling. Such high amount of reactive silica is known as the *upper* critical limit. The concrete is in that case said to have a 'buffer' of reactive silica. If sufficient alkalies are introduced from external sources into the pore fluid of the concrete at a later stage, for example from de-icing salts, the excess reactive silica can undergo alkali-silica reaction to produce sufficient gel to cause distress to the concrete upon absorption of water and subsequent swelling.

On the basis of the foregoing, the pessimum behaviour of an aggregate can be established if there is sufficient reactive silica in the concrete 'aggregate mix' and there is also sufficient alkali available in the pore fluid of the concrete.

1.3 Suitability of the UAMBT for assessing alkali-silica reactivity of aggregates

For many years, one of the methods that is commonly used to rapidly assess the potential alkali-silica reactivity of aggregates for use in concrete is the ultra-accelerated mortar bar test method. Several UAMBT methods exist [11-16], but the one that is very often used and appears to be suitable regardless of the type of aggregate, is the RILEM TC 106-2 ultra-accelerated mortar bar test method [17]. Essentially, mortar bars are exposed to 1 M NaOH at 80 °C and expansion of the bars is monitored over a period of 21 days. This method, which was originally developed by Oberholster and Davies [15], has been developed further and currently incorporated in various concrete and aggregate standards in several countries, including CUR Recommendation 89 [3] and the ASTM standard C 1260 [11-13].

In recent years, results of various studies have indicated that the RILEM TC 106-2 and ASTM C 1260 methods [11, 17] can give rise to misleading results and inappropriate approval of certain types of aggregates. This is the case if aggregates contain more than 2 % of reactive constituents, in the form of porous chert or flint and chalcedony. Using the method by Oberholster and Davies [15], Soers [18] tested samples of gravel and sand dredged from the southeast coastal waters of England and found that these aggregates showed similar (insignificant) expansions as the non-reactive reference aggregate. The tested sea-dredged aggregates contained substantial amounts of porous chert or flint and chalcedony, which exceeded the 2 % by mass allowable limit. On the other hand, when the same materials were tested using the Danish ultra-accelerated mortar bar test method [12] (which uses 1 M NaCl instead of 1 M NaOH solution), a clear distinction was made between the sea-dredged aggregates and the reference non-reactive aggregate: the sea-dredged aggregates showed expansions beyond the allowable limit. Similar observations have been made by other workers [19, 20].

1.4 Objectives of the investigation

The purpose of the study was twofold:

- to examine whether or not a particular sample of North Sea gravel, dredged from the southeast coastal waters of England exhibits a pessimum effect in this UAMBT;

- to investigate why the RILEM ultra-accelerated mortar bar test (using 1M NaOH solution at 80 °C) is not effective in assessing the potential alkali-silica reactivity of aggregates containing high contents of chert or flint, such as this North Sea-dredged gravel.

2 Experimental procedures

2.1 Materials

The sea gravel used was dredged from the southeast coastal waters of England and contained about 12.5 % reactive constituents. A non-reactive limestone obtained from a quarry in the area of Namur, Belgium was used as a reference complementary aggregate to prepare the mortar specimens. The total silica content of this limestone was about 1 % (by mass) and had been found from petrographic analysis and mortar bar test to be a non-reactive rock [18]. Both aggregates were crushed and graded to conform to the requirements of the RILEM TC 106-2 [17] ultra-accelerated mortar bar test method. After crushing and homogenising, fractions of the crushed sea gravel amounting to 0, 25, 50, 75 and 100 % of the total aggregate and corresponding to 0, 3.1, 6.3, 9.4 and 12.5 % reactive constituents, were used to prepare the mortar bars, which were subsequently subjected to the ultra-accelerated mortar bar expansion test. The mortar bars were prepared with a reference Portland cement, CEM I 42.5 obtained from Norcem in Brevik, Norway. The alkali content of this cement, expressed as Na_2O-equivalent was 1.25 % and the specific surface, measured according to the method of Blaine, was 450 m^2/kg.

2.2 Ultra-accelerated mortar bar expansion test

For the UAMBT, five series of mortar bars, each series consisting of three bars, each measuring 160 mm x 40 mm x 40 mm were prepared and initially moist-cured for 24 hours at 20 °C. Thereafter, the specimens were placed in a demineralised water at 80 °C for 24 hours after which they were subjected to ultra-accelerated test conditions of 1 M NaOH solution at 80 °C as described in the RILEM TC 106-2 Recommendation [17]. The grading requirement of the aggregate according to this method is given in Table 1.

Table 1. Grading requirements of crushed fine material, gravel or coarse material.

Sieve size		Mass
Passing	Retained	(%)
4 mm	2 mm	10
2 mm	1 mm	25
1 mm	500 µm	25
500 µm	250 µm	25
250 µm	125 µm	15

The aggregate-cement ratio (by mass) of the mortar bars was 2.25 : 1 and the water-cement ratio (by mass) was 0.47. The formulation of the mortar bars, which included mixing, casting into moulds and compaction, as well as conditioning and storage were carried out according to the procedures detailed in the European Standard EN 196-1 [21]. The expansion of the mortar bars was measured at specific intervals up to 21 days, after which the extent of cracking in the mortar bars was noted.

