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RADIOMETRIC METHODS FOR THE DETERMINATION OF
MAGNESIUM AND CALCIUM IN PORTLAND CEMENT

by

Charles T. Brown
James E. Howes, Jr.
Thomas S. Elleman
Charles W. Townley
Duane N. Sunderman

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Charles T. Brown, James E. Howes, Jr., Thomas S. Elleman,
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Radiometric methods of analysis for magnesium and calcium have been developed as part of a program for the U. S. Atomic Energy Commission, Office of Isotopes Development, which are applicable to the determination of these elements in portland cement. Both methods employ, as a precipitant, a standard solution of $(\text{NH}_4)_2\text{HPO}_4$ labeled with phosphorus-32. In the presence of NH_4OH , this reagent precipitates MgNH_4PO_4 or $\text{Ca}_3(\text{PO}_4)_2$ from a solution of magnesium or calcium ions. The reduction in the radioactivity level of the labeled phosphate solution after precipitation serves as a measure of the phosphate reacted and thus a measure of the quantity of magnesium or calcium present. Studies have been made of the effects of reagent concentration, NH_4OH concentration, and other experimental variables. The interference of other elements present normally in portland cement and its raw materials has been determined. The concentration ranges for highest accuracy have been found to be 5 to 15 mg of MgO per 100 ml and 15 to 30 mg of CaO per 50 ml.

INTRODUCTION

The chemical analysis for magnesium and calcium is an important quality-control problem in the portland cement industry. The analytical procedure currently employed in the industry for magnesium, a time-consuming gravimetric method requiring the digestion, filtration, ignition, and weighing of a precipitate, is not well suited to production operations. As part of a research program for the Office of Isotopes Development, United States Atomic Energy Commission, radiometric methods for the determination of MgO and CaO in portland cement were investigated in an effort to both simplify and perform more rapidly these analytical steps.

To make the analytical technique most suitable to the needs of the industry, every effort was made during the program to adapt the radiometric methods to the equipment and procedures conventionally used for quality control in the manufacture of cement. Radiometric analytical methods for magnesium were based on the MgNH_4PO_4 precipitation method specified by the ASTM.⁽¹⁾ The only modification was that the $(\text{NH}_4)_2\text{HPO}_4$ was labeled with phosphorus-32 so that the radioactivity of the solution after the MgNH_4PO_4 precipitation could serve as the indicator of the amount of magnesium reacted.

Although the methods currently employed for the determination of calcium by the cement industry are simple and straightforward, the radiometric technique was developed because of the chemical similarity of calcium and magnesium, and thus the analytical application was an obvious extension of the technique developed for magnesium.

(1) References at end.

A similar application of the radiometric titration technique to the analysis of magnesium was suggested by Langer.(2) However, this method required the addition of precipitant to a basic magnesium solution, and, as pointed out by Willard and Furman, the addition of phosphate ion to an ammonical solution tends to promote the incorporation of foreign ions in the precipitate, yielding high results.(3)

RADIOMETRIC ANALYSIS FOR MAGNESIUM

Experimental Method

Apparatus and Reagents

Radioassay Equipment. The apparatus consists of a dip-tube counter (Type 1B85, Victoreen Instrument Company) surrounded by a glass chamber of about 10 ml in capacity. The solution which is to be radioassayed is drawn into the chamber by means of a 100-ml syringe attached to the chamber side arm. Any precipitate present is prevented from entering the chamber by means of a coarse glass frit at the bottom. The level of the solution in the radioassay chamber is adjusted to a mark on the side arm by clamping the rubber tubing between the side arm and the syringe. A schematic drawing of this equipment is shown in Figure 1.

Counting rates are measured with a Nuclear-Chicago Model-183 scaler. As the solution is always brought to the same level and the sample chamber and tube are fixed in position, the radioassay geometry remains constant. The chamber is flushed with the solution to be radioassayed before each determination, and the tube and chamber are surrounded by a lead shield to minimize background fluctuations.

Magnesium Oxide Solution. The solution is prepared by dissolving 1.000 g of reagent grade MgO in 80 ml of 1:3 HCl, transferring to a 1-liter volumetric flask, and diluting to the mark. The solution is standardized gravimetrically.

