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Construction and Building Materials 22 (2008) 1183–1190

Construction and Building MATERIALS

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Evaluation of the alkali reactivity of cherts from Turkey

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Received 24 March 2006; received in revised form 24 January 2007; accepted 6 February 2007
Available online 26 March 2007

Abstract

Chert, which is a crypto and/or microcrystalline sedimentary rock, may lead to alkali–silica reaction in concrete when the conditions are favorable. However, cherts vary in composition and consequently may demonstrate different reaction characteristic. In this study, eight different chert types were investigated. Accelerated mortar bar test, ASTM C1260, was performed on aggregate blends of limestone and chert. Ten sets of mortar bars with varying amount of cherts, 1 to 100%, were tested for each chert type. Additionally, sonic velocity measurement and petrographic examination were conducted on the mortar bars. The mortar bar test revealed that all cherts show pessimum behavior with maximum expansion peak attained in the range of 5–15% chert content: the expansion due to the alkali–silica reaction increases up to pessimum content and decreases thereafter. The sonic velocity measurements and the petrographic examinations have supported the expansion data that the minimum velocity and the maximum cracking occur in the peak expansion range. The different testing methods have complemented each other that the pessimum content for all the cherts investigated was found to be 7.5–10%.

Keywords: Alkali–silica reaction; Chert; Pessimum; Sonic velocity; Petrographic examination

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1. Introduction

Chert is one of the well-known activators of alkali–silica reaction (ASR) when used as concrete aggregate. It is involved in ASR cases that have been reported from different parts of the world – North America, Australia, UK, and Japan [1].

ASR initiates with the dissolution of silica by reactions involving the hydroxyl ion (OH^-). Alkalis (Na^+, K^+) in the concrete pore solution react with the dissolved silica to form alkali–silica gel. The gel imbibes water and creates expansive force which may be high enough to disrupt hardened concrete. The silica dissolution is controlled by mineralogical and chemical factors such as silica content, thermodynamic property, specific surface area, grain size and crystallinity [2]. The mineralogical composition of cherts varies from very fine-grained opaline silica to cryptocrystalline silica and from chalcedony to microcrystalline quartz [3]. The finely crystalline nature of chert constituents provides an increased reaction surface. Moreover, a special emphasis is given to the degree of crystallinity: the reactivity is linked to low crystallinity. In a study with Irish cherts and English flints, quartz crystallinity index (QCI) was utilized to demonstrate the difference and it was shown that the cherts from the Irish aggregate samples, which had no reaction history, had an average QCI of 7.0, whereas the ones from the English aggregates, which were known to be reactive, had an average of 2.2. The lower crystallinity of the English cherts was attributed to their kinetic instability compared to the Irish cherts [4,5]. The QCI, which is established in a 0–10 scale, is derived from the intensity of the $d(2\,1\,2)$ X-ray peak at 2θ of 67.74°. As the intensity of this peak increases the quartz tends to have higher crystallinity. Details of the procedure are explained in [6]. Nishiyama et al. [7] also found that the reactive cherts from Japan had relatively low crystallization indices. Furthermore, Jones [8] postulated that factors other than mineralogy

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doi:10.1016/j.conbuildmat.2007.02.002

must have significant influence on the reactivity of cherts and flints. Jones revealed that all the British cherts and flints examined in his study were petrographically and mineralogically indistinguishable and concluded that the reactivity is a function of the micropore system: the smaller the micropores, the higher the dissolution of the silica.

In nature, chert is found as nodules in limestone layers or as a blended portion of gravel in river beds. Therefore, chert is generally found as a percentage of aggregate in concrete. This quantity is very important in terms of expansion potential. Some reactive aggregates like chert and opal do not show an increasing expansion trend with increasing amount: expansion proportionally increases up to a certain percentage and decreases thereafter. The amount at which

Table 1
Chemical composition of ordinary portland cement

Chemical composition (%)									
CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	Na_2O_{eq}	LoI[a]
63.18	19.27	5.59	2.52	3.00	2.77	0.24	1.10	0.96	1.59

[a] Loss on ignition.

