EXPANSION BEHAVIOUR OF SPRATT AND PITTSBURG LIMESTONES IN DIFFERENT TEST PROCEDURES

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Abstract

The expansion behavior of two limestone aggregates from Canada, i.e. Spratt siliceous limestone (SL) and Pittsburg argillaceous dolomite-bearing limestone (PL), in Accelerated Mortar Bar Test (AMBT), Concrete Prism Test (CPT), Accelerated Concrete Microbar Test (CMBT) and autoclave test was studied for exploring the expansion mechanisms when the rocks react with alkalis. The SL gives high expansion in all the tests and sufficient fly ash or LiOH could significantly reduce its expansion, thus showing high ASR behavior. The PL however shows high and rapid expansion in the tests using relatively coarse aggregate particles, but limited expansion in the AMBT and reponse to fly ash and LiOH. The significant difference, even contrary behavior of the two limestones in the various tests and responses to fly ash and LiOH, suggests that two different mechanisms are involved in their expansion processes.

Keywords: Alkali-silica reaction, Alkali-carbonate reaction, Lithium compounds   Fly ash

1   INTRODUCTION

Carbonate aggregates (limestone and dolostone) are widely used as concrete aggregates around the world. Damage due to alkali-silica reactivity in concrete incorporating siliceous carbonate aggregates has been reported in Canada and other areas [1,2,3]. Certain types of argillaceous dolomite–bearing carbonate aggregates were also found to react with the cement alkalis and cause large expansion and disruption of concrete structures within only a few years [2], in many aspects exhibiting a different behavior from classical ASR that usually needs a longer time to occur. The latter, which was originally defined as alkali-carbonate reaction (ACR) by Canadian researchers, was reported in the USA, China and Austria in past years [4-6]. Although a lot of work has been carried out on this type of reaction, the mechanism involved is still not fully understood, even the term itself is still a matter of controversy among researchers [7]. For exploring the expansion mechanism of dolomite-bearing carbonates, the expansion behavior in different test procedures of the two well-known alkali-reactive Spratt and Pittsburg limestone aggregates were compared in this paper.

2   MATERIALS AND METHODS
2.1   Aggregates

The Spratt limestone (SL) is a fine-grained siliceous limestone from the Spratt quarry near Ottawa, Canada. The reactive phase in the Spratt limestone is cryptocrystalline quartz disseminated in the matrix of calcite (micrite) in the rock. Concrete structure deterioration associated with the use of this kind of aggregate has been reported in various region of eastern Canada [1,2]. The aggregate has commonly been used as a reference aggregate worldwide and generates high ASR expansion.

The second aggregate, Pittsburg limestone (PL), is an argillaceous dolomitic limestone from the Pittsburg quarry, Kingston, Canada. It has been defined as a "typical" alkali-carbonate reactive rock in the early literature and has caused rapid concrete deterioration in Kingston area of Canada [2]. A sample of aggregate from the Kingston quarry has been stockpiled in the 1980s by the Ontario Ministry of Transportation in Canada and distributed since as a reference aggregate for expansion testing; the average composition of the rock is about 30% dolomite, 60% calcite and 10% acid insoluble residue. It displays typical petrographic features charaterized by rhombic crystals of dolomite, 20-50μm in size, disseminated in a matrix of microcrystalline calcite (typically 2-6μm in size) and clay minerals(mainly illite) (<2μm in size).

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2.2   Chemical composition of cement and fly ash

A high-alkali cement (HAC) with 0.91% Na_2Oe and a low-alkali cement (LAC) with 0.46% Na_2Oeq were used. A moderate calcium fly ash (FA) was used to assess the effect of fly ash on concrete microbar expansion. The chemical compositions of cements and fly ash are given in Table 1.