2.3 Petrographic examination of mortar bars after expansion tests

Optical microscopic examination of the bars was performed after the ultra-accelerated mortar bar test. The purpose was to gain insight into the type of constituents responsible for the attack and to determine the extent of the alkali-silica reaction in the bars. Initially, the interior of the bars were exposed by fracturing and subsequently examined with the aid of a stereomicroscope.
To obtain more detailed information on the type of reactive constituents, the extent of reactivity and the microstructural differences between the interior and the reacted 'skin', one thin section was prepared from each of the mortar bars showing maximum expansion in each series and examined by means of polarising and fluorescent microscopy. The specimens for the thin sections were removed from the middle of the bars as shown in Figure 2. Each specimen was first vacuum-impregnated with an epoxy resin containing a fluorescent dye prior to preparation of the sections. This method simplified the examination of the thin sections by clearly distinguishing the voids, cracks, cement paste and aggregate particles, especially the porous ones.

2.4 Pore water expression analysis

For the pore water extraction analysis, three mortar mixes were prepared using demineralised water. Each mix consisted separately of 100 % aggregate of crushed limestone (reference mix), a standard non-reactive river sand (reference mix) and crushed sea gravel in accordance with the mix composition given in Table 1. The water-cement ratio was kept constant at 0.50 for all the mixes. For each mix, three specimens were cast into plastic bottles and after being tightly sealed, they were transferred into a conditioned room at a temperature of about 20 ºC for further hydration. At the ages of 2 and 7 days, the specimens were demoulded and immediately loaded into a pore water expression chamber and the pore water extracted. Shortly after extraction, the hydroxide ion concentration, OH^-, was determined by titration against HNO_3 using phenolphthalein as an indicator. The Na^+ and K^+ concentrations were determined by flame emission spectroscopy.

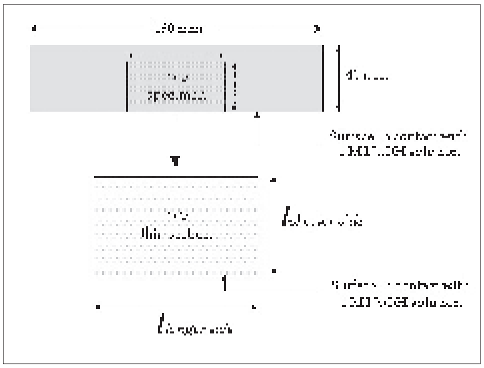


Figure 2. Schematic representation of the way the specimens used for the thin sections were removed from the mortar bars.

3 Results

3.1 Ultra-accelerated mortar bar expansion tests

The UAMBT was carried out on mortar bars with five different aggregate combinations of crushed sea gravel and crushed limestone. For each aggregate combination, three mortar bars were prepared and tested. The average of the three expansion data for a particular age of testing in the UAMBT is presented in Figure 3 and Table 2.

From Figure 3 and Table 2, it appears that the expansion of the mortar bars prepared with 25 % or more of the crushed sea gravel is similar. Only the mortar bars prepared with 100 % crushed limestone show smaller expansions than the mortar bars containing the crushed sea gravel.
For the five tested mortar compositions the expansion after 14 or 20 days is smaller than the maximum allowable value of 1 ‰. This maximum allowable value of 1 ‰ is the acceptable limit above which the aggregate material may be considered as potentially alkali-silica reactive.

The expansion as a function of the percentage crushed sea gravel is given in Figure 4. From the figure, it appears that for the tested samples, there is no pessimum behaviour or effect.

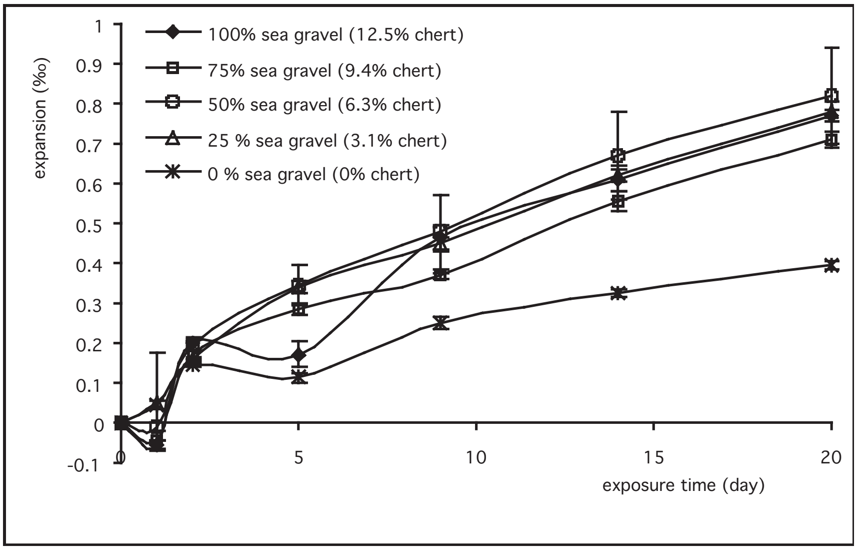


Figure 3. Expansion (‰) as a function ofexposure time of mortar bars containing various percentages of crushed sea gravel as percentage of the total aggregate in the UAMBT. The other aggregate component is crushed limestone

Table 2. Expansion (‰) of mortar bars prepared with various fractions of crushed sea gravel after 20 days of exposure.

