UNEXPECTED EXPANSION OF CONCRETE MADE WITH LAUMONTITE CONTAINING AGGREGATES UNDER SEAWATER CONDITION

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ABSTRACT

Deterioration of steam-cured concrete specimens made with laumontite containing aggregates, under marine submerged, tidal, and atmospheric exposures for 30 years, was investigated. The expansion of the specimens exposed to the marine submerged and tidal exposures ranged from complete disintegration to the moderate deterioration. The deteriorated regions contains little calcium hydroxide as well as calcium silicate hydrates, but rich with ettringite, brucite, and calcite. At the deteriorated region, white rim of ettringite crystal is found around the aggregates. Ettringite, brucite, and calcite are also found at the voids as well as along the cracked path. No visible crack was found on the surface of the atmospheric specimens. It is clearly understood that exposure condition is a governing factor related to the expansion caused by the laumontite mineral. No expansion of 30 years old atmospheric and tidal specimens is found after further wetting and drying exposure utilizing natural seawater of temperature 60°C.

Keywords: laumontite, ettringite, seawater, submerged, tidal, expantion

1. INTRODUCTION

Deterioration of concrete structures due to the use of problematic aggregates having reactive minerals, such as aggregates containing reactive silica or carbonate is found in the literature since 1940, Refs [1-4]. These minerals react with free alkali in concrete and produce a product having volume larger than the initial volume of the reactants involved, and therefore result in expansion. The reaction is known as alkali-aggregate reaction and more specifically as alkali-silica reaction or alkali-carbonate reaction depending on the type of minerals involved in the reaction. Besides these reactions, abnormal expansion under marine exposure due to the use of aggregate containing significant amount of special minerals, such

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as laumontite (CaO.Al$_2$O$_3$.4SiO$_2$.4(H$_2$O)) was also reported in Japan [5]. Severe expansion was also observed by the authors in 1973 after exposing a series of specimens made from a new source of aggregate in seawater for a short period of time. Based on the mineralogical investigation of the aggregates used, a significant amount of laumontite mineral was found. For further investigation, a series of specimens was made in 1973 with the aggregates collected from the same source and exposed to the marine atmospheric, tidal, and submerged exposures. The investigation was continued till the age of 30 years. At 27 years of exposure, aggregates from some severely and moderately deteriorated specimens were collected and crushed into fine aggregates. Mortar specimens utilizing the crushed aggregates were made for further expansion test. Furthermore, at 30 years of exposure, some specimens from tidal and atmospheric exposures were exposed to a wetting and drying exposure utilizing natural seawater of temperature 60°C. The results of all investigations are summarized here.

2. FLOW DIAGRAM

The flow diagram of investigation of a 30-year experimental plan is shown in Figure 1. Concrete specimens were made in 1973 and exposed to the marine exposure facility (submerged, tidal, and atmospheric zones) of Port and Airport Research Institute, Yokosuka, Japan (PARI). The specimens were investigated for visual observation, mineralogy of matrix and aggregates, microstructure of concrete (SEM) after 15 and 27 years of exposure.
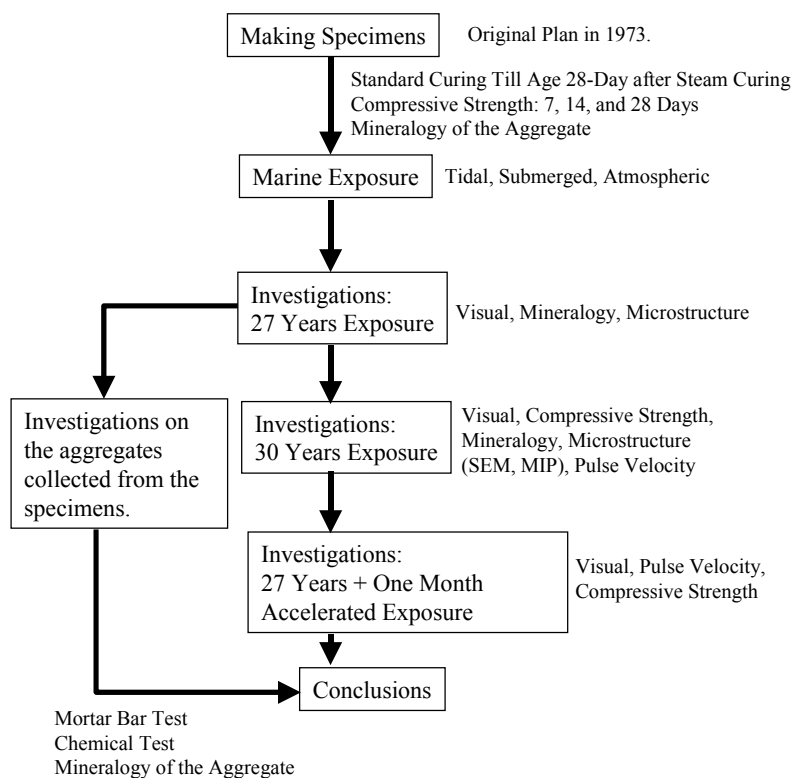
Figure 1. Flow diagram of total investigation

