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DIVISION OF HIGHWAYS

CONTROL OF GYPSUM

IN

PORTLAND CEMENT

By
Bailey Tremper

Prepared for presentation
at
62nd Annual Meeting of
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This is an advance copy of a paper to be presented at the Sixty-Second Annual Meeting of the American Society for Testing Materials (1916 Race St., Philadelphia 3, Pa.) to be held in Atlantic City, N.J., June 21-26. This advance copy is primarily to stimulate discussion. Discussion is invited and may be transmitted to the Executive Secretary. The paper is subject to modification and is not to be published as a whole or in part pending its release by the Society through the Executive Secretary.

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IN

PORTLAND CEMENT

By
Bailey Tremper
Supervising Materials and
Research Engineer
California Division of Highways

CONTENTS

CONTROL OF GYPSUM IN PORTLAND CEMENT

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SYNOPSIS

Progress in devising simple, practical tests to demonstrate the relationship of the SO_3 content of portland cement to its optimum value is discussed. Test methods have been patterned on the principles set forth by Lerch in 1946. These are that for each cement there is an optimum percentage of SO_3 which produces maximum strength and minimum volume change and which is related to the rate of depletion of gypsum during the early stages of setting and hardening. Emphasis is placed on results of co-operative testing for short-time expansion in water and contraction in air of mortars containing the cement in question and the same cement to which pulverized gypsum is added in the laboratory to increase the SO_3 content 0.5 percentage point.

*Supervising Materials and Research Engineer, California Division of Highways, Sacramento; Member, Working Committee on SO_3 Content, ASTM Committee C-1.

CONTROL OF GYPSUM IN PORTLAND CEMENT

In 1946, William Lerch(1) reported the results of extensive tests on the effect of varying percentages of gypsum in portland cement on the properties of the paste during setting and hardening. Using a conduction calorimeter, he demonstrated that variations in SO_3 produced major differences in the rate of reactions in cement paste during the setting period. These differences affect the hardened paste. For each cement, there is an optimum content of gypsum that produces maximum strength, minimum expansion in water and minimum contraction in air. In many cases the optimum value of SO_3 was found to be higher than, then current, specifications would admit.

Lerch also found that the optimum percentage of SO_3 is related to the rate of depletion of the gypsum through interaction with other components of the cement. This was demonstrated by analyses of water extracts of the paste (or mortar) at varying ages. He concluded that when gypsum is present in optimum amount, the water extract contains at least 1.0 gram of SO_3 per liter at the age of 18 hours, but less than 0.07 gram of SO_3 per liter at the age of 24 hours. The determination of SO_3 in water extracts thus appeared to offer a convenient means of determining the relationship of gypsum content to its optimum value.

STUDIES BY WORKING COMMITTEE ON SO_3

As a result of Lerch's disclosures, ASTM Committee C-1 organized a Working Committee on SO_3 Content in 1946. Its scope as outlined was to consider all aspects of the effect of SO_3 in portland cement and to devise means whereby gypsum could be controlled by practical tests at its optimum percentage.

ASTM Bulletin No. 169, (Oct. 1950) contains the first report of the Working Committee. Co-operative testing of clinkers interground with varying amounts of gypsum confirmed the findings of Lerch with respect to an optimum value of SO_3 for greatest strength, minimum expansion in water and minimum contraction in air. Tests for freeze-thaw resistance of concrete also pointed to an optimum value of SO_3 which appeared to be slightly lower than for strength and volume change. The tests were made on non-air-entrained concrete. In the light of present knowledge, the results of freeze-thaw tests of such concrete are of academic more than practical significance. Determinations of SO_3 in water extracts of pastes and mortars were made. In general, these extraction, or leach, tests indicated about the same percentage of SO_3 for optimum* as was indicated by physical tests of mortars for strength and volume change. Reproducibility between laboratories was not considered to be good enough to warrant a recommendation for specification control of both maximum and minimum percentages of SO_3 by such

*based on criteria of more than 0.2 g of SO_3 per liter at 18 hrs. and less than 0.5 g at 24 hrs.

a test. The Working Committee did, however, recommend deletion of maximum numerical limitations on percentage of SO_3 in specifications for cement and the substitution therefor of a maximum limitation of 0.5 gram of $CaSO_4$ (expressed as SO_3) per liter of water extract at the age of 24 hours. It was believed that such a provision would enable manufacturers to proportion gypsum in optimum amount and at the same time would afford protection against an overdose.