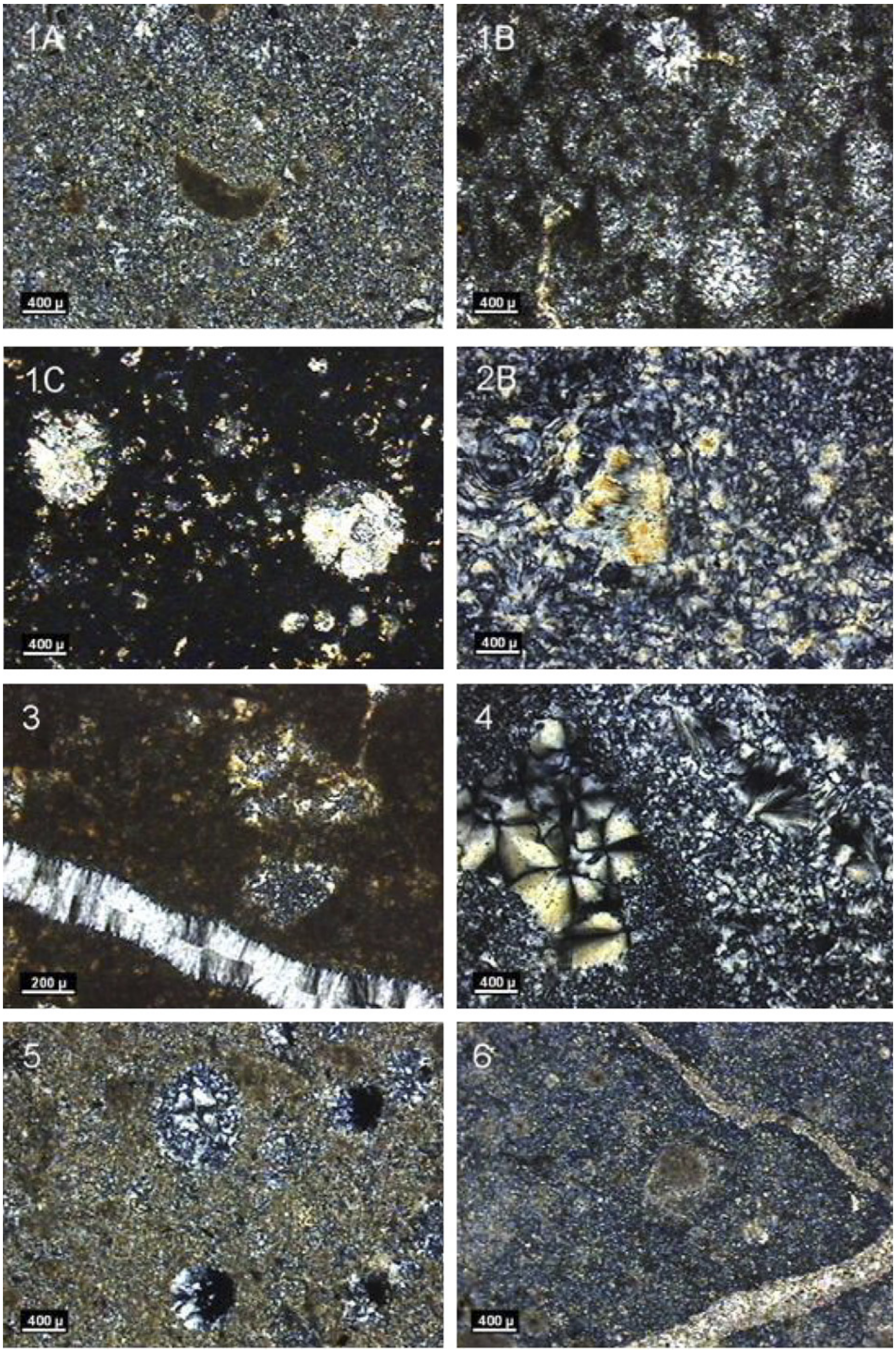

Fig. 1. Microphotographs of the chert samples (thin section).

peak expansion is attained is called ‘pessimum’ content. The pessimum content of chert may be as low as 10% or as high as 60% with varying peak expansions depending on several factors such as reactivity of constituents and available alkali [9,10]. The chert content at which the reaction expansion can be tolerated is not universally agreed and merits attention. ASTM C33 limits chert content as 3% and 8% for fine and coarse aggregates, respectively, and the Dutch specifications [11] allow 2%. However, even 1% chert may lead to high expansion in accelerated tests as shown by McNally et al. [12], although harmful expansion in service will not occur unless alkali loads are high.. A previous research study on Indian rocks stated that 5% or more chert would cause deleterious expansion [13]. On the other hand, the British experience claims that, in the absence of any other potentially reactive constituent, aggregates either containing no more than 5% or alternatively containing more than 60% chert and flint are to be regarded as ‘unlikely to be reactive’ [1]. The term chert denotes a relatively wide scale of materials having different composition, thus, possessing different alkali reactivity. Therefore, it is important to establish expansion characteristics of the local materials.

