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The behavior of silicocarbonatite aggregates from the Montreal area

J.E. Gillott[a,*], C.A. Rogers[b]

[a]Department of Civil Engineering, University of Calgary, 2500 University Drive, Alberta, Canada T2N 1N4
[b]The Ministry of Transportation, Ontario, Canada M3M 1J8

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Abstract

In a previous paper, it was concluded that silicocarbonatite aggregates from the Francon quarry, Montreal contributed to durability problems in Portland cement concrete. Results show that, at 2 days after casting, concrete made with silicocarbonatite aggregates contained over 1.5% more Na_2O than similar bars made with Exshaw limestone aggregates. A reaction involving the rare mineral dawsonite in the silicocarbonatite is thought responsible for the higher Na_2O content. In turn, this caused increased expansion of concrete bars made with alkali expansive aggregates. Also, concrete made with alkali–carbonate reactive Pittsburg aggregate showed more expansion when cured at 80 °C than bars cured at 23 °C. Concrete bars made with Exshaw limestone aggregates cured for 4 h at 85 °C showed late-stage expansion, which is attributed to delayed ettringite formation (DEF). However, no expansion was shown by heat-cured concrete prisms or mortar bars made with silicocarbonatite aggregates. Release of alkalis, aluminates and carbonates by the dawsonite reaction may have inhibited DEF. Concrete bars made with nonreactive Nelson dolostone and 10% silicocarbonatite cured at 80 °C for 4 h showed up to 0.15% expansion after several years at 23 °C and 100% relative humidity (R.H.), indicating that a deleterious reaction did occur.

Keywords: Expansion; Alkali–aggregate reaction; Delayed ettringite formation (DEF); Dawsonite; Alkalis

1. Introduction

Aggregates in the Montreal area of Canada have been made from crushed Ordovician limestones, which have been associated with durability problems in concrete which in precast units included large numbers of rail ties [1–4]. The limestones were intruded during the Cretaceous period by sills and dykes composed of an unusual “carbonatite-type rock” which is referred to as a “silicocarbonatite” to recognize that it contains a “ higher proportion of silicates—chiefly feldspar” [5] than is usual in carbonatites. Various exposures have been described and at the Francon quarry, for example, the silicocarbonatite intrudes the limestone as a sill which forms “ a two metre thick sheet” [5]. The unusual nature of the silicocarbonatite attracted interest from geologists and mineralogists [6–11], who showed that it contains a suite of rare minerals of hydrothermal origin including dawsonite [$NaAl(CO_3)(OH)_2$] described as “the principal carbonate mineral” [5]. The exact percentage amount of dawsonite is not known but is shown to be considerable by the high intensity of peaks attributed to dawsonite on X-ray diffractograms and infrared spectra (see Figs. 10, 11, 12 in Ref. [12]) confirming the conclusion of previous investigators. Aggregates made from rocks in that area sometimes contain silicocarbonatite in addition to limestone, and previous work [12] indicated that the silicocarbonatite may have played a part in the durability problems.

In the earlier study [12], length change and analytical data were reported for concrete bars made with and without silicocarbonatite. The silicocarbonatite was used as a partial replacement of other aggregates, some of which were known to be alkali-expansive and some nonexpansive. The bars made with reactive aggregates only were found to be less expansive than companion bars in which the reactive aggregates were partially replaced by silicocarbonatite. The higher expansion of the companion bars was attributed mainly to an increase in their NaOH content, caused by a reaction between dawsonite in the silicocarbonatite and $Ca(OH)_2$ in the cement paste. It was further suggested that the reaction of the dawsonite itself may

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[*] Corresponding author. Tel.: +1-403-220-5830; fax: +1-403-282-7026.

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Table 1
Percent water-soluble alkalies in concrete prisms

Cure	Aggregates	Percent alkalies at given age							
		2 days		1 year		4¼ years		5½ years	
		Na_2O	K_2O	Na_2O	K_2O	Na_2O	K_2O	Na_2O	K_2O
Fog room	Exshaw	0.181	0.237	0.048	0.056	0.062	0.009	0.003	0.006
	Si–carbonatite	2.21	0.187	1.375	0.052	1.098	0.037	1.208	0.040
Accelerated	Exshaw	0.085	0.164	0.056	0.066	0.045	0.008	0.015	0.007
	Si–carbonatite	1.712	0.092	1.55	0.054	1.204	0.041	0.992	0.045

have contributed directly to the higher expansions because the proposed equation implies an increase in solid volume [12].

In this paper, results of work at the University of Calgary and at the Ontario Ministry of Transportation are reported. Results are shown in Table 1 and in Figs. 1–6.

The objectives were to confirm the increase in NaOH content of concrete containing silicocarbonatite and the associated increase in expansion due to alkali–aggregate reaction (AAR). That topic has been reviewed recently by Fournier and Bérubé [13]. It was also intended to determine whether the dawsonite reaction itself is expansive, to investigate other effects of the dawsonite reaction and to reexamine the later-age expansion of bars made by accelerated curing, which in the previous work was attributed to delayed ettringite formation (DEF).