Acting upon this recommendation, the Society in 1952, adopted tentative specifications for Portland Cement, C 150-52 T, containing such a provision and also adopted C 265-51 T as a test method for the determination of Calcium Sulfate in Hardened Portland Cement Mortar. The specifications, although ostensibly permitting sufficient latitude in SO_3 content for optimum results, did not in any way provide assurance that the cement would not contain less than optimum.

Subsequently, the Working Committee conducted another series of co-operative tests for $CaSO_4$ in the water extract. In these tests, the details were prescribed within much narrower limits than in C 265-51 T and followed very closely the method now designated as C 265-57. Again the results were disappointing in precision.

In the meantime, a number of producers and consumers had conducted extraction tests and physical tests of mortars. Such data led to the conclusion that the direct specification for maximum SO_3 would achieve the same objective as the requirement for maximum $CaSO_4$ in the hardened mortar, provided limiting values of SO_3 were varied for different types of cement in the light of information then available. In 1956, the Society adopted such specifications and has from time to time made upward revisions of permissible SO_3 in certain types of cement.

In 1957, a revision was made in the stated "Scope" of the Tentative Test for Calcium Sulfate in Hydrated Cement Mortar. The scope now states that the method is "intended for use primarily by manufacturers of portland cement and those interested in research." The age at which the extraction is made is, as formerly, 24 hours. In the opinion of the writer, the method would be better suited to research purposes if provision for extraction at other ages as well were made.

In 1957, the writer observed that plots of contraction in air versus SO_3 content appeared to produce similar curves for all cements. This suggested the possibility of controlling gypsum by the determination of contraction of the original cement and the same cement to which pulverized gypsum is added to increase the SO_3 content by a fixed amount. 0.5 percent SO_3 was considered to be a suitable increment.

The suggested method of control can best be explained by reference to Figure 1.

The upper curve is a parabola conforming to the general equation:

$$C = pg^2 \qquad (1)$$

where C = contraction in percent relative to the contraction at optimum SO_3

g = content of SO_3 in percent relative to content at optimum.

p = a coefficient which is dependent on test conditions and characteristics of the cement. For constant test conditions, p is a property of the cement and for convenience in the discussion to follow, is termed the "coefficient of contraction."

In the curve as drawn in Figure 1, the value of p is 0.018. When tested by the method to be described, experimental results for many cements have been found to agree quite well with this value within the range of -1.0 to about +0.75 percent SO_3 relative to optimum. For higher SO_3 contents, the observed contraction tends to be lower than the equation indicates, possibly because of the restraining effect of unreacted gypsum particles. For some cements the coefficient of contraction is higher or lower than 0.018.

The lower curve of Figure 1 is a plot of the change in contraction produced by increments of 0.5 percent of SO_3. It is parallel to the tangent of the parabola which is a straight line, and is offset by one-half of the test increment of SO_3 or 0.25 percent. The equation of the rate-of-change curve is:

$$r = p(g + 0.25) \qquad (2)$$

where $r = \frac{dC}{dg}$ or change in contraction, percent per unit (1 percent) of variation in SO_3.

