CLEANING MODEL STUDY: SUGAR SOIL REMOVAL BY ALKALINE CLEANING SOLUTIONS

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Carlos Borrero Angel
1964

ABSTRACT

CLEANING MODEL STUDY: SUGAR SOIL REMOVAL BY ALKALINE CLEANING SOLUTIONS

By Carlos Borrero Angel

Studies of the rate of sugar removal from a sugar soil model were performed using distilled water and alkaline cleaning solutions of varying concentration. Sugar soils were exposed to cleaning solutions for a defined time interval at constant temperature and rate of agitation and the quantity of the sugar soil dissolved was determined by weight loss.

Results suggest that in this model system the soluble sugar soil removal was controlled by the concentration gradient of the cleaning solution. Cleaning solutions having the smallest solute concentration exhibited the largest rate of soil removal.

Cleaning solution additives were studied; an increase in trisodium phosphate concentration significantly decreased the rate of soil removal; tetrasodium phosphate and sodium gluconate had no significant effect on the rate of soil removal; the addition of EDTA to the cleaning solution in concentrations of 2.5% and 5% by weight of caustic had no effect whereas the addition of 10% EDTA to the cleaning solution enhanced the rate of cleaning by 16%.

The rate of soil removal was increased by increasing the temperature and rate of agitation; the rate of soil removal was found to be constant with respect to time, the amount of the soil with the cleaning solution.

The commercially used cleaning solutions studied suggest that the increase in soluble solids not caustic of the cleaning solution with extensive usage is not large enough to decrease the efficiency of the cleaning solution.

CLEANING MODEL STUDY: SUGAR SOIL REMOVAL BY ALKALINE CLEANING SOLUTIONS

By

Carlos Borrero Angel

A THESIS

Submitted to the School for Advanced Graduate Studies
of Michigan State University in partial
fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Food Science

1964

a mis padres

ACKNOWLEDGEMENTS

The author is greatly indebted and appreciative of his major professor, Professor I. J. Pflug, for encouragement, guidance and constructive criticism during his graduate work.

The author also wishes to convey his sincere appreciation to Professor O. W. Kaufmann and J. M. Jensen for their consideration and interest in their review of this manuscript.

This project was initiated and sponsored by the American Bottlers of Carbonated Beverages. This organization has supported the work financially; however, members of the organization have individually contributed knowledge and testing materials. We appreciate the active support of this industry. Special recognition is due Mr. H. E. Korab for his interest, counsel and enthusiastic support of this study.

Thanks go to Professor B. S. Schweigert, Chairman, Food Science Department, for his interest and support of this program; to Mr. Allen Stewart and Mr. John Schamel for their assistance in the laboratory; to Dr. John Blaisdell for his helpful suggestions; to Mr. P. J. Fellers for proofreading the manuscript; and to Miss D. Fang for the typing of the manuscript.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The cleaning of reusable carbonated beverage bottles is a relatively old operation, yet little is known about the process of soil removal from these containers. Analytical data regarding the effect of variables on the soil removal operation is practically non-existant.

Increasing production costs and a decreasing profit margin in the food processing industry necessitates that the efficiency of processing equipment be increased in order for this process to be economically feasible. Returnable bottles are used and the bottle washing operation is undertaken because it is less expensive for the bottler to reuse the bottles than to use one trip bottles; however the washer is a large item of capital investment. The bottle washer must be used efficiently.

The objective of this study is to investigate some of the variables involved in the bottle washing operation which should be considered to optimize the design of bottle washer and the bottle washing operation. One way of increasing washer efficiency is to reduce bottle washing time which increases bottle capacity of the machine; however this requires improved washing rate and perhaps a more effective washing solution. If we knew when a cleaning solution no longer acted as an effective cleaning agent, it could be replaced to maintain maximum washer efficiency. If, however, bottle washing solutions do not wear out then the cost of recharging the soak compartment of the bottle washing machine could be saved.

The variables of caustic concentration, soluble solid concentration temperature, rate of agitation and time were studied to determine their effect on the rate of soil removal. These variables are the controlling factors in the bottle washing operation.

The water used for cleaning reusable containers may contain calcium and magnesium ions generally classified as hardness; many of the proprietary compounds used contain sequestering agents of either an organic or inorganic nature to remove these ions which effect bottle cleaning and final bottle appearance. The sequestering agents studied included: trisodium phosphate, tetrasodium pyrophosphate, sodium gluconate, and tetrasodium ethylenediaminetetraacetate. Tests were made using these compounds in 3% sodium hydroxide solution to determine the effect of an increase in the sequestering agent concentration on the cleaning rate.

This investigation is part of a study sponsored by the American Bottlers of Carbonated Beverages (ABCB) to evaluate the effect of some of the variables which may affect the rate of soil removal in reusable carbonated beverage bottles by caustic cleaning solutions.

This thesis describes an experimental procedure for studying the rate of removal of a soluble sugar soil by caustic solutions; the effect of increasing the concentration of sequestering agents on the rate of soil removal, and the effect of the variables of time, temperature, and the rate of agitation on the rate of soil removal.

REVIEW OF LITERATURE

Present Cleaning Specifications

The cleaning of reusable carbonated beverage bottles is one of the most important processes in the manufacture of carbonated beverages. This process has suffered little change in the past 70 years. The recommendations appearing in the 1893 Bottle Washing Bulletin of the Nordberg Manufacturing Co. of Milwaukee, Wisconsin, were: "The cleaning solution consists of caustic soda dissolved in water. This solution can be made of any strength, but for economical reasons about 3% caustic in a tank full of water is ordinarily used. Heating the solution adds to the efficiency of the soaking solution." These recommendations are similar to those of the ABCB (1951), "unclean bottles shall be exposed to 3% solution of which not less than 60% is caustic (sodium hydroxide) for a period of not less than 5 minutes at a temperature of not less than 130°F, or to an equivalent cleansing and sterilizing process." These conditions express the minimum conditions to which an unclean container should be submitted. Forty-three states have requirements controlling the type and strength of bottle washing solution and 26 of these states restrict the bottle washer operators to one solution concentration, a minimum temperature and a minimum contact time. A general rule of thumb used by bottlers states that for each 10°F increase in solution temperature of 50% increase in the caustic solution concentration, the necessary contact time will be reduced by one-half.