Ammonium Monohydrogen Phosphate Solution. In preparing this solution, 4.000 g of reagent grade $(\text{NH}_4)_2\text{HPO}_4$ is dissolved in 100 ml of water, the solution is transferred to a 1-liter volumetric flask, and is diluted to the mark. The solution is standardized gravimetrically. The standard $(\text{NH}_4)_2\text{HPO}_4$ solution is labeled with phosphorus-32 by adding 75 microcuries of phosphorus-32 in the phosphate form. This quantity of phosphorus-32 will give counting rates on the order of 8,000 to 10,000 cpm under the conditions described in the procedure. Since phosphorus-32 has a half-life of 14 days, it is necessary to supplement the tracer at regular intervals if the solution is to be used over a long period of time.

Procedure

The analytical procedure used for the radiometric determination of magnesium was as follows:

A - High-voltage lead.

B - G-M tube connector and socket.

C - Shaped rubber stopper.

D - G-M tube, thin-wall aluminum Type 1B85, Victoreen Instrument Co.

E - Glass solution chamber.

F - Rubber tubing.

G - Coarse glass frit.

H - Rubber tubing to 100 ml syringe.

I - Glass chamber side arm.

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FIGURE 1. RADIOMETRIC TITRATION APPARATUS

To a solution containing approximately 10 mg of MgO, 10 ml of the standard $(\text{NH}_4)_2\text{HPO}_4$ solution was added. The solution was diluted to 100 ml, 3 drops of methyl red indicator were added, and the solution was then cooled in an ice bath to less than 4 C with continuous stirring. The frit of the radioassay assembly was placed in a position such that it was below the solution level when the sample chamber was full. The sample chamber and tube were flushed with the solution, and then refilled and radioassayed. Concentrated NH_4OH was added drop by drop with stirring to the methyl red color change, then 10 ml in excess was added. After 5 min of stirring at a temperature of less than 4 C, the sample chamber and tube were flushed again with the solution, then refilled and the radioassay was performed. In the procedure outlined, the decrease in the radioactivity level is a direct measure of the amount of phosphate reacted to precipitate MgNH_4PO_4 . This measured radioactivity must be corrected for background radiation, and the counting rate after precipitation must be corrected for the dilution due to the addition of NH_4OH . A sample calculation follows:

Net counting rate before precipitation = 7570 cpm

Net counting rate after precipitation = 2040 cpm

Initial quantity of $(\text{NH}_4)_2\text{HPO}_4$ = 40.0 mg

Quantity of $(\text{NH}_4)_2\text{HPO}_4$ after precipitation = $40.0 \times \frac{2040}{7570} = 10.8 \text{ mg}$

$(\text{NH}_4)_2\text{HPO}_4$ reacted = 29.2 mg

Weight of MgO = $29.2 \times \frac{\text{mol. wt. MgO (40.3)}}{\text{mol. wt. } (\text{NH}_4)_2\text{HPO}_4 (132.1)} = 8.93 \text{ mg.}$

Results

Effect of Reagent Concentration

The effect of a large excess of $(\text{NH}_4)_2\text{HPO}_4$ on the analytical results was studied by preparing solutions containing 9.70 mg of MgO and 40, 100, 200, and 300 mg of $(\text{NH}_4)_2\text{HPO}_4$ in 100 ml of solution. In each case the radiometric procedure was performed as described above. The results are summarized in Table 1.

TABLE 1. EFFECT OF EXCESS $(\text{NH}_4)_2\text{HPO}_4$

Determination	$(\text{NH}_4)_2\text{HPO}_4$ Added, mg	Initial Solution Radioassay, cpm	Final Solution Radioassay, cpm	Change in Radioassay, cpm	MgO Found, mg
1	40.0	7,122	1,468	5,654	9.69
2	100	5,058	3,460	1,598	9.63
3	200	9,829	8,375	1,454	9.04
4	300	14,487	13,050	1,437	9.07

When a large excess of $(\text{NH}_4)_2\text{HPO}_4$ was used the initial counting rate was very high, and it remained high after the MgNH_4PO_4 was precipitated. The determination of MgO on the basis of a small difference between two large numbers is inaccurate, as can be seen from the results in Table 1. Small errors in background and dilution corrections have a greater effect on the results when the difference between the initial and final counting rates is only 10 to 20 per cent of the initial activity. An optimum value for this difference would be 50 to 75 per cent of the initial counting rate.