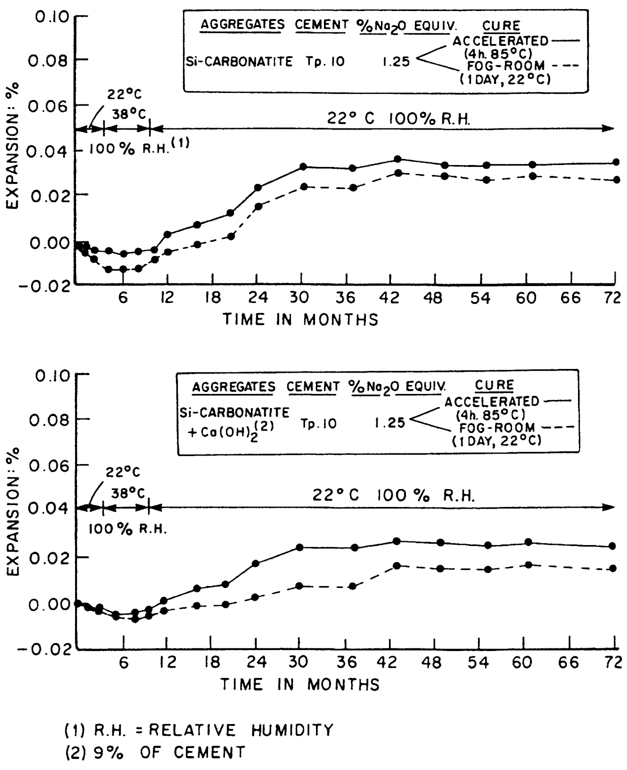


Fig. 1. Length change of mortar bars (1 × 1 × 11 in., 2.5 × 2.5 × 28 cm).

2. Materials and methodology

At the University of Calgary, aggregates used in concrete were made from samples of the feldspathic silicocarbonatite from the Francon quarry, Montreal and from samples of the calcitic limestones from the Exshaw quarry, Alberta. Both types of rock were closely similar to those described previously [12]. Rocks were crushed and sieved and used for coarse and fine aggregate. The concrete was made with Type 10 Portland cement and was similar to that described previously [12]. Concrete mixtures had a cement content of 420 ± 10 kg/m^3 with a water:cement ratio of 0.51 and a slump of 70 ± 10 mm. Mixture proportions, cement and curing conditions were similar to those used in the previous study, but in the earlier work, concrete bars made only with silicocarbonatite aggregates were not made so no data are available for comparison with those now reported.

Two batches of concrete were made. One batch of concrete contained silicocarbonatite aggregate and the other batch contained Exshaw limestone aggregate. In each batch, pairs of prisms (75 × 75 × 360 mm) were made in two sets. Duplicate cylinders (75 × 150 mm) were also cast. In each batch one set of samples was cured in a fog room (24 h at 100% relative humidity [R.H.], 22 °C) and the other set was cured by an accelerated procedure similar to that described previously (2 h controlled heating to 85 °C, 4 h at 85 °C and overnight cooling to room temperature. No moisture was added). Accelerated curing was used to favor possible expansion from DEF.

After curing, all prisms were continuously conditioned at 22 °C, 100% R.H. and measured for length change. Cylinders, similarly conditioned, were sliced at increasing time intervals and samples were used for petrographic examination and chemical analysis. A pair of cylinders, cured and conditioned in a fog room and made with Exshaw limestone aggregate, was tested for compressive strength at 28 days. An average value of 28.1 MPa was obtained. No strength test was carried out on concrete made with silicocarbonatite aggregate as there was insufficient material to manufacture the extra cylinders required.

In addition, mortar bars (25 × 25 × 280 mm) were made using silicocarbonatite aggregate. Type 30 Portland cement (CSA A23.1-94; similar to Type III, ASTM C 150) was used with a sulphate content of 3.58% and SO_3/Al_2O_3 mole

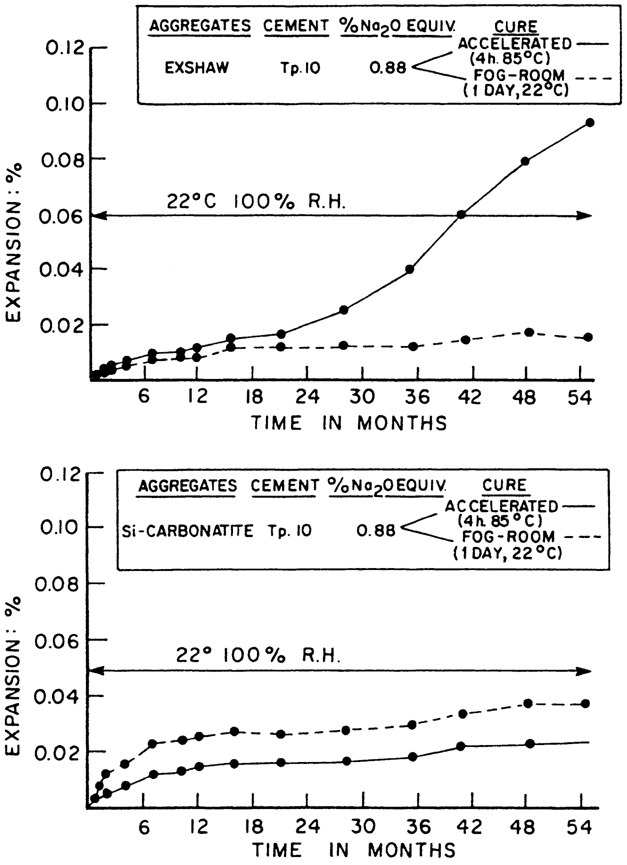


Fig. 2. Length change of concrete prisms (3 × 3 × 14 in., 7.6 × 7.6 × 35.6 cm).

ratio of 0.998, which are all reported to favor DEF [14]. Analytical grade NaOH was added to the mixing water to give an Na_2O equivalent of 1.25% to favor possible expansion from alkali–silica reaction (ASR) since the silicocarbonatite contained cherty material.

