hydration at 7-days age ranged from 63 to 88 cal/g with an average value of 75 cal/g, while at 28-days age the range increased to 77 to 96 cal/g with an average value of 88 cal/g.

#### CONCRETE TEST RESULTS

The expansive-cement concrete portion of this study was done to get an indication of any variability effects the cements from across the entire industry might have on such concrete characteristics as air content, slump, compressive strength, and restrained expansion. The proportions of each batch were the same with only the cement being varied. The results of the physical tests of the concrete are contained in Table 5. Each result represents the average of test specimens from two batches of concrete. The restrained-expansion bars were made from concrete which was wet-sieved over a 3/4-in. (19.0-mm) sieve. This was necessitated by the maximum size of the aggregate (1-1/2-in. (38.1-mm) MSA), the least dimension of the bar (3-in. or 76-mm), and the centrally located restraining rod in the bar.

#### Air Content (Concrete)

The air content of the concrete varied for the individual batches from 2.2 percent for RC-698 to 6.0 percent for RC-700. The average air content for concrete made with all 19 cements was 4.1 percent. The Type II control mixture had an average air content of 3.8 percent.

#### Slump

The slump of the individual batches of concrete varied from a low of 2-1/4 in. (57 mm) for RC-702. The average slump for all the expansive cement concrete rounded to the nearest 1/8 in. (3.2 mm) was 3-1/4 in. (83 mm). The average slump of the Type II control concrete was 3-7/8 in. (98 mm).

#### Compressive Strength (Concrete Cylinders)

The compressive strength of the concrete was determined from testing 6-in. by 12-in. (152-mm by 305-mm) cylinders. Each batch of concrete had two cylinders evaluated at both 7 and 28 days age. The values shown in Table 5 represent the average of two batches for each cement or hence four cylinders evaluated at each age.

The 7-day compressive strengths of the individual batches varied from 2970 psi (20.5 MPa) for RC-709 to 4740 psi (32.7 MPa) for RC-707. The average 7-day strength for all 19 cements was 3830 psi (26.4 MPa). The Type II control strength at the same age was 3410 psi (23.5 MPa). The 28-day strengths varied from 4250 psi (29.3 MPa) for RC-709 to 6130 psi (42.2 MPa) for RC-695(2). The average 28-day strength for all 19 cements was 5130 psi (35.4 MPa). The Type II control strength at the same age was 4700 psi (32.4 MPa).

### Restrained Expansion (Concrete Bars)

The restrained-expansion values shown in Table 5 represent the average expansion of four bars, two each from two batches made with each cement. The 7-day restrained expansions ranged from 0.024 percent for RC-687 to 0.130 percent for RC-690 with an average restrained expansion of 0.044 percent. The 28-day restrained expansion ranged from 0.027 percent for RC-687 to 0.133 percent for RC-690. It should be noted that both these cements also established the range limits for the 7-day expansions. The average 28-day restrained expansion for all 19 cements was 0.045 percent which was not significantly different than the average expansion at 7 days.

The average restrained expansions for the Type II control mixture at 7 and 28 days were -0.002 percent and +0.002 percent, respectively.

#### DRYING SHRINKAGE TEST RESULTS

Drying shrinkage of cement paste, mortar, and concrete is usually measured on unrestrained prisms of the material. Restraint is the mechanism by which expansive cements effectively use their expansions; however, this restraint should also then be present when the expansive cements begin to lose their effectiveness through drying. The data contained in Tables 6 and 7 represent the restrained drying shrinkage of the same restrained expansion prisms used for the mortars and concretes, respectively. Although the prisms were allowed to dry for 90 days, most of the length change had occurred after 60 days of drying. The shrinkage values reported in both Tables 6 and 7 are referenced to the length of each bar after 28-days expansion.

### Restrained Mortar Bar Shrinkage

The length changes of the restrained mortar bars after 90 days of curing at 73 F and 50 percent relative humidity shown in Tables 6 and 7 varied from a low value of 0.065 percent for RC-695(2) to a high value of 0.103 percent for RC-709. The average shrinkage for all 19 cements was 0.080 percent, which was slightly more than the 0.063 percent shrinkage experienced by the Type II control cement.

When these shrinkage values are combined with the observed expansions which preceded the shrinkage, the net change in bar lengths was observed to vary from a net increase of 0.007 percent for RC-707 to a net decrease of 0.044 percent for RC-695. The average net length change for all cements was a shrinkage of 0.028 percent as compared to a net shrinkage of 0.058 percent for the Type II portland-cement control.