Jennings (1963) defines soiling as "the result of a decrease in the free energy of a system", implying that removal of soil necessitates work to add enough energy to reverse the process. This work is generally supplied to the system in two forms: (1) mechanical energy, and (2) physiochemical energy. The mechanical energy in the bottle washing process is supplied by means of turbulence of the cleaning solution, abrasion (brushes), or hydrosprays, whereas the physiochemical energy comes from the detergent and additives in the cleaning solution.

Pflug et al. (1961) using radioactive soils determined that soil build up was greatest on a dirty surface than on a clean surface. This would be assumed from the former statement that soiling results from a decrease in the free energy of a system. The initial soiling would then be the most difficult to incur, and subsequent soiling once the first soil was deposited would not involve as great an energy change, therefore it would recur at a faster rate.

Various techniques have been suggested for estimating soil deposits. Jensen (1946) used light transmittance readings by a spectrophotometer, Kaufmann et al. (1960a,b) used the bacterial count, with or without swab test for determining soil deposits. Jennings (1960), and Pflug et al. (1961) used P^{32} labeled milk soils in their cleaning studies. Jennings (1961) found a high correlation between the soil removed and the radioactivity removed.

Pflug et al. (1961) studied the effect of stainless steel finish on the rate of soil removal using dry milk residues. His data indicated no significant differences in the rate of radioactive soil removal among the finishes. These results were confirmed by Kaufmann et al. (1960a) in their studies of the bacteriological cleanability of stainless steel finishes.

Pflug et al. (1961) and Jenning (1960) have both shown that soil removal from a surface is a complicated process that requires increasing quantities of energy to remove the last remaining traces of soil from the critical surface.

In reusable bottle washing the cleaning solution should remove the soil from the container and sterilize the bottle through the action of heat and caustic during washing or subsequent rinsing. The containers from the washer may be slightly contaminated; therefore, they are classified as commercially sterile. The disinfectant action of alkalies, as summarized by Carpenter (1961), was found to be due largely to the presence of hydroxyl ions in the solution, with the greatest degree of dissociation having the most effective germicidal action. The additives in the caustic solution affect the permeability of the cell membrane causing either a loss of protoplasmic material or enhancement of the effect of the sodium hydroxide. An example is trisodium phosphate increasing the germicidal efficiency of the solution.

Effect of Variables on Rate of Cleaning

Ruff and Becker (1955) listed the following factors influencing the effectiveness of the cleaning solution: (1) the concentration of caustic in the solution, (2) the temperature of the solution, (3) the time of contact of the solution and container, (4) the composition of the cleaning solution (type and composition of additives), (5) the type of washer, (6) the condition of the containers to be cleaned, (7) the nature of the water supply, and (8) the amount of soil residues in the solution.

Information pertaining to cleaning and soil removal in carbonated beverage bottles is practically non-existant, but there has been a great deal of work done on other systems such as the cleaning of dairy equipment, textiles, etc. In studying the effect of detergent concentration, Ladewig (1955) stated that the presence of excessive amounts of caustic in the cleaning solution inhibited the efficiency of the cleaning solution; however, there was no quantitative data given, nor was the degree of inhibition stated.

Parker et al. (1953) summarized the effect of temperature on CIP (cleaning in place) systems by stating that the higher temperatures gave more efficient cleaning. The work of Jennings (1959) ascertained that the removal of cooked-on-milk films from CIP lines by solutions of sodium hydroxide exhibited a $Q_{18°F}$ of 1.6 within the temperature range 115-180°F. He speculated that "increasing the temperature of the solution continues to increase the cleaning efficiency until one reaches a point where detergents decompose or the vapor pressure of the fluid interferes with the operation."

Shand (1958) explains the effect of temperature on glass by saying that "when glass is suddenly heated, the initial stress developed is compressive so that the hazards of fracture are slight, but when suddenly chilled, the stresses are tensile so that the probability of fracture is increased greatly." Fracture because of increased tensile stress due to expansion or contraction produced by temperature change is called thermal shock.

Dungfelder (1957) found thermal heat shock breakage was higher when hot glass was chilled than when cold glass was subjected to a hot environment. He estimated a maximum temperature difference between the glass and the cooling solution of 35-45°F and that very slight breakage occurred upon introducing the bottles in the hot solution.

It is the heat shock effect which imposes limitations on the operating temperatures of bottle washers. The washing cycle includes the immersing of the bottles in a hot cleaning solution and then the rinsing of the bottles to remove the detergent solution from the bottle. The rinsing operation is carried on at a lower temperature than the soaking operation, thus the cooling of the bottles is one of the controlling factors in determining an operating temperature. Buchanan and Levine (1939) reported a great variation in the temperatures of cleaning solutions. They found temperatures from 105-170°F in usage throughout the bottling industry. Ruff and Becker (1955) confirmed the preceding temperature data, but indicated a majority of washers operating between 140-170°F. When bottles are cooled in a step process by immersing in cooler soaker solutions where changes in temperature are within a ΔT of 35°F, a washing temperature of under 170°F is not critical in glass breakage.

Longevity of Solutions

There is no definite way to know when a cleaning solution is no longer effective due to soil pick up during usage. McCallion (1961) tested two soaker solutions using different formulations to determine when they became ineffective; the testing criteria was the ability of the cleaning solution to clean glass without an increase in the reject rate. No difference was observed over an extended period of time. Dormuth (1956) summarized the extent of the knowledge on the life of cleaning solutions when he stated that "when the contamination reaches a certain point it is necessary to dump the solution from the tanks and recharge with fresh solution." From this statement it is evident that the solution is discarded whenever the operator judges it to be ineffective.