Day	Proportions of crushed sea gravel / limestone (% total aggregate)				
	100 / 0	75 / 25	50 / 50	25 / 75	0 / 100
1	-0.05 (0.01)	-0.05 (0.00)	-0.01 (0.01)	0.05 (0.12)	0.05 (0.01)
2	0.20 (0.02)	0.17 (0.01)	0.2 (0.01)	0.16 (0.01)	0.15 (0.01)
5	0.17 (0.03)	0.29 (0.01)	0.35 (0.05)	0.34 (0.02)	0.11 (0.01)
9	0.46 (0.03)	0.37 (0.01)	0.48 (0.09)	0.45 (0.02)	0.25 (0.01)
14	0.61 (0.03)	0.56 (0.03)	0.67 (0.11)	0.62 (0.02)	0.33 (0.01)
20	0.77 (0.02)	0.71 (0.02)	0.82 (0.12)	0.78 (0.02)	0.40 (0.01)

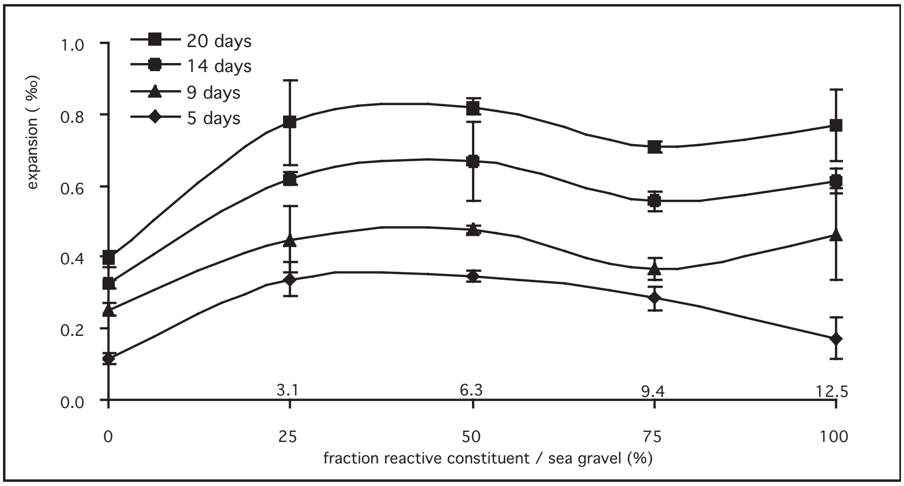


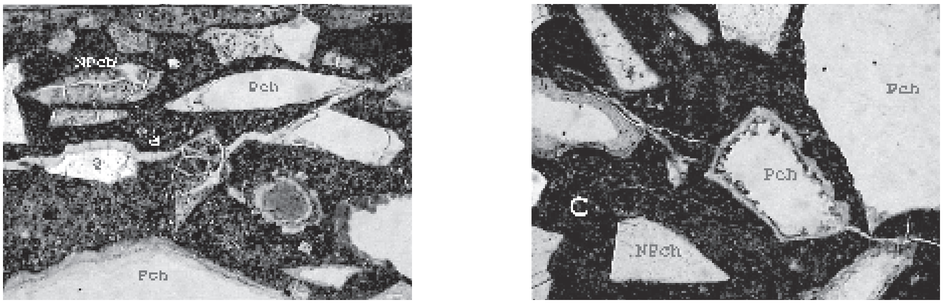
Figure 4. Expansion (‰) as a function of percentage of crushed sea gravel (as percentage of the total aggregate)

3.2 Petrographic examination

Evidence for attack due to ASR

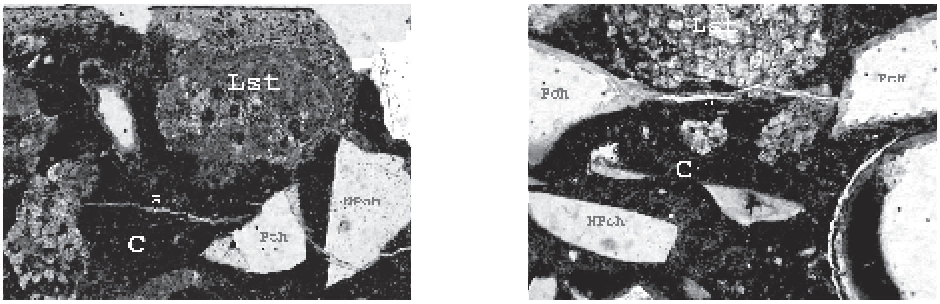
From the stereomicroscopic examination of the fractured surfaces of the mortar bars, the mortar bars containing various amounts of crushed sea gravel showed a distinct interior or core where the particles appeared to be unaffected. In the outermost zone (about 2 to 4 mm thick from the surface in contact with the NaOH solution) where reaction appeared to have been dominant, the reactive constituents, mostly chert and sandstone particles around the edges exhibited clear evidences of attack. Cracks were not visible on the bars even when the stereomicroscope was used.