Two batches of mortar were cast. In one batch the binder was Portland cement and in the other batch the same cement was used plus an addition of 9% $Ca(OH)_2$ since that compound appeared to be mainly responsible for attack on the dawsonite and has also been shown to aggravate ASR [15]. Each batch was used to cast two sets of bars, one of which was cured in a fog room and the other by the accelerated procedure described above using a relatively high temperature (85 °C) to favor expansion due to DEF. Mortar bars were conditioned at 38 °C, 100% R.H., for some months before being returned to 22 °C, 100% R.H. The objective was to accelerate possible expansion from ASR, as in ASTM C227, and to facilitate comparison with concrete prisms in the previous study [12], some of which were stored at 38 °C for several months in accordance with Canadian Standards Association (CSA) A23.2-14A. The bars were measured for length change following a procedure similar to that in ASTM C227.

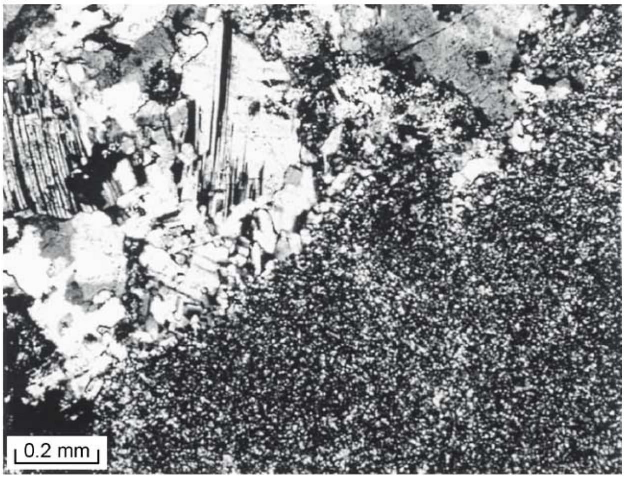
Thin and polished sections of concrete were examined on binocular and petrographic microscopes at ages of 2 days, 1 year, 54 months and 66 months. At the same ages, water-soluble alkalies were extracted from concrete samples by the method of Rogers and Hooton [16], and the content of K_2O and Na_2O was determined by chemical analysis (Table 1).

At the Ontario Ministry of Transportation, four groups of concrete bars were cast in which the coarse aggregate consisted of:

(a) alkali expansive Pittsburg dolomitic limestone;
(b) alkali expansive Pittsburg dolomitic limestone of which 10% was replaced by silicocarbonatite;
(c) nonreactive Nelson dolostone; and
(d) nonreactive Nelson dolostone of which 10% was replaced by silicocarbonatite.

Each group was divided into two sets, one of which was given an initial cure at 80 °C for 4 h while the other set was

(a) CROSSED POLARIZERS



(b) Fog-Room Cure

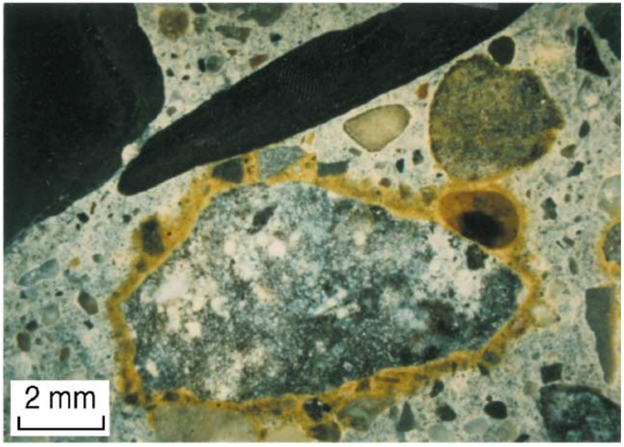


Fig. 3. Optical micrographs of silicocarbonatite aggregate. (a) Chert, plagioclase feldspar and carbonate. (b) Brown rim surrounding silicocarbonatite aggregate in fog-room-cured concrete. Age ~ 1 year.