Effect of Excess NH_4OH

The optimum excess of NH_4OH required to assure the complete precipitation of the MgNH_4PO_4 was determined by measuring the solubility of MgNH_4PO_4 in 100 ml of water containing different quantities of NH_4OH . Labeled MgNH_4PO_4 was prepared for the study by precipitation from a solution of 100 ml each of the standard MgO and $(\text{NH}_4)_2\text{HPO}_4$ solutions and 20 ml of concentrated NH_4OH . The precipitate was filtered, washed with dilute NH_4OH , and placed in a 100-ml volume of water and NH_4OH . This mixture was stirred until equilibrium was established, and the solution was radioassayed to determine the fraction of the MgNH_4PO_4 dissolved. The experimental conditions and results are summarized in Table 2. One determination was performed at 25 C to illustrate the necessity of cooling the solution.

The NH_4OH concentration listed in Table 2 represents the excess NH_4OH added after the methyl red color change. At least 5 ml of excess NH_4OH should be added to assure complete precipitation. The addition of 2.5 g of NH_4NO_3 to the solution containing an NH_4OH excess of 10 ml did not appreciably decrease the solubility of the MgNH_4PO_4 .

TABLE 2. EFFECT OF NH_4OH CONCENTRATION AND TEMPERATURE ON THE SOLUBILITY OF MgNH_4PO_4

Temperature, C	Volume of NH_4OH , ml	Radioassay of Solution, cpm	Theoretical 100 Per Cent Solubility, cpm	Solubility, per cent
25	0	477	17,400	2.74
4	0	289	17,400	1.66
4	2	95	17,400	0.55
4	5	66	17,400	0.38
4	10	91	17,400	0.52
2	10 + 2.5 g of NH_4NO_3	82	17,400	0.47

Effect of MgO Concentration

The accuracy of the procedure over a MgO concentration range of 1 to 25 mg per 100 ml was studied by performing MgO determinations on solutions containing nominal MgO concentrations of 1 mg per 100 ml, 5 mg per 100 ml, 10 mg per 100 ml, and 25 mg per 100 ml. The results of these determinations are summarized in Table 3.

The precision and accuracy of the MgO determinations are within 1 per cent except for the nominal MgO concentration of 1 mg per 100 ml. The lower limit for the MgO concentration should be taken as 5 mg per 100 ml for accurate results.

TABLE 3. PRECISION AND ACCURACY OF MgO DETERMINATIONS AS A FUNCTION OF MgO CONCENTRATION

Theoretical	MgO Concentration, mg per 100 ml		Standard Deviation, mg MgO	Absolute Error, per cent
	Experimental	Experimental Average		
0.97	0.90	0.91	± 0.026	6.19
	0.95			
	0.89			
4.85	4.86	4.85	± 0.022	0.00
	4.88			
	4.84			
	4.82			
9.70	9.93(a)	9.72	± 0.030	0.21
	9.68			
	9.70			
	9.72			
	9.78			
24.25	24.51	24.42	± 0.11	0.70
	24.55			
	24.32			
	24.31			

(a) Determination excluded since its deviation from the average of the other four is more than four times their average deviation.

Effect of Interfering Elements

The effect of interfering elements on the radiometric method of analysis for magnesium was investigated. Samples containing 10 mg of MgO and 10 mg of a specific contaminant in 100 ml of solution were run under the normal experimental conditions. The following contaminants were used: $\text{Al}_2(\text{SO}_4)_3$, CaCl_2 , $\text{Fe}(\text{NO}_3)_3$, MnSO_4 , NaCl , and KCl . Calcium and manganese were the only elements found to interfere. The MgO results were 17 per cent high with the calcium present and 14 per cent high with the manganese present. Two-milligram quantities of MnSO_4 and CaCl_2 per 10 mg of MgO in 100 ml of solution did not interfere, while 4-mg quantities of these same two compounds per 10 mg of MgO yielded results 3 per cent high in the case of manganese and 8 per cent high in the case of calcium.

In a typical cement sample only 0.25 mg of Mn_2O_3 will be present for each 10 mg of MgO; so interference due to manganese is no problem. However, CaO is present in a ratio of about 265 mg of CaO to 10 mg of MgO. In this latter case a separation must be effected before the magnesium is determined.