#### Restrained Concrete Bar Shrinkage

The length changes of the restrained concrete bars after 90 days of curing at 73.4 F (23.0 C) and 50 percent relative humidity are shown in Table 7 and varied from a low value of 0.033 percent for RC-707 to a high value of 0.052 percent for RC-691. The difference in the high and low values for the concrete was 0.019 percent, which was one-half the difference observed for the mortar. The average shrinkage for all 19 cement samples was 0.044 percent, which was not significantly different than the 0.045 percent shrinkage observed for the Type II portland-cement control bars.

Combining these shrinkage values with the observed expansions which preceded the shrinkage, the net change in bar lengths was observed to vary from a net increase of 0.082 percent to a net decrease of  $\div 0.025$  percent for RC-687. The range of these length changes was approximately twice the range observed for the mortar bars. Average net length change for all the cements was 0 percent as compared to a net shrinkage of 0.043 percent for the Type II portland-cement control.

### THE CONSTITUTION OF THE CEMENTS

#### X-Ray Diffraction Test Procedures

Each cement was examined in the as-received condition, front loaded and tight packed in a sample holder giving a sample surface about 2-3/4 in. (70 mm) long. All examinations were made in a static nitrogen atmosphere. Another sample of each cement, weight 5.0000 g, was treated with maleic acid in absolute methanol to remove the calcium silicates and leave calcium aluminoferrites, tricalcium aluminate ( $C_{3}A$ ), calcium sulfates, tetracalcium trialuminate sulfate ( $C_{4}A_{3}S$ ), and magnesia (MgO) in the insoluble residue. The residue was weighed after drying to a free-flowing condition and was examined on the diffractometer. A few of the residues insoluble in maleic acid were treated with 10 percent ammonium chloride (NH4C1) solution to remove calcium sulfates and were then examined on the diffractometer.

The diffractometer was standardized using an external quartz standard before each examination. Although the x-ray diffraction work covered a period of 10 months the diffraction charts are regarded as comparable because of the standardization and adjustment of the ratemeter, kilovoltage (kv), and milliamperage (ma) to comparable intensity levels at low-power and high-power settings. Low power was used from 5 to 20 deg two theta, with 27 kilovolts constant potential (kvcp) and 41 ma, using a 1 deg beam slit, 3 deg beam slit as a soller slit, and a 0.2 deg detector slit. The chart range was approximately logarithmic from 10 to 4000 counts for full-scale deflection. High-power settings were used for the range from 20 deg two theta to 65 deg, at 50 kvcp and 21 ma, using a 3 deg beam slit

and the same scale, with the rest of the x-ray collimation as for low power. All of the x-ray diffractometer charts were compared and intensities in chart units were measured on the charts of as-received cements and of maleic acid-insoluble residues, after a background had been drawn to bisect the background level from 20 to 65 deg two theta and sketched from 5 to 20 deg two theta on the diffraction charts. Table 8 shows the most easily measured intensities of alite (substituted tricalcium silicate), belite (substituted dicalcium silicate), the strongest line of  $C_4A_3\bar{S}$ , two tricalcium aluminate lines, the strongest line of magnesia (MgO), and an aluminoferrite line of fairly high intensity that is not interfered with.

It is possible that some of the maleic acid used to remove silicates in fact contained other materials that also affected other constituents, because some of the nominal maleic acid was not satisfactory in determining cement in hardened concrete.

#### Identification of Constituents

Calcium sulfate was found in these cements as CaSO<sub>4</sub> (anhydrite),  $CaSO_4$  · 0.5H $_2O$  (plaster of paris), and  $CaSO_4$  · 2H $_2O$  (gypsum). In 10 of the cements gypsum was shown clearly to be present and made a considerable contribution to the total calcium sulfate. In four it was barely detectable; and in the remaining five it was not detected by x-ray diffraction in the as-received samples. All 19 cements contained CaSO $_4$  (anhydrite). All of the cements contained CaSO $_4$ 0.5H<sub>2</sub>O after treatment with maleic acid, but it was not surely identified, although it was suspected in the diffraction charts in several of the cements as received. Because of the uncertainty as to identifying  $CaSO_4$  • 0.5H<sub>2</sub>O in the as-received cements, because of the distribution of calcium sulfate in two or three compounds in most of the cements, and since each sulfate differs from the others in absorption coefficient and thus somewhat in diffracting ability, there was no satisfactory measurement of total calcium sulfate by x-ray diffraction and Table 8 shows  $SO_3$  by chemical analysis as a measure of calcium sulfate. Tricalcium aluminate (C<sub>3</sub>A) was identified in 17 of the 19 cements.