After 27 years of exposure, coarse aggregates from the specimens were collected and tested for mineralogy of the aggregates. Some aggregates were crushed to make mortar specimens and the expansion of the specimens was tested under seawater and tap water exposure at temperature 40°C. Three years later, i.e. at the age of 30 years, some specimens were again tested for visual observation, compressive strength, mineralogy, microstructure (SEM, MIP), and pulse velocity. Moreover, to understand further deterioration of the specimens, some specimens from tidal and atmospheric zones were exposed to an accelerated seawater exposure facility to check the further expansion of the specimens. The possibility of alkali-silica-reaction (ASR) related expansion was also checked by various tests. Finally, conclusions were made based on the results of all investigations.

3. EXPERIMENTAL MEATHODS, RESULTS AND DISCUSSIONS

In this section, the information related to the concrete specimens is summarized.

3.1 Materials, Mixture Proportion, Specimens, and Exposure Conditions
High early strength Portland cement was used. Physical properties and chemical composition of the cement are given in Table 1. Mixing water was potable tap water. River sand and gravel were used. The density, absorption, and fineness modulus of the fine aggregate was 2.65 g/cm^3, 2.30%, and 2.84, respectively. The values were 2.75 g/cm^3, 1.04%, and 6.80, respectively for coarse aggregate. Mixture proportion of concrete is presented in Table 2. Cylinder specimens of diameter 100 mm and length 200 mm were made. Compressive strength of the control specimens was 51 MPa at 3 days, 60 MPa at 7 days, and 69 MPa at 28 days. The mixture proportion was similar to the typical mixture proportion used for prestressed concrete. Steam curing was applied. The process of steam curing was, 1) Specimens were kept in the casting room for 3 h after making the specimens, 2) Air temperature was raised at the rate of 15°C/h, and kept constant at 60°C for 4 hours, 3) Air temperature was lowered gradually to 20°C.

Table 1. Physical Properties and Chemical Composition of Cements

Specific Gravity	Blaine Fineness (cm^2/g)	Ignition Loss (%)	SiO$_2$ (%)	Al$_2$O$_3$ (%)	CaO (%)	MgO (%)	SO$_3$ (%)	Fe$_2$O$_3$ (%)	Na$_2$O (%)	K$_2$O (%)
3.13	4290	1.1	20.6	5.2	65.3	1.2	2.5	2.0	0.37	0.54

After lowering the temperature to 20°C, the specimens were cured for 28 days at relative humidity more than 90%. Then the specimens were exposed to the marine submerged, tidal, and atmospheric exposure zones. The latitude and longitude of the exposure site were 35°N and 138°E, respectively. The amount of rainfall at the exposure site was 1650 mm/year. The

average monthly temperature varied from 6 to 30°C at the exposure site in a year. The exposure site was free from freezing-and-thawing effect. The tidal pool is located beside the sea. Seawater was directly pumped into the pool from the sea and drained out to the sea automatically at 6 hours intervals. The marine atmospheric zone is located about 10m from the sea and above 5m above the mean seawater level. Physical properties and chemical composition of seawater are given in Table 3.