The aim of this study was to evaluate the alkali-reactivity characteristics of chert samples collected from Ankara, Turkey. The study was carried out on mortar bars, which were cast and tested in accordance with the method outlined in ASTM C1260. The experimental program included length change determination, sonic velocity measurements and petrographical analysis of cracked sections.

2. Materials

The cement used in the study was an ordinary portland cement – CEM I 42.5 N according to EN 197-1 (equivalent to ASTM C150 Type I). The chemical composition of the cement is shown in Table 1. Eight chert samples were taken from different parts of Ankara, Turkey. Although they are all described as cherts due to microcrystalline nature of the materials, they are associated with different geological environment and display differences in their petrographical features. Geologically, some are formed as nodules, the others as layers. They have differences in color, calcite/dolomite content, micro-textures and mineralogy (Fig. 1). Detailed descriptions of the petrography are also given in Table 2. A limestone was used as inert aggregate, composed of 100% calcite ($CaCO_3$).

3. Experimental study

Cherts may be found as embedded layers or nodules in other rock formations. Surrounding impurity, if any, was discarded (by simple techniques such as sawing, scraping) so that the chert quantity used would reflect true percentage. For each chert type, firstly, ten sets of mortar bars, each set containing three bars, were cast in accordance with ASTM C1260. Limestone was substituted by chert at 1, 3, 5, 7.5, 10, 15, 20, 30, 50 and 100% levels in the ten mixes. The bars were demolded after 24 h and placed into a water bath at room temperature then heated to 80 °C as specified in the test method. The bars were cured for 1 day, and then

Table 2
Petrographical properties of the cherts

Sample	Petrographic description
1A	*Nodular beige chert:* the sample includes microcrystalline quartz with about 35% chalcedony, existing as irregular patches. Includes scattered calcite crystals. Microcrystalline quartz (3–12 μm) displays well-developed mosaic texture
1B	*Pink radiolarian chert:* spherical shaped radiolarian tests (approx. 80%) in a matrix of cryptocrystalline quartz with tiny hematite flakes. Radiolarians (0.02 mm) are filled mainly with fan-shaped radial chalcedony with minor microcrystalline quartz. Chalcedony occurs in cross-cutting veinlets, <0.001 mm in width
1C	*Brownish radiolarian chert:* the rock consists of microcrystalline quartz partly replaced by calcite and includes almost 25% hematite flakes. The radiolarian tests are also partly replaced by calcite. Calcite occurs as neoformed minerals in the microcrystalline quartz matrix. Cross-cutting veins, 0.2 mm wide, are filled with fine-grained calcite
2B	*Brownish gray chert I:* the sample is made up of mosaic of microcrystalline quartz and includes a network of larger, fan-shaped chalcedony (up to 40%). Irregularly distributed patches of hematite-rich microcrystalline quartz are observed. The chalcedony is also formed as vein-fills, perpendicular to the wall. The sample includes tiny cracks with chalcedony-fill
3	*Pinkish gray radiolarian chert:* microcrystalline quartz showing conchoidal fracturing. The sample is made up of microcrystalline quartz with coarser grains of fan-shaped chalcedony. In this matrix, irregular patches of up to 3 mm long, brownish colored, hematite stained and radiolarian-bearing areas are observed. These former pieces of radiolarian mudstone are completely replaced by cryptocrystalline quartz. The rock is cut by irregular veins, filled with calcite and chalcedony
4	*Brownish gray chert II:* the sample is made up of microcrystalline quartz with irregular patches (1–2 mm) and veins filled with chalcedony (up to 45%)
5	*Brownish gray radiolarian chert:* the sample is made up of microcrystalline quartz with spherical and chalcedony filled radiolarian tests. Locally enriched in calcite crystals (up to 25%) and carbonate rich pellets. Very few radiolarian tests have calcite infilling. In contrast to other chert samples studied, this one does not include chalcedony-filled veins
6	*Brown chert:* the sample is made up of cryptocrystalline quartz (72%) and microcrystalline calcite (28%). The calcite bearing parts occur as angular fragments in the cryptocrystalline quartz matrix. The cross-cutting veins and fossil tasks are filled with calcite

immersed in 1 N NaOH solution at 80 °C after the initial (zero-day) length measurement. The expansions were recorded at 0, 3, 7, 14, 21, and 28 days. In the second part of the experimental program, sonic velocity (P-wave) of the mortar bars was measured. For the sonic velocity testing, pulse method was used on 7-day air-dried bars with lengths ranging between 95 and 125 mm. In the pulse method, an impulse is imparted to the sample and the time required for the transient pulse to traverse the length of the specimens is used to calculate the velocity of the waves. Pundit Plus with P-54 kHz transducers were used for the sonic wave measurements. Lastly, thin sections were cut from the same bars used for sonic velocity testing, and examined under polarizing microscope. For the petrographic examination, the length and the width of cracks on the thin sections together with the cracking per unit area ($1 \times 1\ \mathrm{mm}^2$) were evaluated.

