

IN-PLANT USE OF AN ATOMIC ABSORPTION SPECTROPHOTOMETER TO MONITOR CALCIUM IN CIP CLEANING SOLUTIONS

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ABSTRACT

An atomic absorption spectrophotometer was installed in an automated CIP dairy plant cleaning system to detect the amount of calcium in the cleaning solution as it flowed from milk-processing equipment and storage tanks during each phase of the cleaning cycle. A major portion of the milk residue was removed from the equipment during the first half of the rinse phase. Most of the residue remaining after rinsing was removed during the first 2 min of the alkaline cleaning phase.

In a previous study (1) in which an atomic absorption spectrophotometer was used for measurements, it was shown that major ingredients of commercial detergents do not, for practical purposes, interfere with measurements of calcium in cleaning solutions. The feasibility of quantitating the amount of milk (based on calcium detected) flowing in a simulated CIP cleaning system has been shown (2). The literature (3, 4, 5) indicated that calcium is present in most residue on milk contact surfaces. The objective of this research was to determine whether an atomic absorption spectrophotometer performs satisfactorily for on-line monitoring of milk in cleaning solutions during different phases of the cleaning cycle.

MATERIALS AND METHODS

Materials

A standard stock solution with 2000 mg calcium/l was prepared by dissolving 4.9945 g of dried CaCO₃ (analytical

grade) in 10 ml of 6 N HCl and diluting with distilled water to one liter. Standard solutions for quantitating amounts of calcium in cleaning solutions were prepared by adding stock solution to water used in prerinse and postrinse phases and to solutions of the alkaline (1.0% Klenzade HC-41; Economics Laboratory, Inc., St. Paul, Minnesota) and acid (0.1% Klenzade AC-3) detergents.

An atomic absorption spectrophotometer (Varian Techtron, Model 1000, equipped with a calcium hollow cathode lamp) with a dual-channel strip chart recorder was installed in the dairy plant at the University of Missouri-Columbia to measure the amount of calcium in the cleaning solution as it flowed from the processing equipment. Acetylene was the fuel gas, and nitrous-oxide was the support gas. The lamp current was 6 ma. The dimensions of the nitrous-oxide burner were 6.324 cm × 0.457 mm. The slit width was 0.5 nm.

To remove a small portion of the cleaning solution, a 1/8-inch tube, directed upstream, was installed in the return line. A stainless steel needle valve was attached to the tube to regulate the flow of solution. Solution flowed from the needle valve to a stainless steel channel assembly (Fig. 1). Air bubbles were removed as the thin film of solution flowed between the silicon rubber dikes. The solution was drawn through the aspirator tube into the spectrophotometer.

Methods

Alkaline or acid detergent was added to water in the solution supply tanks to give desired concentrations, and solutions were heated to the desired temperature.

Before each phase of the tank-cleaning cycle or processing-line cleaning cycle was started, standard solutions of calcium that were appropriate for that phase were aspirated into the spectrophotometer, and instrument responses were recorded. These peak responses were used to prepare a stand-

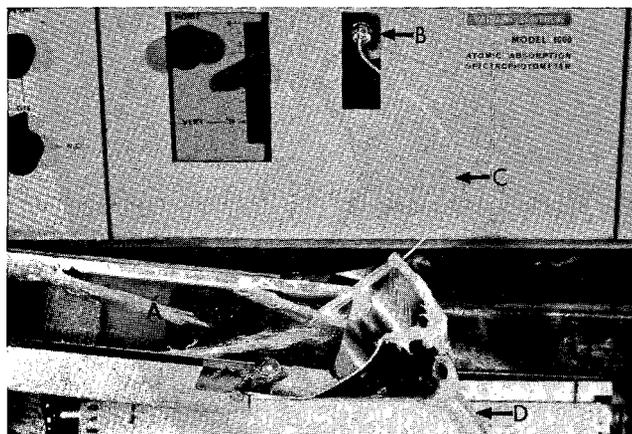


Figure 1. Stainless steel channel assembly with plastic tubing used to aspirate solution during in-plant studies. A—stainless steel channel with silicon rubber dikes, B—nebulizer, C—aspirator tube, and D—solution drain tube.