For the particular curve plotted in Figure 1, the equation is:

$$r = 0.018 (g + 0.25) \quad (3)$$

Plots of rate-of-change derived from experimental data approximate straight lines in the region of -1.0 to about +0.75 percent SO_3 relative to optimum. For cements containing SO_3 within this range, the determination of change in contraction for an increment of 0.5 percent in SO_3 yields the data necessary for estimating the relationship to optimum by means of equation (2). For example, if no change in contraction is produced, the cement contains optimum minus 0.25 percent SO_3. If the change in contraction is +0.0045 percent, the SO_3 content is optimum for cements having a coefficient of contraction = 0.018. If the change is -0.0045 percent, the SO_3 content is optimum minus 0.5 percent if the coefficient of contraction is 0.018. When the observed change is in excess of about $\pm$ 0.012 percent, the estimate is less certain but such values clearly indicate a substantial departure from optimum.

This concept was applied in co-operative tests by the Working Committee on SO_3 Content to four cements varying in type, chemical composition and fineness. Test specimens were 1x1x11-1/4-inch bars molded from 1:2 (by weight) graded Ottawa sand mortar. Bars were removed from the molds at 24 hours and measured for length. They were immersed in water to the age of 72 hours and expansion was measured. They were then placed in a cabinet for drying to the age of 7 days. Contraction was expressed as the shortening from 72 hours to 7 days. Increments of SO_3 were obtained by blending computed amounts of pulverized gypsum (terra alba) with the cement at the time of batching with sand. An inexpensive drying cabinet was used which depended upon a saturated solution of sodium bichromate for control of humidity. Temperature was held within the limits specified for the room in which cement mortars are made, i.e., between 60 and 81.5 F. The test is termed the "expansion-contraction" test.

The results of these co-operative tests are reported in an appendix to the Report of Committee C-1 for 1959, which also gives details of the expansion-contraction test. The four cements of the series produced curves of contraction vs. SO_3 content that approximated parabolas, but the coefficient of contraction varied somewhat between cements. Interlaboratory reproducibility of change in contraction produced by an increment of 0.5 percent SO_3, was found to be slightly less than 0.005 percentage points. This is interpreted to mean that, for the cements involved, a test for change in contraction could afford effective control of SO_3 within $\pm$ 0.25 percentage point of optimum. At the extremes of this range, the contraction is only slightly greater than at optimum. Results of expansion tests were studied and found to provide additional safeguards against an overdose of gypsum.

Concurrently with the expansion and contraction tests, some of the co-operating laboratories made C 109 tests for compressive strength. The effect of variations in SO_3 content on strength could be evaluated in the same manner as that on contraction. The reproducibility of the strength test however, did not yield as high a degree of discrimination as did the contraction test. This was particularly true for a Type II cement which produced a rather flat strength curve. One of the laboratories made compressive strength tests at 24 hours with 1:2 mortar. These tests appeared to afford greater discrimination but since they were performed in one laboratory only, an estimate of reproducibility could not be made.

The study indicated quite conclusively that the percentage of SO_3 that produces minimum contraction also produces maximum strength.

The use of 24-hour strength tests for controlling gypsum has considerable appeal because of the short elapsed time relative to the 7-day period required to complete the expansion-contraction test. The Working Committee plans to make further co-operative tests based on strength as a criterion.

STUDIES BY CALIFORNIA DIVISION OF HIGHWAYS

California Division of Highways has felt concern over wide variations in SO_3 content in cement furnished for its use and inability to obtain acceptable explanations for such variations.

Acting upon the favorable results obtained in the expansion-contraction tests reported by the Working Committee, the Division of Highways has inaugurated a co-operative series with each of the 13 producing cement mills in the State. The study is confined to modified* Type II, low-alkali cements meeting the requirements of the specifications of the Division. Under the plan, each mill makes tests for expansion and contraction over a suitable range of SO_3 content for a cement considered to be typical of its production. The cements are compared for response to change in SO_3 as expressed by the coefficient of contraction. Values of the observed coefficient are given in Table I for those mills from which the tests have been reported. The mean coefficient of contraction is 0.018. The coefficient for individual mills varies between 0.014 and 0.022. The data to follow have been analysed on the assumption that the use of the mean coefficient does not introduce serious error into computations of optimum SO_3.

