PRELIMINARY REPORT
ON
INVESTIGATIONS OF THE EFFECT OF BORON ADMIXTURES
ON CONCRETE PROPERTIES

REPORT TO STANFORD LINEAR ACCELERATOR CENTER - ABA NO. 97
STANFORD UNIVERSITY SUBCONTRACT S-136
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SYNOPSIS

Two test series were conducted by ABA to determine the effects of various types of boron additives on the properties of normal job concrete. The first investigations were made prior to construction of the Positron Radiator structure in the Linear Accelerator Housing using boron frit and also a finely graded colemanite from U. S. Borax and Chemical Corporation. The second series, as a part of the preliminary investigations for the Beam Switchyard, explored the use of colemanite from the mines of the Kern County Land Company. Following the completion of the first test series, additional routine tests were conducted on concretes with frits used in the construction of the Positron Radiator structure. Results of both test series and the tests of the Positron Radiator structure concrete are summarized and comparisons are made.

Colemanite samples from the second source were also washed thoroughly to remove the excessive fines. In addition, unwashed raw ore as delivered was upgraded to a size range not finer than the No. 30 sieve size or larger than 3/8 inch. These beneficiated colemanites were also tested. The results of these beneficiations are described.

Test results indicated that quality concretes comparable to the concretes used in normal project construction can be obtained with boron frit or washed colemanite admixtures.
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INTRODUCTION

Several thousand cubic yards of concrete with "Elemental Boron" will be required to complete the construction of facilities in the Target Area of the Stanford Linear Accelerator.

Approximately 300 cubic yards of "Boron Loaded" concrete were needed in the Positron Radiator structure construction. Limited time was available for preliminary concrete studies. These studies indicated that the use of frit as a boron additive presented few problems and/or detrimental effects on the various concrete properties. Tests made with colemanite, another boron source, were less favorable in this respect. The decision was made to use frit as a means for boron loading. No placing problems were encountered nor were harmful effects noted.

Cost studies during these initial investigations showed that use of frit was from 200 to 300 percent higher than with the colemanite ores. Therefore, in view of the remaining volume of boron loaded concrete required, it appeared necessary to conduct additional studies regarding the use of colemanite as a practical source of elemental boron.

Additional concrete tests were made with colemanite from a second source. Materials from this source were washed to remove excessive fines. Samples were also Dry Screened to produce a coarser gradation. Results with these beneficiated materials were compared with the basic ore as delivered and also with mixes without the additives.

Test results and observations during the testing of both types of additives and later results with the frit used during construction are summarized in this report.

MATERIALS

The selected concrete materials used in the Accelerator Housing and Research Complex and for the preliminary investigations were all from the
same sources. With the possible exception of the water reducing admixture, they are expected to be similar to those which will be used for the Beam Switchyard construction.

Cement

Type II, "modified" cement was used. Specifications limited the tri-calcium silicate to a minimum of 42% and a maximum of 50% and not more than 6% tri-calcium aluminate. The compressive strength (2" x 2" cubes) was specified at not less than 4500 psi at 28 days of age. Note Table 2 for the properties of cement used in the testing and Positron Radiator structure construction.

Fine Aggregates

Fine aggregate from the Monterey Bay - Santa Cruz area was used. These sands are reasonably well graded feldspathic sands composed predominately of quartz and feldspar. The particle shape ranges from subangular to angular. The sand used in the concretes with Colemanite No. 1 and the tests and job concrete with the boron frit had a fineness modulus of 2.65. The sand used in the tests with Colemanite No. 2 had a fineness modulus of 2.45. Both sands were within ASTM gradation limits.

Coarse Aggregates

Granite aggregates from the Watsonville area were used. This aggregate is quarried material from the Santa Lucia granite formation and is composed chiefly of quartz and feldspar with minor amounts of hornblende and biotite mica. The rock is sound, strong and only slightly weathered. Particle shape ranges from subangular to angular after processing. Aggregates used were in two size ranges, #4 to 3/4 inch and 3/4 inch to 1-1/2 inches. Gradation was within ASTM limits with no more than 3% significant undersize.
Water Reducing Admixture

The admixture used was Lignosulfonic acid, delivered in solution. Normal dosage was 6 ounces per sack of cement.

Air Entraining Agent

A Vinsol Resin type agent was used. Normal dosage was 1/2 to 3/4 ounces per sack of cement in the concretes with the water reducing admixture and up to 1-1/4 ounces per sack in the plain mixes.