4. Results and discussion

4.1. ASR expansion

All levels of chert addition caused length change due to the ASR expansion. Fig. 2 shows the expansion curves plotted against chert content of the mortar bars for various chert types. The data of sample 1 A has been previously published by the authors [9]. For each chert type the curves from lowest to uppermost refer to expansion at different ages from 3 to 28 days and are in chronological sequence. There was no consistent relationship between chert content and expansion at the end of first week; however, the relation became apparent starting at 14 days. All the chert samples showed pessimum behavior. The peak expansions at 28 days were observed at 5% for sample 2B; at 7.5% for sample 1A, 1B, 3 and 4; at 10% for 1C and 5; and at 15% for sample 6, and the values

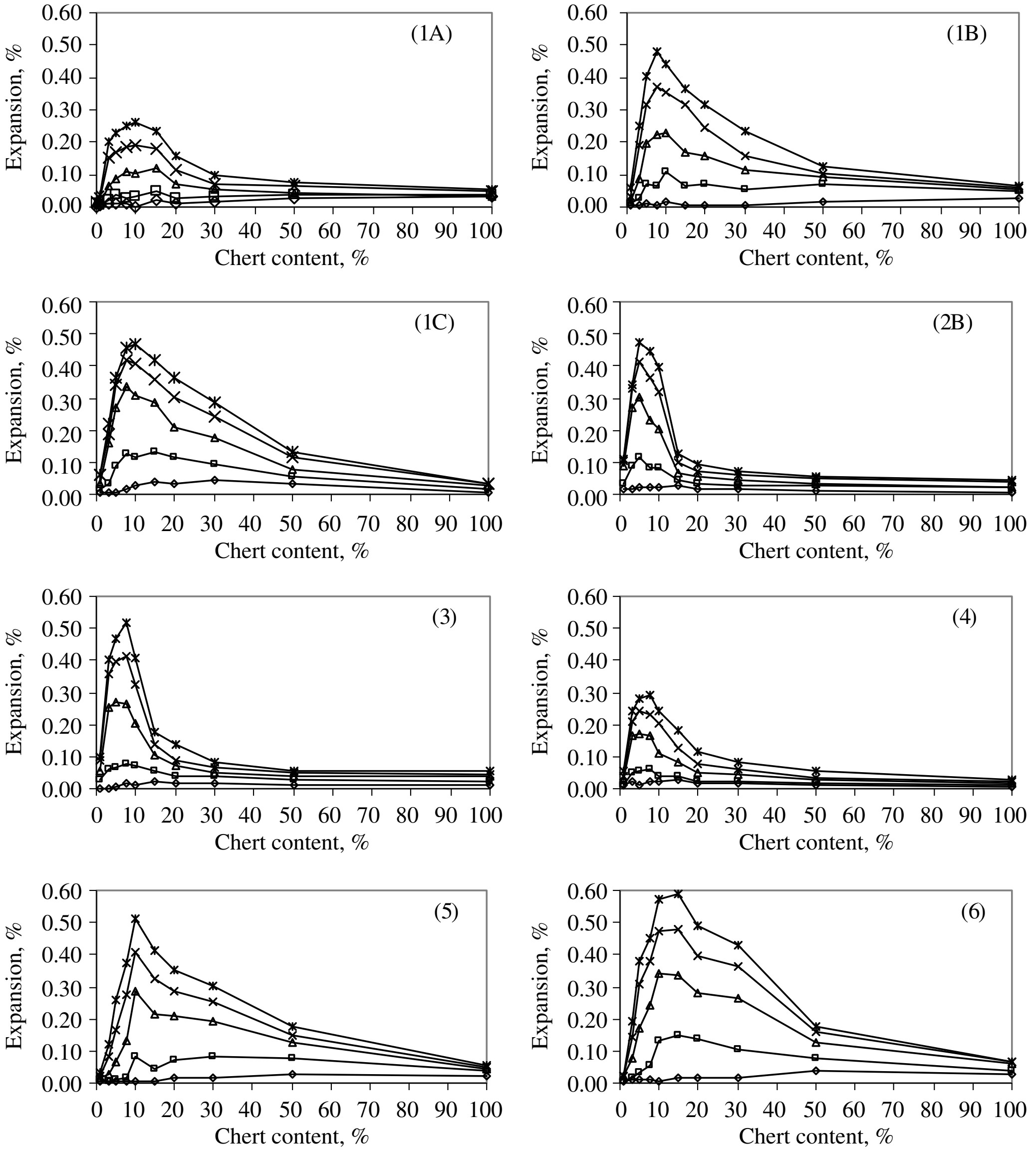

Fig. 2. Variation of the ASR expansion with chert content. (The curves from lowest to uppermost correspond to 3-, 7-, 14-, 21-, and 28-day expansions).

were lying between 0.25% and 0.59%. The classical theory explains the pessimum concept based on the optimum alkali–silica ratio at which maximum expansion occurs. For a given level of alkali, the expansion increases with the increase of reactive aggregate content up to a certain point. Beyond that point with the increase of reactive aggregate the alkali is diluted and the alkali–silica ratio drops and little expansion occurs. This explanation fails in the accelerated test at which the alkali–silica ratio would be practically infinite at any reactive aggregate content. Shayan [14] has suggested that, in the presence of high opal contents, large amount of ASR gel is produced that impregnate the hydrated cement paste and any cracks at the outer zones, and form a barrier to further penetration of alkali ions into the interior of the mortar bar, thereby preventing the reaction take place and reducing the total expansion. However, this postulation has not been further supported.

Other than the pessimum content, the quantity of chert that is considered to be deleteriously reactive differs as stated earlier. Setting the limit to 0.10% at 14 days the cherts under investigation demonstrated different behavior: the range in percent was 7.5–15, 5–30, 3–30, 3–10, 3–15, 3–10, 7.5–50, and 5–50 for the samples 1A, 1B, 1C, 2B, 3, 4, 5 and 6, respectively. The results seem to confirm the British study mentioned before that high percentage levels do not possess deleterious expansion. On the other hand, low amounts, i.e., <5%, is capable of producing harmful expansion.

4.2. Sonic velocity measurements

Measurement of ultrasonic pulse velocity in damaged concretes is a common non-destructive method to find out the degree of cracking and also has been utilized to test