*The modification consists of elimination of the requirement for maximum percentage of tricalcium silicate.

In addition to the above described tests, each mill at monthly intervals, makes the expansion-contraction test on a selected sample of cement and on the same cement blended with pulverized gypsum to increase the SO_3 content by 0.5 percentage point and computes the change in contraction produced by the added gypsum. Each sample is sent to the laboratory of the California Division of Highways for check testing. Some of the mills are nearing completion of a planned 12 sample program. Comparative results at first were disappointing, but as experience with the test was gained, better interlaboratory agreement was obtained. Test results, excepting the earlier ones, are summarized in Table II. The table lists the standard deviations computed from the differences in change in contraction as reported by the two laboratories.

These standard deviations appear to indicate that the reproducibility is at least as good as that determined in the study reported by the Working Committee. The results can be visualized more readily by expressing the differences between laboratories in terms of estimated departure of each cement from optimum as shown in Table III. Comparisons have been made on the assumption that the applicable coefficient of contraction for each cement is 0.018. In 83 percent of the comparisons, the difference between laboratories does not exceed 0.25 percent SO_3. Of the nine comparisons in which this value is exceeded, all but one were obtained on cements that were deficient in SO_3 by 0.5 percent or more relative to optimum.

The results appear to indicate that, provided cement were manufactured to contain SO_3 within 0.25 percent of optimum as determined by expansion-contraction tests at the mill, the purchaser upon making these tests, would obtain similar results in the majority of cases. Only occasionally would the purchaser obtain results indicating a divergence from optimum as high as 0.50 percent. In cases of uncertainty, repeat tests by the two laboratories should produce good agreement.

Should the cement contain a substantial overdose of gypsum, contraction data, which may be erratic in such cases, might not disclose the fact. The results of the expansion test are not detailed in this report but examination of the data indicates that excessive values of expansion are reliable signals of excess gypsum.

More data on the coefficient of contraction of the various cements are needed to afford proper evaluation of the expansion-contraction test as a control of gypsum in portland cement. Much of the data submitted to date consists of results of a single round of tests through a range of 2 percent in SO_3. The range in SO_3 does not always provide a good bracket above and below the optimum. The results reported by Mill K in Table I, include cements of similar composition and specific surface but which were ground in mills of different types.

Haskell(2) has shown by statistical analysis, that optimum SO_3 is closely related linearly to the percentages of alkalies and tricalcium aluminate and the specific surface.

He concludes that "any manufacturer could develop a similar linear equation for his own materials and processes." By this means, the manufacturer could control the gypsum within close limits without awaiting the results of expansion-contraction tests. The latter tests would serve to produce confirmatory data and could point to the need of revision from time to time of the equation based on chemical analysis and specific surface.

CONCLUSIONS

If it may be assumed that the coefficient of contraction of the cements under study does not vary outside the range of 0.014 and 0.022, the test data appear to warrant the following conclusions:

1. For cements of the type specified by California Division of Highways, it should be feasible for cement manufacturers to control the percentage of SO_3 within $\pm$ 0.25 percentage point of optimum by means of the expansion-contraction test and intimate knowledge of materials and processes used.
2. If the SO_3 content of the cement were controlled at the mill within the limits given in (1), other laboratories using the expansion-contraction test should obtain results within these limits in the majority of tests and only occasionally should the indicated deviation be as great as 0.50 percent. Repeat tests should serve to eliminate or confirm questionable results.

