Extraction of Free Lime in Portland Cement and Clinker By Ethylene Glycol

Preface

The authors of this ethylene glycol extraction method evaluated the effects of extraction time, extraction temperature, and sample fineness on the results. The method extracts the free lime with ethylene glycol and then titrates the resulting extract with 0.05 *N* hydrochloric acid. Their basic recommendations are that normal cement fineness (3000 Blaine or higher) is adequate, a temperature range of 80 to 100°C is suitable, as is an extraction time of up to 30 min with a preferred range of 5 to 10 min.

The unique feature of this method is that the glycol is preheated to the desired temperature before adding it to the flask containing the sample. Filtration and washing is done hot as, apparently, is the titration. The titration will be at a temperature below extraction temperature because of the addition of deionized water, presumably at room temperature, immediately before titration.

Editor

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STP985-EB/May 1988

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ABSTRACT

Free lime in portland cement and clinker has been determined by extraction with hot ethylene glycol. Our determinations show that times of 5-10 minutes and temperatures of 80-100°C are adequate. This method is as accurate as the ASTM method and has the distinct advantage of simplicity and rapidity.

Introduction

Uncombined calcium oxide or "free lime" usually occurs in small amounts (1-2%) in portland cement clinker. The free lime value generally indicates the completeness of the clinkering reactions and the quality of the burning practices. A high free lime clinker usually is due either to inhomogeneity and coarseness of the cement raw mix or to improper burning and cooling conditions in the kiln. For this reason, determination of free lime in portland cement clinker, together with some other physical characteristics, provide a convenient and useful method for assessing clinker quality.

The most widely used methods for the determination of free CaO in cement and cement clinker are based on its extraction in an organic solvent. The ASTM recommended methods are based on the work of Lerch and Bogue (1), which uses the solubility of CaO in a glycerol-absolute alcohol solvent, and that of Franke (2,3), which uses CaO dissolution in acetoacetic ester-isobutanol solvent. However, these methods are tedious and time-consuming.

A simple and relatively rapid method, described by Schlapfer and Bukowski (4,5), is based on the extraction of CaO by ethylene glycol heated to 60-70°C. This method gives results in reasonable agreement with those obtained by the glycerol-alcohol method and reduces the extraction time to about half an hour. Recently, Wang et al (6) used the same method to show that ethylene glycol at 80-85°C reduced extraction time to less than 5 minutes and still provided results that agreed well with those obtained by other methods. In view of this information, we have evaluated the ethylene glycol procedure in some detail as a function of time, solvent temperature, and cement clinker fineness.

It is not our purpose to discuss the chemistry of CaO dissolution in organic solvents. This subject has been discussed in detail by Swenson and Thorvaldsen (7) and Longuet et al (8). The present work stresses the experimental aspects of CaO extraction by ethylene glycol with the objective of establishing a rapid and reliable method for determination of free lime in cement and cement clinker for possible application to quality control problems in cement production.

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Experimental

Equipment

Burette (0.5-ml subdivision)
Erlenmeyer flask with rubber stopper (250 ml)
Hot plate with stirrer
Thermometer
Teflon-coated magnetic stirring bar
Vacuum filtering flask (250 ml)
Gooch crucible with holder
Glass fiber filter

Reagents

Anhydrous ethylene glycol
0.05 N hydrochloric acid (standardized against 0.05 N sodium hydroxide which is standardized with potassium acid phthalate)
Phenolphthalein indicator (1% solution in ethanol)

Materials

Several cement and clinker samples were used for this evaluation. The cement samples were supplied by the Cement and Concrete Research Laboratory of the National Bureau of Standards as part of the CCRL test. The clinkers were obtained from Martin Marietta cement plants.

Procedure

A sample (usually 1 g) of ground cement or clinker was accurately weighed into a clean, dry, 250-ml Erlenmayer flask. It is important that the sample does not come in contact with moisture before extraction. About 50 ml of ethylene glycol, heated to the desired temperature (50-100°C), were added to the flask and stirred for the desired amount of time (5 min to 3 hr) using a magnetic stirrer on a hot plate. The temperature was maintained at the desired value and checked frequently. The hot suspension was filtered under suction through a glass fiber filter fitted onto a Gooch crucible and the clean filtrate was collected in a 250-ml vacuum filter flask. The filter should be wetted with ethylene glycol before filtering. The Erlenmeyer flask was rinsed at least twice with about 10-15 ml hot ethylene glycol which, after filtering, was added to the original filtrate.

About 25 ml of deionized water and 1 ml of phenolphthalein indicator solution were added to the filtrate and then titrated to a colorless endpoint with 0.05 N HCl. Addition of water to the ethylene glycol filtrate facilitates the endpoint determination. Free lime is calculated as follows:

$$\% \text{ Free CaO} = \frac{\text{ml HCl} \times \text{normality of HCl}}{10 \times \text{sample weight}} \times 28$$

For comparison the free lime was also determined by the ASTM method using the glycerol-ethanol solvent (9).

Results

Comparison of Methods

The results of the free-lime determination by the ethylene glycol and ASTM methods are given in Table 1.