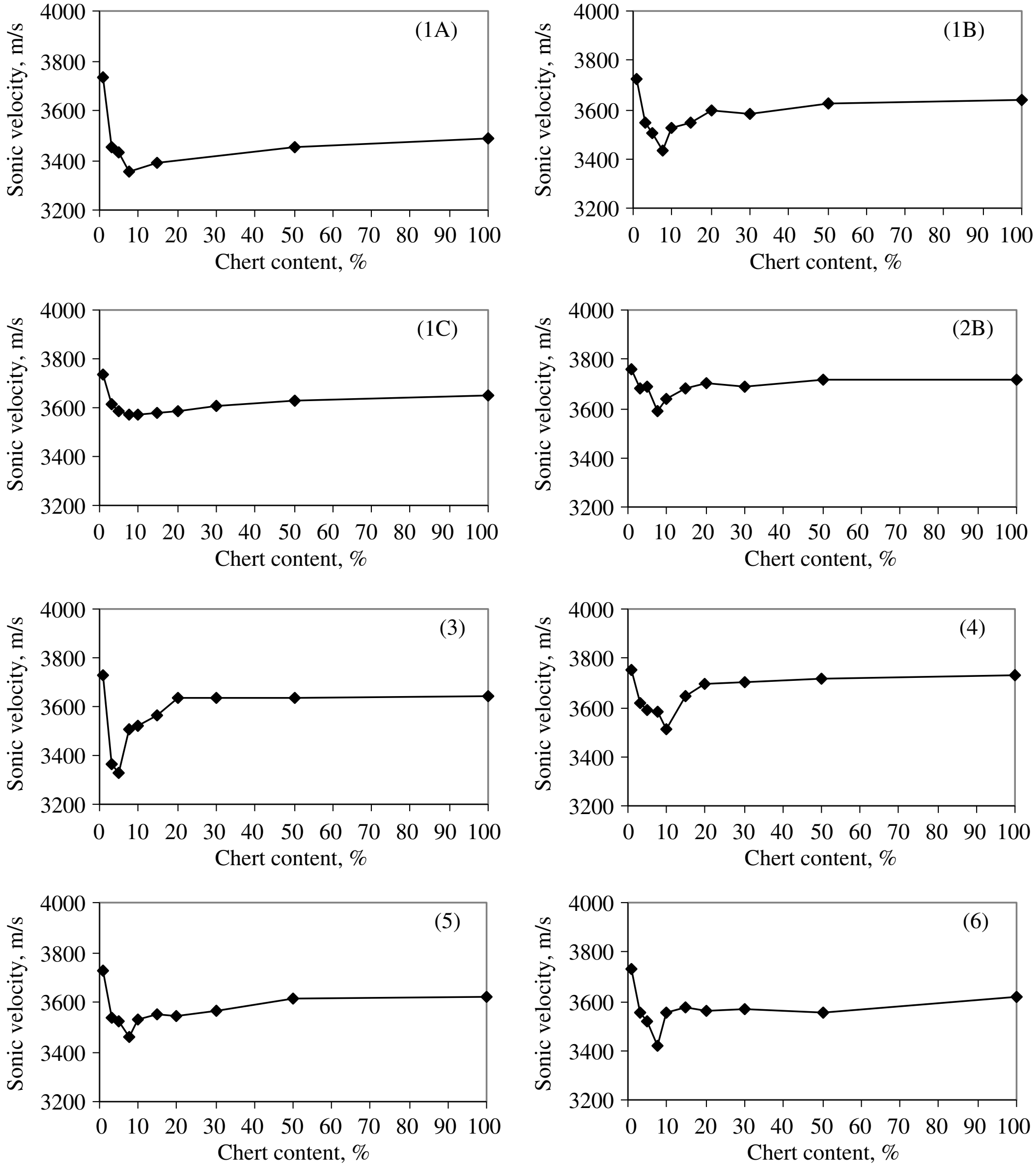

Fig. 3. Variation of the sonic velocity with chert content for each type.

concrete that has undergone ASR [15]. Obviously sonic velocity decreases as concrete cracking increases. Variation of the sonic wave velocity of the dry mortar bars for various chert contents is plotted in Fig. 3. The sonic velocity measurements have also confirmed the pessimum behavior since the velocity is a function of cracking associated with ASR. The results indicate that maximum expansion occurs at 5% to 10% chert content. Although there are some shifts, which could be attributed to the relatively small mortar sections used in the measurements, it is prudent to state the expansion and the sonic velocity results almost perfectly match (see Table 3).

Table 3
Correlation of expansion, sonic velocity and petrographical results

Sample	Chert content (%) with		
	Maximum ASR expansion	Minimum sonic velocity	Maximum number of cracks
1A	7.5	7.5	7.5
1B	7.5	7.5	7.5
1C	10	10	10
2B	5	7.5	7.5
3	7.5	5	7.5
4	7.5	10	7.5
5	10	7.5	10
6	15	7.5	7.5–10

4.3. Petrographic examination

Petrographic examination provides valuable information to evaluate cracking pattern of mortar or concrete. Kerrick and Hooton [16], Hornain et al. [17] and Ringot and Bascoul [18] performed successful applications of this technique. In this study, for the petrographic examination under the microscope, thin sections were prepared from each chert