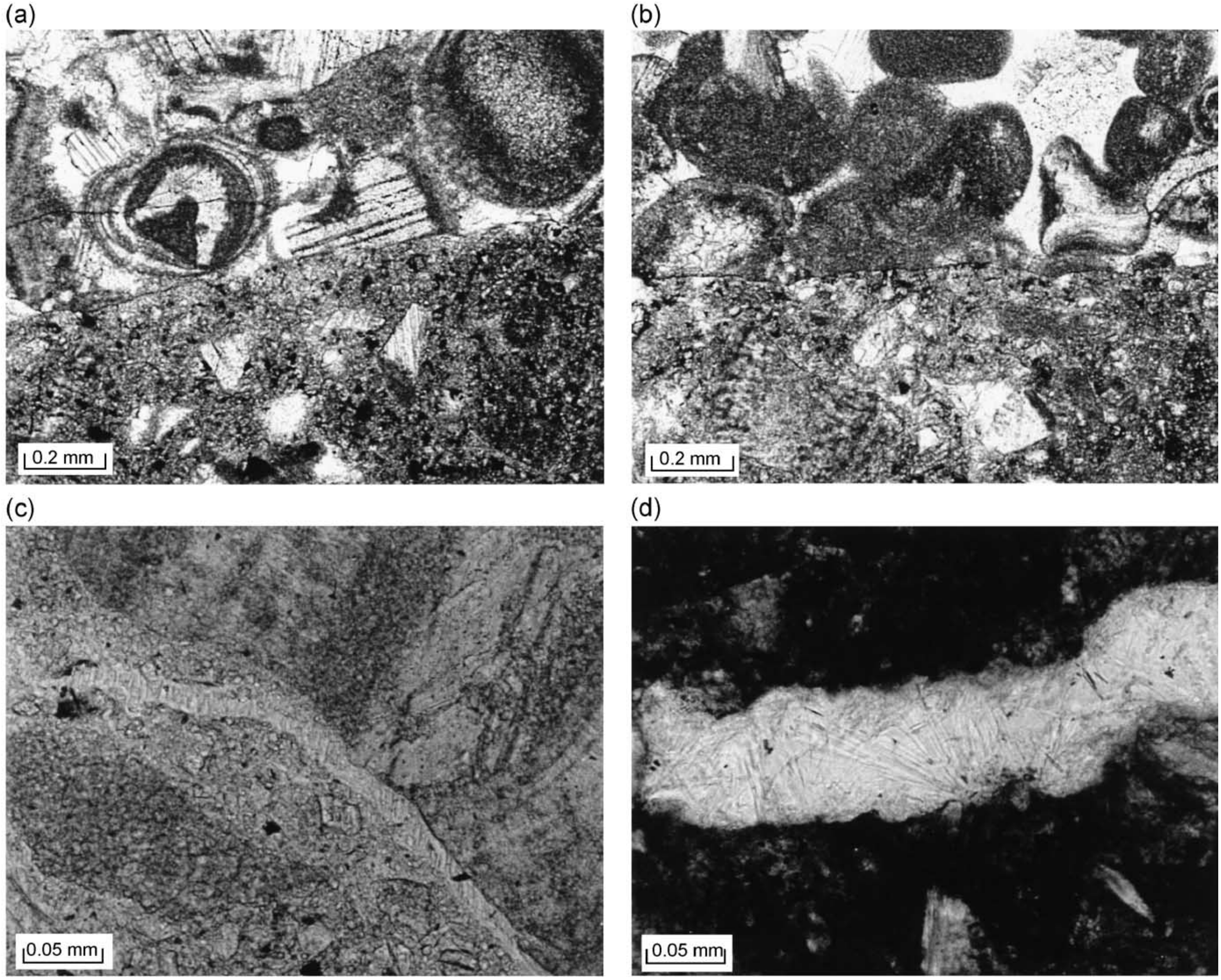


Fig. 4. Optical micrographs of concrete made with Exshaw aggregate. (a) and (b) Age ~1 year. No ettringite or crack at cement–aggregate interface. (c) Age 54 months. Ettringite in crack at and near cement–aggregate interface. (d) Age 54 months. Ettringite in crack in cement paste. (a), (c) Accelerated curing. (b), (d) Fog room curing.

given an initial cure at 23 °C. All bars were stored at 23 °C, 100% R.H., for 9 years and length change was recorded at regular intervals.

3. Results

Length-change data for mortar samples made at the University of Calgary are shown in Fig. 1. All the mortar bars decreased slightly in length (< 0.02%) for the first 12 months. At greater ages, bars expanded a little to between about 0.01% and 0.03% after 30 months. Some bars were measured to an age of about 9 1/2 years (126 months of 28 days). The maximum expansion was about 0.04% for the bars made by accelerated curing and which belonged to the batch to which there was 0% addition of $Ca(OH)_2$. Minimum expansion was about 0.02% recorded on bars cured in the fog room belonging to the batch to which there was an addition of 9% $Ca(OH)_2$.

Concrete prisms made with silicocarbonatite aggregates and cured either in a fog room or by the accelerated method showed less than 0.04% expansion by an age of 54 months (Fig. 2). A single bar of each set was retained in the fog room and at an age of about 9 years (116 months of 28 days) expansion was 0.04% for the fog-cured bar and 0.03% for the heat cured bar. Concrete prisms made with normally nonexpansive Exshaw limestone aggregates and cured in a fog room or by the accelerated method showed less than 0.02% expansion for the first 20 months.

At greater ages, length-change data diverged for the two sets of bars. By 54 months, the set cured by the accelerated method had expanded by about 0.09% whereas the fog-cured set of bars had expansion values of less than 0.02% (Fig. 2). A single bar of each set was retained in the fog room and length change was measured at an age of about 9 years (116 months of 28 days). Expansion was about 0.13% for the heat-cured bar and about 0.02% for the fog-cured bar. The form of the graphs of expansion vs. time for concrete prisms made with Exshaw limestones are similar to those reported in the earlier study. Bars cured in the fog room showed only very small changes in length whereas bars made by accelerated curing expanded at later ages. Rate and magnitude of expansion of those bars were, however, lower in this work than in the previous study—perhaps because of a difference in storage conditions. In the previous experiments prisms were conditioned at 38 °C, 100% R.H., for about 18 months prior to conditioning at 22 °C in a fog room whereas in this work specimens were held at 22 °C or 23 °C, 100% R.H., for the entire program.

Concrete was examined petrographically at ages of 2 days, 1 year and 54 months. Results showed that the silicocarbonatite contained carbonates, feldspars, chert, dawsonite and other unusual minerals previously described [5–11] (Fig. 3a). At an age of 1 year the cement paste surrounding the silicocarbonatite aggregate particles was reddish-brown, forming a reaction rim which was present in both fog room and accelerated-cured concretes (Fig. 3b). This behavior was reported in the previous paper. Evidence of carbonation was also present. Concrete made with silicocarbonatite aggregates and cured by the accelerated method did not always show microcracks at the cement–aggregate interfaces at 1 year (Fig. 5a), and by 54 months cracks were generally free of ettringite though some had a thin lining, possibly of $Ca(OH)_2$ (Fig. 5c). Likewise, ettringite was not present in cracks in fog-room-cured concrete at 1 year or 54 months (Fig. 5b, d). Concrete made with Exshaw aggregate was relatively free of cracks, and cracks which were present showed little sign of ettringite in either