Sequestering Agents Used and Their Chemical Behavior

Cleaning solutions used for bottle washing in the carbonated beverage industry are adversely affected by the action of hard water salts with the sodium hydroxide in the solution. The free calcium and magnesium salts present in the solution react with the sodium hydroxide to form insoluble magnesium hydroxide and calcium carbonate. These precipitates form scale on washer tank, heat transfer surface and moving parts of the machine. The operating efficiency of the washer is lowered and costly damage to the equipment is the end result. Sequestering agents are used to prevent the precipitation of the aforementioned salts from the solution by forming soluble complexes with the ions of calcium and magnesium. The precipitation of magnesium hydroxide on the bottle surface causing a cloudiness or haze condition can be alleviated by use of chelated caustic solutions (Ladewig, 1955). The inorganic phosphates or the organic sequestering agents such as the sodium salts of the organic acids--sodium gluconate or sodium salts of the aminopolycarboxylic acids EDTA are the materials used to sequester the calcium and magnesium ions present in hard water. These compounds act on the metal salts by forming a soluble complex, which in turn prevents the formation of precipitates on both the washer and the surface of the bottles. These sequestering agents also improve the wetting ability and the free rinsing qualities of the solution.

Schwartz et al. (1958) defines free rinsing as "freedom from waterbreak, a condition where water drains in a continuous film without breaking into droplets or streams". This condition indicates a surface free of soil and reduces the carry over by the bottles of caustic solution from one tank to another. Bottles are clear and shiny indicating a clean bottle whereas if bottle washing solutions are free rinsing, opaque spots on the bottle can be used to indicate an unclean and undesirable bottle. The inorganic phosphates have a wider usage at present as free rinsing agents because of their lower cost as compared to the organic sequestering agents (Chabereck and Martell, 1959).

The compounds to be examined in this study are: trisodium phosphate, tetrasodium pyrophosphate, sodium gluconate, and ethylenediaminetetraacetate (EDTA). Trisodium phosphate has been widely used because of its cleaning properties; however, when added to a caustic solution prepared using hard water, ions are removed as insoluble phosphate salts. Trisodium phosphate is different from the sequestrants in that it precipitates the calcium salts rather than tying them in a soluble chelate (Schwartz, et al. (1958). Overman (1964) indicated that normally used concentrations of trisodium phosphate ran from 0-10% of the caustic present in solution.

The inorganic polyphosphates have had extensive usage due to their sequestering properties and low cost. Martell and Calvin (1953) state that "the relative effectiveness of the polyphosphates increase with increasing chain length." A disadvantage of the polyphosphate sequestering agents is their tendency to hydrolyze to orthophosphate (reversion), causing precipitation of the insoluble salts of the phosphates. Chabereck and Martell (1959) indicate that "the degree of hydrolysis of polyphosphates increases with an increase in chain length." They also found tetrasodium pyrophosphate to have the slowest rate of reversion of the polyphosphates at 100°C. Reversion is highly accelerated at the high temperatures used for bottle washing, and is undesirable because upon reversion there is precipitation of the insoluble phosphates of the metal salts in the solution. In their description of the polyphosphates they describe an additional effect encountered with the usage of these compounds, namely the "threshold effect". The "threshold effect" is described as the use of sequestering agents in small concentrations to prevent the formation of insoluble salt precipitates. Thus it is possible to maintain higher quantities of calcium and magnesium ions in solution that would stoichiometrically combine with the available polyphosphate. The "threshold effect", however, does not work when the concentration of available calcium is greater than 20 ppm. Mehltretter et al. (1953) reported that another advantage derived from the use of polyphosphates, in addition to the deactivation of metal ions, was "the ability to defloculate and suspend water insoluble substances such as clays and hard soils." Benson (1956) states that polyphosphates promote the wetting of glass by the caustic solution and also promote the free drainage of water allowing for lower carry over loss and generally cleaner bottles. Use of tetrasodium pyrophosphate depends on the conditions to be met. Concentrations from 0-12% (expressed as a percentage of the caustic) were reported by Korab (1964) as being in use by the industry.

One of the major considerations in the choosing of the concentration of additives to be used appears to be the cost of the cleaning compound ingredients. The two main organic sequestering agents used in the bottle washing industry today are sodium gluconate and tetrasodium ethylenediaminetetraacetate salts.

Chabereck and Martell (1959) stated that the industrial value of sodium gluconate salts lies in the fact that at pH values greater than 11 the sodium gluconate salts become very efficient sequestering agents in the presence of free caustic. Also, that in the presence of free sodium hydroxide, sodium gluconate compared with tetraphosphate and citric acid was the most effective sequestering agent in the normal pH range over a wide range of sodium hydroxide concentrations. In a similar manner to the polyphosphates, sodium gluconate also exhibits the "threshold effect" in caustic solutions. Pfizer Gluconates in Caustic Bottle Washing (1959) listed the recommended amounts of sodium gluconate to be used in caustic solutions based on the hardness of the water used. These values are tabulated in Table 1.

Table 1. Average levels of gluconate required in practice.

	Sodium Gluconate Required Per 100 Pounds Caustic Soda at Caustic Concentrations of				
Water Hardness	1%	2%	3%	4%	5%
grains/gal.	lb.	lb.	lb.	lb.	lb.
1 to 5	2.0	1.0	1.0	0.5	0.5
6 to 10	5.5	3.0	2.0	1.5	1.0
11 to 15	9.0	4.5	3.0	2.0	2.0
16 to 20	12.5	6.0	4.0	3.0	2.5
20 or over	14.0	7.0	5.0	3.5	3.0

The organic chelating agents offer some advantages over the polyphosphates, especially as regards thermal stability in aqueous solutions. The metal chelates have a higher stability than the polyphosphates, and they remove rust by forming stable chelates with ferrous and ferric ions (Mehltretter et al., 1953). The maximum efficiency of ethylenediaminetetraacetate (EDTA) is attained at a pH greater than 8. The action of EDTA differs from the polyphosphates in that it forms a chelate with the metal ions. Martell and Calvin (1953) define a chelate as formed by the combination of a metal with a substance containing two or more donor groups so that one or more rings are formed. The high cost of this compound has inhibited its more widespread usage even with its greater efficiency as a sequestering agent.