2.3   Testing methods

A number of expansion tests were carried out in the laboratory. The accelerated mortar bar test (AMBT) and concrete prism test (CPT) were carried out in accordance with CSA A23.2-25A (equivalent to ASTM C 1260) and CSA A23.2-14A (equivalent to ASTM C 1293), respectively.

The Concrete Microbar test (CMBT) was carried out in accordance with RILEM AAR-5, Rapid preliminary screening test for carbonate aggregates. The effects of fly ash (30% replacement of the HA cement) and aggregate particle size (2.5-5.0 mm vs 5-10 mm) on expansion in the CMBT were also examined.

The fourth method used in the program consists of the Autoclave Concrete Minibar Test (ACMT), which was originally developed for the identification of the alkali reactivity of carbonate rocks [5]. However, modifications were made in the type of alkalis both in the cement matrix and in the storage solutions to evaluate the effect of alkalis on expansion. The main parameters of the accelerated tests are listed in Table 2.

3   TEST RESULTS
3.1   Expansion in the AMBT and CPT

Figure 1 shows the expansion curves for the SL and PL aggregates in the AMBT. The expansion of the mortar bars incorporating SL and PL reached 0.30% and 0.11% at 14 d, respectively. The expansion of SL mortar bars increased relatively uniformly with time, reaching 0.69% at 28 d. On the other hand, the PL mortar bars expanded slowly throughout the testing period, reaching only 0.16% at 28 d. According to CSA and ASTM limits, SL is considered as potentially-reactive, while PL is considered as non-reactive. The expansion behavior of PL in the AMBT does not correlate to its rapid and deleterious expansion observed in field concrete, indicating that the AMBT could not adequately identify its reactivity.

Figure 2 shows the CPT expansion of SL and PL cured at 38 and 60°C respectively. At 38°C, after a 4-week induction period, the concrete prisms made with the SL aggregate entered a main expansion phase up to about 24 weeks, reaching the 0.040% expansion limit after only 8 weeks of testing. The expansion rate then started to decrease and the expansion progressively leveled off; it developed the typical "S-shape" expansion curve reported in the literature [8]. Under the same curing conditions, however, concrete prisms incorporating the PL aggregate expanded rapidly, reaching 0.040% and 0.35% after one week and 8 weeks of testing, respectively. The expansion rate slowed down after that, but the test prisms kept expanding throughout the testing period to finally reach about 0.80% level at one year.

3.2   Expansion in the CMBT

Figure 3 shows that no significant difference is observed between the expansion behaviour of the two limestones in the CMBT, both inducing rapid and linear expansion with time. It should be noted that white gel deposits formed on the surfaces of the concrete microbars incorporating the SL and PL aggregates, although the amount of gel deposited on the PL specimens was significantly smaller than those with SL. This suggests that siliceous material in both aggregates was involved in the reaction with alkalis and may have contributed to the expansion in this method. Concrete microbars with fly ash (FA) however showed a significantly difference in expansion. With 30% of FA, the expansion of SL concrete microbars was largely suppressed (76% reduction at 28 days), while the use of FA did not show much impact on PL expansion (only 12% reduction at 28 days).

The different response of SL and PL to FA correlates well with the results reported in the literature that indicates that there is no real efficient preventive measure against alkali-carbonate reaction [9]. This suggests that the expansion mechanisms involved for the two limestones may totally different. However, the similar behaviour of control PL and SL concrete microbars indicates that the CMBT procedure cannot efficiently differentiate the two types of reaction

Figure 4 illustrates the effect of the aggregate particle size on SL and PL expansion in the CMBT. In the case of the SL aggregate, a decrease in the aggregate particle size resulted in a significant increase in expansion over the 28-day testing period. This is considered as a typical ASR behaviour observed with several reactive aggregates where, within a certain aggregate size range, the

finer the aggregate particles, the faster and higher the reaction rate and expansion when tested in AMBT or CMBT conditions. On the other hand, in the case of the PL aggregate, the two size fractions, 2.5-5.0 mm and 5.0-10.0 mm, induced relatively similar rates of expansion and final expansion levels over the 28-day testing period. Considering the low expansion of PL in the AMBT, in which over 60% of the aggregate particles are smaller than 1.25 mm, the use of the CMBT in which 100 percent of aggregate are larger than 2.5 mm, not only suggests that the expansion behaviour of PL is different from a typical ASR, it also suggests that the use of relative coarse particles is critical for reliable identification of its expansivity.