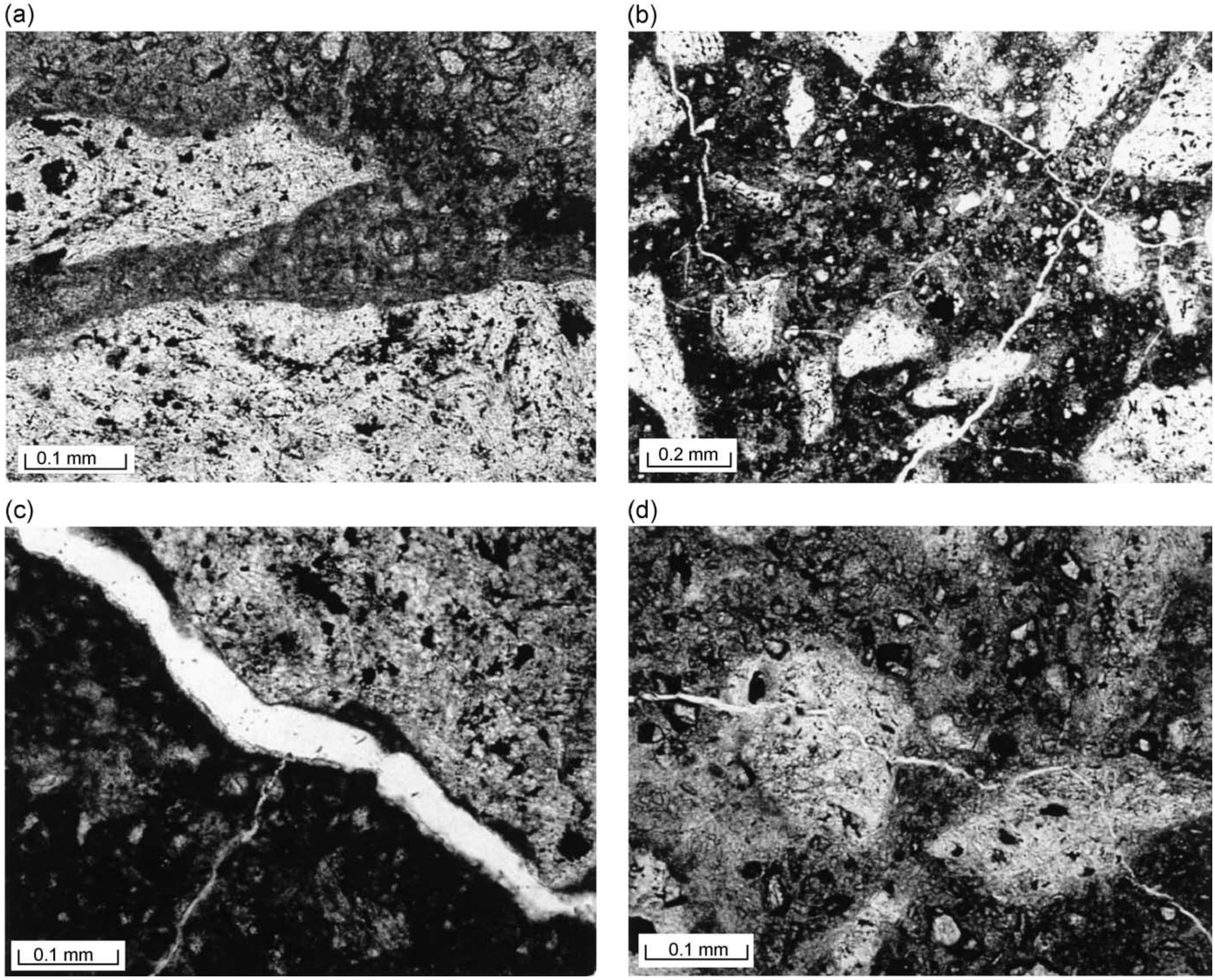


Fig. 5. Optical micrographs of concrete made with silicocarbonatite aggregate. (a) Age ~ 1 year. No ettringite or crack at cement–aggregate interface. (b) Age ~ 1 year. No ettringite in cracks crossing cement paste, aggregates and interfaces. (c) Age 54 months. No ettringite, possible $Ca(OH)_2$ lining crack at cement–aggregate interface. (d) Age 54 months. No ettringite in crack crossing cement paste, aggregates and interfaces.

the accelerated or fog-room-cured material at an age of 1 year (Fig. 4a, b). However, at 54 months microcracks at the cement–aggregate interfaces contained ettringite in the accelerated-cured concrete (Fig. 4c). Some voids and wider cracks in the fog-room-cured concrete also contained ettringite needles (Fig. 4d).

Results of the chemical analyses of water-soluble alkalies (Table 1) showed that the pore solutions of 2-day-old concrete made with silicocarbonatite aggregates contained much more NaOH than companion specimens made with Exshaw limestone aggregates. The difference was of the same order in concrete bars cured by the accelerated method as in bars cured in the fog room, and although the difference decreased with time it was greater than 1% even after 4 1/4 years exposure in a high-humidity fog room. The difference in K_2O content between concrete made with the two types of aggregates was small. Alkali contents showed a general decrease with time.

Length-change data of samples made at the Ontario Ministry of Transportation are shown in Fig. 6. It can be seen that the concrete made with the alkali–carbonate expansive Pittsburg dolomitic limestone, stored moist at 23 °C, continued to expand up to an age of 9 years. The prisms, which were given an initial cure at 80 °C, expanded more than the prisms cured at 23 °C and in both sets, the group containing silicocarbonatite expanded slightly more than the group with no silicocarbonatite.

The prisms made with nonreactive Nelson dolostone aggregate did not expand except in the mixture containing silicocarbonatite that was cured at 80 °C. Expansion of this set of prisms had substantially stopped after about 3 years. The bottom curve in Fig. 6 is an overlap of three sets of results for prisms made with Nelson aggregate with and without silicocarbonatite cured at 23 °C and for the prisms made with Nelson aggregate and cured at 80 °C for 4 h. Expansion of the three sets of prisms was minimal.