RADIOMETRIC ANALYSIS FOR CALCIUM

Experimental Method

Apparatus and Reagents

Radioassay Equipment. The apparatus employed in the calcium analysis is the same as that described for use in the magnesium analysis. The same sample chamber, dip counter, and scaling equipment are used.

Calcium Nitrate Solution. The solution is prepared by dissolving 5.90 g of reagent grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 100 ml of water, transferring to a 1-liter volumetric flask, and diluting to the mark. The solution is standardized gravimetrically.

Ammonium Monohydrogen Phosphate Solution. The $(\text{NH}_4)_2\text{HPO}_4$ solution is prepared in the same manner as described for the magnesium procedure, except only 30 microcuries of phosphorus-32 is used to label the phosphate. Under the conditions described for the calcium determination this quantity of phosphorus-32 will give counting rates on the order of 8,000 to 10,000 cpm.

Procedure

The analytical procedure used for the radiometric determination of calcium was as follows:

Ten milliliters of the standard $(\text{NH}_4)_2\text{HPO}_4$ solution was diluted to 40 ml, the sample chamber and counting tube were flushed with this solution, the chamber was refilled, and the solution was radioassayed. Approximately 15 mg of CaO and 2 to 5 drops of concentrated NH_4OH were added. (All calculations of calcium concentration have been made on the basis of CaO.) After 15 min of stirring at room temperature, the sample chamber and tube were flushed again with the solution, refilled, and radioassayed.

Under this procedure, the fraction of the radioactivity remaining in solution after the precipitation of $\text{Ca}_3(\text{PO}_4)_2$ represents the fraction of the $(\text{NH}_4)_2\text{HPO}_4$ unreacted. The counting rates must be corrected for background radiation, and the counting rate after precipitation must be corrected for dilution due to the addition of the CaO solution. A sample calculation follows:

Net counting rate before precipitation = 8234 cpm

Net counting rate after precipitation = 2795 cpm

Initial quantity of $(\text{NH}_4)_2\text{HPO}_4$ = 40.00 mg

Quantity of $(\text{NH}_4)_2\text{HPO}_4$ after precipitation = $40.00 \times \frac{2795}{8234} = 13.57 \text{ mg}$

$(\text{NH}_4)_2\text{HPO}_4$ reacted = 26.43 mg

Weight of CaO = $26.43 \times \frac{3 \times \text{mol. wt. CaO (56.08)}}{2 \times \text{mol. wt. } (\text{NH}_4)_2\text{HPO}_4 (132.1)} = 16.83 \text{ mg.}$

The difference between the initial and final counting rates should be 50 to 75 per cent of the initial counting rate for optimum accuracy in the results; so a sufficient excess of $(\text{NH}_4)_2\text{HPO}_4$ should be used to give this difference.

Results

Effect of Stirring Time and NH_4OH Concentration

Studies were performed to determine the optimum stirring time and NH_4OH concentration required to yield accurate results in the CaO determination. The quantity of concentrated NH_4OH added to the solution was varied from 0 to 1.0 ml, and the analysis was performed as described in the procedure. The results of these determinations are given in Table 4. Included also in the table are the results of determinations made with stirring times of 1, 5, 10, 15, and 20 min with a constant 0.1-ml volume of concentrated NH_4OH . A 16.66-mg quantity of CaO was used in each analysis.

TABLE 4. EFFECT OF NH_4OH CONCENTRATION AND STIRRING TIME ON THE CaO DETERMINATION

Volume of NH_4OH , ml	Stirring Time, min	CaO Found, mg	Absolute Error, per cent
0	15	12.19	26.8
0.05	15	16.29	2.3
0.1	1	16.95	1.7
	5	16.90	1.4
	10	16.95	1.7
	15	16.70	0.2
	20	16.66	0.0
0.2	15	16.55	0.7
0.5	15	16.80	0.8
1.0	15	16.40	1.6

The absolute error in the analysis of CaO was found to be as high as 26.8 per cent when no NH_4OH was added, but only a few drops of concentrated NH_4OH are necessary to reduce this error to less than 1 per cent. The NH_4OH is apparently necessary to shift the phosphate equilibrium in solution toward the PO_4^{-3} ion and to thus obtain complete precipitation of the calcium as $\text{Ca}_3(\text{PO}_4)_2$. The best results were achieved with 0.1 to 0.2 ml (2 to 5 drops) of concentrated NH_4OH . A stirring time of at least 15 min was found necessary to attain equilibrium between the solution and precipitate and to thus obtain accurate results.