With the exception of the mortar bar specimen containing 100 % crushed limestone as aggregate, all the other mortar bars showed clear evidence of attack due to ASR. These evidences are illustrated in the PFM-micrographs in Figures 5, 6 and 7.



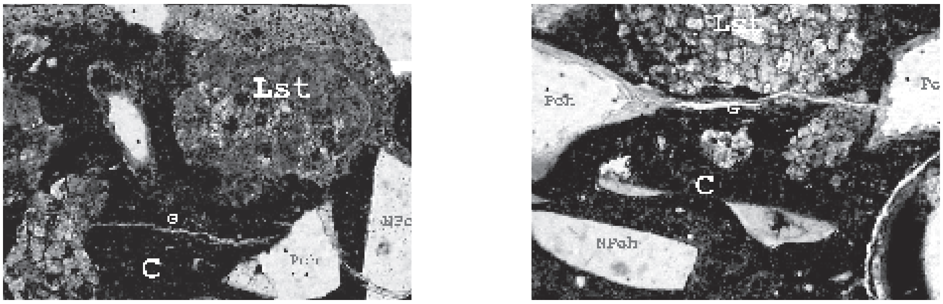
a = outermost part
b = circa 3 mm from surface

Figure 5. Thin section micrographs showing ASR-attack of porous chert particles in the mortar bar containing 100 % crushed sea gravel. Pch = porous chert; NPch = non-porous chert; Q = quartz; G = ASR-gel; C = cement paste. Image is 1.4 mm by 0.9 mm.



a = outermost part
b = circa 2 mm from surface

Figure 6. Thin section micrograph (transmitted light) showing ASR-attack of porous chert particles in the mortar bar containing 50 % crushed sea gravel. The limestone particles, Lst, are not affected. Pch = porous chert; NPch = non-porous chert; G = ASR-gel; C = cement paste. Image is 1.4 mm by 0.9 mm.



a = outermost part
b = middle of the mortar bar

Figure 7. Thin section micrographs (transmitted light) showing an overview of the mortar bar containing 100 % crushed limestone. None of the limestone particles, Lst, is affected by the alkali-silica reaction. V = void; C = cement paste. Image is 1.4 mm by 0.9 mm.

The depth of attack (estimated from the surface of the mortar bar in direct contact with the NaOH solution) varied from 1-2 mm (in the specimens containing 25 and 50 % of crushed sea gravel) to 2-3 mm in the specimens containing 75 and 100 % of crushed sea gravel. No evidence of attack due to ASR was found in the mortar bar specimen containing 100 % crushed limestone as aggregate. Also none of the quartz particles and none of the minor mineral constituents such as calcite, oxides, micas and feldspars showed any attack due to ASR regardless of the high temperature of exposure. A summarised overview of the results obtained is presented in Table 3.

Table 3. A summarised overview of the results of the petrographic examination.

Mix composition		Reacted constituents				Depth of attack from mortar surface (mm)
Sea gravel	Crushed limestone	Porous chert	Non-porous chert	Chalcedony	Sandstone	
100	0	Yes (see Figure 5)	Yes (superficial)	No	Yes	2 – 3
75	25	Yes	No	No	No	2 – 3
50	50	Yes (see Figure 6)	No	No	No	1 – 2
25	75	Yes	No	No	No	1 – 2
0	100	No (see Figure 7)	Absent	Absent	Absent	Absent

N.B. Porous chert, non-porous chert and chalcedony were absent in the specimen containing 100 % crushed limestone.

Other aspects

With the exception of the specimen containing 100 % crushed limestone, almost all the air-voids in the zone of attack or the 'skin' were fully or partially filled with ASR-gel. Also the cement paste showed an inhomogeneous microstructure (especially in the zones of attack) in the form of high and low capillary porosity. In the specimen containing 100 % crushed limestone, the microstructure of the cement paste was found to be homogeneous.

3.3 Pore water expression analysis

For analyses of the data, it was assumed that since the mortar mixes were sealed in plastic containers against ingress or loss of water throughout the curing time, four mechanisms could be responsible for the variations in the concentrations of ions in the extracted pore fluids. These include:

- Release of ions into the pore fluid by the hydrating Portland cement.
- Decrease in the amount of *free water* by virtue of the fact that the cement was progressively using some of the water for hydration (bound water in the cement hydrates).
- Interaction of the aggregate with the ions from the pore fluid.
- Possible release of ions into the pore fluid by constituents of the aggregate in the mortars.

The first two and the last mechanisms cause an increase in the amount of ions in the fluid while the third mechanism may decrease or increase the ionic concentration depending on the nature of the interaction. However, the net result of all mechanisms together is represented by the concentrations of the various ions that were measured at that particular time.

