Effect of pH on EDTA Method of Measuring Calcium

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Abstract

The purpose of this study was to evaluate the interference of pH on the EDTA titrimetric method of measuring calcium. Solutions with various calcium ion concentrations were prepared by using $CaCl_2$. EDTA test was conducted with varying the pH from -0.8 to 12. Sulfuric and hydrochloric acids were used to lower the pH. Preliminary results indicate that the EDTA method is reliable in the pH range of 0 to 12 to measure calcium concentrations from 1 to 1000 ppm.

1. Introduction

Concrete is one of the most widely used material in the construction of wastewater collection and treatment systems, chemical and petrochemical plants and pipelines. Concrete corrosion takes place because of the biological and/or chemical attack of the material. In the sewer infrastructure sulfur reducing bacteria (SRB) reduce the sulfide and produce hydrogen sulfide, H_2S, gas that is oxidized to sulfuric acid by the Thiobacillus species which are sulfur oxidizing bacteria. The sulfuric acid then reacts with the cement binder in concrete to form expansive end products by affecting the integrity of concrete. Calcium is leached out of the concrete when concrete corrosion is underway. Hence measuring the calcium can be the first step in monitoring the concrete corrosion.

2. Objective

Since various pH solutions are used in studying the corrosion of concrete, it is important to evaluate the interference of pH on the EDTA method. The objectives of this study are (1) to determine the effect of pH on the EDTA method and (2) to determine the minimum volume of sample required for titration.

2.1 AWWA EDTA Titrimetric Method

a. *Principle*: When EDTA (ethylenediaminetetracetic acid or its salts) is added to water containing both calcium and magnesium, it combines first with the calcium. Calcium can be determined directly, with EDTA, when the pH is made sufficiently high that the magnesium is largely precipitated as the hydroxide and an indicator is used that combines with calcium only. Several indicators give a color change when all of the calcium has been complexed by EDTA between a pH of 12 to 13.

b. *Interference*: Under conditions of this test, the following concentrations of ions cause no interference with the calcium hardness determination: Cu^{2+}, 2 mg/L; Fe^{2+}, 20 mg/L; Fe^{3+}, 20 mg/L;

Mn^{2+}, 10 mg/L; Zn^{2+}, 5 mg/L ;Pb^{2+}, 5 mg/L; Al^{3+}, 5 mg/L ; and Sn^{4+}, 5 mg/L. Orthophosphate precipitates calcium at the pH of the test. Strontium and barium give a positive interference and alkalinity in excess of 300 mg/L may cause an indistinct end point in hard waters.

2.2 Materials

a. *Base:* Sodium hydroxide, NaOH, 1 N, was used to increase the pH of the solution.

b. *Acid*: Concentrated sulfuric acid and hydrochloric acid were used.

c. *Indicator:* Murexide (ammonium purpurate) was used as the indicator in detecting the calcium end point. This indicator color changes from pink to purple at the end point. Facilitate end-point recognition by preparing a color comparison blank containing 2.0 mL NaOH solution, 0.2 g solid indicator mixture, and sufficient standard EDTA titrant (0.05 to 0.10 mL) to produce an unchanging color.

d. *Titrant:* Prepared standard EDTA titrant (0.01 M) as described in the EDTA total hardness method (AWWA Section 2340). Standard EDTA titrant, 0.01 M, is equivalent to 400.8 �g Ca/1.00 mL.

3. Testing Program

All tests were done at room temperature.

a. Sample preparation: 50 mL samples were mainly used but 10 through 40 mL samples were also used to evaluate the sensibility of test.

b. Titration: 0.1 to 490 mL NaOH solution were added to increase the pH of 12.5 to 13. And 0.1 to 0.2 g indicator mixture was added.

c. EDTA titrant was added slowly, with continuous stirring to the proper end point. This procedure included checking end point by adding I to 2 drops of titrant in excess to make certain that no further color change occurred.

d. Calculation of Ca^{2+}: {EDTA(mL) X 400.8(μg Ca/1.00 mL)}/ volume of solution(mL) = mgCa/L

4. Results and Discussion

Preliminary results indicate that EDTA test could be used to measure Ca^{2+} in the pH range of 0 to 12. No interference was observed with sulfuric and hydrochloric acids in this range of pH when the calcium concentrations were varied from 1 to 1000 ppm. Varying the sample size from 10 mL to 50 mL had only a slight effect the Ca^{2+} measurement.

When the $[Ca^{2+}][SO_4]$ ionic product is greater than the Ksp of $CaSO_4$, the calcium ions would be precipitated. Hence with the 30 % sulfuric acid solution (pH = -0.8) lower than expected calcium was measured. Further studies to confirm this observation are underway.

5. CIGMAT standard

CIGMAT CH 1-99 Standard outlines the testing procedure used in this study.

6. Conclusions

Based on the experimental results and initial analysis following observations are advanced.

a. EDTA method could be used to measure calcium concentrations between 1 to 1000 ppm in the pH range of 0 to 12.

b. Sample volume from 10 to 50 mL didn't affect the Ca^{2+} measurement.

7. Acknowledgment

This work was supported by the Center for Innovative Grouting Materials and Technology under grants from the City of Houston, National Science Foundation (CMS-9526094) and various industries.

8. References

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If you have any questions, please contact **Dr. C.Vipulanandan**