3.3   Expansion under autoclave condition (ACMT)

Figures 5 and 6 show the expansion of concrete minibar with SL and PL autoclaved in different alkali solutions. The above figures indicate that both SL and PL concrete minibars gave large and rapid expansion when autoclaved in NaOH and KOH media, with SL giving larger expansion than PL after similar autoclaving periods. When cured in LiOH and water, however, minibars with SL and PL showed quite different expansive behaviours. Minibars incorporating the SL aggregate showed basically no expansion when autoclaved in water and developed noticeable but relatively limited expansion (0.12%) when autoclaved in LiOH for 150 hours. On the other hand, while concrete minibars made with the PL aggregate developed noticeable but limited expansion in water, the companion set of bars immersed in LiOH reached an expansion of 0.29% after 150 hours of autoclaving. The expansion of SL and PL concrete minibars in water may due to various processes such as the absorption of water by clay matrix in the rocks, nonreversable thermal expansion, the dedolomitization of dolomite crystals in the rocks matrix (since the dedolomitization might take place at low pH condition). It is reasonable to attribute the "net" expansion of both aggregates (i.e. the expansion in the lithium solution less that in water) to non ASR reasons considering that the ASR-induced expansion could be largely suppressed when enough lithium is available (both in the concrete minibar and in the autoclave solution). Concrete minibars with PL developed a higher "net" expansion than that of SL throughout the testing period (0.19% vs 0.10%), thus suggesting that the dominant mechanism leading to higher expansion of PL is different from that in SL.

4   DISCUSSION
4.1   Experimental findings

The results presented in the previous sections and in the literature confirmed that PL aggregate shows many different features from typical ASR aggregates. Firstly, concrete prisms made with the PL aggregate expand significantly at 23°C with 310 kg/m^3 cement content (i.e. original version of the concrete prism test), under which conditions most ASR aggregates will not expand significantly or will expand very slowly [10-12]. The current CPT conditions, i.e. high cement and alkali contents (420 kg/m^3 cement content, 1.25% Na$_2$Oeq)), as well as higher testing temperatures (38 or 60°C), results in the development of rapid and high expansion. Secondly, the use of sufficient amounts of fly ash, slag and lithium additives can largely suppress ASR expansion in both laboratory and field conditions, but cannot satisfactorily control the expansion of the PL aggregate. For example, Fig. 7 shows the expansion of control concrete blocks and blocks incorporating 50% ground granulated blast-furnace slag made with the Spratt and Kingston aggregates [13,14]. The results shows that, over the five-year testing period reported, 50% slag was totally effective in controlling expansion with the Spratt aggregate but ineffective with the Kingston limestone. Thirdly, rock cylinders with PL aggregate expand significantly in alkali solution at low temperatures (ASTM C 586) [11,15]. Figure 8 show the expansion of PL rock cylinders in 1 M KOH solution at 20 and 40°C. TEM analysis performed on specimens extracted from the rock cylinders indicates that the quartz was not involved in the reaction process with the alkalis under those conditions (Fig. 9). Also, the AMBT failed to correctly identify the expansivity of PL, the use of relatively larger coarse particle size, such as in the CMBT, being however effective in assessing its expansivity.