EXPERIMENTAL DESIGN

General Considerations

The design of this experiment required a homogeneous test soil which would be representative of soils which might be encountered in the commercial practice of washing reusable bottles. The selection of a soil for use in carbonated beverage bottle cleaning studies is a critical part of this cleaning study. More than 99% of the returned carbonated beverage bottles contain only the residual beverage plus extraneous materials such as straws, cigarettes and silt or dust from the air. A sugar soil was selected because the problem of washing carbonated beverage bottles is mainly one of removing the sugar soil from the bottle's inner surface. The sugar glass used in this study is a soil similar to that encountered in the bottles after the water has evaporated and is therefore a logical soil to use to simulate the conditions inside the bottle. A sugar glass is more difficult to remove than a crystalline sugar. Bottlers will generally set aside bottles containing oils, tar, heavy clays or cement to wash them separately or they may destroy these bottles. Therefore, the washer operation is geared for normally soiled returned bottles and for these conditions this study should provide data to improve this operation.

A preliminary experiment was made in which a sugar glass was cut into rectangular pieces 3" x 1-1/2" x 1/4". Wire loops were imbedded in the sugar glass and these pieces were suspended in the solution and the weight loss determined by difference. The nature of the sugar glass, namely its fluidity at high temperatures was as encountered in these tests giving poor results which led to the improved beaker test method where area is accurately controlled and it is necessary to only remove soil from a horizontal surface.

A second preliminary test was made in which the soils were produced in the bottom of 250 ml beakers. A sufficient amount of soil was added to assure the exposure of a constant surface area to the cleaning solution in each test vessel. The sides and bottom of the soil layer adhered to the glass, therefore were not exposed to the action of the cleaning solution. The soil could be separated from the solution and reweighed to determine the weight loss by decanting the cleaning solution from the beaker following a test. Preliminary tests made using these vessels with 200 ml of cleaning solution at 150°F under 150 rpm of agitation for 5 minutes, indicated that this method was unsatisfactory. The agitation conditions in the beaker caused the formation of several vortexes in the solution. The resulting effect was uneven removal of soil from the surface, with a greater amount of soil removed where the vortex inpinged on the soil. The lack of reproducibility of results made the preceding method of testing undesirable. Further experimentation showed that when the soil was poured into 600 ml beakers, conditions of turbulence did not appear, thus an even surface, free of indentations, was maintained and reproducible results could be obtained.

A carbonated beverage contains acid and flavor in addition to sugar. In preparing the synthetic soil we can start with a sugar-acid-flavor mix; however, acid and flavor will be evaporated by the time the end of the cook was reached. To add acid and flavor to the sugar glass it is best to add it in the dry form and blend it into the hot molten glass by mixing. In general these additions will not make the soil any harder.

Description of Test Equipment

The testing equipment consisted of three basic parts: the stirring unit with six agitators; the beaker holder; and a constant temperature bath. The stirring unit was designed so the blade in each beaker would produce equal agitation. The system was assembled to minimize the "without agitation" contact time of the solution with the soil. It was important to place the agitator on the test beakers immediately upon their immersion in the bath and at the end of the time of agitation to remove the unit allowing decantation of the cleaning solution. The beaker holder maintained the six test beakers equidistant from each other and directly beneath the agitator blades (see Figure 1). This holder also enabled the operator to place and remove the six beakers simultaneously from the constant temperature bath. The flask holding unit with the six 500 ml Erlenmeyer flasks was used to pour 500 ml of cleaning solution at the test temperature into the beakers in the holder. The flasks were spaced such that solution could be poured directly into each beaker (see Figure 2).

The constant temperature bath was equipped with a thermostat which maintained a test temperature ± 1°F.

Test Materials

Experimental Soils

Sugar Soil. The sugar soil was prepared by mixing 1600 g of sucrose and 400 g of corn sugar with 1500 ml of distilled water. This solution was heated until the temperature reached 310°F. A hard crack consistency resulted upon cooling. When the solution reached 310°F, a sufficient quantity was poured into each of the 600 ml beakers to produce a soil thickness of 1/4 to 3/8 inch. After the soil had cooled to room temperature, the beakers with the soil were weighed to ±0.01 g.

Sugar plus milk soil. 1600 g of sucrose, 400 g of corn sugar, 100 g of powdered milk, and 1500 g of water were mixed to make a solution which was heated to 310°F, at which time it was poured into 600 ml beakers to a depth of 1/4 to 3/8 inch. The beakers were weighed to ± 0.01 g after cooling to room temperature.

Cleaning Solutions

The cleaning solutions used consisted mainly of NaOH solutions of varying concentrations, 3% NaOH solutions with varying concentrations of sequestering agents, and several commercial proprietary compounds.

NaOH solutions. The solutions of NaOH were prepared using distilled water and anhydrous NaOH. Solutions were prepared by weight, i.e. (3% NaOH - 3 g NaOH to 97 g H_2O). Solutions were prepared in the following concentrations: 3%, 5%, 10%, and 20% NaOH.

NaOH solutions containing soluble solids. These solutions were prepared as above and to each concentration, 20%, 40%, 60% soluble solids (sucrose) was added, i.e. (to 3000 g of solution 600 g sucrose for 20% soluble solids). The solutions were then placed in the 150°F bath and held at this temperature overnight. On the following day these solutions were restandardized to their respective normalities.

3% NaOH solutions containing sequestering agents. Solutions of 3% NaOH were prepared as above and to these solutions were added 2.5%, 5%, and 10% of the sequestering agents based on the NaOH concentration i.e. (for a 10% sodium gluconate solution in 3% NaOH - 30 g NaOH/1000 g of solution and 3 g of sodium gluconate were added to the 3% NaOH solution). The sequestering agents used in this study were trisodium phosphate, sodium pyrophosphate, sodium gluconate and tetrasodium ethylenediaminetetraacetate.

Commercial cleaning solutions made from proprietary compounds. Cleaning solutions were prepared using commercial proprietary compounds (supplied by several manufacturers) plus distilled water to make a 3% caustic concentration. To these solutions were added 20%, 40%, 60% soluble solids (sucrose), the resulting solutions being kept at 150°F overnight and restandardized to their original normality before using.

