



Method Validation

Examination of Environmental Error Contributing to Imprecise and Inaccurate Data on the CMA Test.

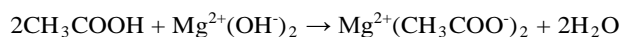


J.K. Ladet

Over the past months, CMA results have been skewed to indicate longer reaction times. Since these higher results were observed across all manufacturing facilities, the materials at any one facility being faulty were immediately ruled out. The more obvious route was to look at error in and around the laboratory. Several aspects of the procedure were examined and ruled out as a significant contributor of error. These were the acetic acid being contaminated, the phenolphthalein being out of specification, the blender speed contributing significant energy to the reaction, and the overall volume of water in the reaction. It was found that the major contributing factors were temperature and water quality.

Introduction

The CMA procedure outlines a typical acid/base reaction that produces water and a salt. The reaction takes magnesium hydroxide and acetic acid and produces water and magnesium acetate.



The acetic acid reactant was replaced with a fresh container of acid. The pipet tip used during the slurry transfer was rinsed repeatedly to ensure a more quantitative transfer. The phenolphthalein indicator solution was replaced with fresh solution and titrated to its endpoint. The endpoint was recorded to be at a pH of 8.2, which is in specification. The water used in the reaction was changed from tap to distilled and the volume increased up to double the amount specified. The blender speed was evaluated at several different settings. The temperatures of the water, acetic acid, and environment were monitored.

The variables were adjusted one at a time, with all others being held constant. The data was collected via VWR SB20 pH probe and at the end of the experiment, via Vernier Labpro with pH probe.

Results and discussion



The result of changing the acetic acid and the phenolphthalein indicator made a negligible effect on the results and was eliminated as being suspect.

Altering the volume of water also produced negligible results. The volume of the water was increased to double its initial quantity in order to ascertain if adding hot or cold water to adjust the water temperature in the vessel gave imprecise results. It was observed that with double the initial volume of water (600 mL), that the results varied within the data sets recorded as with 300 mL of water. This was a valuable observation to allow for greater temperature control within the reaction vessel.

Distilled water made a noticeable decrease in the overall reaction time when compared to tap water. The improvement of time was not largely substantial but when coupled with rinsing the pipet tip, made up to a 25 second improvement to Martin Marietta products.

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	R&D		
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The largest contributor to the reaction rate was found to be temperature. Temperature of the water, acetic acid, and the laboratory were the primary contributing factors. As can be seen on figure 1 and tabulated at points of interest on table 1, when the reaction was run at temperatures that varied by 12°F, time was affected significantly. This follows an old rule of thumb in inorganic reactions that states that for every 10°C change in temperature, a change of 2x in reaction time will be observed. While just a general rule of thumb (thumbtimes it's true, thumbtimes it's not), it loosely fits this particular reaction. It can be observed on figure 2 that even when all environmental variables are controlled with care, that being $\pm 1^\circ\text{F}$ can still slightly curve the results and when compared to a faster reaction such as that illustrated on figure 3, can make a noticeable percent difference.

Temp(F)	65°	77°	77°	89°	90°
Time(s)	351	273	249	177	157
pH	7.80	7.80	7.80	7.80	7.80
Time(s)	373	320	278	200	178
pH	8.20	8.20	8.20	8.20	8.20

Table 1(data points of interest for figure 1)

A large portion of error can also be attributed as subjective, being that the colour indicator gives a very gradual and subtle change to pink at a pH of approximately 7.8 on Martin Marietta and Tetra products and a sudden change to red at a pH of 8.2 on Aspers, Gabbs, and Superior products. This gives quite a large opportunity to introduce significant error by the observer.

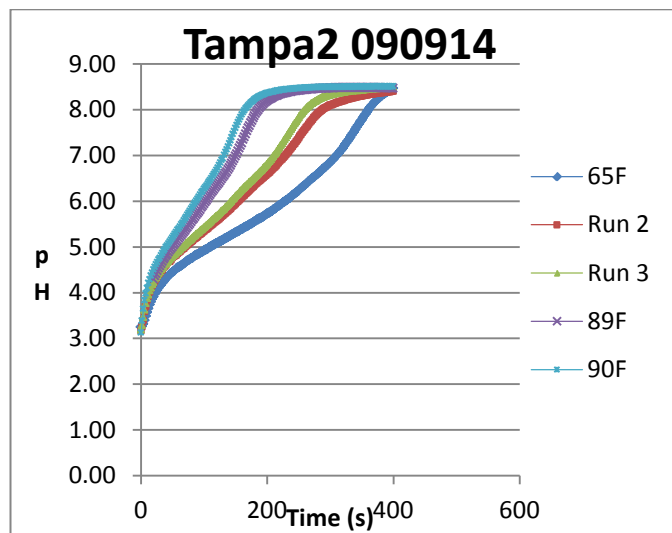


Figure 1 (illustration of effects of temperature)