REFERENCES

(1) "The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes" by William Lerch, Proceedings, ASTM Vol. 46, p. 1252 (1946)

(2) "Three Factors Govern Optimum Gypsum Content of Cement" by W. E. Haskell, Rock Products, Vol. 62, No. 4, p. 108 (April, 1959)

TABLE I

Coefficients of Contraction of Test Cements

California Modified Type II, Low-alkali Cements

Mill		Coefficient of Contraction, "p"
B		0.015
C		0.021
D		0.014
E		0.021
H		0.019
J		0.017
K	0.020	
	0.014	
	0.015	
	0.019	
	0.014	
	0.015	0.016
L		0.017
Average		0.018

Report of Working Committee on SO_3 Content, 1959

Cement No.	"p"
1	0.011
2	0.015
3	0.015
4	0.013

Note: Coefficients represent rate of change in contraction produced by increment of 0.5 percent SO_3 when added to the cement containing SO_3 in the range of ± 0.25 per cent relative to optimum.

TABLE II

Comparison between Laboratories of Test Results for Change in Contraction based on Single Tests in each Laboratory

Values given are standard deviations of differences in test results expressed in percentage points

Mill	No. of Samples	Standard Deviation
A	5	0.0032
C	6	0.0026
D	7	0.0021
E	7	0.0038
F	7	0.0051
H	7	0.0017
I	7	0.0049
J	8	0.0028
Average of Mills		0.0037

Note: Comparisons are between laboratory of mill submitting sample and laboratory of California Division of Highways.

TABLE III

Comparison between Laboratories of Indicated Optimum SO_3 as Estimated from Single Tests for Change in Contraction

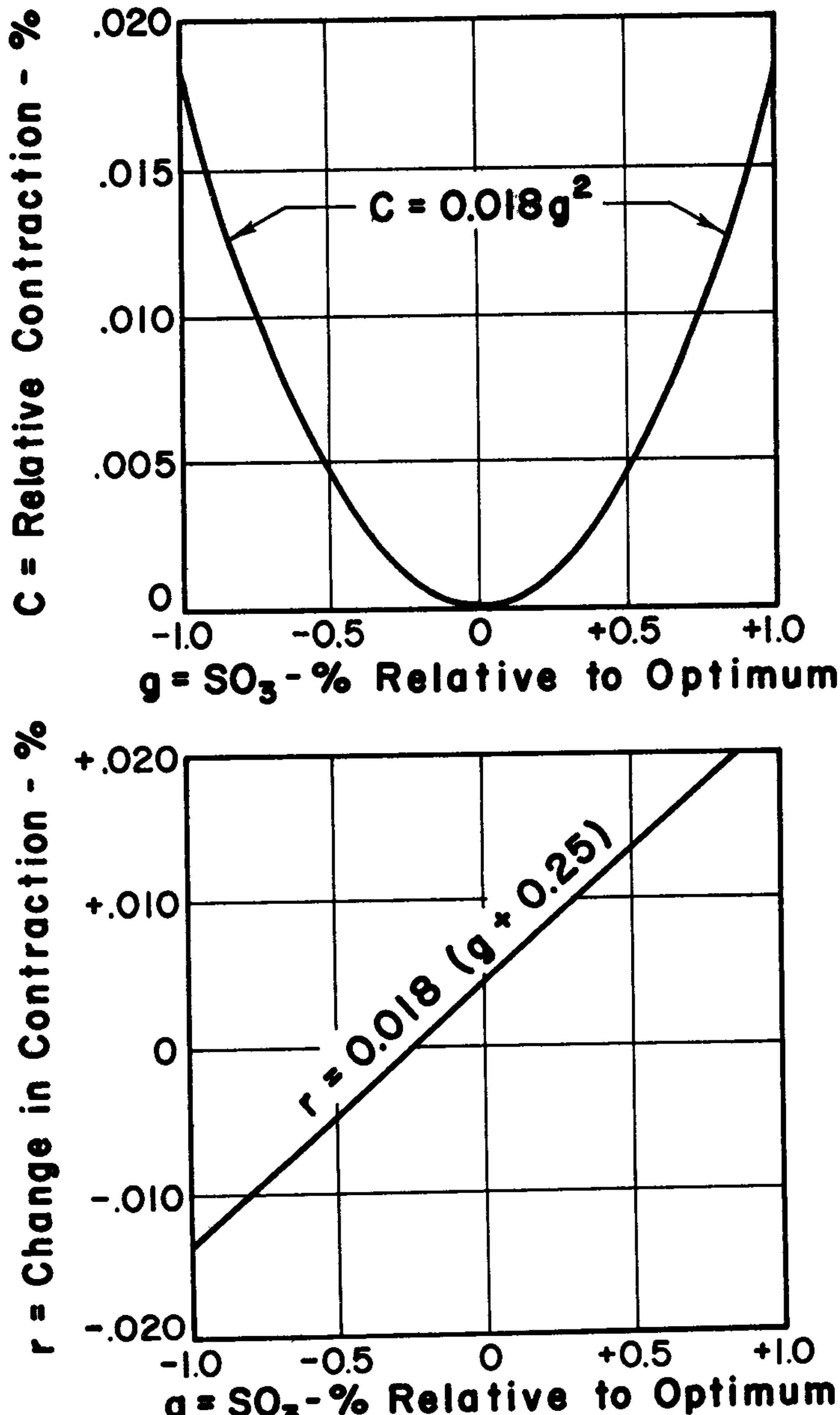
Values are given in terms of percentage points of excess or deficiency of SO_3 relative to optimum, calculated by Equation (3)