Finally, compacted cylinders (φ10 mm × 40 mm) were made with various size fractions of pure dolomite, magnesite or calcite powders (without silica) and cement at high pressure (300 MPa) to simulate the environment of dolomite crystals distributed in matrix of rocks. The size fraction of rock powders include <0.04 mm, 0.04-0.08 mm, 0.08-0.15 mm, 0.15-0.35 mm, 0.35-0.56 mm, 0.56-0.80 mm. The rock powder-to-cement ratio and water-to-cement ratio of the compacts are 4 and 0.1, respectively. As shown in Figs. 10 to 12, all compacted cylinders with magnesite, dolomite and calcite powders without silica suffered expansion in alkali solution, and the expansion increased with decreasing powder sizes. However, the decreases of solid volume in reactions of magnesite, dolomite and calcite with alkalis are 7.4%, 8.6% and 11.8%, respectively. It indicates that solid-volume-

decreasing reaction can induce expansion when appropriate conditions are met, and that the silica is thus not necessarily involved in the expansion process [16].

4.2   Existence of harmful ACR?

The main argument for denying that the dedolomitization process can by itself induce deleterious expansion is that dedolomitization reaction is a solid-volume-decreasing process. Also, dolomitic limestone very often includes some silica impurities, which may also be involved in the reaction process with alkali hydroxides, especially in accelerated laboratory tests (high alkali, high temperature). Therefore, some researchers have suggested that the so-called ACR is essentially another type of ASR, based on the existence of ASR product, the non-expansivity of dedolomitization reaction itself, and the existence of non harmful dedolomitization in field concrete [7].

There is no doubt that not all dedolomitization process is harmful. Chemical reactions also not necessarily cause harmful expansion. In that sense, alkali-carbonate reaction (ACR) may not be an accurate or appropriate term for referring to the harmful dedolomitization process occurred in certain type of carbonate rocks with special petrographic features. However, it is insufficient to deny the existence of harmful dedolomitization (ACR). Actually, compacts with pure dolomite, magnesite and calcite without silica suffered expansion in alkaline solution indicating that solid-volume- decreasing reaction can induce harmful expansion under appropriate conditions, and the silica is not necessarily needed in the expansion process. Extensive study and experimental findings presented above have suggested that the harmful reaction occurred in PL is not a special type of ASR, either a classical ASR bothered by a non-harmful dedolomitization.

4.3   Interaction between ASR and so called ACR

Silica "impurities" in dolomitic limestones will likely be involved in the reaction with alkali hydroxides (high pH) under high temperature conditions. Actually, gel deposits on the PL concrete microbar surfaces were noticed. On the other hand, small amounts of dolomite in some siliceous linestones may also react with alkali hydroxides. It is likely that, in practice, alkali-silica reaction and dedolomitization coexist within some carbonate rocks. The expansion mechanism of such rocks is more complicated than that with only one reactive constituent. The order and time of the two reactions, alkali-silica and alkali-dolomite, may not only depend on the amount and chemical reactivity of silica and dolomite; the distribution of these constituents in the rock is also, and even probably more important. The contribution of each reaction, ASR and dedolomitization, to the resultant expansion, and whether there are synergetic effects between the above, has not been clearly established and needs further study.

For selecting appropriate preventative measures to control deleterious expansion of these rocks, it is necessary to clarify the dominant expansion mechanism of these rocks. The different response of the PL and SL to FA, slag and lithium additives has thrown some light in this respect.

5   CONCLUSIONS

- The SL and PL aggregates have shown significant differences in their expansion behaviour in various laboratory tests, including AMBT, CPT, CMBT and autoclave tests, and in their respons to additives such as FA, lithium, slag etc, the latter being often effective in suppressing ASR expansion when used in sufficient amounts.
- The SL aggregate shows typical ASR features and gives high expansion in various laboratory tests. Sufficient FA and lithium could effectively suppress its expansion. While the PL aggregate gives rapid and high expansion in the concrete prism and concrete microbar tests, it results in low accelerated mortar bar expansion. It's response to FA, lithium, temperature, and aggregate particle size, etc., is also different, sometimes contrary to that of the SL aggregate.
- The use of coarser aggregate particles is a critical factor for correctly identify the expansivity of the PL aggregate.
- The high expansion mechanism involved in the reaction of PL with alkalis is totally different from that with SL, a typical ASR aggregate.
- In some carbonate rocks, ASR and harmful dedolomitization may coexist and the use of their different response to FA, slag and lithium is helpful to clarify the dominant expansion mechanism.