Used commercial proprietary compound cleaning solutions. Bottle washing solutions from the bottle washers of 11 commercial carbonated beverage bottlers were obtained from the ABCB. These solutions were tested to determine percent soluble solids and the normality of each solution.

Testing Procedure

Procedure for tests on the rate of soil removal. The cleaning solution to be used in the test was first equilibrated in a large container to approximately the test temperature and then poured into the 500 ml Erlenmeyer flasks and allowed to equilibrate to the test temperature in the constant temperature bath. Six beakers with sugar soil were attached to the beaker holder, the solution poured in (Figure 2), and the beakers placed into the constant temperature bath. The stirrer unit was quickly lowered over the beakers and agitation begun. The elapsed time between pouring the solution into the beakers and the start of agitation was approximately 15 seconds and was constant for all tests. At the end of the five minute test period the stirrer was stopped and removed from the beakers. The beakers were removed from the bath and the solution was decanted. The interval from the end of

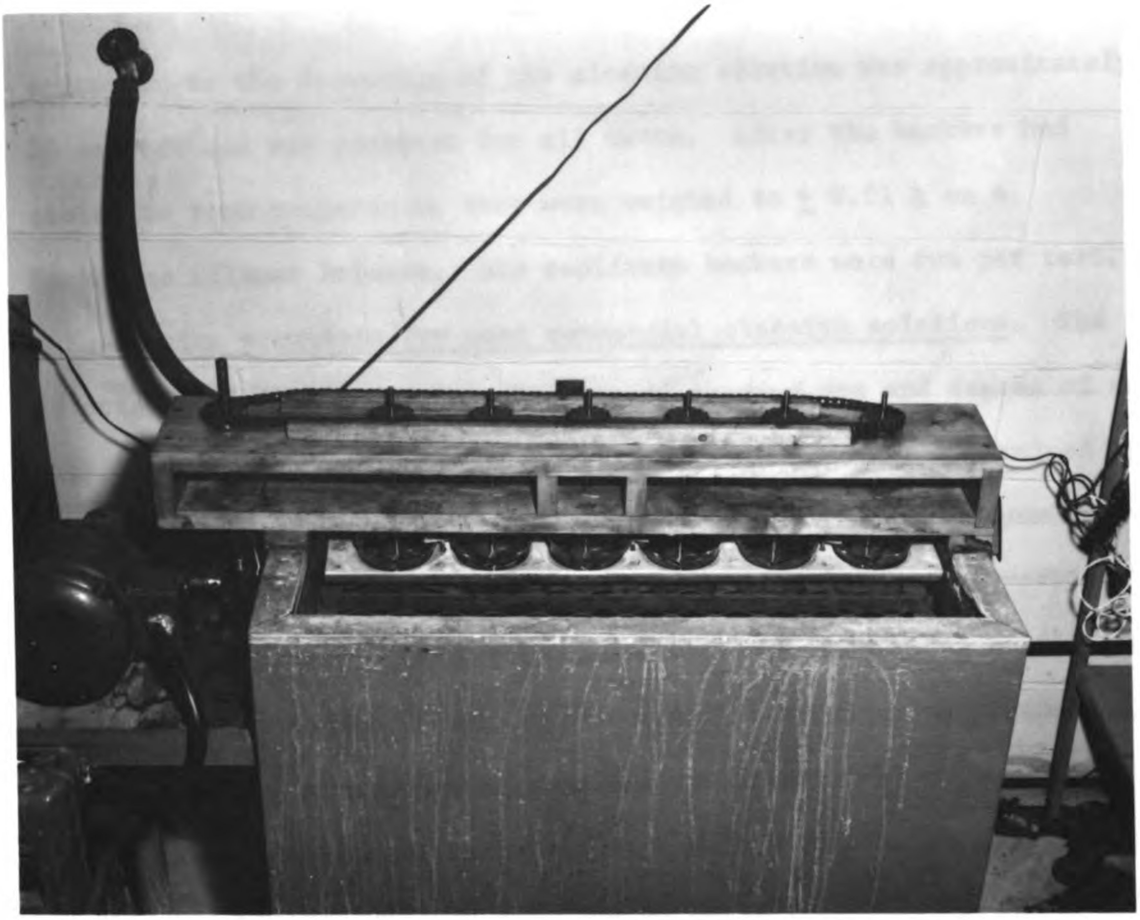

Figure 1. Test equipment, agitator mechanism with beaker holder beneath it.

Figure 2. Flask holding device and beaker holder.

agitation to the decanting of the cleaning solution was approximately 20 seconds and was constant for all tests. After the beakers had cooled to room temperature they were weighed to ± 0.01 g on a Sartorius Kilomat Balance. Six replicate beakers were run per test.

Testing procedure for used commercial cleaning solutions. The solutions obtained from the ABCB were of varying age and degree of use. The total soluble solids in each of these solutions was determined by evaporating the water in a 200 g sample of solution in a vacuum oven at 70°C then determining the soil content by the weight of the residue left in the beaker. The normality of the solution was obtained by titrating a 10 ml sample of the caustic solution with 1 N HCl using phenophthalein indicator. The percent soluble solids not caustic was obtained by taking the difference between the total solids and the weight of caustic, as determined from solution normality, divided by the weight of the original sample.

RESULTS

The results are reported under four headings: (1) Apparatus performance tests, (2) Effect of concentration gradient on the rate of soil removal, (3) Effect of temperature, time and rate of agitation, (4) Tests of commercially used cleaning solutions.

Apparatus Performance Tests

The results of tests to establish the reproducibility of the experimental procedure, equality of different batches of sugar soil, and reproducibility of agitation conditions at each agitator position were treated using the analysis of variance method (Dixon and Massey, 1957). The results of the analysis of variance are tabulated in Table 1. The data in Table 1 indicate no difference at the 5% level of significance between batches of soil, procedure, or agitator position.

