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# Colorimetric Test
FOR
# Organic Impurities in Sands

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Experimental work carried out in cooperation with Committee C-9 on Concrete and Concrete Aggregates, of the American Society for Testing Materials. Published by permission.

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# Colorimetric Test for Organic Impurities in Sands

## INTRODUCTION.

During the past few years the subject of impurities in sands for mortar and concrete has been receiving rapidly increasing attention from testing engineers and inspectors. Experience has shown that on account of the presence of impurities, certain natural sands do not give satisfactory results when used in concrete, and many failures and much inferior work have been attributed to impurities in the fine aggregate. However, when it comes to determining before the sand is used in construction or subjected to tests in mortar, whether or not the sand is suitable for fine aggregate, there has been no well-established criterion regarding the impurities. Practically all specifications have required that the sand be clean; the so-called dirty sands have generally been in bad repute. Organic matter has been the principal source of trouble, yet many publications stating that as much as 10 per cent of loan in sand was not harmful and might even increase the strength of the mortar, are to be found in the engineering journals.

An investigation initiated by Committee C-9 on Concrete and Concrete Aggregates, of the American Society for Testing Materials, showed the desirability of a simple and reliable test which would make it possible to detect sands which contained harmful impurities before they were used in concrete. Commercially, it was also desirable to develop some remedial measure which would make it possible to use sands which in their present condition, on account of impurities, are not satisfactory for concrete.

Engineers and chemists have recognized the danger of using sands which contained appreciable amounts of organic matter which may come from surface loan or other sources of contamination, and have used various methods for detecting such impurities. A method which has probably been most used depends upon the loss on ignition. Obviously the loss-on-ignition test drives off, besides the organic matter, the water of crystallization, hydration, etc., and the carbon dioxide ($CO_2$). In certain "limestone sands" the loss on ignition due to carbon dioxide alone may amount to more than 10 per cent, and yet the sand may be entirely free from organic matter. The determination of the organic matter by combustion has little advantage over the loss-on-ignition method, unless a correction be made for the carbonates present. Methods which depend upon the moist oxidation of the organic matter have some advantage, but are not entirely satisfactory. None of these methods determines directly the amount of organic matter in the sands. Most of them determine the amount of carbon by first converting it into carbon dioxide. The organic matter is then calculated by multiplying the per cent of carbon by some factor, the accuracy of which is often questionable.

The colorimetric test for organic impurities in sands represents one phase of the work which has been done at the Structural Materials Research Laboratory, Lewis Institute, Chicago, under the direction of the Committee mentioned above. The fact that the sand has passed the colorimetric test does not by itself prove that the sand is suitable for mortar or concrete, since its fineness and other characteristics must also be considered as they affect the strength. The result of the researches, however, indicate that it is a reliable test for organic impurities, which are the most common source of danger in a sand of satisfactory granulometric composition.

It is intended at this time to give only a description of the methods of making the test so that it may be tried out further in commercial and private laboratories. The experimental data obtained in the course of these studies will furnish the subject-matter of a subsequent report.

It will be of assistance to the Committee having this investigation in charge, if other experimenters will report the details of their tests and observations to the Chairman, Mr. Sanford E. Thompson, 136 Federal Street, Boston, Mass., or to the authors.

The colorimetric test may be described briefly as follows:

A sample of sand is digested at ordinary temperature in a solution of sodium hydroxide ($NaOH$). If the sand contains certain organic materials, thought to be largely of a humus nature, the filtered solution resulting from this treatment will found to be of a color ranging from light yellow up through the reds to that which appears almost black. The depth of color has been found to furnish a measure of the effect of the impurities on the strength of mortars made from such sands. The depth of color may be measured by comparison with proper color standards.

Two methods of procedure have been developed: (1) For Field Tests; (2) For Laboratory Tests.

## METHOD FOR FIELD TESTS.

Fill a 12-oz. graduated prescription bottle to the 4½-oz. mark with the sand to be tested. Add a 3% solution of sodium hydroxide until the volume of the sand and solution, after shaking, amounts to 7 oz. Shake thoroughly and let stand over night. Observe the color of the clear supernatant liquid.

In approximate field tests it is not necessary to make comparison with color standards. If the clear supernatant liquid is colorless, or has a light yellow color, the sand may be considered satisfactory in so far as organic impurities are concerned. On the other hand, if a dark-colored solution, ranging from dark reds to black is obtained the sand should be rejected or used only after it has been subjected to the usual mortar strength tests.

Field tests made in this way are not expected to give quantitative results, but will be found useful in:

(1) Prospecting for sand supplies;
(2) Checking the quality of sand received on the job;
(3) Preliminary examination of sands in the laboratory.

