Dimensional Change of Self-Leveling Materials Developed by Mixing Aluminous Cement, Portland Cement and Anhydrite at 35ºC

Yoshinobu Hirano, Koji Makida, Ryuichi Komatsu* and Ko Ikeda*

Ube Center ,Ube-Mitsubishi Cement Research Institute Corporation
(1-6 Okinoyama, Kogushi, Ube, Yamaguchi 755-8633, Japan)
Fax: 81-836-22-6151, E-mail: y.hirano@ube-ind.co.jp
*Department of Advanced Materials Science and Engineering, Yamaguchi University
(2-16-1 Tokiwadai,Ube, Yamaguchi 755-8611, Japan)
Fax: 81-836-85-9631, E-mail: r-komats@po.cc.yamaguchi-u.ac.jp

Relationship between mixing proportions and linear dimensional changes of mortars measured under nearly restraint-free conditions has been studied in order to obtain basic knowledges on the self-leveling materials developed in aluminous cement-Portland cement-anhydrite system at 35ºC. Generally, a sequence of shrinkage-expansion-shrinkage was noted during hardening of mortars. After casting, the mortars began to shrink to reach a point called the first inflection point and then, turned upward to expand until the second inflection point was reached. However, some mortars did not show any expansion even after the first inflection point was reached. Subsequently, the mortars shrinked again toward 28d age point gradually. Some distinct trends of expansion and shrinkage were observed in terms of ettringite formation and were discussed on the basis of XRD intensities. Finally, optimal mixing proportions of the source materials were determined on the basis of desirable expansion and shrinkage ranges.
Key words: Self-leveling material, Dimensional change, Ettringite, Portland cement, Aluminous cement, Anhydrite

1. INTRODUCTION
Nearly 30 years have passed since self-leveling materials appeared on the market in Japan. Since then, consumption of self-leveling materials has been growing steadily due to the capability of shortened finishing time in high precision flatness. Self-leveling materials have wide applications especially for condominiums whose construction numbers are rapidly increasing in urban areas in Japan.

An old type of self-leveling materials called "gypsum system" was developed in 1965 and was applied to a lot of buildings in Japan. This material excelled in fluidity and had an advantage of early hardening. However, it had a disadvantage of insufficient water-proof so that frequent degradation troubles were reported on this material. Furthermore, this material is acidulous and rusts steel [1]. To solve these problems another type of self-leveling materials called "cement system" was develop. However, shrinkage stress became larger, when working thickness was larger. As a consequence, cracks propagate to bottom surfaces and flaking off of basal concretes takes place so frequent.

Recently in Japan, floors of condominiums are requested to be barrier-free due to aged society. Therefore, reforming to adjust the floor levels is required sometimes. In addition, excellent flatness of floor surface should be maintained to meet super-high-strength concretes applied to pillars and beams so as to realize large spans and section reductions in buildings. Currently, 10-40 mm thickness is very common for self-leveling works. To meet this demand, a novel type of self-leveling material called "aluminous cement-Portland cement-anhydrite system" has been developed recently[2]. Results of dimensional change of this novel type of self-leveling materials have already been published by preparing mortars at 20ºC [3]. Subsequently, dimensional change will be studied at 35ºC in this paper, supposing the self-leveling works during hot summertime in Japan.

2. EXPERIMENTAL
Raw materials used are shown in **Table** I and mixing proportions in **Table** II. Mixtures of high early strength Portland cement (H), aluminous cement (A), and natural anhydrite (G) were used as principal binder materials in various proportions. Water quenched blast furnace slag (B) was introduced to the principal binder materials in constant amount. Some super plasticizer and stabilizer were mixed in order to add smooth self-leveling property. The dosage of raw materials other than the principal binder materials was kept constant as seen in **Table** II. Thus, 22 kinds of mixture were prepared as indicated in **Fig. 1**. Silica sand, not JIS standard, was applied to prepare mortars for convenience.

Table I   Principal raw materials and additives

Symbol	Materials
H	High early strength Portland cement (Blaine 4560 cm²/ g)
A	Aluminous cement (Blaine 3050 cm²/ g)
G	Natural anhydrite (Blaine 4330 cm²/ g)
B	Blast furnace slag (Blaine 4320 cm²/ g)
S	Silica sand, maximum partical size (1.0mm>)
P	Superplasticizer (Polycarboxylate type)
Z	Stabilizer (Hydroxypropyl methylcellulose)

Table Ⅱ   Mix proportion of raw materials

H	A	G	B	S	P	Z
200			200	600	1.5	0.8
Variable proportion			Constant			

Fig. 1   Mix proportion in A-H-G system

Fig. 2   Apparatus for dimensional change measurement

Water/solid ratio was standard 0.65. Mixing duration was 3 min in a mixer at 400 rpm rotation. Then, the charge was transferred into a mold having 520×40×20 mm dimension. Then, it was wrapped with a polyethylene film and cured under 35ᵒC and 65%RH condition, supposing daytime of mid-summer in Japan.