Table 2. Mixture Proportion of Concrete

| G$_{max}$ (mm) | Slump (cm) | Air (%) | W/C (%) | s/a (%) | Unit Content (kg/m^3) | | | | |
					W	C	S	G	Chemical Admixture
20	5±1	4±1	37	40.5	167	460	710	1080	1.84

Table 3. Physical Properties and Chemical Composition of Seawater

Specific Gravity	pH	Na ppm	K ppm	Ca ppm	Mg ppm	Cl ppm	SO$_4$ ppm	CO$_3$ ppm
1.022	7.77	9290	346	356	1167	17087	2378	110

3.2 Methods of Evaluation

The appearance of the specimens was checked frequently to visualize the formation of cracks on the surface of the specimens. Compressive strength of the specimens was tested at 3, 14, and 28 days as per JIS A1108. Unfortunately, the specimens were not tested for gradual loss of compressive strength till the age of 30 years. At the age of 30 years, pulse velocity and compressive strength were tested. Ultrasonic pulse velocity was measured at the center of the specimens (frequency of the pulse was 54 kHz).

The mineralogy of the mortar portion and aggregates of deteriorated and sound concrete was investigated at 15, 27 and 30 years of exposure by X-ray diffraction (XRD) analysis. The fractured surfaces of the sound and deteriorated regions (matrix and aggregate-matrix interfaces) were investigated by scanning electron microscope (SEM). Microstructure of the mortar portions at the outer and inner regions of the specimens was also evaluated by Mercury Intrusion Porosimetry (MIP).

3.3 Test Results and Discussion Appearance of the Specimens

Cracking over the specimens was identified after 5~6 years for tidal and submerged specimens. Appearance of the specimens at 15 years of exposure is shown in Figure 2. The specimens exposed to the atmospheric exposure show minute hair cracking without any advance stage of deterioration. In the tidal exposure, the extent of deterioration is varied from severe cracking on the specimens to the moderate cracking. In the submerged zone, the extent of deterioration is varied from complete disintegration of the specimens to the

moderate cracking. Lateral expansion as well as distortion of the specimens was clearly found for some specimens. The submerged specimens were deteriorated very quickly compared to the tidal specimens. At 30 years of exposure, some specimens of the tidal exposure showed severe lateral expansion. Some tidal specimens showed moderate deterioration. Interestingly, no significant deterioration was visualized for atmospheric exposure. The above-mentioned observations indicate that deterioration of the specimens strongly influenced by the type of marine exposure; severe for submerged exposure, moderate for tidal exposure, and no significant influence for atmospheric exposure.

(a) Atmospheric

(b) Tidal

(c) Submerged

Figure 2. Appearance of some specimens (at 15 years of exposure)

(a) Tidal 15 Years   (b) Tidal 30 Years

Figure 3. Transverse section of the tidal specimens

The cut surfaces of the specimens are shown in Figure 3. Severe cracking in the specimens is observed due to the expansion of aggregates with the presence of seawater at

15 and 30 years of exposure. Cracking in concrete is not necessarily uniform around the specimens (Figure 3, Left). It is due to the variation of the distribution of reactive aggregates in the specimens. The mortar portion of the deteriorated region becomes relatively softer but not necessarily porous due to the deposition of the new products, such as ettringite, calcite, brucite, etc. in the pore structures. The results related to this deposits are explained later. White deposit around the aggregate at the deteriorated region was clearly observed. The deposit was confirmed as ettringite based on the SEM investigation. The central portion of the specimens remains as normal concrete. Condition of the fractured surface after spraying phenolphthalein solution is shown in Figure 4. The deteriorated region surrounding the specimens is carbonated. No carbonation was found for atmospheric specimens even after 30 years of exposure due to the rich mixture proportion with W/C=0.37 (Table 2).