At an age of 9 years, the prisms were removed from storage and thin sections made for petrographic examination. The Nelson dolostone concrete cured at 23 °C showed some carbonation of the paste at the coarse aggregate/paste boundaries. There were trace amounts of ettringite lining some air voids. The concrete cured at 80 °C was similar except that there were larger amounts of ettringite, which lined or filled most air voids. The mixtures of Nelson with 10% silicocarbonatite showed similar amounts of ettringite to the mixtures without silicocarbonatite. Small hexagonal crystals were found in some air voids adjacent to silicocarbonatite particles. These were tentatively identified as gibbsite $[Al(OH)_3]$. The paste adjacent to the silicocarbonatite particles was usually extensively carbonated and calcium carbonate crystals were also observed in voids associated with the possible gibbsite crystals. These observations indicate that at 23 °C the silicocarbonatite did not cause expansion. High initial curing temperatures did cause a deleterious reaction of the Nelson concrete containing silicocarbonatite, resulting in up to 0.15% expansion after several years.

The mixtures made with the alkali–carbonate expansive Pittsburg aggregate showed ettringite filling cracks and

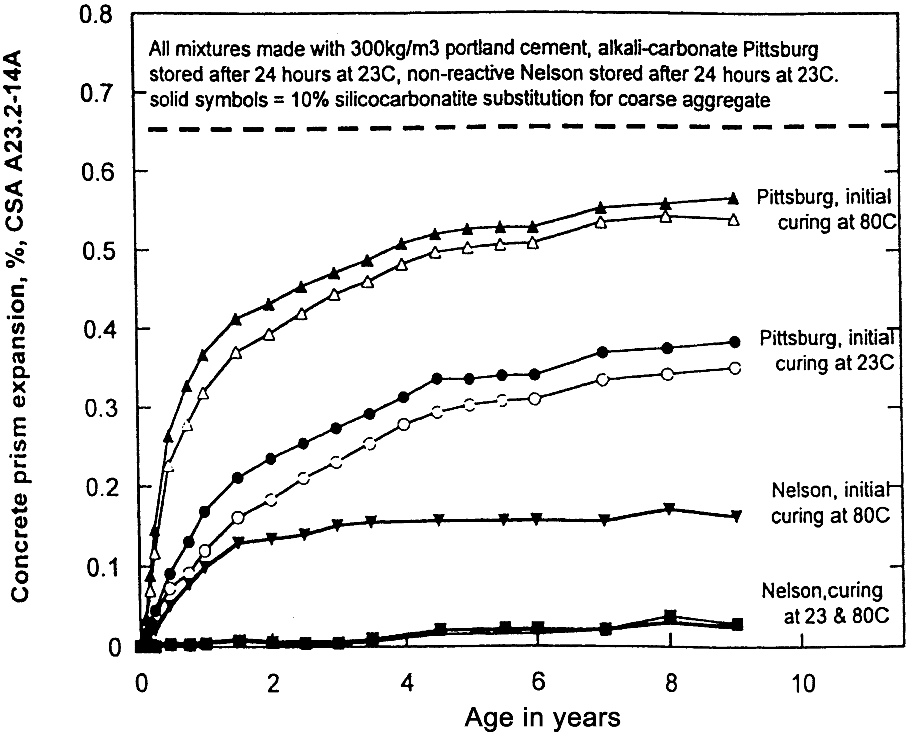


Fig. 6. Length change of concrete prisms.

filling and lining air voids in all samples. Those prisms subjected to 80 °C curing showed substantially greater amounts of cracking and larger amounts of observable ettringite than those cured at 23 °C. Cracks ranged in width from about 20 to 100 μm. In the 80 °C cured samples there were many undulating or wavy ribbons of cracks present in the mortar and at coarse aggregate/paste boundaries. The cracks were filled with ettringite crystals, which were generally growing perpendicular to crack walls and in randomly oriented groups of crystals in air voids. Nearly all small air voids (<100 μm) were filled but larger ones had only a lining of ettringite. Cracks in the middle of coarse aggregate particles were usually empty. The presence or absence of silicocarbonatite did not seem to have a significant effect on the amount of cracking or deposition of secondary deposits. In this alkali–carbonate expansive concrete, initial high curing temperatures caused substantially greater expansion in the long term compared with curing at more normal temperatures. The slightly greater expansion of both sets of Pittsburg prisms containing silicocarbonatite may be due to an increase in alkali content caused by the dawsonite reaction.

4. Discussion

The chemical analyses (Table 1) confirm previous findings [12] that NaOH is released at an early age into concrete pore solutions when silicocarbonatite from the Montreal area is used as aggregate in Portland cement concrete. As described previously [12] it is very probable that the rare mineral dawsonite in the silicocarbonatite rock reacts with $Ca(OH)_2$ in the pore solutions and NaOH is produced as indicated by the following equation:

$$\begin{aligned} &NaAl(CO_3)(OH)_2 + Ca(OH)_2 \\ &\quad \rightarrow CaCO_3 + Al(OH)_3 + NaOH \end{aligned} \tag{1}$$

Release of alkalies from a number of minerals found in aggregates has been proposed by other authors [17–21]. In the previous paper [12] it was demonstrated that the release of NaOH due to the dawsonite reaction led to an increase in expansion of concrete prisms made with alkali–carbonate reactive and alkali–silica reactive aggregates and also expansion with Pittsburg aggregate was shown to be increased by accelerated curing. Similar results are shown in this paper (Fig. 6) confirming that the NaOH released by the dawsonite reaction is able to increase expansion caused by AAR. Nonetheless, the concrete prisms and mortar bars made with silicocarbonatite showed only very small changes in dimensions. The mortar bars not only had a very high alkali content but also contained added $Ca(OH)_2$ both of which are known to favor expansion due to alkali–silica reaction [15]. Possibly, there is too little disordered silica in the silicocarbonatite or the proportion is too far from the pessimum for significant expansion due to ASR to occur.