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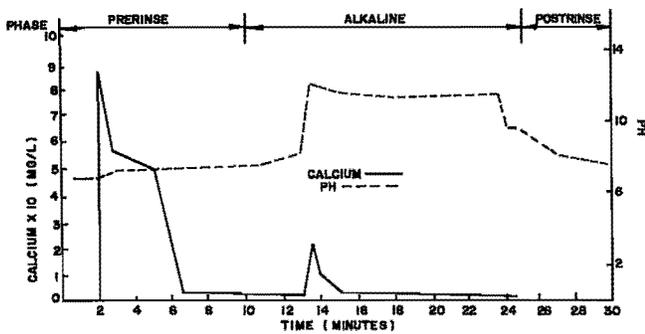


Figure 2. A plot of the calcium content and pH of the cleaning solution versus time as the solution flowed from a 2,500-gal milk storage tank during the cleaning cycle.

ard curve to quantitate the amount of calcium for that phase. Next, the automated CIP system was started, and solution was pumped to the equipment to be cleaned. A CIP return pump forced the solution back to the CIP tank where it was diverted to the drain.

A small portion of the solution was diverted to the spectrophotometer, via the channel assembly, as it flowed back to the CIP tank. The cleaning solution flowed as a thin layer in the channel to remove small, entrained air bubbles. At the end of the respective phases, standard solutions were again aspirated into the instrument for 10 sec to verify standard readings taken at the beginning of the test.

Samples of the solutions were collected intermittently during each phase. These samples were analyzed by aspirating them into the spectrophotometer at the end of the phase to verify readings obtained from the continuous analyses.

RESULTS AND DISCUSSION

Tank cleaning cycle

Figure 2 is a plot showing calcium content of the cleaning solution being removed from a 2,500-gal, raw milk storage tank during the three phases of the cleaning cycle (pre-rinse, alkaline, and post-rinse). After the cleaning cycle was started, approximately 2 min were required for the CIP return pump to remove the rinse solution from the milk storage tank and return it to the CIP tank for analysis by the spectrophotometer. This accounts for the initial delay in recording increased calcium content of rinse water.

The CIP pump was started and stopped three times during the pre-rinse phase to give three burst rinses. Burst rinses removed loosely held milk residue from walls of the tank and allowed time for the previous rinse solutions to be removed. The first burst sprayed water into the tank for less than 1 min. The first solution from the milk storage tank contained a high amount of calcium, approximately 90 mg/l. The amount decreased rapidly to about 55 mg/l in about 1 min. Therefore, the initial rinse water removed a large portion of the milk residue from the walls and floor of the tank.

Return of the second burst began at about 3 min

(Fig. 2) and continued for about 2 min. Mixing of solutions from the first two burst rinses in the bottom of the tank produced a gradual dilution of calcium to 50 mg/l.

The third burst rinse lasted for about 2 min with calcium concentration decreasing to less than 4 mg/l. Most residual milk was rinsed from the walls and floor during the rinse cycle. The phase should have been stopped and the alkaline phase started after about 8 min; the next 5 min accomplished little further cleaning.

A plot of the pH (Fig. 2) of the returning solution indicated that the milk did not materially affect the pH of the solution. There was an unexplained increase in the pH of the rinse solution with time.

During the alkaline phase of the cleaning cycle, the CIP pump operated continuously, and the returning solution was diverted to the drain. The initial returning alkaline solution contained about 22 mg calcium/l. This amount decreased to about 12 mg/l after 1 min and more slowly to about 5 mg/l after approximately 2 min. During the remaining 10 min of the alkaline phase, a small decrease in calcium concentration was noted. During the post-rinse phase, no calcium was detected in the rinse water.