### Effects of Composition

Although  $C_3A$  as well as  $C_4A_3\bar{S}$  can participate in forming ettringite, and although  $C_3A$  was as abundant as or more abundant than  $C_4A_3\bar{S}$  in several of the cements, it appears that the  $C_3A$  did not affect the restrained expansion significantly with the possible exception of RC-707, which contained more  $C_3A$  than any of other cements. The restrained expansion at 7 days was significantly higher than in several other cements with similar intensity of  $C_4A_3\bar{S}$  but RC-707 also contained more  $S_{03}$  than any of the others. It seems reasonable to conceive that  $C_4A_3\bar{S}$  blended with portland cement is more easily accessible to hydration and formation of ettringite than  $C_3A$  which may be protected in part from hydration by other cement constituents and thus hydrate more slowly to, or convert to monosulfate ( $C_4A\bar{S}H_{12}$ ) rather than forming and persisting as ettringite. The apparent absence of effect of  $C_3A$  in these shrinkage-compensating cements was somewhat surprising.

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Aluminoferrite is recorded in Table 8 but no effect on the behavior of the shrinkage-compensating cements was expected from it or found.

The Influences on restrained expansion that appear to be most active include the amount of  $\text{C}_4\text{A}_3\bar{\text{S}}$  (as indicated by the height of the line at 3.76 Å), the fineness of the cement, the amount of alite, and the total amount of sulfate. Strength at early ages is also significant, and extremes of fineness. Examples are given in the discussion that follows. RC-687 had the lowest fineness recorded, low  $C_4A_3S$ , high alite; the 7-day compressive strength was above average, which all suggests that there was too little  $C_4A_3S$  to form enough ettringite to expand the fairly strong framework developed in the first days of strength gain. Six cements in the group failed to meet ASTM specification requirements for expansion of 0.040 percent at 7 days (RC-687, -690(2), -694, -695, -700, -711); all had  $C_4A_3\bar{S}$  intensity below 24, alite ranging from 27 to 43, SO<sub>3</sub> from 5.2 to 6.4 percent, fineness ranging from 3550 to 5360 cm<sup>2</sup>/g (the highest recorded), and 7-day strengths from 3840 to 4730 psi, the latter being the highest 7-day strengths in the group. On the other hand, two cements with  $C_4A_3S$  intensities of 19 and 21 met the 7-day expansion requirement; one met it barely and had low total sulfate (5.1 percent) and low alite. The other had the highest sulfate of any of the cements and moderately high alite. RC-690, which had the highest expansion at 7 days had rather low alite and the lowest 7-day strength in the group. Four cements had expanded at 28 days more than the allowed 115 percent of the 7-day expansion; one had the highest C4A3S and alite close to the average; three had average  $C_{LA3}S$  and alite average or below.

 $C_4A_3\bar{S}$  intensities from 23.5 to 29 with alite intensities ranging from 30 to 41 associated with finenesses from 3730 to 5240 cm<sup>2</sup>/g produced cements that met the requirements of the ASTM specifications; the sulfate contents in the group of acceptable cements ranged from 4.6 to 7.5 percent. The regression equation using amount of  $C_4A_3\bar{S}$ as X and the 28-day restrained expansion as Y is a straight line function of the form

$$Y = -0.0214 + 0.0032 X$$
(1)

The correlation coefficient is R = +0.56. For n - 2 = 17, this correlation would occur by chance less that 2 times in 100 (1). Considering that the behavior in restrained expansion of these cements must be affected by compression and tensile strength of the specimens, which depends on fineness, cement composition, and sulfate available to provide early strength, it is somewhat surprising to find a significant relation between these two variables. The correlation of SO<sub>3</sub> and restrained expansion at 7 days was calculated but was just below significant at the 5 percent level.

A regression equation was calculated between MgO determined chemically (X) and MgO in x-ray diffraction chart units (Y) and was

best represented by a simple power function of the form

$$Y = 4.4 \times \frac{1.3}{2}$$
 (2)

with a correlation coefficient of  $\pm 0.94$ , which for n - 2 = 17 has substantially less than one chance in 100 of the relation occurring by change (Fig. 1).

CaO (free lime), a significant constituent of self-stressing cements, was not certainly identified in any of the cements of this group. While it may have been present in some of the cements in small amounts, it appears that the Ca needed to combine with  $C_4A_3\bar{S}$  and  $CaSO_4$  to form ettringite was obtained as  $Ca(OH)_2$  from the hydration of alite.