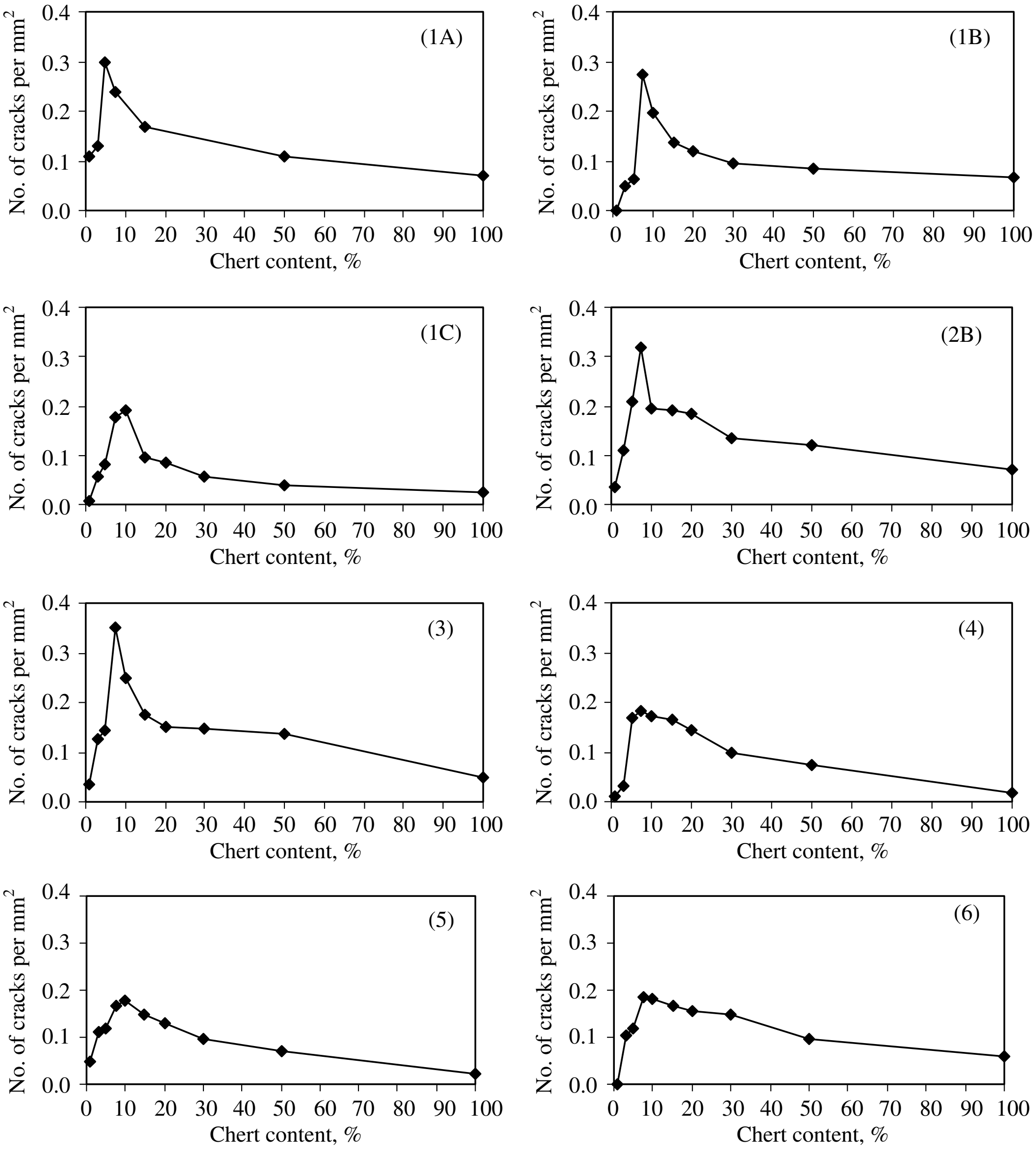

Fig. 4. Variation of the number of cracks with chert content for each type.

type. The petrographic description of the cherts is summarized in Table 2. In addition to the descriptions of the chert samples, parameters such as the number of cracks per unit area, the form, distribution, length and width of cracks across the mortar bar, the type and extent of gel infilling in cracks and voids, the shape of the aggregates and the distribution of the voids on the thin-sections from the bars were also considered. Among these, it was observed that the number of cracks per unit area, and the length and the width of cracks vary at different chert contents.

Variation of the number of cracks with the chert content for each chert type (Fig. 4) indicated that the number increases as the chert content increases and reaches a maximum value at 7.5–10%, then, decreases as the chert content further increases revealing pessimum behavior. The number of cracks per mm^2 ranges from 0.18 to 0.35. The chert content corresponding to the maximum values are generally in good agreement with the expansion and the sonic velocity data. Similar relationship was observed in the crack width analysis. The findings are given in Fig. 5. Expectedly, the maximums were attained around 7.5–10% chert content. Table 3 gives a comparison of the data from obtained from different investigation techniques.

Evaluation of the test results including the length change determination, the sonic velocity measurement and the petrographic examination has demonstrated that the pessimum proportion of the cherts under investigation is validated by the maximum expansion at 7.5–10% chert contents. It was stated that the measurement of mortar bars in longitudinal direction only as an indication of ASR cracking might be misleading since the bars also undergo lateral deformation [19]. Similarly, field concrete also experiences multi-directional expansion and the linear expansion based test is therefore a modeling misconception. This study provides validation for the mortar bar technique as it proves that the sonic velocity and the thin