An approximate volumetric determination of the silt in sand can be made by measuring or estimating the thickness of the layer of fine material which settles on top of the sand. The per cent of silt by volume has been found to vary from 1 to 2 times the per cent by weight.

## METHOD FOR LABORATORY TESTS.

To a 200-gram sample of dry sand add 100 cc. of a 3% solution of sodium hydroxide (NaOH) and digest at ordinary temperature, with occasional stirring, for 24 hours. Filter this solution through a good grade of filter paper; refilter if necessary. The filtrate *must* be clear. Place 10 cc. of the *clear* filtrate in a 50 cc. Nessler cylinder and dilute to 50 cc. with distilled water. Shake thoroughly and let stand until all foam and bubbles disappear. Determine the color value of this cylinder by comparing it with cylinders containing standard solutions of alkaline sodium tannate. Compare the colors by looking through the full depth of the solution with the cylinders held toward a good natural light.

*Standard Tannic Acid Solution for Color Comparison.* The preparation of the standard tannic acid solution for comparing the color of the filtrate should be begun at the same time as the treatment of the sand. Add 10 cc. of a 2% solution of tannic acid in 10% alcohol to 90 cc. of a 3% solution of sodium hydroxide. The sodium hydroxide combines with the tannic acid to form sodium tannate. Let the solution stand 24 hours at room temperature. Place 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 cc., respectively, of this solution in 50 cc. Nessler cylinders and dilute to the mark with distilled water. The amounts of tannic acid in the different cylinders will then be as shown in the following table:

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Alkaline Sodium Tannate in each cylinder—cc. ... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Tannic acid in each cylinder — milligrams ..... | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 |
| Color value in parts of tannic acid per million of sand by weight | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |

It is desirable to have good sunlight for comparing the colors; if sunlight is not available, the amount of tannic acid in each of the cylinders containing the standard solutions may be decreased by one-half and the other values in the table modified accordingly.

In case the solution obtained by digesting the sand with the sodium hydroxide is very dark, use less than 10 cc. for the comparison and make the necessary modifications in the calculation of the color values. With very light-colored solutions use more than 10 cc. of the filtrate for the comparisons. The depth of color of the solution decreases on standing, and for that reason the solution should be made up fresh for each day's work.

*Method of Calculation.* An example will make clear the method of calculating the color value of a sand. Suppose that 10 cc. of clear filtrate obtained by digesting the sand with 100 cc. of a 3% solution of sodium hydroxide when diluted to 50 cc. corresponds in color to the Nessler cylinder containing 12 milligrams of tannic acid, or 6 cc. of the alkaline tannate solution. The sand will then have a color value of 600. The 10 cc. of the filtrate placed in the Nessler cylinder is 1/10 of the 100 cc. of 3% sodium hydroxide solution which was added to the sand, and the sample of sand (200 grams) is 1/5 of a kilogram; therefore, the milligrams of tanic acid per kilogram of the sand, by weight, are 12 x 10 x 5 = 600; or the tannic acid equivalent when expressed in parts per million of the sand, by weight, is 600.

## BASIS OF COLORIMETRIC TEST.

The colorimetric test has been applied to sands from about 40 widely distributed deposits in 20 different states. The research to date has brought out the following:

1. Examinations of deposits of defective sands show that surface loan is the principal source of contamination.

2. All natural sands which have been found to be defective on account of the presence of organic impurities have responded to the colorimetric test with sodium hydroxide, and all sands which have given high color values have shown low values in mortar tests.

3. Sands which were similarly graded by screening out and recombining the different sizes to a definite sieve analysis, showed a fairly definite relation between the compressive strengths of 1-3 mortars at 7 and 28 days and the color values of the sands.

4. The motar-making quality of sands known to contain organic impurities has been much improved by removing the organic matter, either by repeatedly digesting them with sodium hydroxide and then washing free from alkali, or by driving off the organic impurities by ignition.

5. When the sodium hydroxide extracts from sands which mortar tests had shown to be defective were purified and applied as coatings on high-grade sand, that sand was made "defective" or gave much reduced mortar strength.

6. It is impracticable to give exact values for the relation between the color value of a sand and the strength of mortars made from the same sand. However, the tests made thus far show this relation to be about as follows:

| Color Values of sand | Reduction in Compressive Strength of 1-3 Mortar Per cent |
|---|---|
| 250 | 10-20 |
| 500 | 15-30 |
| 1000 | 20-40 |
| 2000 | 25-50 |
| 3000 | 30-60 |

The reduction in strength is based on compression tests at ages of 7 days, 28 days, and 3 months, of 1-3 mortars made from the same sand, before and after coating with different per cents of organic impurities which had been extracted from defective sands and purified. Tests on mortars made from defective sands as received and after removal of the organic impurities, either by repeated extractions with sodium hydroxide or by ignition, showed that in some cases the reduction in strength for a given color value was even greater than the higher values given above. Frequently the test pieces completely disintegrated in the storage water. The higher reductions in strength for a given color value for a natural sand as compared with the same color value for an artifically coated sand is probably due to the artificial coating being more easily removed by the sodium hydroxide.