Moving distance of the piston at the one end of the test-piece was measured against the original mold length by a contact-free remote sensor as shown in **Fig. 2[4]**. A Teflon sheet was placed on the bottom of the mold to mitigate frictions between the mold and the test-piece to allow nearly restrain-free condition.

Pastes were prepared separately according to **Table Ⅱ** without blending the silica sand in the same W/S condition, 65%. Hydration was ceased by soaking the pastes in acetone. Then, XRD samples were prepared by crushing and grinding the paste in an agate mortar to obtain powders under 90μm in size. Then, peak intensities were measured on (100) reflections (2θ =9.1° ,CuK α) for ettringite and on (001) reflections (2θ =18.0° ,CuK α) for portlandite under 50kV - 130mA and 1° (DS)-1° (SS)-0.3mm(RS) slit conditions, employing a powder X-ray diffractometer, Rigaku RU200B.

3. RESULTS AND DISCUSSION

3.1 Dimensional change pattern

Two typical curve patterns of linear expansion and shrinkage were encountered in this study as seen in **Fig. 3**. One was a down-up-down pattern (Pattern A), namely shrinkage was generated so steep after some induction period and turning up to expand also so steep at a point called "first inflection point, P1", and then, turning down again at a point called "second inflection point, P2" to shrink gradually toward the 28-d age
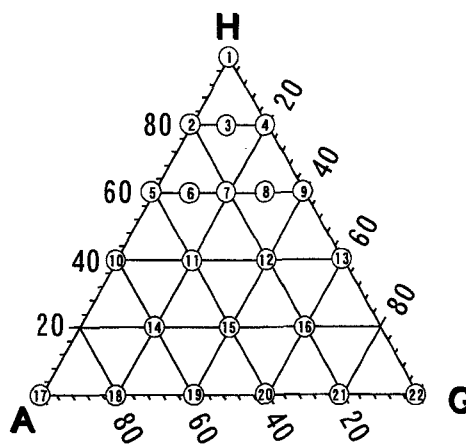
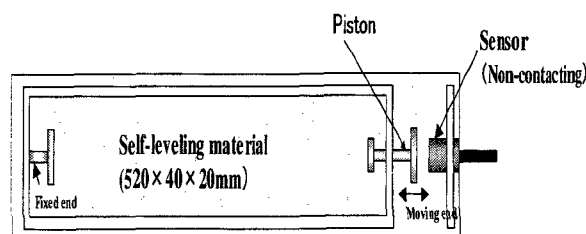point, P28. Another one was down-flat-down pattern (Pattern B), namely shrinkage was generated so steep after some induction period as seen in the pattern A. However, no turning up took place just after P1 and nearly flat and constant variation curve with a slight decreasing was noted until P2 was reached. Finally, gradual shrinkage toward P28 was noted after P2.

Classified results of present mixes into two patterns A and B are shown in **Table Ⅲ** . Following two comments can be drawn in terms of principal binder material combination, aluminous cement (A), Portland cement (H), and anhydrite (G):

●Pattern A included such samples mixed with H, G and/or A in which G contents are relatively higher against H and A contents.

●Pattern B included such samples mixed with H, G and/or A in which G contents are relatively lower against H and A contents, or such samples mixed with A and G excluding H.

3.2 Conditions of expansive ettringite formation

The expansion after final setting would be closely related to ettringite formation as argued extensively so far. As shown in **Fig. 4**, XRD peak intensities of ettringite in pastes at P2 age were plotted against the dimensions obtained by deduction between P2 and P1, where P1 is regarded as final setting time[3]. Two trends are obviously seen. The first group is represented by a trend line of marked high expansion running

Table III Grouping of expansion and shrinkage patterns, A and B, according to mixes

Mix	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Pattern A	O		O	O			O	O	O			O		O	O	O	O					
Pattern B		O			O	O				O	O							O	O	O	O	O

through mix 7 and 12 from the origin and the second group is represented by a trend line of a little expansion including nearly entire mixes belonging to the pattern A. In addition, the third group is seen as represented by a trend line of a little shrinkage including all mixes belonging to the pattern B.