Mill	Tested by Hwy.*	Tested by Mill**	Difference Hwy-Mill
A	+0.70	+0.50	+0.20
	+0.11	+0.24	-0.13
	+0.09	+0.27	-0.16
	-1.14	-1.31	+0.17
	-0.70	-0.89	+0.19
C	+0.16	0.00	+0.16
	+0.22	+0.27	-0.05
	+0.13	+0.05	+0.08
	+0.22	+0.21	+0.01
	-0.78	-0.52	-0.26
	-0.38	-0.38	0.00
D	-0.70	-0.61	-0.11
	-0.05	-0.13	+0.08
	-0.75	-0.81	+0.06
	-0.73	-0.57	-0.16
	-0.56	-0.64	+0.08
	-0.54	-0.51	-0.03
	-0.35	-0.70	+0.35
E	+0.28	+0.12	+0.16
	-0.67	-0.60	-0.07
	-0.33	-0.50	+0.17
	+0.11	-0.09	+0.20
	+0.09	+0.08	+0.01
	-0.12	-0.12	0.00
	-0.45	-0.23	-0.22
F	-0.76	-0.33	-0.43
	-0.48	-0.39	-0.09
	-0.32	-0.72	+0.40
	-0.59	-0.95	+0.36
	-0.47	-0.61	+0.14
	-0.49	-0.48	-0.01
	-0.43	-0.51	+0.08
H	+0.23	+0.19	+0.04
	+0.19	+0.31	-0.12
	+0.14	+0.13	+0.02
	+0.29	+0.25	+0.04
	-0.09	+0.05	-0.14
	+0.13	+0.02	+0.11
	-0.03	-0.05	+0.02
I	+0.39	+0.41	-0.02
	+0.57	+0.39	+0.18
	+0.28	-0.06	+0.34
	+0.34	+0.38	-0.04
	+0.35	-0.18	+0.53
	+0.33	+0.19	+0.04
	-0.83	-1.13	+0.30
J	-0.77	-0.50	-0.27
	-0.32	-0.34	+0.02
	-0.18	-0.15	-0.03
	-0.42	-0.42	0.00
	-0.36	-0.15	-0.21
	-0.11	-0.33	+0.22
	-0.68	-0.60	-0.08
	-0.64	-0.53	-0.11

*Laboratory of California Division of Highways

** Laboratory of cement mill submitting sample

Fig. 1



EFFECT OF SO_3 ON CONTRACTION