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DETERMINATION OF SULPHUR OCCURRING AS SULPHIDE IN PORTLAND CEMENT

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ABSTRACT

A modification of the usual evolution method for the determination of sulphur is described wherein stannous chloride is used during solution of the sample to prevent the oxidation of hydrogen sulphide by the higher oxides of manganese and iron.

CONTENTS

I. INTRODUCTION

Among the minor constituents of certain portland cements are small amounts of sulphides associated with compounds of manganese and iron. The manganese is usually in valence states higher than 2 and interferes with any determination of sulphides based on the amount of hydrogen sulphide that is evolved when a sample is dissolved in hydrochloric acid. Ferric iron, which is practically always present in portland cements, likewise interferes. Sulphides and higher oxides of manganese in portland cement may seem incompatible, but both may be present, particularly in blended cements.

Watson [1] has recommended the use of stannous chloride to overcome the effect of ferric iron. Stannous chloride for this purpose was independently used at this Bureau in connection with an investigation on the reducing and oxidizing constituents of cements. As will be shown later, it was found that the addition of this salt also prevented interference by higher oxides of manganese. Titanous chloride and zinc dust were not as efficient as stannous chloride. The procedure developed at this Bureau is given in section II.

II. PROCEDURE

Transfer 5 g of the sample to a *dry* 500-ml flask and connect the latter as shown in figure 1. Place 15 ml of an ammoniacal solution of zinc sulphate and 285 ml of distilled water in the tall-form beaker.[2]

[1] Cement 5, 49 (1932).

[2] For very small amounts of sulphides, an ammoniacal solution of $CdCl_2$ can be substituted, as the yellow CdS facilitates detection of traces of sulphides.

Add 10 ml of water through the thistle tube, and shake the flask to wet the cement completely. Add 25 ml of stannous chloride solution, shake several times to mix, and then add 65 ml of diluted hydrochloric acid (10+3). Connect the inlet tube, pass a *slow* stream of air [3] through the system, and heat the flask and contents slowly until boiling ensues. Boil gently for 5 to 6 minutes, cut off the heat and continue the passage of air for 3 to 4 minutes. Disconnect the delivery tube, and leave it in the solution for use as a stirrer.[4] Add 2 ml of starch solution and then 40 ml of diluted hydrochloric acid (1+1). Titrate immediately with the iodate solution until a permanent blue color is obtained. Subtract the blank obtained with the reagents alone, and calculate the percentage of sulphur.

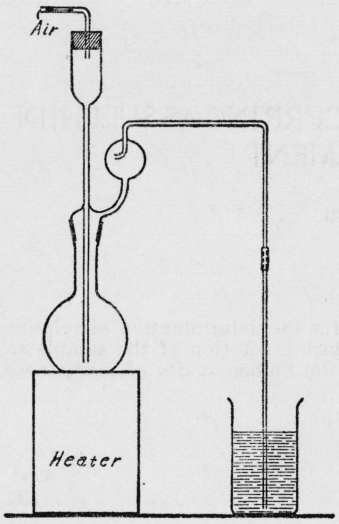

FIGURE 1.—*Apparatus for the determination of sulphide sulphur.*

Ammoniacal zinc sulphate.—Dissolve 50 g of $ZnSO_4.7H_2O$ in 150 ml of water and 350 ml of NH_4OH (sp gr 0.90). Let stand 24 hours and filter.

Stannous chloride.—To 10 g of $SnCl_2.2H_2O$, in a small flask, add 7 ml of diluted HCl (1+1). Warm gently until the salt is dissolved. Cool, and add 95 ml of water. This reagent should be made up daily as needed, as the salt tends to hydrolyze.

Starch solution.—To 500 ml of boiling distilled water, add a cold suspension of 5 g of soluble starch in 25 ml of distilled water, cool, add a cool solution of 5 g of NaOH in 50 ml of distilled water, then add 15 g of KI, and mix thoroughly.