Effect of CaO Concentration

The accuracy of the radiometric procedure was studied over a CaO concentration range of 3 to 33 mg per 50 ml. Analyses were performed under the same experimental conditions and with a constant percentage excess of $(\text{NH}_4)_2\text{HPO}_4$. The CaO concentrations studied were 3.33, 8.33, 10.00, 13.32, 16.66, and 33.32 mg per 50 ml. The results of these determinations are given in Table 5.

TABLE 5. PRECISION AND ACCURACY OF CaO DETERMINATIONS AS A FUNCTION OF CaO CONCENTRATION

Theoretical	CaO Concentration, mg per 50 ml		Standard Deviation, mg CaO	Absolute Error, per cent
	Experimental	Experimental Average		
3.33	2.94	2.88	± 0.08	13.5
	2.83			
8.33	7.86	7.92	± 0.08	4.9
	7.98			
10.00	9.31	9.70	± 0.34	3.6
	9.91			
	9.89			
13.32	13.36	13.28	± 0.10	0.3
	13.30			
	13.17			
16.66	16.63	16.67	± 0.08	0.06
	16.60			
	16.81			
	16.80			
	16.63			
	16.60			
	16.67			
33.32	33.26	33.52	± 0.35	0.6
	33.92			
	33.39			

The precision and accuracy of the CaO determinations were within 1 per cent for CaO concentrations higher than 13 mg per 50 ml. The lower limits for the CaO concentration should be taken as 15 mg per 50 ml for accurate results.

Effect of Interfering Elements

The effect of interfering elements on the radiometric method of calcium analysis was investigated. A CaO concentration of 16.66 mg per 50 ml was used, and other experimental conditions were the same as those described in the procedure. In each determination the concentration of contaminant was maintained at approximately the same order of magnitude as would be expected in a sample of portland cement. The following contaminants were used: $\text{Al}(\text{NO}_3)_3$, MgO , $\text{Fe}(\text{NO}_3)_3$, MnSO_4 , and K_2SO_4 . The elements found to interfere were aluminum, iron, and magnesium. The CaO results were 6 per cent high with 1 mg of iron present, 13 per cent high with 1 mg of magnesium, and 9 per cent high with 1 mg of aluminum.

Manganese did not interfere even at a concentration 20 times that found in a typical cement sample. The interference of aluminum, iron, and magnesium is a problem, however, and the calcium must be separated from these elements before an analysis is performed.

DISCUSSION

The accuracy and precision of the radiometric procedures developed for the determination of magnesium and calcium in portland cement are within 1 per cent. For these analytical methods, the recommended concentration ranges are 5 to 15 mg of MgO per 100 ml and 15 to 30 mg of CaO per 50 ml.

The primary advantages of the radiometric methods are speed and simplicity. Excluding the necessary separations of interfering ions, a magnesium or calcium determination may be made in less than 1 hr. There is no need for close pH control or the preparation and storage of a large number of standard solutions. The apparatus is simple and easy to maintain, and a laboratory technician with analytical experience could easily adapt himself to radioassay techniques.

The only other magnesium or calcium method that compares to the radiometric method in simplicity and speed is the EDTA titration with an Eriochrome Black T indicator.⁽⁴⁾ Here, as in most EDTA titrations, pH is very important and properly controlled buffering must be employed. Special precautions must be taken to mask interfering elements, and complexing agents must be added to prevent the precipitation of metal hydroxides of such elements as aluminum and iron, since the titrations are carried out at pH 10.

REFERENCES

- (1) ASTM Standards on Cement, American Society for Testing Materials, Philadelphia (1955).
- (2) Langer, A. "Radiometric Titration of Magnesium", J. Phys. Chem., 45, 639 (1941).

- (3) Willard, H. H., and Furman, N. H., Elementary Quantitative Analysis, 3rd edition, D. Van Nostrand Company, New York (1950), p 331.
- (4) Diehl, H., Goetz, C. A., and Hach, C. C., "The Versenate Titration for Total Hardness", J. Am. Water Works Assoc., 42, 40 (1950).

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