Fractured Surface (Transverse)   **Close-up View**
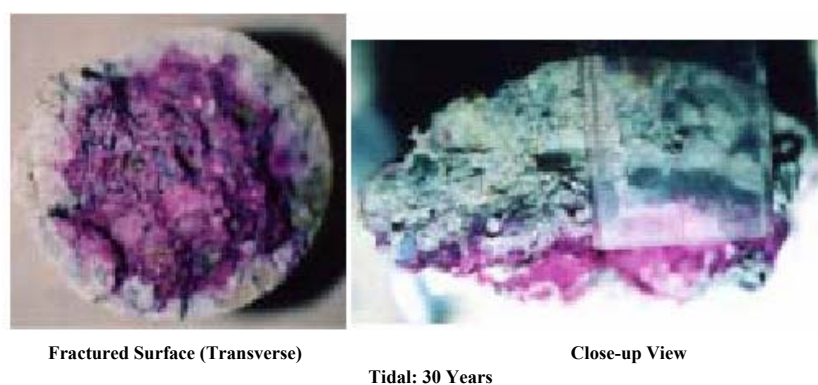**Tidal: 30 Years**

Figure 4. Appearance of the fractured surface after spraying phenolphthalein solution

4. COMPRESSIVE STRENGTH AND PULSE VELITY (30 YEARS EXPOSURE)

The remaining specimens of the tidal and atmospheric zones were tested for pulse velity at the age of 30 years. Some of them were crushed to evaluate the compressive strength. Compressive strength of concrete varies widely for tidal exposure. The cumulative distribution function of pulse velity obtained from normal distribution is shown in Figure 5. The key statistical parameters are summarized in Table 4. The variation of the data for atmospheric specimens is very low. In atmospheric exposure, the average strength loss of the specimens was about 17% compared to the 28-day strength. Contrary, in tidal exposure, the pulse velity varies in a wide range from 2.1 km/s to 5.09 km/s; 10% of the data show a strength value less than 4 MPa, 50% of the data about 17 MPa, and 90% of the data below 52 MPa. The variation of the data in the case of tidal exposure is expected due to the variation in content of reactive aggregate in a specimen. It is important to note that pulse velity was converted to strength value based on the established numerical relations for tidal and atmospheric exposure (from known strength and velity data). The strength and pulsevelity data clearly indicate that the deterioration of the specimens was strongly

influenced by the exposure conditions.

Table 4. Statistical Parameters

Parameters	Tidal	Atmospheric
Number of Samples	70	23
Maximum Value	5.09	4.76
Minimum Value	2.1	4.35
Average Value	4.16 (17 Mpa)	4.59 (57 Mpa)
Standard Deviation	0.88	0.138
Coefficient of Variation	0.21	0.03
10 Percentile Value	3.03 (4 Mpa)	4.41 (54 Mpa)
90 Percentile Value	5.33 (52 Mpa)	4.76 (61 Mpa)

Compressive Strength and Pulse Velity (30 Years Marine Exposure Plus 4 Cycles of Artificial Exposure) to understand possible future expansion of the specimens, some specimens of the tidal and atmospheric zones were exposed to a tank regulated by a wetting and drying cycle using seawater (submergence in 60 seawater for 3.5 days; and drying at atmospheric temperature for 3.5 days).
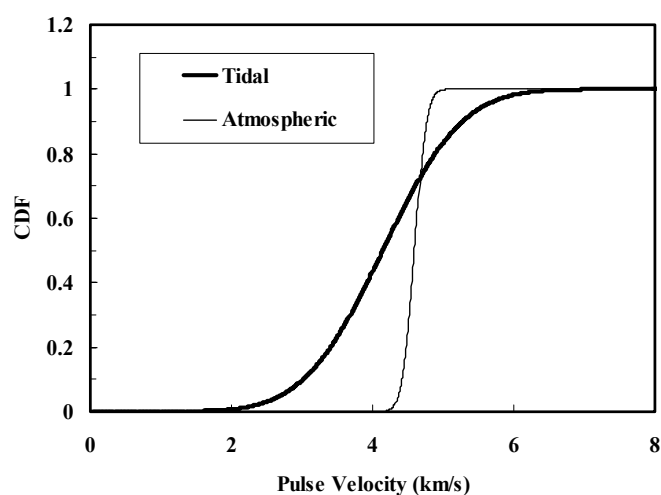