The equation describing the dawsonite reaction indicates formation of carbonate and aluminate ions in addition to NaOH and also implies an increase in solid volume. The additional ions are released at an early age, and in the case of carbonate ions the supply is likely to be much more vigorous than that available from additions of finely ground limestone, for example [22]. When carbonate ions originate internally the time required for carbonation to affect components within a concrete element may well be relatively short. Externally derived atmospheric CO_2 enters via cracks and pores at exposed surfaces and the time required for it to reach internal cement hydration products or reinforcement depends upon the thickness of cover, concentration of CO_2 and degree of saturation which affects diffusion rate, etc. [23].

Carbonation causes a decrease in pH, which can lead to destruction of the passive layer on steel and thereby reduces corrosion resistance of reinforcement. Also, carbonation may release chlorides from some cement minerals and if the chloride concentration exceeds a certain limit, the possibility of corrosion is much increased. The release of carbonate ions by the dawsonite reaction may therefore increase the risk of corrosion of steel reinforcement in concrete though this possibility is minimized by the simultaneous release of strongly alkaline NaOH, which should largely counteract the effect of the weak carbonic acid.

In cement paste, carbonate ions are known to react mainly with $Ca(OH)_2$, forming $CaCO_3$. Its formation is accompanied by an increase in hardness and strength and a decrease in porosity and permeability of the cement paste. Carbonate ions may also attack other cement hydration products including C-S-H, Ca-sulphoaluminates and Fe-bearing compounds with formation of hydrated silica, alumina, ferric oxide and Ca carboaluminates [24,25]; the latter compound was tentatively identified by X-ray diffraction in the previous work [12].

As described above, reddish-brown reaction rims were observed in the cement paste surrounding silicocarbonatite aggregates. Those rims and implied other changes to the transition zone probably resulted from formation of hydrated Fe_2O_3 following internal carbonation of Fe-bearing minerals in the cement paste. Other evidence of carbonation included the identification of calcite and $Al(OH)_3$, some of which may have formed by internal carbonation of minerals in the cement paste supplementing the $CaCO_3$ and $Al(OH)_3$ formed by the dawsonite reaction itself.

Carbonation causes shrinkage of cement paste with maximum shrinkage occurring at a R.H. of about 50%. It seems possible that the early-age decrease in length of the mortar bars made with silicocarbonatite aggregates (Fig. 1) may have been partly due to carbonation shrinkage caused by internal release of carbonate ions in the dawsonite reaction. However, shrinkage was not shown by the concrete prisms made with silicocarbonatite aggregates.

It was suggested above that the dawsonite reaction may contribute to expansion of concrete because the combined molecular volumes of probable solid reaction products are greater than that of the reactants. In previous work, this suggestion could not be verified as the concrete used for length-change tests contained aggregates in which the silicocarbonatite was present only as a partial replacement for other rocks, some of which were known to be alkali expansive. In the present work in Calgary, only silicocarbonatite aggregate was used in some samples so complications from that cause were avoided. As stated above, however, those concrete prisms and mortar showed only small increases in length up to an age of about 9 years. Hence, if the increase in solid volume, implied by Eq. (1), does occur it does not translate into immediate expansion of the concrete or mortar bars. Perhaps the dawsonite reaction occurred while the cement paste was still sufficiently plastic to accommodate the increase in solid volume. After all, the analyses did show that the NaOH concentration had already increased significantly by an age of only 2 days.

Nonetheless, the concrete prisms cured at 80 °C and made in Ontario with nonreactive Nelson aggregates together with 10% silicocarbonate expanded whereas the companion bars, made with Nelson aggregate only, did not (Fig. 6). Similarly, in the previous work early-age expansion was recorded on concrete prisms made with normally nonreactive Exshaw limestone aggregate when combined with silicocarbonatite regardless of curing method (see Figs. 2 and 3 in Ref. [12]). Evidently, the presence of silicocarbonatite in the aggregates can lead to deleterious early-age expansion in concrete made with normally innocuous aggregates. So length change behavior, at least, is different when silicocarbonatite and another normally nonreactive aggregate are both present together from when the aggregate is composed only of silicocarbonatite.

Changes in solid volume due to chemical or physical reactions have long been considered to play a part in rock weathering and in some processes affecting the durability, strength and other physical properties of concrete. Volume increases are associated with a number of reactions such as the oxidation of some sulphides [26–28], the formation of many hydrates and the freezing of liquid water. Conversely, a decrease in solid volume accompanies the conversion reaction in high alumina cement (Refs. [29], p. 328; [30]), the formation of αC when Portland cement is autoclaved without addition of SiO_2 (see Ref. [31], pp. 316–318) and dedolomitization in the alkali–carbonate reaction [17,32]. However, the magnitude of expansion or contraction of polycomponent materials may be affected by dimensional changes in more than one constituent and/or by other variables. These include the "form energy" [33] or "crystallization pressure" (see Ref. [34], p. 119) of the new products and the location or site at which recrystallization or precipitation of new products takes place [35].

Microcrack tips are sites of stress concentration at which distorted interatomic bonds may favor the nucleation of new crystals. Other factors having an influence on dimensional change include the porosity and pore size distribution, the permeability, the possible presence of complex ions, the course of the reaction, the presence or formation of hygroscopic gels and the fabric and microstructure of the material. Possibly the dawsonite reaction is accompanied by side reactions or is more complex than indicated by Eq. (1) as suggested by some evidence mentioned in the earlier paper [12]. These considerations or other factors have a major influence on the dimensional change behavior of the concrete and mortar bars stored at constant temperature and high humidity.