Tests of the Effect of Concentration

The means of six replicate tests on the effect of sodium hydroxide concentration on the rate of soil removal are presented in Table 2; the mean values of six replicate tests on the effect of increasing the concentration of soluble solids on the rate of soil removal of distilled water, 3% sodium hydroxide, and 5% sodium hydroxide cleaning solutions are presented in Table 3; the effects of increasing the concentration of soluble solids in solutions prepared using commercial proprietary compounds are tabulated in Table 4; and the results of the study conducted to observe the effect of increasing the concentration of soluble solids in distilled water and alkaline cleaning solutions on the rate of soil removal of a sugar plus milk soil are listed in Table 5.

An analysis of variance was performed on the values obtained from tests on the effect of the addition of 2.5%, 5%, and 10% sequestering agents in sodium hydroxide cleaning solutions. The sequestering agents used were trisodium phosphate, tetrasodium pyrophosphate, sodium gluconate, and tetrasodium ethylenediaminetetraacetate; the results of the analyses are tabulated in Tables 6, 7, 8, and 9, respectively. The means of six replicate tests performed on each of these concentrations of sequestering agent are presented in Table 10.

Study of Time, Temperature and Rate of Agitation

The results of a study conducted to observe the effect of an increase in temperature on the rate of soil removal of distilled water and alkaline cleaning solutions are listed in Table 11.

The effects of varying agitation on the rate of soil removal of sugar soil by distilled water cleaning solutions of varying concentrations of soluble solids are tabulated in Table 12.

An analysis of variance test was made on the results of tests made varying the contact time between the cleaning solution and the soil. Time intervals of 5, 10 and 20 minutes were used in this study. The solution used was distilled water. Table 13 represents the analysis of this test.

Tests of Commercially Used Cleaning Solutions

From the cleaning solutions obtained from the ABCB data were gathered to determine the percent concentration of soluble solids and the normality of the cleaning solution. Table 14 shows values for all treatments.

TABLES

Table 1. Analysis of variance table of weight loss of six batches of sugar soil, experimental procedure, and agitator position.

Source	Degrees of freedom	Sum of squares	Mean squares	F
Batches of soil and procedure	5	1.26	.252	1.28
Position in agitator	5	.42	.084	
Residual	25	4.92	.197	
Total	35	6.60		

Table 2. Weight loss of sugar soil with increased sodium hydroxide concentration at 150°F and agitation speed of 147 rpm, mean of 6 replicates.

NaOH Concentration percent	Rate of soil removal mg/cm^2 min	
	mean	range
0%	24.65	(21.85-26.09)
3%	20.12	(19.38-20.80)
5%	16.65	(16.10-17.24)
10%	12.51	(11.67-14.15)
20%	4.62	(4.36- 5.02)

Table 3. Rate of sugar soil removal by distilled water and alkaline cleaning solutions at 150°F and agitator speed of 147 rpm, means of 6 replicates.

% Soluble solids	Rate of soil removal (mg/cm^2 min)		
	Distilled water	3% NaOH	5% NaOH
0%	24.65	20.12	16.65
20%	19.87	14.98	11.16
40%	15.63	7.85	3.25
60%	10.36	4.07	.93 .

Table 4. Rate of sugar soil removal by solutions of proprietary cleaning compounds and 3% NaOH at 150°F and agitator speed of 147 rpm, means of 6 replicates.

% soluble solids	Rate of soil removal (mg/cm^2 min)			
	3% NaOH	Solution 1	Solution 2	Solution 3
0%	20.12	19.05	19.01	17.31
20%	14.98	12.40	10.14	11.16
40%	7.85	7.09	4.43	7.05
60%	4.07	.690	1.53	.70

Table 5. Rate of sugar plus milk soil removal by distilled water and alkaline cleaning solutions containing soluble solids at 150°F and agitator speed of 147 rpm, means of 6 replicates.

% Soluble solids	Rate of soil removal (mg/cm^2 min) Distilled water	 3% NaOH
0%	24.70	20.12
20%	19.14	13.51
40%	12.02	7.15
60%	5.30	1.59

Table 6. Analysis of variance table of the rate of soil removal of sugar soil of 3% sodium hydroxide cleaning solution with 2.5%, 5%, and 10% trisodium phosphate by weight of caustic.

Source	df	Sum of squares	Mean squares	F
Concentration	2	11.08	5.54	13.19**
Within	51	22.04	.42	
Total	53	33.12		

$F_{.95}$ (2,51) = 3.19

Table 7. Analysis of variance table of the rate of soil removal of sugar soil of 3% sodium hydroxide cleaning solutions with 2.5%, 5%, and 10% tetrasodium pyrophosphate by weight of caustic.

Source	d_f	Sum of squares	Mean squares	F
Concentration	2	1.11	.555	1.79
Within	51	15.91	.31	
Total	53	17.02		

$F_{.95}$ (2,51) = 3.19

Table 8. Analysis of variance table of the rate of soil removal of sugar soil of 3% sodium hydroxide cleaning solutions with 2.5%, 5%, and 10% sodium gluconate by weight of caustic.

Source	d_f	Sum of squares	Mean squares	F
Concentration	2	4.44	2.22	5.8**
Within	44	16.71	.38	
Total	46	21.15		

$F_{.95}$ (2,44) = 3.23

Table 9. Analysis of variance table of the rate of soil removal of sugar soil of 3% sodium hydroxide cleaning solutions with 2.5%, 5%, and 10% tetrasodium ethylenediaminetetraacetate by weight of caustic.

Source	d_f	Sum of squares	Mean squares	F
Concentration	2	8.5	4.25	8.67**
Within	51	25.13	.49	
Total	53	33.63		

$F_{.95}$ (2,51) = 3.19

Table 10. Rate of soil removal from sugar soil by 3% sodium hydroxide solutions with varying concentrations of four sequestering agents at 150°F and agitator speed of 147 rpm. 18 replicates per concentration.

Sequestering agent concentration as % of cuastic	Rate of soil removal (mg/cm^2 min)			
	Na_3PO_4	$Na_4P_2O_7$	Na gluconate	Na_4 EDTA
0	20.12	20.12	20.12	20.12
2.5%	19.09	20.15	18.25	19.96
5%	16.04	21.41	20.36	20.87
10%	15.31	21.20	20.11*	23.35

*11 replicates for this test.