6   REFERENCES

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TABLE 1: Chemical composition of cement and fly ash (%).									
Sample	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	Na$_2$O	K$_2$O	SO$_3$	LOI	Total
HAC	60.82	19.57	4.88	2.91	2.52	0.27	0.97	3.32	2.82	95.16
LAC	64.60	22.10	4.76	3.28	0.82	0.07	0.59	--	0.91	96.22
FA	13.40	52.40	23.40	4.70	1.30	3.60	0.60	0.20	0.30	100.70

| TABLE 2: Parameters in accelerated tests used in this study.				
Parameters	**AMBT**	**CMBT**	**ACMT**	**CPT**
Water-to-cement ratio	0.47	0.32	0.30	0.45
Cement alkalis (Na$_2$Oeq.)	1.0 ± 0.1%*	1.0 ± 0.1%*	1.5% **	1.25% ***
Aggregate size (mm)	0.15-5.0 ****	5-10; 2.5-5.0	5-10	5-20
Bar Size (mm)	25×25×285	40×40×160	20×20×60	75×75×300
Cement-aggregate ratio	1:2.25	1:1	1:1	
Curing temperature	80ºC	80ºC	150ºC	38ºC
Storage solution	1.0 M NaOH	1.0 M NaOH	10% KOH or NaOH or LiOH	Moist >95% R.H.
Zero length	24h in water @ 80ºC	24h in water @ 80ºC	24h moist @ 23ºC plus 4 h steam (100ºC)	24h moist @ 23ºC
Criteria	0.10% @ 14 d	0.10% @ 28 d	--	0.04%@ 1 year
* Use high-alkali cement				
** Use low-alkali cement, add KOH, NaOH or LiOH to mixture water				
*** High alkali cement added with NaOH in mixing water				
**** Five required size fractions.				
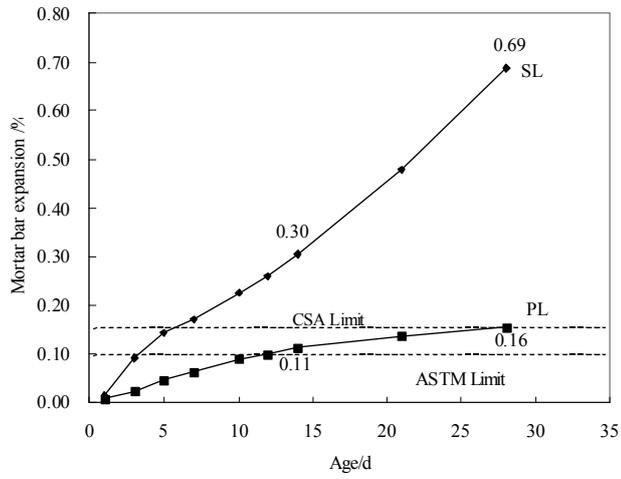
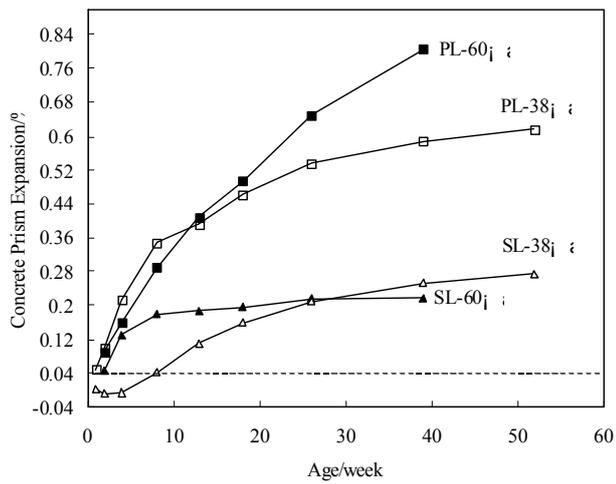Figure 1: Expansion of SL and PL in the AMBT.