The means, standard deviations, and variances of several variables are shown in Table 9.

From the examinations by x-ray diffraction it seems probable that five of the shrinkage-compensating cements have their portlandcement portion low in  $C_3A$ ; sufficiently so as to have this portion regarded as like Type V portland cement. In these five, no  $C_3A$  line was detected at 1.558 Å. Possibly the portland-cement portion of a few others had Type II compositions. Several apparently contained Type I portland cements. The factors on which the behavior of these Type K shrinkage-compensating cements depend appear to be more difficult to assess than was the case with 15 self-stressing cements examined previously (2).

#### DISCUSSION OF RESULTS

#### Specification Compliance

None of the cements had any difficulty meeting the mandatory chemical requirements of the specifications although cements from two mills did not meet the optional maximum requirement for total alkalies.

None of the cements appeared to have a problem meeting the physical requirements of air content, compressive strength, and time of setting. There was a problem with the principal feature for which these cements were designed however, that is expansion. Of the initial sampling, five cements did not meet the minimum expansion requirements, having values 0.028, 0.034, 0.033, 0.039, and 0.037 percent. A review of these values together with the 0.036 percent value obtained from the second sample of one mill (RC-690(2)) points out a feature of the specification which warrants further definition.

The length change of the restrained bars is measured in a comparator to the nearest 0.0001 in. (0.0025 mm). Expressed as a percentage of length change, measurements are then made and reported to the nearest 0.001 percent, which is a number of three significant

figures. The minimum and maximum expansion limits of the specification are 0.04 percent and 0.10 percent, respectively, which are numbers of two significant figures. Having made measurements to three significant figures, they are then rounded to two significant figures for compliance to the specification. The result of the rounding is that three of the six cements which failed the minimum expansion requirement (RC-690(2), -700, and -711) and the one cement which failed the maximum expansion requirement (RC-690) at three significant figures, now meet the specification at two significant figures. On this point, the intent of the proposed specification is not clear. To eliminate this dilemma and insure that cements with adequate and safe expansive potentials are being used, the limits of expansion in the specification probably should be expressed to three significant figures as 0.040 percent and 0.100 percent for minimum and maximum limits, respectively.

The problem of two versus three significant figures also carries over into the requirement that the 28-day expansions be not more than 115 percent of the 7-day expansions. Using the three significant figures obtainted in the actual length change measurements, four cements (RC-690(2), -703, -709, and -711) failed this requirement. If the numbers had been rounded to two significant figures prior to determining the increase, only three of those four cements would have failed. The proposed specification should contain more explicit language as to how this increase in percentage is to be determined.

The allowable later expansions expressed as a 115 percent increase should also be reviewed from the standpoint of the actual expansions that occur. Under this requirement, cements expanding to the minimum level of 0.04 percent or 0.004 in. (0.102 mm) for a 10-in.(254-mm) restrained bar, would be allowed to increase in length by an additional 0.006 in. (0.0152 mm). At the maximum allowable level of 0.10 percent, or 0.010 in. (0.254 mm) for a 10-in. (254-mm) restrained bar, the acceptable increase could be 0.0015 in. (0.0381 mm) or 2-1/2 times the increase of the bar at the minimum level. For two concretes of identical proportions, all other things also being equal, except for the expansive potential of the cement, a concrete having a large initial expansion (0.010-in. (0.0254-mm)) will probably not tolerate an additional expansion of 0.0015-in (0.0381-mm) as well as would a concrete having a low initial expansion [0.004-in. (0.102-mm)]. This is not to say that an additional expansion of 0.0015-in. (0.0381-mm) would be harmful to a concrete expanding 0.10 percent. This fact is not known to the authors but if in fact it is not harmful, that amount of additional increase could also be safely tolerated by a concrete expanding 0.04 percent at 7 days This suggests that the additional expansion requirement should age. perhaps be stated as a fixed amount over the entire range rather than as a percent increase. The amount of this fixed value would have to be defined and substantiated by additional testing.

The x-ray diffraction analysis indicates that the performance of the cements with regard to expansion is affected by the amounts and

types of constituents not identified in the chemical requirements. This suggests that chemical requirements might be expanded to include other chemical requirements that may provide a more rapid indication of the expansive potential of the cements. These additional requirements might include upper and lower limits on  $SO_3$  and  $Al_2O_3$ .