Sufficient data are not available to indicate whether or not the effect of a given quantity of organic impurities varies with the grading of the sand. The reduction in strength seems to decrease slightly with the age of the test pieces.

## APPARATUS.

The apparatus required for making the colorimetric test of sands will vary according to the nature of the investigation. Two lists are given below: (1) Apparatus for Field Tests; (2) Apparatus for Laboratory Tests. Sufficient apparatus has been included in each list for tests on 5 samples at a time.

| *For Field Tests.* | *Approximate Cost* |
|---|---|
| 5 12-oz. graduated prescription bottles........ | $ .25 |
| Stock of 3% solution of sodium hydroxide (dissolve 1 oz. of sodium hydroxide in enough water to make 32 oz.)................... | .50 |
| | $ .75 |

*For Laboratory Tests.*

| | |
|---|---|
| 15 Nessler cylinders | $ 7.50 |
| 5 3-in. glass funnels | 1.00 |
| 10 250-cc. beakers | 2.00 |
| 1 test tube support | .50 |
| 100 qualitative filter papers, 11 cm. diam. (good grade) | .50 |
| 1 100-cc. graduated cylinder | .75 |
| 2 oz. 2% solution of tannic acid in 10% alcohol. | .50 |
| 1 lb. sodium hydroxide (NaOH) (sufficient for 150 tests) | .50 |
| 1 32-oz. bottle containing 3% solution sodium hydroxide | .25 |
| 1 10-cc. Mohr's pipette, graduated in 1/10 cc. | .50 |
| | $14.00 |

## CONCLUDING REMARKS.

Impurities in sands other than organic, such as clay or similar admixtures, if present in considerable quantities, may be expected to affect the strength of the concrete. However, the examination of a large number of defective sands has shown that it is the organic impurities of a humus nature which are responsible for the abnormally low strengths of such sands. The presence of these impurities can be detected by the methods described above.

It has been found that the colorimetric test can be made with a greater degree of uniformity by different operators than can the strength tests of mortars from the same sands.

The fact that the colors produced by digesting certain natural sands with sodium hydroxide are similar to those produced by treating tannic acid in the same manner must not be intepreted to mean that the organic matter in sands is necessarily tannic acid, or even a tannate. The chemical compounds which make up the organic material are probably numerous and complicated.

The time actually required for a single determination by the laboratory method is about ½ hour. If tests on as many as 5 samples can be made at once, the total time consumed need not exceed 1 hour. The time required from the beginning to the end of the test is about 24 hours.

Inexperienced operators without technical training or previous experience in work of this character have secured satisfactory results at their first trials.

The strength test of mortar is used as the criterion of the effect of impurities in sand. In making strength tests of sand mortars and interpreting the results of such tests, the following points require particular attention:

(a) Sampling of sand,
(b) Grading of sand,
(c) Quantity of water used in mixing,
(d) Methods of mixing, molding and testing,
(e) Form and size of test piece.

(a) Great care is necessary to insure that the sample tested is representative of the larger lot of sand. Good judgment and considerable experience are necessary to secure representative samples from an undeveloped deposit. Some form of sampler should be used in the laboratory in selecting a test sample from a larger lot.

(b) The size and grading has an important influence on the concrete and mortar-making qualities of sands. A sand graded from coarse to fine, with the coarse particles up to about ¼ in. in diameter, is desirable for use in concrete. Fine sands when mixed to the same plasticity, give mortar strengths much below those of coarse, well-graded sands. The infiuence of the grading of sand on the strength of the mortar must not be confused with the effect of impurities.

(c) The quantity of water used in mortar tests has just as important an influence on the strength as the amount of cement. The quantity of water required for normal consistency of mortar made from a given cement is a function of the grading of the sand.

(d) The methods used in mixing, molding the test pieces, storing and testing the specimens, etc., used in standard tests of cement should be followed in making strength tests of sand mortars.

(e) Compression tests of mortar are believed to be more significant than tension tests. A 2 by 4-in. cylinder has been found to give satisfactory results as a compression test piece. This is the form of test piece recommended by the American Society for Testing Materials in their proposed tentative specification for compression tests of cement.

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The study of impurities in natural sands is being continued as a part of the work of the Structural Materials Research Laboratory, Lewis Institute, Chicago. Special attention will be given to further improvements in the colorimetric test, and to discovering remedial measures which can be used in a commerical way for counteracting the effects of such impurities.