It must be pointed out that at the ages of 2 and 7 days, the Portland cement was still actively hydrating and for that matter thermodynamic equilibrium between the ions in the pore fluid and the hardened mortar was not yet attained. However, for purposes of comparison of the net ionic concentration, and assuming that release of ions into the pore fluid by the aggregates used was considerably limited, then one could reasonably compare the concentration in each of the mixes. The pore water analysis was performed on four mortar mixes each consisting of 100 % crushed aggregate of limestone (0 % reactive constituents), sea gravel (12.5 % reactive constituents) or standard river sand (0 % reactive constituents). The chemical evolution of the extracted pore water in terms of pH, OH^-, Na^+ and K^+ at ages of 2 and 7 days are presented in Table 4. Each value represents the average of three tests with the standard deviation reported in brackets.

Table 4. Results of the pore water extraction analyses of the mortars at the ages of 2 days. Standard deviations given in brackets.

	pH	OH^- (eq/l)	Na^+ (eq/l)	K^+ (eq/l)
Crushed sea gravel	13.81 (0.02)	0.65 (0.03)	0.20 (0.01)	0.46 (0.01)
Crushed limestone	13.89 (0.00)	0.78 (0.01)	0.22 (0.01)	0.59 (0.01)
Standard river sand	13.90 (0.01)	0.79 (0.01)	0.22 (0.01)	0.57 (0.01)

Table 5. Results of the pore water extraction analyses of the mortars at the ages of 7 days. Standard deviations given in brackets.

	pH	OH^- (eq/l)	Na^+ (eq/l)	K^+ (eq/l)
Crushed sea gravel	13.82 (0.00)	0.66 (0.01)	0.22 (0)	0.46 (0.00)
Crushed limestone	13.90 (0.00)	0.79 (0.00)	0.24 (0)	0.61 (0.01)
Standard river sand	13.90 (0.01)	0.80 (0.02)	0.24 (0)	0.57 (0.02)

The pH values have also been presented graphically in Figure 8. The concentrations of OH^-, Na^+ and K^+ are shown graphically in Figure 9.

The following deductions can be made from the tables and figures regardless of the aggregate composition:

- The pH and the concentrations of OH^-, Na^+ and K^+ 7 days are greater than those at 2 days.
- The total concentration of K^+ and Na^+ is nearly equal to the concentration of the hydroxide ion OH^- in all cases. This is normal for plain Portland cement concrete or mortar.
- With the exception of the mix containing 100 % sea gravel, the pH of the other mixes is almost equal. The pH of the pore water of the mix containing sea gravel (pH = 13.8) is about 0.1 lower than that of the other mortar mixes (pH = 13.9). This is for pH a relatively big difference.

- The OH- concentration of the mortar containing crushed sea gravel (0.66) is thus quite lower than that of the other mortar mixes (0.79).
- The sodium contents are almost same for all the mixes (about 0.24 eq/l).
- The potassium contents vary almost in the same way as that of the hydroxide contents; about 0.6 for limestone and sand, 0.46 for sea gravel; the maximum difference is 0.15 eq/l.

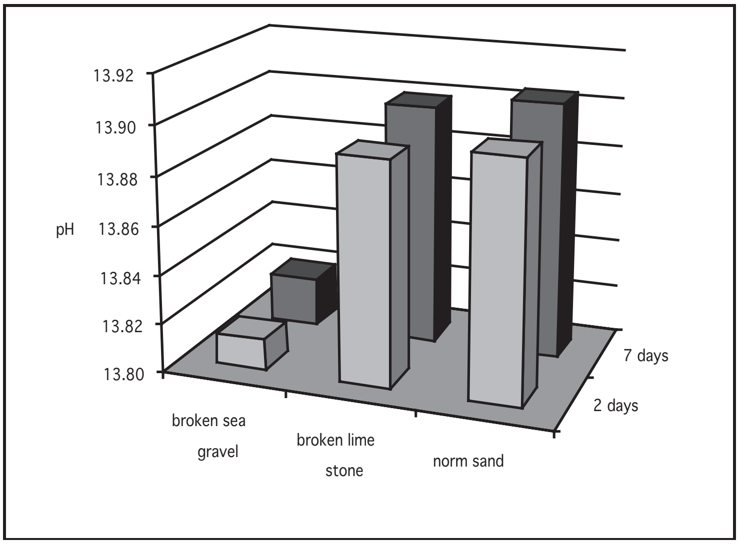
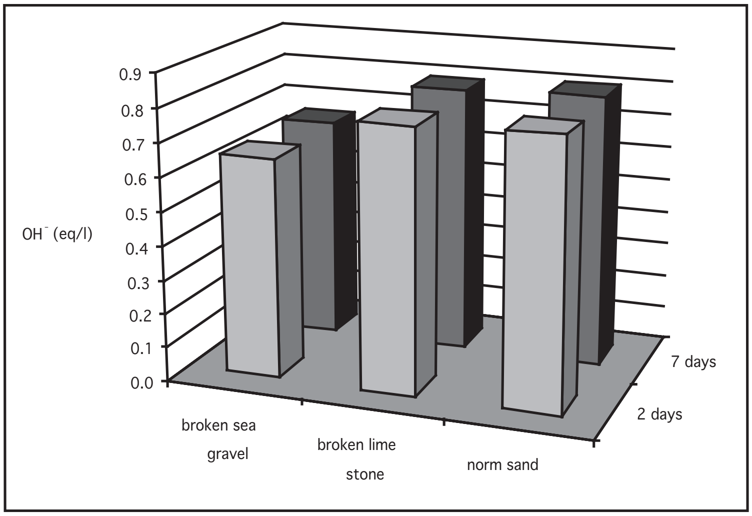
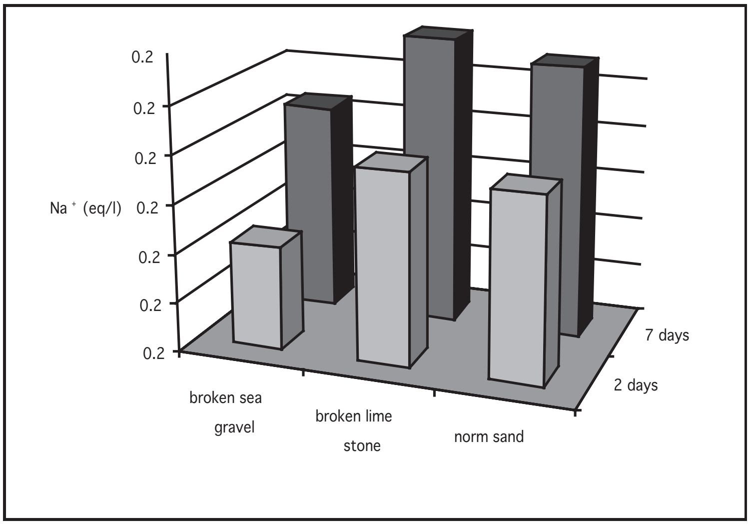