It is generally seen that much formation of ettringite gives rise to expansion at P2 age as indicated by the pattern A. However, there are some differences of degree of expansion as indicated by the trend lines in **Fig. 4**. When compared mix 12 located on the first trend line with mixes 15 and 16 located on the second trend line, presence and lacking of portlandite are markedly noted in XRD results. Therefore, it is considered that copresence of portlandite with ettringite would be required to high expansion. The ettringite-portlandite combinations are frequently pointed out in some literatures to obtain expansive type ettringite[5]. It is believed that a crystal growth pressure of ettringite similar to a growth of young bamboo is a cause of expansion. On the other hand, some authors indicated precipitation of sulfur defect in ettringite due to substituting $2OH^-$ for $[SO_4]^{2-}$[6,7], presumably taking place in excess portlandite presence. Although compositional analysis of ettringite is difficult due to easy disintegration of this mineral under electron beams such as EPMA and TEM, the sulfur deficiency was actually pointed out by some authors[8,9]. As a consequence, the crystal structure of ettringite becomes loosened and expansive due to sulfur deficiency in view of a crystallographic theorem[10]. That is, sulfur-rich ettringite may form firstly in the beginning of hydration. Then, the sulfur-rich ettringite may dissolve to precipitate sulfur-poor ettringite with the advancement of hydration due to much supply of portlandite potential, leading to expansion, eventually.

3.4 Optimal mixing proportions for stable solidification

The dimensional difference of P28-P1 obtained by deduction versus the XRD peak intensity of ettringite at P28 age is shown in **Fig. 5**. Generally, the values of dimensional change markedly decreased from the values of P2-P1 mentioned in section 3.3 according to advancement of solidification of hardened bodies. The mixes belonging to the pattern A were plotted in both of the positive and negative regions. The mixes belonging to the pattern B were plotted in the negative regions including the Portland cement (H) free mixtures. As a consequence, nearly all
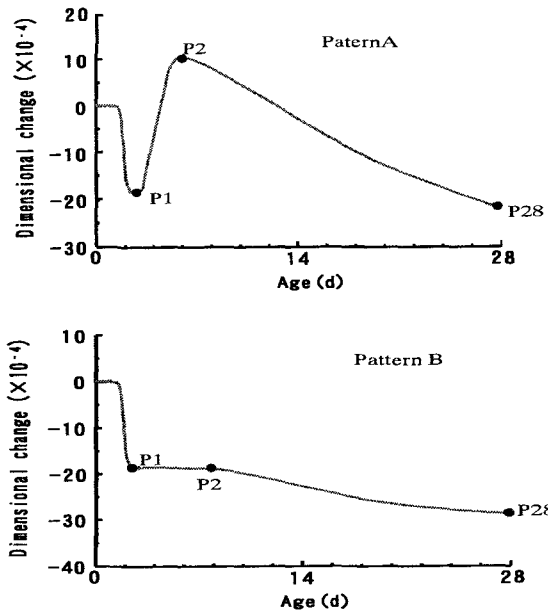

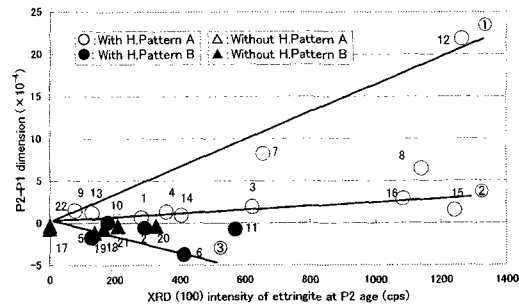Fig. 3 Two typical evolution patterns of linear dimensional change for mortars.

Fig. 4 Relationship between P2-P1 dimention and XRD intensity of ettringite at P2 age.
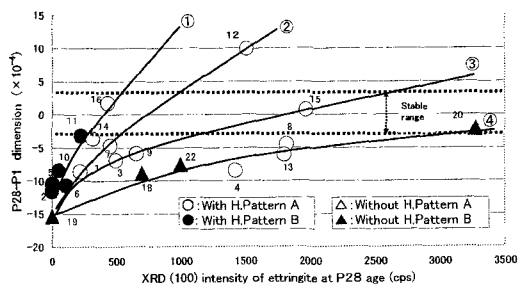

Fig. 5 Relationship between linear dimensional change, P28-P1 and XRD intensity of ettringite at P28 age.

mixes were found in the negative region and only three mixes were resulted in the positive region. Therefore, the P28-P1 values are decreased from the P2-P1 values as much as nearly 10×10^{-4} to 15×10^{-4}. Nevertheless, the first trend line connecting mixes 7 and 12 seems to be maintained. The second and third trend lines were completely altered due to extremely different X-ray peak intensities of ettringite between P2 and P28. As a consequence, four trend lines were recognized as indicated in **Fig. 5**, starting from the coordination point, $(0, -15 \times 10^{-4})$.