#### Expansive Potential Requirements

The principal reason for using expansive cements in concrete is, of course, to provide an overall combination of expansion and drying shrinkage such that the resulting dimensions of the element made with the concrete will not cause tensile stresses of such magnitude so as to cause cracking to occur within the element. The data in Table 6 indicate that after 90 days restrained drying shrinkage, all but two of the cements had shrunk to less than the original length of the test specimens before expansion had occurred. The average change from initial length was a shrinkage of 0.028 percent. With additional time in the same curing environment, even more shrinkage will take place. Even the concrete (Table 7), which had less cement per unit volume to contribute to shrinkage and which also had its shrinkage restrained by the presence of coarse aggregate, had 10 of the 19 cements exhibit more shrinkage than expansion. Although not measured, the shrinkage trends indicated that by 120 days age, 16 of the 19 cements would have had more shrinkage than expansion.

It is not known whether these values of shrinkage for either the mortar or concrete would induce shrinkage cracking in a concrete element because of the many factors which can influence shrinkage in concrete. They do suggest however that if volume stability (zero length change after expansion and shrinkage) will insure the elimination or significant reduction in drying shrinkage cracking, the minimum specification limit of 0.04 percent may not be adequate and perhaps should be increased. The amount of this increase would have to be determined through additional testing.

### Other Cement Characteristics

The specific gravities of the expansive cements were generally less than those normally associated with Type I and II portland cements although a few exceptions occurred. This presents no problem to their use except that this fact should be called to the attention of the cement user so he will make the necessary determinations of this value before beginning mixture proportioning.

The fineness of the expansive cements is generally higher than that of Type I and II portland cements and is comparable to those normally associated with Type III portland cements. These higher fineness values may be the result of the increased amount of gypsum in these cements. The gypsum, being softer than cement clinker, will reduce more readily during grinding and thus increase the apparent fineness of the cement. The heats of hydration of Type K expansive cements apparently are not significantly different from the usual portland cements and thus could be used in larger concrete sections without increasing thermal problems.

In fact that air contents in concrete varied from 2.4 to 6.0 percent for the same amount of a given brand of air-entraining admixture in each concrete batch and varied from 7.2 to 11.3 percent in mortar suggests that there is a compatibility requirement for airentraining admixtures and expansive cements which may warrant further study.

The slumps of concretes made with Type K expansive cements have historically been reported as always being <u>less</u> than comparably proportioned Type I and II portland-cement concrete mixtures. This has been attributed to both increased cement fineness and the need for additional water in the formation of ettringite. In general, most of the cements did not produce a lower slump than the Type II cement control; however, some exceptions were noted.

As with slumps, compressive strengths of Type K expansive cements have historically been reported as being <u>more</u> than those achieved with comparable proportioned mixtures made with Type I and II cements. This has usually been attributed to the increased fineness of the Type K cements, the reduction of free water in the concrete as more of the batch water is used for the development of hydration products, and also to the densification of the paste caused by the formation of larger amounts of ettringite. In general, the 19 cements evaluated exhibited this behavior, but again, there were some exceptions.

#### CONCLUSIONS

In assessing the significance of the data reported herein it must be appreciated that cements evaluated were from production in 1974 and do not necessarily reflect the condition of the Type K expansive cement industry at the time this paper was published. What the data do indicate, however, are some apparent shortcomings in the proposed specification for these cements. The proposed specification, as presently written, may satisfy most user requirements; however, there are a number of aspects of it which could be revised to form a much stronger and responsible specification. These include (1) use of additional chemical requirements to assess expansive potential more quickly, (2) a restatement of expansion requirements to three significant figures, (3) an upgrading of the minimum expansion requirement of the specifications, and (4) the revision of the later age expansion requirement to a constant value requirement rather than a percentage requirement.

When moist cured, Type K expansive cements do in fact expand substantially more than normal portland cements. When they undergo

drying shrinkage, the amount of that shrinkage is similar to that of normal portland cements. The combined expansion and shrinkage produce less total shrinkage in test prisms than occurs with normal portland cements.

The other characteristics of the Type K expansive cements such as specific gravity, fineness, and heats of hydration present no special problems for their use in a wide variety of different applications. When used in concrete they tend to reduce slumps and slightly increase compressive strengths at 28-day ages over those of comparably proportioned Type I and II cement concretes. There may be some slight compatibility problems between individual cements and air-entraining agents, but these should be evaluated on an individual basis.

The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the Civil Works Research Program of the United States Army Corps of Engineers by the U. S. Army Engineer Waterways Experiment Station. Permission was granted by the Chief of Engineers to publish this information.

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