Colemanite

Colemanite is a naturally occurring mineral used principally as a source of boron. It occurs in crystalline masses interbedded with clay shales, sandstones and other sedimentary rocks in California and Nevada. Colemanite as extracted from the ground usually contains impurities such as sodium, clays, sands and silts, and small amounts of gypsum. These impurities in excessive amounts may produce significant adverse effects on the properties of concrete.

Colemanite Number 1 was from the U. S. Borax and Chemical Corporation, Los Angeles. Colemanite Number 2 was from the Kern County Land Company's mines in Death Valley, California. The samples from U. S. Borax were very fine with approximately 50 percent minus the #50 sieve and 15 percent minus the #200 sieve. The material from Kern County was much coarser with 20 percent minus the #50 sieve and 5 percent minus the #200 sieve. Comparative gradations are shown in Figure 1. Significant amounts of clayey materials were present in both samples. These clays exist throughout each size fraction and are not isolated in the minus #200 size range. A part of the fines are bentonitic clays. Limited tests were conducted to establish the amounts of clayey materials. The samples contained approximately 45 percent clayey materials, 2 percent of which were hard rock fragments.
Approximately 600 pounds of the sample of the colemanite from Kern County were washed prior to use in the concrete. The material was pre-soaked for 24 hours followed by simple washing, comparable to conventional methods used to remove excessive fines from concrete sands. This pre-soaking appears advisable as nearly 35 percent fines were removed as a result of the washing. It should be noted, however, that the amount of fines in the various raw samples varied from 20 to 40 percent which will significantly affect total quantities, the amount of washing, and possibly the need for pre-soaking. This may or may not be true in colemanites from other sources or from selective mining from the above source. The $B_2O_3$ content of the colemanites checked ranged from 18 percent unwashed to 25 percent washed. Depending upon the amounts of the impurities, the total dosage of colemanite per cubic yard of treated concrete could vary from approximately 200 to 300 pounds.

Several definite advantages were noted as a result of the washing. These are:

1) A significant reduction in the adverse effects noted with the unwashed colemanite on the properties of the fresh and hardened concrete.

2) Increased $B_2O_3$ content for equal dosage. Total $B_2O_3$ content expressed as a percent of the total sample increased from 18 to 25 percent as a result of the washing.

3) Uniform addition of elemental boron per cubic yard of concrete at minimum dosage.

4) Stabilized unit water requirement.

5) Removal of sodium and other water soluble salts.

**Frit**

Boron frit is a refined product produced by fusing boric acid, calcium carbonate, silica and alumina and quenching the melted product in water. When used as a boron additive in concretes, these frits must be free of compounds of sodium and potassium.
The $B_2O_3$ content of the high grade frit used is approximately 52 percent. At this $B_2O_3$ content, 100 pounds of frit are required to add 16 pounds of elemental boron to each cubic yard of concrete.

The frit used in the preliminary testing and the Positron Radiator structure construction was fairly coarse with an average of 97 percent plus the No. 30 sieve size and 100 percent minus the 3/8" size screen. Note Figure 1. No problems were encountered in the handling, storage, batching or introduction of the material into the concrete mix during construction. Placeability, workability and finishing time, etc. were comparable to the normal concrete used in construction of the Housing.

**CONCRETE MIX DESIGN**

The concrete mixes were designed in accordance with the "Recommended Practice for Selecting Proportions for Concrete" (ACI 613-54). The amount of boron additive per cubic yard replaced an equal weight of sand.

**TESTING METHODS AND PROCEDURES**

The trial mixes were batched at the concrete batch plants furnishing concrete for the Accelerator Housing and the Research Complex. The minimum batch size was one-half cubic yard. The batches were mixed in transit mixers for a total of 80 revolutions after addition of all materials. Tests of the fresh concrete and the casting of the specimens for compressive strength, shrinkage, etc., were conducted at ABA's field laboratory or the batch plant immediately following the mixing period. The test specimens were stored in the field laboratory or batch plant for 24 hours following casting (in a moist atmosphere with controlled 70°F temperature), then transported to the testing laboratory of the University of California for curing and testing.

All tests were performed in accordance with applicable ASTM and/or ACI practices or procedures. Specimens for compressive strength were standard cured 6" by 12" cylinders. The specimens for the shrinkage determinations were 5" by 6" by 16" prisms. Moist curing period for the shrinkage tests
was 14 days. Drying occurred at 50 percent relative humidity and at 70°F.
Tests of the rate of hardening were made on mortars wet screened from the
trial batches.