Processing line cleaning cycle

Cleaning solutions were initially pumped from the solution makeup tank (CIP tank) into a 110-gal batching tank, through the processing line (approx-

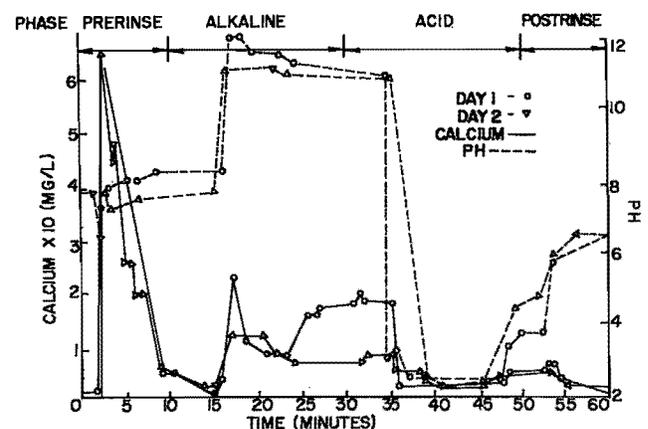


Figure 3. Plots of the calcium content and pH of the cleaning solution versus time as the solution flowed from the milk processing line on two different days. Note that time when the cycle started, indicated by the horizontal line with arrows at top of figure, does not coincide with time when the spectrophotometer detected changes in calcium concentration. This occurred because it took approximately 4 min for solutions to pass from the CIP storage tank through the system to the spectrophotometer. Initial lag time was only 2 min because part of the rinse solution originated in the constant level tank.

mate volume 40 gal), and back to respective compartments of the CIP tank for recirculation.

Rinse water initially picked up more than 60 mg calcium/l in flowing through the processing line (Fig. 3). Concentration decreased rapidly during the first part of the phase (4-9 min), and then more slowly at the end (9-14 min), to approximately 2 mg/l. The irregular tracing observed on day two may have been caused by the recirculation (diversion to the constant level tank) of approximately 10% of the solution from the system each time the flow-diversion valve pulsed to clean the leak detector line. This was programmed into the system. However, pulsing of the flow-diversion valve and control of the CIP cycle were independent. This allowed pulsing of the flow-diversion valve to occur at different times in the cleaning cycle and account for minor differences in tracings (Fig. 3) on the two days.

Next, alkaline solution was pumped through the processing line and recirculated (14-37 min). A high peak was noted on day one at 18 min. This peak was lower and wider on day two. The difference was attributed to pulsing of the flow-diversion valve with consequent recirculation of solution containing the high concentration of calcium.

The increase in calcium content after 24 min (Fig. 3) for day one was caused by the recirculation of the alkaline solution, with its higher calcium content, through the processing line. Also, additional calcium may have been removed.

The start of the acid phase, as indicated by the change in pH, occurred 34 min after the start of the cycle. The leading boundary of the acid solution was mixed with alkaline solution remaining in the line. This mixing is indicated by the slope of the pH plot that ends at 35-38 min. The quantity of calcium in the acid water was about 2 mg/l. This indicated that very little calcium remained in the processing line after the alkaline phase. If small quantities of calcium and traces of other constituents of milk are not removed, they will tend to build up and may form a visible residue after 3 or 4 days. Previously, the foreman of the University plant had noted that when the processing line was not rou-

tinely washed with acid, a residual film built up after several days.

A small amount of calcium (4 mg/l) was dissolved in the acid solution remaining in the system after the acid phase was stopped. Some of this was removed during the final rinse phase as indicated by the plot of the last 15 min of the cycle. Final rinse water flowing through the system picked up about 1 mg calcium/l.

During the collection of these data, it was observed that fat globules in the returning rinse solution adhered to the inside of the aspirator tube of the spectrophotometer, causing a decrease in the amount of solution aspirated into the nebulizer. To determine whether the aspirator tube or nebulizer was restricted, a solution of known concentration was aspirated, and the instrument response was observed. If the response was not equivalent to earlier readings of the same solution, the operation was interrupted, and the aspirator tube and nebulizer were cleaned.

CONCLUSION

This research demonstrated that an atomic absorption spectrophotometer can be successfully used, with calcium as an indicator, for on-line monitoring of milk in a cleaning solution during the different phases of a cleaning cycle used by a milk processing plant.

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