Firstly, X-ray peak intensities of ettringite for the mixes without the Portland cement (H) became intense remarkable, specifically for mix 20, resulting a new trend line. Secondly, the group represented by the second trend line in **Fig. 5** was disseminated into two portions due to decreasing and increasing X-ray peak intensities occurring during prolonged curing time after P2 age, specifically mix 16. Thirdly, mixes adjusted to the dimension at P1 age, that is zero line in **Fig. 4**, were obtained, which were the mixes 14, 15 and 16 of the second trend line of **Fig. 4** in addition to the mix 11 of the third trend line of **Fig. 4**, since the safety dimensional change, no crack and no pop out, is considered between -4×10^{-4} and 4×10^{-4} range.

4. CONCLUSION

The expansion and shrinkage of the self leveling material of the aluminous cement-Portland cement-anhydrite system have been measured at 35℃ in nearly unrestraint conditions. Following items are summarized as conclusion.

(1)Two types of hardening pattern are recognized in terms of expansion and shrinkage : pattern A and pattern B. Pattern A is characterized by clear P1, P2 and P28 points called first inflection point, second inflection point and 28-day age point, respectively. No sooner than casting mortars, shrinkage takes place abruptly until P1 point is reached. Then, it turns to expansion abruptly until P2 point is reached. Then, it turns gradually to shrinkage toward P28 point. On the contrary, P2 point is lacking and unclear in pattern B due to showing no appreciable expansion.

(2)Deducted P2-P1 dimension versus XRD (100) intensity of ettringite well-explains the relationship of expansion and shrinkage of the bodies at P2 age. Three trend lines are recognized, very high level expansion, high level expansion, and low level shrinkage at P2 age.

(3)Deducted P28-P1 dimension versus XRD (100) intensity of ettringite also well-explains the relationship of expansion and shrinkage of the bodies at P28 age. Three mixes out of twenty-two are judged suitable whose dimensions are so well adjusted to so called stable range, -4×10^{-4} and 4×10^{-4}, when measured on the basis of P1 age dimensions. It should be stressed that one out of three belongs to pattern B, showing extraordinary enhancement of ettringite formation at P28 age.

(4)The conditions obtaining the adjusted bodies to stable dimensional range at 35℃ are as follows: Firstly, cast bodies should expand between P1 and P2 ages, that is pattern A;Secondly, the bodies should line up in the vicinity of the second trend line in the diagram of P2-P1 dimension versus XRD (100) intensity of ettringite measured at P2 age. It is principally pattern A, but one body made from the Portlandite cement-free mixture classified to pattern B are also suitable due to remarkably enhanced formation of ettringite at 28d age after passing P2 age.

5. REFERENCES

[1] K.Omata, self leveling material, Gypsum & Lime, No.222,pp.20-26 (1989)

[2] K.Matuo, Development of low shrinkage self leveling material that can be shortened term of works about below the floor level ground adjustment construction, CONSTRUCTION FINISHING TECHNIQUES, vol.29, No.345, pp.58-59 (2004)

[3]Y.Hirano,K.Makida,R.Komatsu,K.Ikeda,Dimensional Change of Self Leveling Materials Based on Aluminous cement-Portland cement-Anhydrite,Cemnt Science and Concrete Technology, No.58 pp.81-86 (2004)

[4]T.Takahashi,H.Nakata,S.Goto, An Apparatus for Measurement of Autogeneous Shrinkage of Cement Paste, Proceedings of the Japan Concrete Institute, vol.18,No1 pp.621-626 (1996)

[5]P. K. Mehta, Mechanism of expansion associated with ettringite formation, Cem. Concr. Res., 3, pp.1-6 (1973)

[6] K. Ikeda, T. Terai, Y. Nakamura and H. Shima, Synthesis of ettringite and crystal structure, Abst. Ann. Meet. Ceram. Soc. Jpn.. pp.384 (1999)

[7]K. Ikeda, T. Wakae, Y. Nakamura and H. Shima, Synthesis of ettringite and its structure, Abst. Ann. Meet. Ceram. Soc. Jpn.. pp.317 (2001)

[8]E. E. Lachowski, K. Mohan, H. F. W. Taylor and A. E. Moore, Analytical electron microscopy of cement pastes: II, Pastes of Portland cements and clinkers., J. Am. Ceram. Soc., 63 pp.447-452 (1980)

[9]S. Diamond and E. E. Lachowski, Investigations of the composition and morphology of individual particles of Portland cement paste: Calcium sulfoaluminates, Cem. Concr. Res., 13 pp.335-340 (1983)

[10]W. West, "Basic solid state chemistry", Kodansha-Scientific, Tokyo, pp.322 (1996)(Japanese translation)