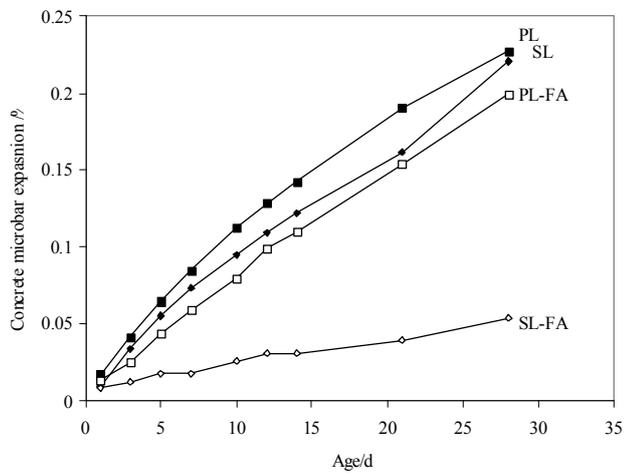Figure 2: CPT expansion of SL and PL cured at 38 and 60°C.

Figure 3: Effect of FA on the expansion of SL and PL in the CMBT.
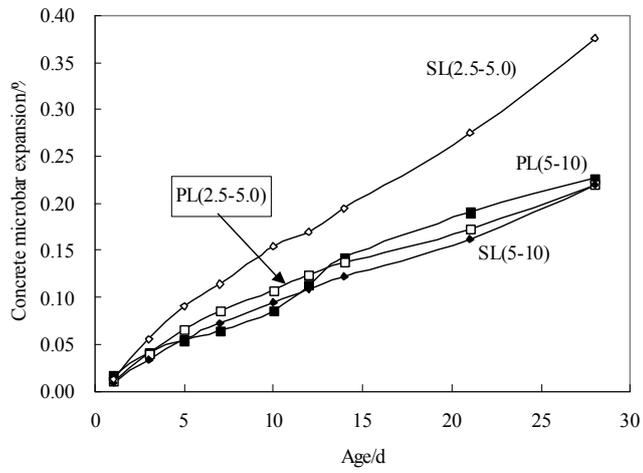
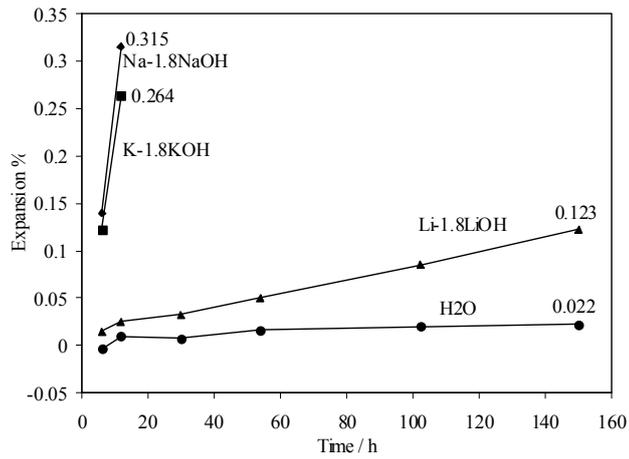Figure 4: Effect of aggregate particle size on expansion of SL and PL in the CMBT.