It was concluded in the previous work that DEF was the cause of higher ultimate expansions of heat-cured concrete bars made with alkali expansive and normally nonalkali expansive aggregates; petrographic and length-change data reported in the current work lead to the same conclusion. It seems reasonable to conclude also that the release of NaOH, carbonate and aluminate ions by the dawsonite reaction itself had a bearing on the progress of DEF in the specimens containing silicocarbonatite aggregates.

Causes of durability failure due to DEF and the underlying mechanism have been reviewed by various authors [14,25,36–42]. In one view, the cement paste itself is thought to expand due to the formation of very small ettringite crystals. Crystal size is likely to be affected by the space available and by the relative rates of nucleation and diffusion. Also Mehta and Wang [43] showed that, in the presence of $Ca(OH)_2$, crystallites of ettringite may precipitate with gel-like properties capable of swelling by adsorption of water. On the other hand, the presence of ettringite crystals at cement–aggregate interfaces led to the alternative suggestion that crystal growth pressure is the root cause of expansion. If crystal growth at the cement–aggregate interface is indeed a factor in the expansive mechanism of DEF differences in behavior between specimens made with different aggregates may result in part from petrographic differences between the types of rock used as aggregate since such differences are known to affect bond strength [45] and the nature of the transition zone [46,47].

High-temperature curing (>70 °C) is often thought to be one important requirement for DEF. It has been suggested, however, that when concrete is placed during warm weather and when large elements are cast the exothermic nature of the hydration reactions themselves may cause a sufficient rise in temperature to set the stage for DEF [44]. In laboratory studies, the small size of the test specimens makes this unlikely, and results in the current study and in the previous work showed that when late-stage expansion occurred, as in concrete made with Exshaw limestone aggregates (Fig. 2), it did so only in heat-cured specimens. Even then, expansion did not occur in all cases. For example, no significant late-age expansion occurred when silicocarbonatite aggregates were used in heat-cured concrete prisms or mortar bars despite the type and composition of the cement used in the mortar (Figs. 1 and 2). Likewise, heat-cured concrete prisms made with Nelson aggregates showed no expansion by 9 years (Fig. 6).

A high alkali content is reported to decrease the reactivity of the aluminates in Portland cement [48] and to stabilize AFm phases at the expense of AFt phases [49] so late-age formation of ettringite is inhibited. This could occur when the aggregate is made with silicocarbonatite since the dawsonite reaction causes a high alkali content in the concrete or mortar. Apart from the effect of increased NaOH concentration, release of $Al(OH)_3$ by the dawsonite reaction would tend to decrease the SO_3/Al_2O_3 mole ratio and thereby also reduce the likelihood of expansion due to DEF [14]. Release of carbonate ions by the dawsonite reaction may also have an influence since it has been suggested that formation of Ca-carboaluminate may affect ettringite formation and the proportion of AFm and AFt phases [25].

Despite these considerations of theoretically beneficial effects of the dawsonite reaction on DEF it should be recalled that heat-cured concrete containing silicocarbonatite plus both Spratt and Exshaw limestone aggregates Fig. 2 in Ref. [12] still managed to show increased late-age expansion! Also heat-cured concrete made with Nelson plus 10% silicocarbonatite aggregates and fog-room-cured concrete made with Exshaw limestone plus silicocarbonatite aggregates showed early-age expansion (Fig. 6 this paper; Fig. 2 in Ref. [12]).

5. Conclusions

1. Concrete made with silicocarbonatite aggregates contained over 1.5% more water-soluble Na_2O than companion prisms made with Exshaw limestone aggregates 2 days after casting. The difference was observed both in samples cured in the fog room and in accelerated-cured samples. The difference decreased with time in the fog room but still exceeded 1.0% after 4¼ years.

2. The higher Na_2O content of the concrete made with silicocarbonatite aggregate is attributed largely to a rapid reaction between the rare mineral dawsonite in that aggregate and $Ca(OH)_2$ in the Portland cement paste.

3. The proposed reaction between dawsonite and $Ca(OH)_2$ (the dawsonite reaction) implies an increase in solid volume. Length-change data recorded for about 9 years on concrete prisms and mortar bars made with silicocarbonatite aggregates and stored at constant temperature and high humidity showed minimal expansion. Expansion was also minimal in accelerated-cured concrete prisms made with Nelson dolostone. However, companion bars containing 10% silicocarbonatite showed 0.15% expansion indicating a deleterious reaction.

4. Concrete prisms made with Exshaw limestone aggregates and subjected to accelerated curing at 85 °C showed late-stage expansion, which is attributed to DEF. Increased expansion of the accelerated-cured Pittsburg aggregate concrete is attributed to aggravated alkali carbonate reaction (ACR) or DEF.

5. Interpretation of results from the present series of tests indicates that damage from AAR was aggravated by the dawsonite reaction and DEF was associated with high temperature curing.

6. The lack of expansion attributable to DEF in heat-cured concrete and mortar made with silicocarbonatite aggregates and recent literature suggests that the release of alkali, carbonates and aluminate ions by the dawsonite reaction may have potentially beneficial side effects if properly exploited and which could help to prevent impaired durability performance by Portland cement concrete.

7. The potentially deleterious nature of sodium-bearing minerals present in aggregate, even in small amounts, should be noted. While such minerals are rare, their presence should be sought when investigating sources of concrete aggregate. When found, a thorough investigation should be conducted before permitting such aggregates to be used in concrete.

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