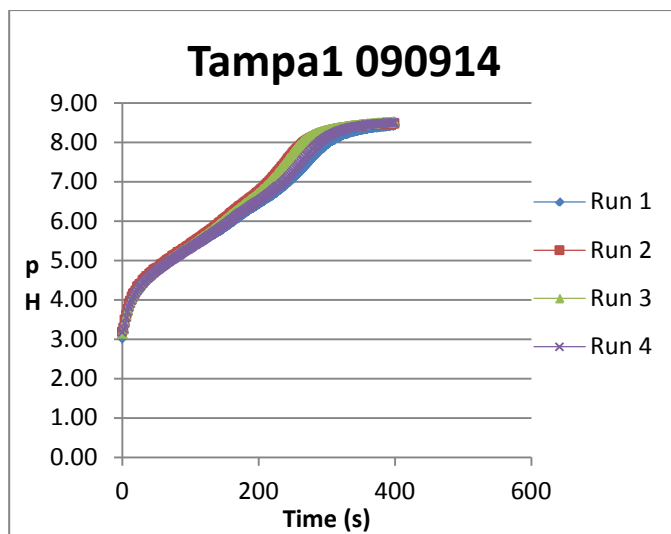


Figure 2(environmental temperature held at 77°F)

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3. APPARATUS

- 3.1 One-quart Waring blender jar and jar holder for a Waring commercial blender or similar model.
- 3.2 Analytical balance, 0.002g readability.
- 3.3 Stop watch.
- 3.4 Thermometer, 0-230°F.
- 3.5 Graduates: 100, 500ml.

4. METHOD

- 4.1 If the slurry solids content and density (lb/gal) are known, the volume (V, ml) of slurry to be added equivalent of 7.2 g solids can be calculated using the following formula: $V = 60.50/D$, where D= density of the slurry in lb/gal.
- 4.2 Measure 300ml of distilled at $77^{\circ}\text{F} \pm 1^{\circ}\text{F}$ into the blender container.
- 4.3 Add the 7.20 gram sample to the water in the blender and add 8-10 drops phenolphthalein indicator.
- 4.4 Mix for approximately 10 seconds at highest speed setting.
- 4.5 Quickly add by graduate 100ml of 1.0N acetic acid at $77^{\circ}\text{F} \pm 1^{\circ}\text{F}$ to the sample slurry while continuing to mix.
- 4.6 Start the stop watch as the acid is being added. Allow the acid to drain from the graduate for about 5 seconds to ensure a more quantitative transfer.
- 4.7 Record the time in seconds for the development of the red phenolphthalein color. If the red color has not developed in the first 45 seconds, add 4 more drops of phenolphthalein indicator and repeat every 30 seconds until end point. This will ensure a concise color change.

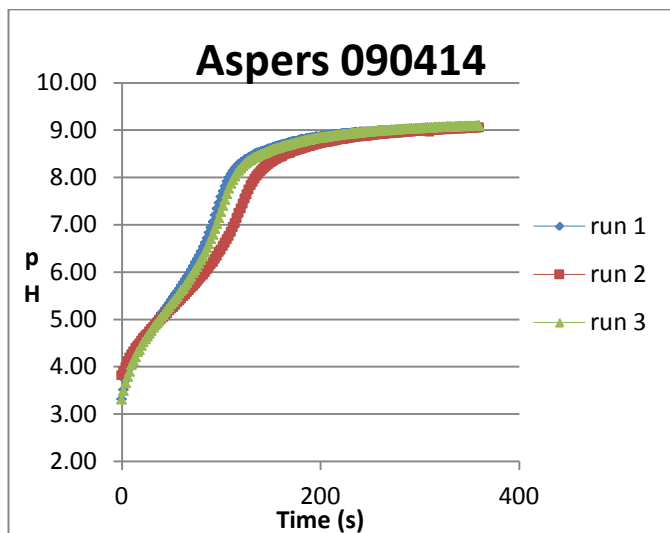


Figure 3 (Environmental temperature held at 77° F)

Experimental

The following procedure is the TP-227 CMA SOP that is in use.



1. SCOPE

- 1.1 This method of test is intended for determining the reactivity of dry $\text{Mg}(\text{OH})_2$ powder by acid neutralization.

2. REAGENTS

- 2.1 Acetic Acid, 1.0N
- 2.2 Phenolphthalein Indicator (See TP-13).

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5. REPORT

- 5.1 The Caustic Magnesia Activity Time is the elapsed time, in seconds, from the acid addition to the development of a red color.

Conclusions

The data collected from the manipulation of controllable variables would indicate that error can be minimized through careful temperature control, implementing a standard pH to utilize as the endpoint, and performing the experiment in triplicate and averaging the results. Because the reaction is open to the environment, temperature can be maintained by keeping the lab within a reasonable tolerance to the 77°F required by the SOP. This will do little to influence temperature increase due to the reaction, but will eliminate inconsistent climbs. Implementing a pH endpoint will remove researcher error due to independent objectivity. A pH of either 7.8 or 8.2 would be consistent with past observed results. When the experiment is performed in triplicate, deviations from the mean can be minimized through averaging or outlier rejection. If all of the controllable independent variables are addressed, the data sets will be both precise and accurate.

Approval Signatures/Dates: (all applicable parties)				
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