Figure 8. pH-values of the pore water of mortar prepared with various aggregates after extraction at ages of 2 and 7 days respectively.



(a)



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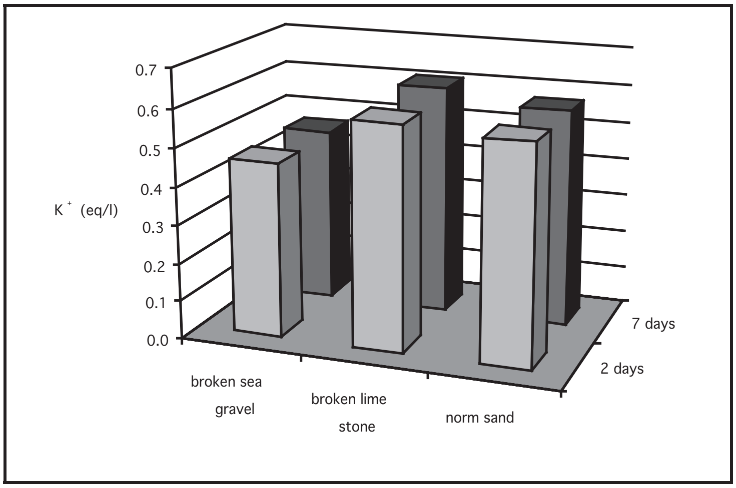

(c)

Figure 10. Concentrations of OH^- (a), Na^+ (b) and K^+ (c) of the extracted pore water of the mortars prepared with various aggregates at the age of 2 and 7 days.

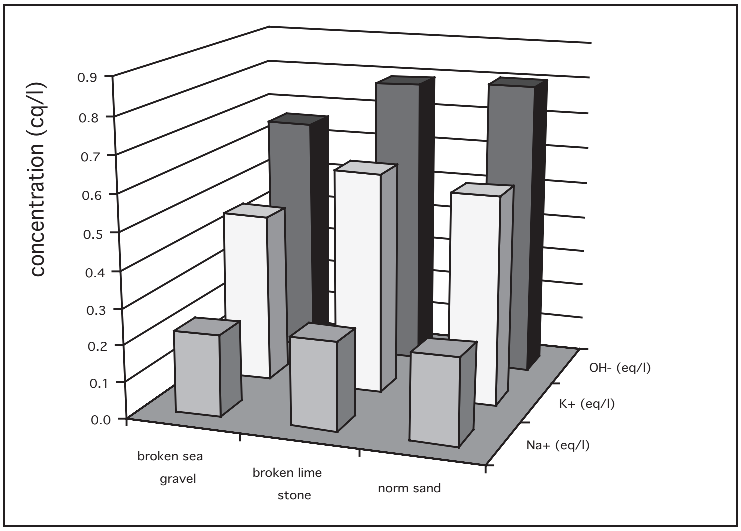

Figure 11. Comparative concentrations of OH$^-$*, Na*$^+$ *and K*$^+$ *of the extracted pore water of the mortars prepared with various aggregates at the age of 7 days.*

On the basis of the foregoing results, the following conclusions can be drawn:

- The pore water composition of the mortars prepared with the standard river sand or with the crushed limestone does not differ considerably from each other.
- The pore water composition of the mortars prepared with the 100 % crushed sea gravel differs considerably from both mixes.