Table 11. Rate of soil removal of sugar soil with varying temperature at agitator speed of 147 rpm.

% Soluble solids	Rate of soil removal (mg/cm^2 min)								
	T=130°F			T=150°F			T=170°F		
	H_2O	3% NaOH	5% NaOH	H_2O	3% NaOH	5% NaOH	H_2O	3% NaOH	5% NaOH
0%	20.51	18.58	13.16	24.65	20.12	16.65	27.64	26.11	21.64
20%	14.95	9.78	8.33	19.87	14.98	11.16	24.25	18.18	16.51
40%	8.33	4.07	2.04	15.63	7.85	3.25	19.09	13.35	10.95
60%	1.89	.98	-2.83	10.36	4.07	.93	12.51	8.25	4.95

Table 12. Rate of soil removal of sugar soil with varying agitation at 150°F using distilled water cleaning solutions.

% Soluble solids	Rate of soil removal (mg/cm^2 min)		
	0 RPM	65 RPM	147 RPM
0%	10.79	13.38	24.65
20%	5.31	8.51	19.87
40%	2.22	5.78	15.63
60%	-2.83	-1.34	10.36

Table 13. Analysis of variance table of rate of soil removal of sugar with respect to time.

Source	Degrees of freedom	Sum of squares	Mean squares	F
Contact time	2	75.47	37.74	.0384
Within	6	5,849.72	982.86	
Total	8	5,925.19		

$F_{.95}(2,6) = 5.14$

Table 14. Normality and concentration of soluble solids for 11 commercial cleaning solutions.

	A	B	C	D	E	F	G	H	I	J	K
Normality	.276	.84	.97	.80	1.03	1.21	1.38	1.04	.93	.60	.61
% Caustic	1.10	3.30	3.90	2.80	4.10	4.80	5.50	4.20	3.70	2.40	2.40
% Soluble solids not caustic	1.03	2.4	2.5	3.2	2.0	3.7	3.5	2.2	2.3	2.2	1.7

DISCUSSION

The results of the analysis of variance tabulated in Table 1 indicate no significant difference at the 5% level in the experimental procedure between runs, different batches of soil, or beaker position in the agitator system. Having established the reproducibility of procedure and soil, studies of the other variables were undertaken.

Studies on the effect of increasing sodium hydroxide concentration indicated a decrease in the rate of soil removal with an increase in the sodium hydroxide concentration. Figure 3 is a plot of the data of Table 2 showing the effect of the increase in the sodium hydroxide concentration on the rate of soil removal. The results from this study indicate that distilled water is more effective sugar soil removing agent than sodium hydroxide. The role of caustic in the cleaning solution appears to be twofold: (1) To act as a germicidal agent during the cleaning cycle, the combined effect of temperature and caustic are bacteriocidal and maintain the soak tank solution in a sterile condition, and (2) To saponify and solubilize any oil or fat residues left in the bottle.

When a sugar soil is to be removed, water is the most effective cleaning agent due to its larger concentration gradient. The mechanism of soil removal is one where a boundary layer is formed between the sugar soil and the solution, consisting of a saturated sugar solution layer in which there is movement of sugar to the solution and water to the soil. The concentration gradient between the solution and the film is controlling and diffusion of the soil to the solution is greater than water to the soil. An increase in the sodium hydroxide concentration decreases this concentration gradient thus lessening the driving force of the sugar to the solution with a subsequently lower rate of soil removal.

To determine more precisely the effect of this factor, a study was designed covering a large range of concentration gradients. To distilled water, 3% and 5% sodium hydroxide cleaning solutions, 20%, 40%, and 60% soluble solids were added. Table 3 lists the mean values resulting from these tests and the graphical representation of this data in Figure 4, indicates that as the concentration gradient is increased, the rate of soil removal is decreased. Figure 4a is the linear regression line drawn from the data obtained from the test, the equation for this line is $Y = -.234\ X + 24.57$, indicating a linear correlation for the rate of soil removal and the concentration of soluble solids present in distilled water cleaning solutions. The plot of rate of soil removal versus percent concentration of soluble solids not caustic for alkaline solutions demonstrates a non-linear relationship. This relationship indicated that the sodium hydroxide content, while lowering the rate of soil removal of the solution at each concentration of soluble solids, also affected the relationship of the percent soluble solids with the rate of soil removal. Linearity was found no longer applicable to this system. An increase in the percent concentration of soluble solids will increase the viscosity of the solution thus making the rate of soil removal also dependent on the viscosity. Increasing the viscosity of a cleaning solution reduces the rate of soil removal. In a highly viscous system the motion of the atoms is slower, and their tendency to go into solution is smaller due to the higher shear forces and resistance to movement. Solutions of higher soluble solids not caustic have notably lower rates of soil removal than those of lower concentrations; this decrease is in part due to their higher viscosity.

Three proprietary cleaning compounds and 3% sodium hydroxide cleaning solution were tested using the sugar soil. The proprietary compounds were formulated to have a 3% caustic strength with the same three concentrations of soluble solids not caustic added to each solution. The results of these tests are listed in Table 4. The data of Table 4 is represented graphically in Figure 5 indicating 3% sodium hydroxide to have the highest rate of soil removal of the four solutions. The three proprietary compounds were observed to have approximately the same rate of soil removal for each of the four concentration gradients. Since the concentration of additives in these solutions was not known, further analysis could not be made.

In order to establish a comparison for the sugar soil a second type of soil was devised. For this soil the same formulation as for the sugar soil was used with the addition of 100 g of powdered skimmed milk. This soil represented a different type of surface and removal of this soil included removal of insoluble particles. Tests were made using distilled water and 3% sodium hydroxide cleaning solutions with the four concentrations of soluble solids. Table 5 shows that an increase in soluble solids decreases the rate of soil removal, again indicating the concentration gradient to be a controlling factor in this system. Due to a smaller concentration gradient for increasing soluble solids concentration, the 3% sodium hydroxide displayed a smaller cleaning ability than the distilled water cleaning solutions at the four soluble solid concentrations. Figure 6 is a graphical representation of Table 5.