DISCUSSION OF TEST RESULTS

Compressive Strength

With Boron Frit

The preliminary tests indicated a strength loss with frit in the mixes
with the water reducing admixture of approximately 12 percent when compared
with the control mix. Comparison, with and without frit, of the concrete
without the water reducing admixture showed a gain of nearly 10 percent
over control. Later, during construction of the Positron Radiator structure,
results of routine strength tests showed strengths through 28 days of age
closely comparable to the original control mix without frit at a cement con-
tent one quarter of a sack higher. These comparisons are shown in Figure 2.
The results also compare favorably with the results obtained with normal job
concrete with the same materials and cement content.

With Colemanite Number 1 (U.S. Borax)

Table 1 and Figure 3 present the compressive strength results with this
additive. A strength gain at 28 days of age and older was noted in the mixes
with the colemanite, with or without the water reducing admixture. A greater
strength increase was noted in the concretes without the admixture. The major
portion of this indicated gain can be attributed to the complete loss of en-
trained air in the mix. It is doubtful if any strength advantage or disadvant-
age results from the use of colemanite at equal water-cement ratios. At
early ages (3 days) strengths of the mixes with the water reducing admixture
were approximately 50 percent lower than the control mix. This slow strength
development is due principally to the excessive retardation as shown in Figure 9.
This will significantly affect the concrete finishing and early form removal,
particularly at lower air temperatures.
With Colemanite Number 2 (Kern County)

Normal concretes with the water reducing admixture were compared with similar concretes with unwashed and washed samples from this source. Also, the control mix was compared with unwashed material "up-graded" to a size range not finer than the Number 30 sieve size and not larger than 3/8 inch.

Compressive strengths of the concrete with the unwashed material (regardless of the grading) averaged 4000 psi at 28 days of age as shown in Figure 4. This is from 28 to 32 percent below the strengths of the control mix. The high water demand (30 percent plus) for these mixes to obtain equivalent consistency and workability is considered the influencing factor controlling the lower strength, not the addition of the colemanite.

Again, as was noted with the first colemanites investigated, the compressive strengths at early ages (2 days) are proportionately lower than the plain mixes, as shown in Figure 5. However, the early strengths show significant improvement over the results with the first sample of colemanite. This slower strength gain is due principally to the moderate retardation illustrated in Figure 10, and is not expected to impose any major problem during construction if the cement content is sufficient to produce overall strengths equal to the control mixes.

Strengths with the washed colemanite were closely comparable to the control mixes except at two days of age, as noted in Figure 4. A slowing of the rate of hardening was noted with the washed colemanite which in all probability can be held accountable for the slower strength gain at early ages.

Strengths of the control mixes compare favorably with job concretes at water/cement ratios equal to those used during construction. Compressive strengths of concretes with the frit and the washed colemanite (combined with the other materials comparable to those used in these tests) should easily meet the strength demands for the Beam Switchyard at cement content no higher than used in the mixes tested. Mixtures with unwashed colemanites similar to
those tested would require considerably more cement due to the high water demand.

**Drying Shrinkage**

Favorable low drying shrinkage was noted in all of the tests. Shrinkage results after 21 days of drying were all below ABA specification limitations of 0.0250%. The results at later ages up to 90 days follow the general pattern and values of the normal job concretes.

The shrinkage with Colemanite Number 1 (U.S. Borax) tested in the first series was extremely low. The total shrinkage at 90 days of age ranged from 26 percent to 42 percent lower than the control mixes with or without water reducing admixtures respectively, as shown in Figure 5. It is the writer's opinion that the water was "used up" by the fine, clayey materials in the boron additives resulting in lower drying shrinkage. This conclusion was supported by the second test series. The mixes with Colemanite Number 2 (Kern County) with approximately 30 percent higher unit water content (for equal consistency and workability) exhibited low shrinkage only slightly higher than the control mixes. Note Table 1 and Figure 6.

Boron frit, comparable to the frits tested, in combination with the materials used in past construction had no significant influence on the drying shrinkage property. These comparisons are shown in Figure 7.

**Volume Change (Expansion)**

During the second test series with Colemanite No. 2, measurements were taken of the drying shrinkage specimens during the moist curing period immediately following the casting of the specimens. No significant expansion was indicated by these tests.

**Flexural Strength (Shrinkage Bar Specimens)**

Tests in flexure, after completion of the drying shrinkage period (104 days of age) indicate that concretes with both types of boron additives can
be expected to possess somewhat lower flexural strengths than normal job concretes. This lower factor is not considered significant in the type of construction connected with the Beam Switchyard. Test results are given in Table 1.