TABLE 1

Comparison of Methods

Sample*	Free CaO (%) Ethylene Glycol	ASTM
CCRL #53	0.61	0.63
CCRL #55	0.81	0.83
CCRL #57	0.56	0.57
CCRL #59	0.77	0.75
CCRL #60	0.54	0.53
CCRL #61	1.18	1.25
CCRL #62	1.36	1.36

*As-received cements (Blaine: approx. 3000 cm^2/g) extracted for 5 min at 80-85°C. Excellent agreement is shown between the two methods.

Effect of Extraction Time

To determine the effect of extraction time on CaO dissolution, extractions for periods of time ranging from 5 minutes to 3 hours were done. The results are shown in Table 2.

TABLE 2

CaO Dissolution in Ethylene Glycol with Time

Sample*	Extraction Time	Free CaO (%)
CCRL #53	5 min	0.61
Free CaO by	10 min	0.65
ASTM Method:	30 min	0.69
0.63%	1 hr	0.81
	2 hr	0.90
	3 hr	0.98
CCRL #61	5 min	1.18
Free CaO by	10 min	1.18
ASTM Method:	30 min	1.27
1.25%	1 hr	1.51
	2 hr	1.55
	3 hr	1.54

*As-received cements (Blaine: 3000 cm^2/g) extracted at 80-85°C.

With time, more CaO is extracted. This result could be due to the dissolution of other calcium-containing clinker minerals after prolonged extraction, e.g. calcium silicates and aluminates, and gypsum. However, times up to 30 minutes do not seem critical.

Effect of Extraction Temperature

The temperature of the ethylene glycol was varied from 50°C to 100°C to determine the effect of solvent temperature on CaO dissolution. The results are given in Table 3.

TABLE 3

Effect of Ethylene Glycol Temperature on CaO Dissolution

Sample*	Temperature of Ethylene Glycol (°C)	Free CaO (%)
CCRL #60	50	0.41
Free CaO by	60	0.45
ASTM Method:	80	0.54
0.53%	100	0.54
CCRL #61	50	1.01
Free CaO by	60	1.13
ASTM Method:	80	1.18
1.25%	100	1.17

*As-received cement (Blaine: approx. 3000 cm^2/g) extracted for 5 min.

With increase in solvent temperature, the CaO dissolution seems to increase, reaching a near constant value at about 80°C. A temperature range of 80-100°C seems suitable for extraction.

Effect of Sample Fineness

Clinkers from two different cement plants were ground to two different finenesses to assess the effect of sample fineness on the CaO dissolution. The results are given in Table 4.

TABLE 4

Effect of Sample Fineness on CaO Extraction

Sample*	Fineness (cm^2/g Blaine)	Free CaO (%) Ethylene Glycol	ASTM
Clinker A	2950	1.89	1.96
	5930	1.98	2.02
Clinker B	3110	1.57	1.58
	6100	1.46	1.38

*Clinker extracted for 5 min at 80-85°C

Increase in clinker fineness above ~3000 cm^2/g Blaine does not seem to show any effect on free CaO extraction within experimental error.

Conclusions

Our work shows that hot ethylene glycol extraction offers a very rapid and convenient method for determination of free CaO in fresh cement and clinkers. Extraction times of 5-10 minutes and temperatures of 80-100°C are quite adequate for this determination. Although this method is as good as the ASTM method for accuracy, its simplicity and rapidity give it a distinct advantage. It is most suitable for quality control during cement clinker production, where time can be an important factor. It is not suitable for cement and clinker stored for long periods of time or in contact with moisture since ethylene glycol would dissolve both CaO and $Ca(OH)_2$. However, the ASTM method suffers from the same shortcomings. In our opinion, the method deserves serious consideration by the ASTM committee on portland cement analysis as an alternate method for free-lime determination in portland cement and clinker.

Acknowledgment

This work was supported by the National Science Foundation through grant no. CME-79-02665. Thanks are also due to A. Kolan for help with this work.

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APPENDIX

This is an independent evaluation of the preceding method. It verifies agreement of the method with the classical glycerin-ethanol method that used to be in ASTM C 114.

Editor

Free Lime Determination by Ethylene Glycol Extraction By N. T. Flores[2]

Two cement samples from R. Pyrdeck were tested for free CaO using the ethylene glycol method as described in the previous paper, as well as the British method (Table 1). The value by the ASTM method was from the Control Laboratory. The extraction time used was 10 min at 80 to 90°C. The data shows that the ethylene glycol value is closer to the value by ASTM as compared to the British method. The method is very easy, reproducible, and not time consuming.

TABLE 1—*Free lime determination (British and ASTM methods versus ethylene glycol method).*

	%Free CaO		
Method	ASTM	Ethylene Glycol	British
Sample 76416	1.53	1-1.56	1.80
		2-1.58	1.82
		3-1.59	
		4-1.59	
		5-1.61	
Sample 76426	0.32	1-0.36	0.51
		2-0.36	0.51

REQUIREMENTS: 0.0496 *N* HCl; ethylene glycol (Anhydrous); phenolpthalein—0.5% in anhydrous and neutralized to faint pink with NaOH dissolved in anhydrous alcohol.

[2] California Portland Cement Company, Colton, CA.