Potassium iodate.—(0.03*N*) Dissolve 1.12 g of KIO_3 and 12 g of KI in 1,000 ml of distilled water. Standardize by means of sodium oxalate through $KMnO_4$ and $Na_2S_2O_3$ as follows: To 300 ml of water in a 500-ml flask, preferably glass-stoppered, add 10 ml of hydrochloric acid (sp gr 1.18) and 1 g of KI. Cool and add 25 ml of 0.03*N* $KMnO_4$ solution which has been standardized against sodium oxalate. Swirl gently, stopper, and let stand for 5 minutes. Titrate the liberated iodine with thiosulphate solution (approximately 0.03*N*) until the color nearly fades. Then add 2 ml of starch solution and continue the titration until the blue color is just destroyed. In another flask, repeat the experiment with the sole difference that 25 ml of the iodate solution is substituted for the standard permanganate solution. The normality of the iodate solution is then found by dividing the volume of $Na_2S_2O_3$ solution required in the second titration by the

[3] Tests indicated that the substitution of hydrogen for air offers no advantages in this particular determination.

[4] If the absorbing solution has warmed up during the evolution, cool it to 20 to 25° C.

volume required in the first, and multiplying by the normality factor of the $KMnO_4$ solution. One ml of N $KMnO_4$=0.01603 g of sulphur.

III. EXPERIMENTAL RESULTS

The accuracy of the procedure was tested on mixtures of CaO, MnO_2, Fe_2O_3, and an amount of ZnS approximately equivalent to the amount of sulphides that may occur in cements. Lime was used in these mixtures because an iron-free portland cement was not available. The results obtained are given in table 1.

TABLE 1.—*Determination of sulphide-sulphur in synthetic mixtures*

ZnS	CaO	MnO_2	Fe_2O_3	Sulphide-sulphur	
				Added [a]	Found
g	g	g	g	g	g
0.0085	----------	----------	----------	----------	0.0027_9
.0057	3.3	----------	----------	0.0018_7	$.0018_8$
.0052	3.3	0.09	----------	$.0017_9$	$.0016_6$
.0084	3.3	.09	----------	$.0027_5$	$.0027_3$
.0080	3.3	.09	0.25	$.0026_2$	$.0026_2$
.0054	3.3	.09	----------	$.0017_7$	([b])

[a] Calculated on the basis of 99.6 percent ZnS.
[b] None found; no $SnCl_2$ added.

The procedure was also applied to several sulphide-bearing portland cements of low manganese content, and to mixtures of these with a cement having a high manganese content. When treated with concentrated hydrochloric acid, 1 g of this cement (labeled *A* in the table) liberated 0.006 g of chlorine per gram, which is in excess of what should be liberated if the manganese were all present in the trivalent state. If all of this chlorine should react with hydrogen sulphide ($H_2S+Cl_2=2HCl+S$), it would destroy 0.0027 g of "sulphide" sulphur. In tests with mixtures of zinc sulphide and the cement it was found that the amount actually destroyed in the evolution method (without stannous chloride) was approximately half theoretical, or about 0.001 g of "sulphide" sulphur per gram of the cement.

The results obtained, together with those obtained in tests in which no $SnCl_2$ was used, were as follows:

	Iodate ml	Sulphur (%)
5 g of cement *A* (0.72% Mn)	0.03	0.000_3
2 g of cement *B* (5.0% Fe_2O_3; 0.10% Mn)	5.95	.149
2 g of cement *B*+3 g of cement *A*	5.98	.150
2 g of cement *B* (no $SnCl_2$ added)	1.23	.031
2 g of cement *C* (5.3% Fe_2O_3; 0.10% Mn)	1.70	.043
2 g of cement *C*+3 g of cement *A*	1.71	.043
2 g of cement *C* (no $SnCl_2$ added)	.78	.020
4 g of cement *D* (0.3% Fe_2O_3; 0.01% Mn)	1.10	.014
4 g of cement *D*+3 g of cement *A*	1.18	.015
4 g of cement *D* (no $SnCl_2$ added)	.40	.005
4 g of cement *D*+3 g of cement *A* (no $SnCl_2$ added)	.00	None

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