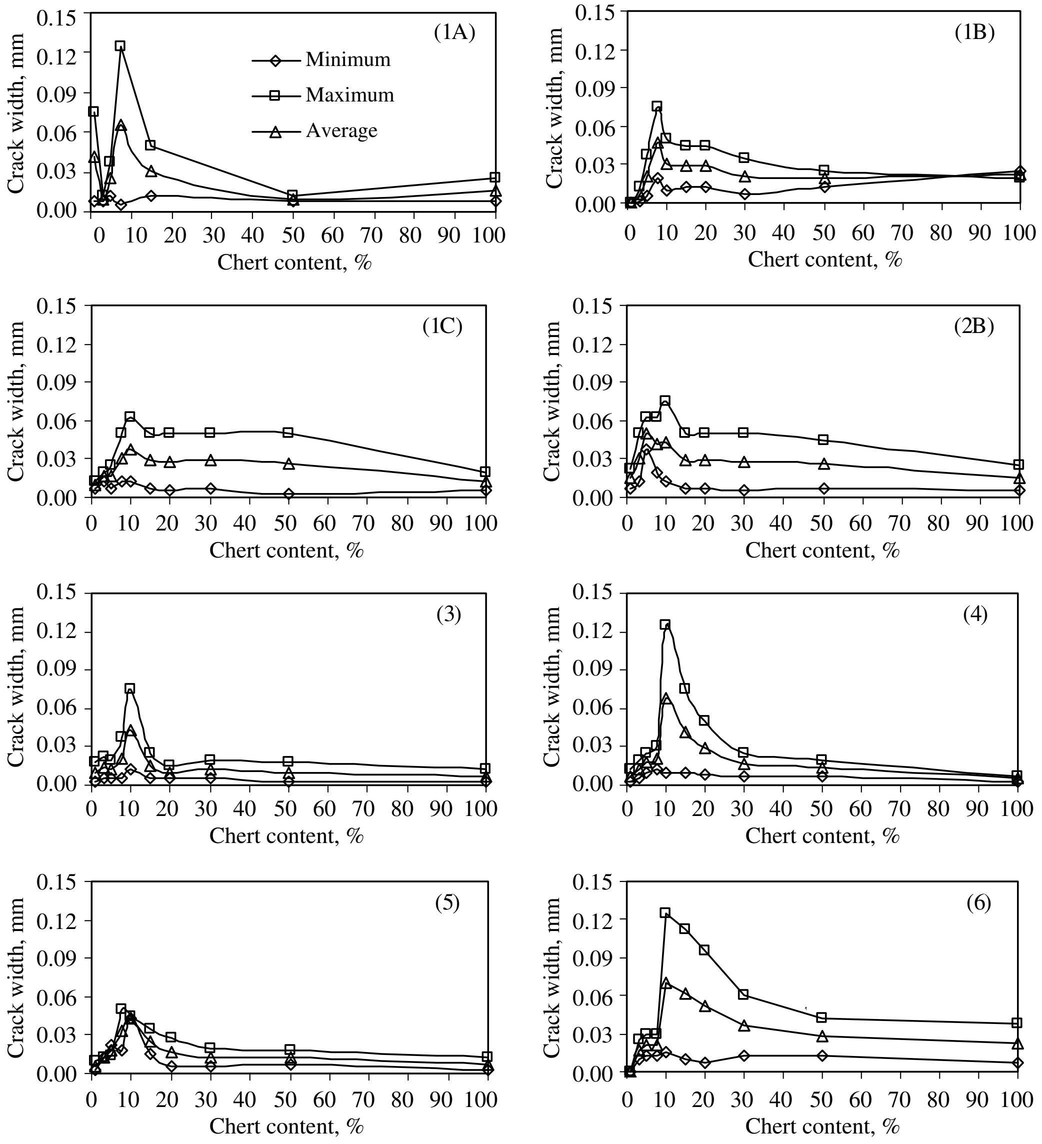

Fig. 5. Variation of the width of cracks with chert content for each type.

section study give useful and supplementary information in addition to the length change measurement: they are in good agreement corroborating each other. In other words, expansion measurement based on longitudinal length change of mortar bars provides quick, reliable information about the potential reactivity; however, it is not a definitive indicator of the field expansion.

5. Conclusions

Eight cherts investigated in this study for alkali–silica reactivity showed pessimum proportion behavior. The length change observation of the bars stored in the alkaline solution, the sonic pulse velocity measurement and petrographic investigation has confirmed the behavior. The pessimum content for all the cherts were concentrated around 7.5–10%. The results from different techniques have complemented each other. The comparison of all the data reveals that the mortar bar test can be supplemented by sonic velocity and petrographic examination. On the other hand, the peak expansion values were different, indicating that the material, although all being named as chert, have different reaction characteristics. The petrography has revealed the differences. The trends identified in this study should be further supported by tests on concrete.

Acknowledgements

The authors thank Middle East Technical University for the financial support of the study under the Project no. AFP-2001-03-03.02.

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