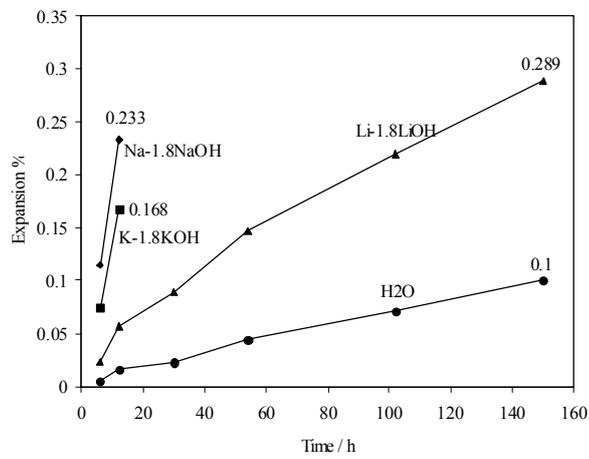Figure 5: Expansion of concrete minibar with SL autoclaved in different media.

Figure 6: Expansion of concrete minibar with PL autoclaved in different media.
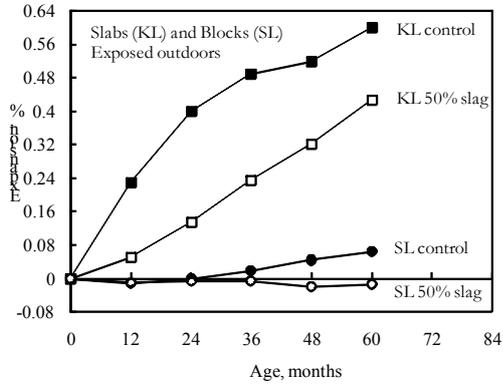
Figure 7: Expansion of concrete blocks and slabs made with the Spratt (SL) and the Kingston (KL) limestones and incorporating 50% ground granulated blast-furnace slag. The total concrete alkali content was kept to about 3 kg/m³, from [13,14].
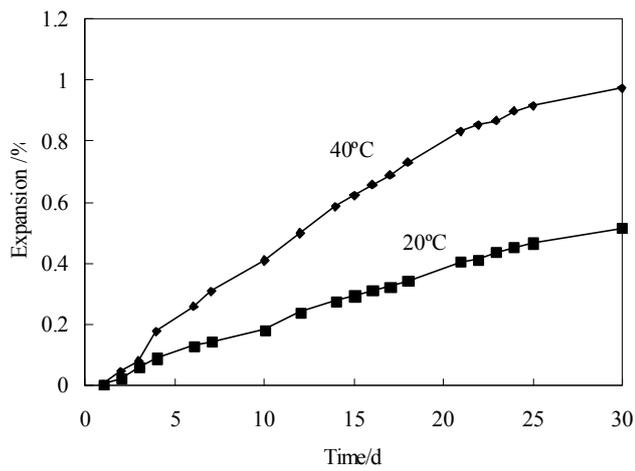
Figure 8: Expansions of φ8×15 mm PL rock cylinders in 1 M KOH solution.
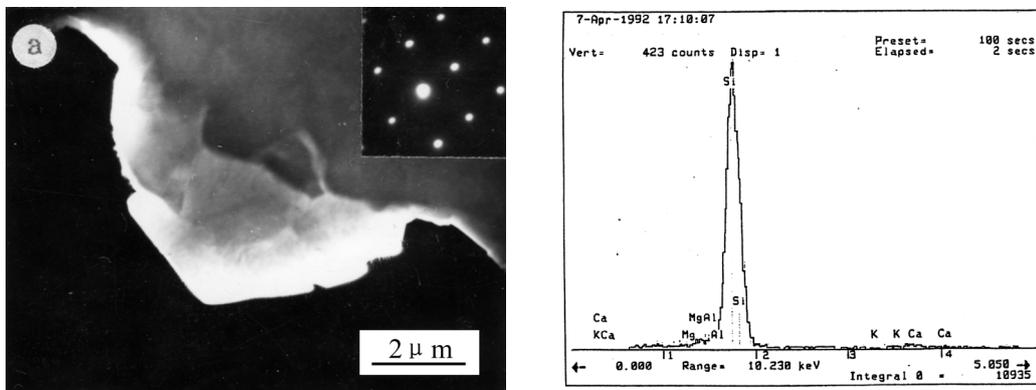
Figure 9: TEM dark field image (a) and EDS spectra (b) of Quartz crystal in PL rock cylinder immersed in 1 mol/L KOH solution at 40ºC, 7 days.
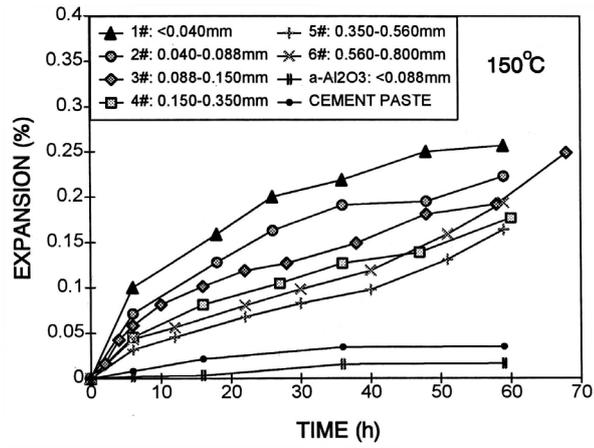
Figure 10: Expansion of compacts with <u>magnesite powders</u> in different size fractions autoclaved in 10% KOH solutions at 150°C (with a-Al$_2$O$_3$ powder and cement for reference), from [16].
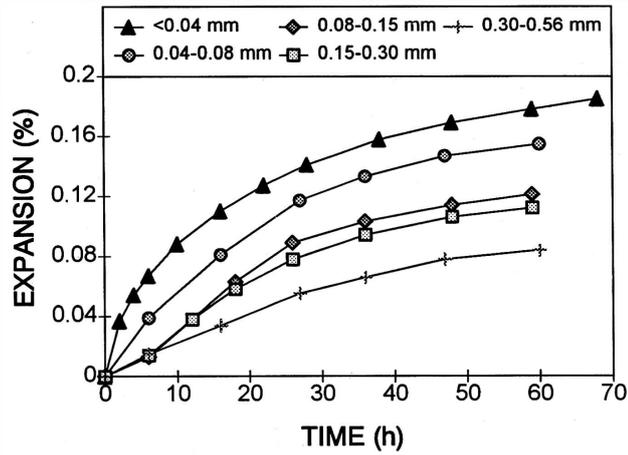