Figure 5. CDF of the pulse velocity data

The pulse velity and compressive strength data are summarized in Table **5**.After two months of accelerated exposure, no significant deterioration of the specimens was found. The results suggest that the deterioration of the specimens becomes stable after 30 years of exposure. The influence of accelerated exposure using seawater was also not observed for

the specimens exposed to the atmospheric exposure for 30 years.

Table 5. Compressive Strength and Pulse Velocity Before and After
Accelerated Exposure

Specimen	Pulse Velocity and Compressive Strength	
	Before Exposure	After Exposure
Tidal	4.8 km/s, 32 Mpa	4.9 km/s, 35 Mpa
Atmospheric	4.5 km/s, 55 Mpa	4.5 km/s, 55 Mpa

5. MINERALOGY, MICROSTRUCTURE, AND AGGREGATE-MATRIX INTERFACES

The XRD chart of the aggregates (after making powder) collected from the severely deteriorated region of the specimens after 15 years of exposure is shown in Figure 6. Peaks for laumontite mineral are clearly found. The SEM micrographs of the fractured region of the aggregates are shown in Figure 7. Bands of laumontite minerals are clearly identified in the aggregates.
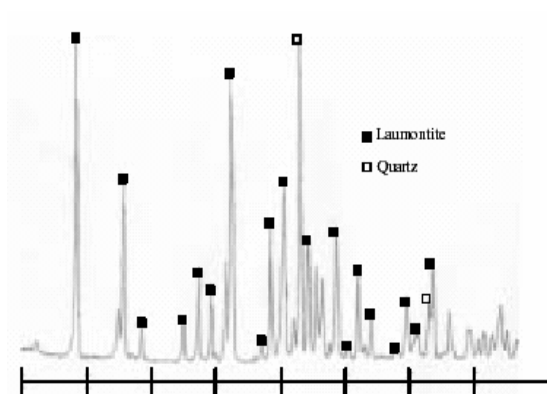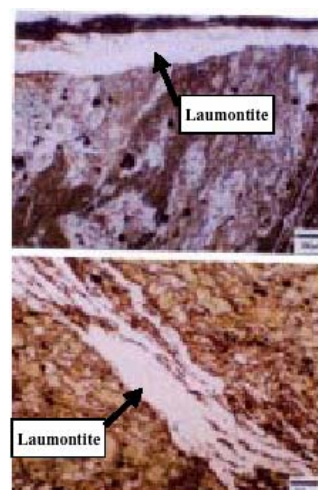

Figure 6. The XRD Chart of the aggregates

Figure 7. SEM micrographs of the fractured surface of aggregates

The XRD charts of the mortar portion of concrete at the center (40~50 mm) and outer (10~20 mm) regions of the atmospheric and tidal specimens after 30 years of exposure are shown in Figure 8. It is found that the peaks of CH at the outer region of the tidal specimens

are very low compared to the inner region of the tidal specimens or the outer region of the atmospheric specimens. Calcium carbonate is observed at the outer region of the tidal specimens indicating carbonation of concrete at the outer region (Figure 4). Peaks for ettringite are also clearly observed at the outer region. CSH was not identified at the outer region of the specimens exposed to the tidal exposure. The presence of gypsum crystals was not found. Peaks for brucite were not detected in the samples tested at 30 years of exposure, however were clearly detected in the samples tested at 15 and 27 years of exposure. The presence of brucite was also found in SEM investigations at 15, 27 and 30 years of exposure.