**Slump Characteristics**

Slump losses are shown in Figure 11. None of the mixes with frit or colemamites exhibited slump losses noticeably different than those of the control mixes. The control mixes also compare favorably with the job concretes. The low slumps with the first sample of colemamite were due to low air and insufficient mixing water (note Table 1). There is no indication that any change in the rate of slump loss results from the use of colemamite.

**Air Entrainment**

Entrainment of air is difficult only in the mixes with the unwashed colemamite. In the second test series the mixes with unwashed colemamite required from 6 to 8 times the dosage of air entraining agent in comparison with the control mixes and 4 times as much as the mix with the washed colemamite, as noted in Table 1. Difficult control, possibly to the point of being dangerously poor, could result from use of these excessive amounts of agent. Poor control of the washing and/or batching could produce air contents from one extreme to the other causing wide variations in the consistency, workability, compressive strength, etc.

**Workability**

Good, plastic, workable mixes were obtained in concretes with both the boron frit and the washed colemamite. The mixes with the unwashed or coarsely graded colemamites were highly plastic, extremely sticky, with nearly a complete loss of flowability at slumps from 3 to 4 inches. The stickiness appeared to be aggravated at higher air contents nearing 5 percent. Discharge from transit mixers, chuting, placing and finishing can be expected to be much more difficult in concretes with unwashed materials.
Rate of Hardening (Retardation)

The rate of hardening was significantly and adversely retarded by the addition of the boron additives.

Only moderate delays were noted in the mixes with the boron frit, as shown in Figure 8. The initial retardation to the vibration limit or to point of maximum penetration was approximately 1½ hours longer than control. Limited delays such as this were not considered significant. Later, during construction of the Positron Radiator structure, the retardation noted during the testing was also apparent causing slight delays of approximately one hour in final finishing.

Severe retardation resulted from the use of colemanite from U. S. Borax. Figure 9 shows that the rate of hardening of the mixes without the water-reducing admixture was delayed nearly 16 hours longer than the control mixes and up to approximately 22 hours longer in mixes with the water-reducing admixture. Corresponding delays in job concrete would result in costly delays in finishing and possibly in form removal. This retardation could possibly be extended much longer at the low concrete temperatures (below 50°F.) proposed for the Beam Switchyard. Winter temperatures, which will be much lower than the 70°F at which the tests were run, will also contribute to increased retardation.

Noticeably less retardation occurred in the mortars with colemanite from Kern County in comparison with similar mortars with Colemanite No. 1. The best test results were obtained with the washed colemanite with the rate of hardening to maximum penetration delayed slightly over two hours longer than control. This delay increased to 3½ hours with the coarse material plus the #30 sieve and up to 5 hours longer with unwashed ore as delivered. Figure 10 compares these values. It was first thought that removal of the heavy clayey materials from the colemanite would eliminate the excessive retardation. However, this has not proven to be true. Time of set is improved with the washing;
other minerals apparently influence this property and some abnormal retardation continues.

Retardation to some degree apparently must be expected with these boron additives. Mr. J. O. Henrie in his report (1) points out the problems of increased setting time with similar types of additives but from different sources. All ABA tests indicate that similar results must be expected with these materials. Unless some type of accelerator is used to overcome the extended retardation, the construction problems resulting from the delays must be accepted.

(1) Reference - Henrie, J.O., "Properties of Shielding Concrete" AI Memo 3503
Atoms International - Issued January, 1959
SUMMARY AND CONCLUSIONS

The preceding text has described the boron admixtures test program. Results of the tests conducted indicate the following conclusions and recommendations:

1) Quality concrete, consistent with the high standards adopted for the construction work on this project, can be obtained with frit or the washed colemanites tested.

2) Only washed colemanite or the boron frit should be considered where boron loaded concrete is required for the Beam Switchyard.

3) Moderate retardation resulting from the use of the frit or washed colemanite should not impose any difficult or costly problems during construction.

4) Specifications controlling the boron admixture to be used should limit or control:
   (a) Amounts of undesirable impurities;
   (b) gradation;
   (c) tests to establish amounts of boron or $B_2O_3$ in material as delivered to the job site;
   (d) maximum quantity of fines minus the #200 sieve permissible in the washed colemanite;
   (e) methods of handling, batching, batching controls and mixing.
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Compressive Strength

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3 day ------------------------- 2481  2337
7 day ------------------------- 3500  3242
28 day ------------------------- 5388  5037

SILO 14 - Used in Tests with Colemanite #1 and Boron Frit
SILO 12 - Used in Tests with Colemanite #2 and Positron Radiator Structure

TABLE 2 - PROPERTIES OF CEMENT