4 Discussion of results and conclusions

4.1 Pessimum effect

One of the objectives of this study was to investigate whether or not the sample of North Sea gravel tested exhibits a pessimum effect, that is, if used in combination with the crushed limestone there will be a proportion of reactive constituent in the total 'aggregate mix', which will lead to a maximum expansion in the UAMBT. From the results of the UAMBT presented in Figure 4, it appears that no pessimum effect occurs for the content of reactive constituents tested. A possible explanation is that the pessimum value is far lower than the minimum content of reactive constituents in the mortar mixes tested. In other words, the amount of reactive constituents in the mixes, that is, 3.1, 6.3, 9.4 and 12.5 %, all fall in the region above the pessimum limit. It implies that there is excess of reactive silica but not sufficient alkalis available in the interior of the mortar bars for sufficient reaction to take place, which will lead to the formation of expansive gels.

Another effect that may have contributed to the absence of the pessimum effect is the formation of the 'outermost reaction zone'. The formation of the outermost barrier, which limits further ingress of alkalies from the buffer of NaOH solution appears to be crucial in the UAMBT, especially in cases where the aggregate contains 2 % by volume or more amount of porous chert / flint and chalcedony.

4.2 The UAMBT and ASR-reactivity of the aggregate mixes

Dutch CUR-Recommendation 89 [3] specifies that aggregates that are found by means of petrography to contain more than 2 % by volume of reactive constituents should by definition be classified as potentially reactive aggregates. Such aggregates would produce excessive expansions due to ASR when used to produce concrete, which is later exposed to moist or aggressive environments. The above recommendation does not recommend further assessment of such aggregates by means of the UAMBT because the expansions produced would definitely exceed the stipulated maximum allowable expansion value of 1 ‰ at 14 days of testing.

The crushed limestone used as reference aggregate in this study contains about 1 % (by mass) of silica, SiO_2 [18]. According to the definition of CUR-Recommendation 89 [3], this aggregate should be classified as non-reactive and should not produce excessive expansions in the UAMBT beyond the maximum allowable expansion value of 1 ‰ at 14 days of testing. From the results of the expansion test (for the mortar bars with 100 % crushed limestone), this lower-critical limit behaviour of the limestone appears to be confirmed in this investigation.

With respect to the crushed sea gravel ‘aggregate mixes’, although each mix used to prepare the mortar bars contained more than 2 % by volume of reactive constituents, the expansion of the mortar bars at 20 days of testing in the UAMBT was lower than the maximum allowable expansion value of 1 ‰. This prompts the question as to why the UAMBT could on the one hand suitably assess the crushed non-reactive limestone aggregate and on the other hand appears to be ineffective in assessing this North Sea gravel (with high content of reactive constituents) as a potentially reactive aggregate?

Two possible explanations can be given for the small expansion in the mortar bars regardless of the relatively high content of potentially reactive constituents:

1. The ASR activity in the outermost reacted zone results in the formation of less viscous type of ASR-gel that blocks the voids and pores of the cement paste and inhibits further ingress of NaOH into the interior of the mortar bars.
2. The pessimum limit is so low (far less than 3.1 %) that all the mortars containing the crushed sea gravel (sea gravel ‘aggregate mixes’) fall in the region above the pessimum limit.

Formation of an outermost barrier

The observations made on the thin sections with 25 %, 50 %, 75 % and 100 % crushed sea gravel (corresponding to 3.1, 6.3, 9.4 and 12.5 % reactive constituents) from the optical microscopic examination suggest the formation of a *barrier* between the outer reacted ‘skin’ and the interior of the mortar bars: the outer zone rich in gels and the interior devoid of gels. This is likely to impede ingress of the NaOH solution into the interior unreacted zone of the bars to react with the reactive constituents there. In the interior of the bars, there were no signs of attack due to ASR: the porous chert, chalcedony and sandstone particles appeared unaffected.

The barrier may have been formed because of the occurrence of a considerably large amount of reactive particles present in the mortar bars, giving rise to a large surface area of the reactive constituents. At the time of exposure of the mortar bars to the NaOH solution (that is, 2 days after casting), they were likely to be permeable because the microstructure of the cement paste was not fully developed allowing a large amount of the NaOH solution to penetrate the mortar bars. The ingress of a large amount of the NaOH solution may have caused a large amount of tiny ASR-gels to be formed in the outermost zone of the bars. These tiny gels may have impregnated, blocked or clogged the voids and pores in the mortar as well as other access routes NaOH solution to penetrate deeper into the interior parts of the bars. Also, since the mortar bars were cured in a moist environment prior to the UAMBT, they contained a considerable amount of moisture. Part of this moisture may have been absorbed by the ASR-gels formed to produce the necessary swelling and subsequent expansion of the bars. As hydration of the cement progressed, the permeability of the cement paste in the interior of the mortar bars decreased, which in combination with the barrier formed in the outermost layer, may have limited further ingress of NaOH solution into the interior of the bars for further reaction. In a similar study, Hudec [22] proposed lack of supply of sufficient moisture to the bars as the cause of the low expansion, however, in this study it is clear that reaction, if any, had not taken place to a large extent in the core of the mortar bars, indicating that the NaOH solution may possibly not have reached the interior of the bars as pointed out by Shayan [10].