P: Portlandite (CH)   H: CSH   F: Feldspar
Fr: Friedel's Salt   C: Calcite   Ac: Actionolite
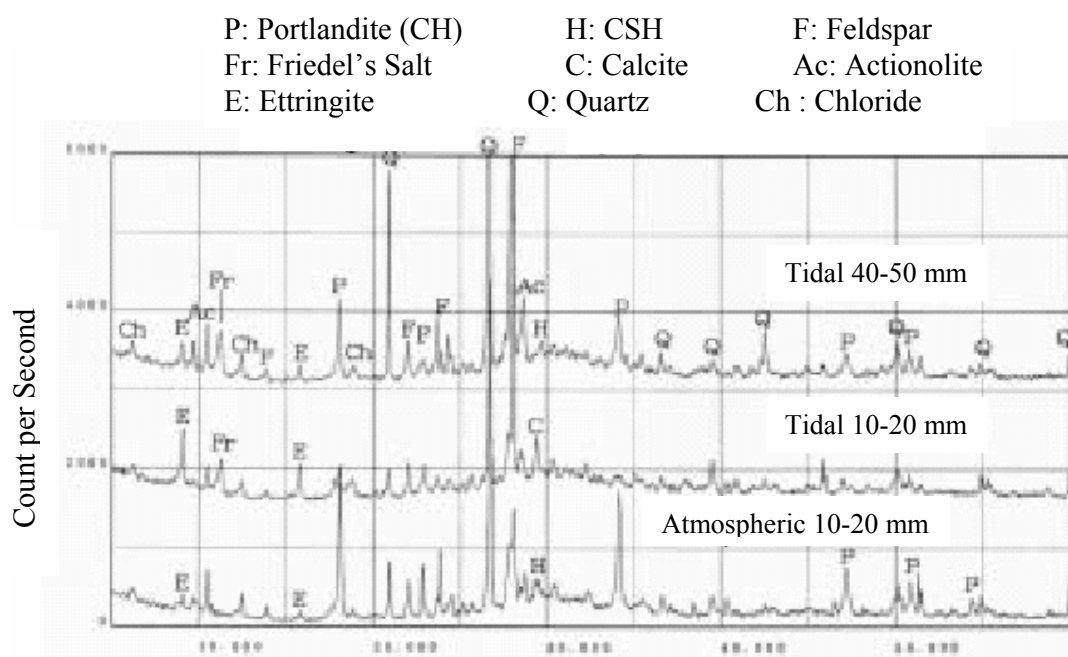E: Ettringite   Q: Quartz   Ch : Chloride

Figure 8. XRD charts of mortar (30 years of exposure)

Count Per Second Aggregate-matrix interfaces are shown in Figure 9 for the atmospheric and tidal specimens. Densely populated ettringite crystals were found at the aggregate-matrix interface at the outer region of the tidal specimens (b)-(d). No significant amount of ettringite was found at the interfaces at the inner region of the tidal specimens as well as the outer region of the atmospheric specimens (a) and (e). White deposit was clearly found surrounding the aggregates. The deposits were confirmed as ettringite (d). The aggregates at the outer region of the tidal specimens lost its adhesion with matrix due to the deposition of ettringite surrounding the aggregate.
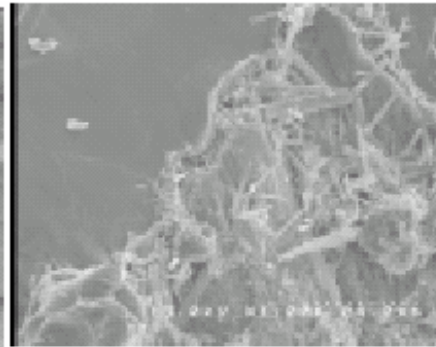