Figure 11: Expansions of compacts with <u>dolostone powders </u>in different size fractions autoclaved in 10% KOH solutions at 150°C, from [16].
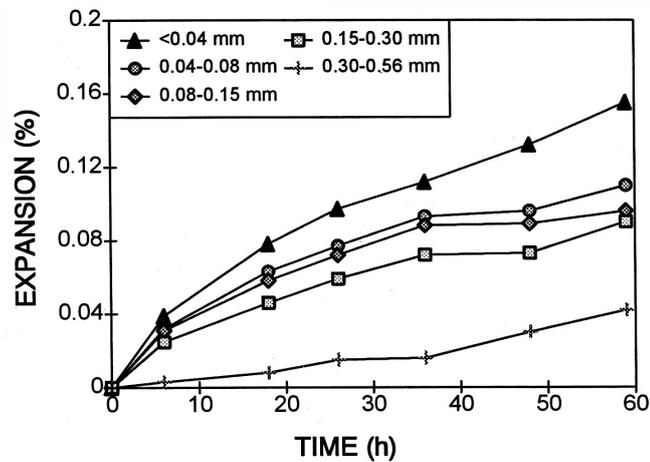

Figure 12: Expansions of compacts with <u>pure limestone powders </u>in different size fractions autoclaved in 10% KOH solutions at 150°C, from [16].