The pattern of the expansion curves in Figure 3 shows that expansion of the bars will continue even after 20 days, suggesting that the alkali-silica reaction will proceed even after the formation of the outermost layer. This is likely to be achieved by means of slow diffusion of Na^+ and OH^- ions into the mortar bars and through the 'barrier' to the reaction front. Because there is a large amount of reactive constituents in the mortar bars and once there is supply of Na^+ and OH^- ions, ASR can take place and subsequently cause expansion. As the formation of ASR-gels increases, microcracking can occur, which will enhance further ingress of Na^+ and OH^- ions into the mortar bars to the reaction front to permit faster reaction and subsequent expansion.

Percent reactive constituents falls in the region above pessimum limit

In this case, the reactive silica-to-alkali ratio (SiO_2/alkali) is quite high and the total quantity of gel that is likely to be formed is so small that it is not able to swell enough, on absorption of water, to cause damage to the mortar bars. Nixon et al. [8] suggested a similar explanation for the behaviour of concretes containing flints with high reactive silica-to-alkali ratios. According to them, the gel formed in that case is more fluid and able to dissipate itself into the cement paste without causing excessive stress in the concrete. They explained also that the widely distributed sites of reaction tend to limit expansion both by altering the composition of the gel so that it becomes more fluid and dissipate easily and by distributing the gel almost homogenously in the concrete so that it has as much paste as possible to dissipate into. Stresses developed from the swelling of such gels are spread throughout the cement paste and causes limited expansion. Damaging expansion and subsequent cracking seem to occur when the reaction is limited to a small number of sites producing local concentrations of gel. The total amount of reaction between silica and alkali is in that case low but the gel produced is present locally in sufficient amounts to produce an expansive stress to which the concrete or mortar may not be able to accommodate itself without cracking.

The fact that the optical microscopic examination did not reveal clear evidences of attack due to ASR in the interior of the mortar bars containing sea gravel does not necessarily mean that ASR has not occurred in there. The results of the pore fluid analysis in Tables 4 and 5, shows that even at an early age of 2 days (the age at which the specimens for the UAMBT were exposed to 1 M NaOH solution) the OH- concentration (or pH) of the mix with 100 % sea gravel (12.5 % reactive constituents) had decreased. The alkali concentration of this mix is considerably lower than the alkali concentration of the other two mixes (crushed limestone or river sand). Since the mix composition of the mortars is otherwise similar, it is reasonable to assume that part of the alkalies in that mix had reacted to form ASR-gels. In a similar work by Nixon et al. [9] on concrete specimens containing high contents of flints (although tested at 20 °C and 38 °C), very little signs of ASR attack on the aggregate particles were observed. The ASR-gels observed consisted of small discrete amounts in voids near to aggregate particles. They found the majority of the cement paste to be darkened and attributed that to impregnation by ASR-gel. In the present study, the cement paste of the mortar bars containing sea gravel were found from optical microscopic examination to be inhomogeneous, consisting of alternating zones of high and low capillary porosities. This pattern is similar to the observations made by Nixon et al. [9] and suggests that very small, discrete amounts of ASR-gels are formed but owing to the chemical composition and fluidity tend to dissipate to impregnate the adjoining cement pastes, and by so doing decrease their capillary porosities.

4.3 Conclusions

From this study, the following conclusions could be drawn:

- Aggregate mix combinations of crushed North Sea gravel and non-reactive limestone containing 0, 3.1, 6.3, 9.4 and 12.5 % reactive constituents in the form of porous chert / flint and chalcedony, were incorporated in mortar bars, which were subsequently subjected to ultra-accelerated mortar bar expansion test. Although each of mortar bar mixes tested contained more than the acceptable limit of 2 % reactive constituents, the expansions of the mortar bars at 14 and 20 days of testing in the UAMBT were lower than the maximum allowable expansion value of 1 ‰ given in the Dutch concrete requirements.
- An explanation has been proposed for this behaviour due to the formation of large amounts of ASR-gel in the outermost 2-3 millimetres zone or ‘skin’ of the bars, blocking the voids and pores, which forms a barrier and inhibits further ingress of NaOH solution to the interior parts of the mortar bars, thereby limiting further reaction and subsequent expansion.
- In the interior of the mortar bars, beyond the zone of reaction, no ASR-gels were observed by means of microscopy, although pore solution analysis suggests that reaction may have occurred in that zone.
- No pessimum effect was observed for the content of reactive constituents tested. The absence of a pessimum effect is most likely caused by the formation of a barrier to ingress of NaOH solution into the interior of the mortar bars, thereby limiting and reducing the rate of occurrence of

ASR in the mortar bars. Thus, although there is sufficient reactive material, very little reaction could take place; consequently, the pessimum effect does not show.

- Another explanation for the absence of the pessimum effect may be that the limit is quite low and far less than the minimum content of 3.1 % studied here. The content of reactive constituents in the mortar mixes tested appears to fall in the region above the pessimum limit. The first stages of reaction of alkalies and reactive sea gravel are very rapid, shown by reduced pH and K concentration after as short as 2 days of storage at 20 °C. That these concentrations were essentially identical after 7 days, may suggest that further reaction at 20 °C is quite slow.

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