6. SUMMARY OF THE RESULTS: POSSIBLE CAUSE OF EXPANSION

It was clearly understood that the expansion of the specimens is not assiated with the alkali-

silica reaction in concrete. Delayed Ettringite Formation (DEF) in concrete is reported due to the late formation of ettringite caused by the decomposition of ettringite at higher temperature or slow hydration of sulfate in clinkers [6-9]. In this study, it was found that the deterioration of the specimens varied in a wide range from complete disintegration to the moderate deterioration of the specimens in the submerged zone. Therefore, it cannot be judged that the expansion is assiated with the problem related to the cement. If the expansion is caused by cement, in that case, the expansion should be observed for all of the specimens more or less uniformly for each exposure zone. No noticeable cracks were found in the atmospheric exposure even though the total amount of rainfall at the exposure site was 1650 mm/year (the specimens were under open sky). Therefore, the possibility of expansion due to DEF cannot be judged.
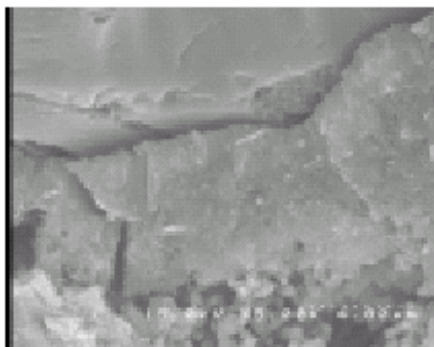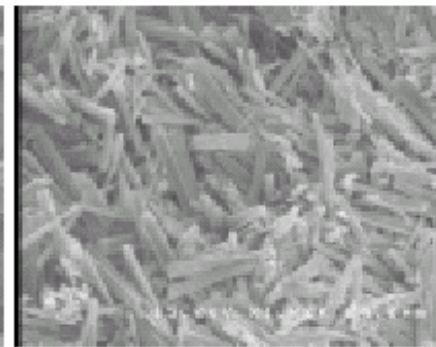

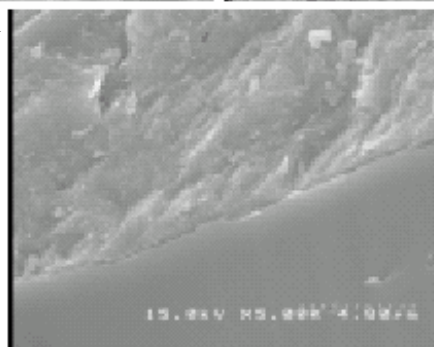(a) Atmospheric 10-20 mm   (b) Tidal 10-20 mm

(c) Tidal 10-20 mm   (d) Tidal 10-20 mm

(e) Tidal 40-50 mm

Figure 9. Aggregate-matrix interfaces (30 years exposure)

Lack of CH and CSH at the outer region of the specimens indicates the possibility of sulfate attack. Gypsum was not identified in any investigation at 15, 27, and 30 years. Looking at the surface of the specimens, it was found that the expansion is caused by the aggregates. Lateral distortion or disintegration of the specimens was visualized due the severe expansion (Figure 2) for tidal and submerged exposure. Conventional chemical sulfate attack of the specimens after cracking by expansion could not be neglected, as micrracking in concrete was supposed to be a prerequisite for sulfate attack [7]. The expansion was not noticeable in atmospheric exposure.

It is understood that exposure condition plays a key role in the press of expansion. But, the basic mechanism of expansion of laumontite minerals could not be judged from this study with the presence of seawater. The mineral may accelerate the formation of ettringite. Further studies are strongly recommended.

7. CONCLUSIONS

The following conclusions are drawn based on the scope of this study:
1. The expansion of concrete made with laumontite containing aggregates is significantly affected by the marine exposure condition: severe for submerged, moderate for tidal, and no traceable influence for atmospheric exposures.
2. Ettringite, calcite, and brucite are rich in the matrix collected from the deteriorated zone. Significant amount of ettringite is found around the aggregates. The aggregate lost the adhesion with the matrix at the deteriorated regions.
3. The microstructure of the matrix in the deteriorated region remains dense due to the deposition of new products, such as ettringite, calcite, brucite, and magnesium silicate hydrate.
4. Main and most realistic reason for unexpected expansion of concrete made with laumontite containing aggregates is ettringite formation at the interfacial zone of coarse aggregate and mortar portion.

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