Studies were made to determine the effect of increasing the concentration of sequestering agents on the rate of soil removal of 3% sodium hydroxide cleaning solution. For these studies, concentrations of trisodium phosphate, tetrasodium pyrophosphate, sodium gluconate, and tetrasodium ethylenediaminetetraacetate of 2.5%, 5% and 10% by weight of caustic were used.

An analysis of variance (Table 6) was performed on the experimental values from the soil removal tests for trisodium phosphate. It was found that the concentration of trisodium phosphate affects the rate of soil removal, with an increase in the trisodium phosphate concentration causing the decrease in the rate of soil removal. Table 10 lists the mean values for these tests. A concentration of 2.5% trisodium phosphate had no apparent effect on the rate of soil removal, but an increase in the concentration from 2.5 to 5% reduced the rate of soil removal from 19.09 to 16.04 mg/cm^2 min. A further increase in the trisodium phosphate concentration from 5 to 10% did not have as radical an effect on the rate of soil removal as an increase from 2.5 to 5%; however, it did lower it.

The effect of trisodium phosphate on the rate of soil removal is not unlike that of sodium hydroxide in that it decreases the rate of soil removal with an increase in concentration. The trisodium phosphate effect on the rate of soil removal is more marked than the sodium hydroxide, i.e. The rate of soil removal of 3% sodium hydroxide with 10% trisodium phosphate cleaning solution is 15.31 mg/cm^2 min. compared to that of 5% sodium hydroxide with no phosphate which is 16.65 mg/cm^2 min. This again could be caused by its effect on the concentration gradient. The solubility of sodium hydroxide at 0°C is 42 g/100 ml of water, whereas that of trisodium phosphate is 8.8 g/100 ml of water. These data explain why the addition of 10% trisodium phosphate by weight of caustic to 3% sodium hydroxide cleaning solution has a lower rate of soil removal than a 5% sodium hydroxide cleaning solution. The effect of increasing the concentration of trisodium phosphate is five fold that of sodium hydroxide. The effect in solution of the trisodium phosphate on the Ca^{++} ions present due to water hardness is to form insoluble precipitates with these ions. Trisodium phosphate is in this manner different in its treatment of water hardness from the other sequestering agents. The fact that it decreases the rate of soil removal may be due to its not forming soluble complexes as the other sequestering agents.

Tests using tetrasodium pyrophosphate as the sequestering agent were performed for the three concentrations. Table 7 represents an analysis of variance for the experimental results, and at the 5% level of significance there was no difference between the three concentrations used. There was also no significant difference between the 3% sodium hydroxide solution and the solution with the sequestering agents. Mean values for these tests are listed in Table 10.

A study of the effect of increasing the concentration of sodium gluconate on the rate of soil removal was performed and the experimental results were analyzed by the analysis of variance method (Table 8). This table indicates significantly different means for the three concentrations. The rate of soil removal for the 2.5% solution was lower than for the 5 and 10% solutions. The mean results of these tests are tabulated in Table 10. A contrast between the 2.5% sodium gluconate solution and the 3% sodium hydroxide solution indicated a difference between the two rates of soil removal, with the 3% sodium hydroxide solution being the more efficient cleaning solution. The decrease in efficiency between the 2.5% sodium gluconate solution and the 3% sodium hydroxide solution was in the order of 9%. At the higher sequestering agent concentrations such as the 5% and 10% concentrations there was no significant effect on the rate of soil removal when compared with the value from the 3% sodium hydroxide solution.

The effect of tetrasodium ethylenediaminetetraacetate on the rate of soil removal was studied using the three concentrations of sequestering agent in 3% sodium hydroxide solution. An analysis of variance (Table 9) on the experimental data indicates a significant difference between the mean values for the three concentrations. There was no effect on the cleaning rate when 2.5% and 5% concentrations of EDTA were added; however, for the 10% concentration, a notable effect was observed. The values listed in Table 10 showed an enhancement in the rate of soil removal of 16% by the addition of 10% EDTA.

The effect of the variables of temperature was studied using distilled water, 3% sodium hydroxide, and 5% sodium hydroxide cleaning solutions. These three concentrations (0-5% sodium hydroxide) were used because they represented the causticity range used in the bottle washing industry. Temperatures of 130, 150, and 170°F were used to study the effect of temperature on the rate of soil removal for the three cleaning solutions at the four concentrations of soluble solids. The data of Table 11 indicate that the rate of soil removal for the three temperatures for any given sodium hydroxide or soluble solids concentration was highest at 170°F. Figures 7, 8 and 9 graphically represent the data of Table 11. From these figures a contrast can be made between distilled water and the alkaline cleaning solutions for the four concentrations of soluble solids. An increase in the temperature of a cleaning solution decreases the viscosity of the solution and increases the solubility of sugar in the solution, thus increasing both the diffusion rate and the concentration driving force. The increase in the diffusion rate is linked to the effect of an increase in temperature on the molecular motion. An increase in the temperature will increase the motion of the molecules due to higher energy thus increasing the transfer rate of material from the film to the solution. The effect of sodium hydroxide concentration on the rate of soil removal at each temperature was the same; an increase in sodium hydroxide concentration or soluble solids concentration decreased the rate of soil removal at all three temperatures tested.

The effect of agitation on the rate of soil removal was studied using distilled water cleaning solutions. The agitation speeds used were 0, 65, and 147 rpm. Agitation was maintained at these low velocities because of the difficulty in reproducing the tests when higher agitation speeds, which caused turbulent conditions in the test vessel, were used. The data in Table 12 showed a greater rate of soil removal for the four concentrations of soluble solids used as the result of a greater rate of agitation. Figure 10 represents the data of Table 12. It is interesting to note that at 0 and 65 rpm the cleaning solution with 60% soluble solids caused a gain in weight in the test vessel. This can only mean that the diffusion of water into the sugar soil was greater than the rate of diffusion of the sugar into the fluid. The low speed of agitation would cause a larger mass transfer film thickness which would effectively cause a greater resistance to the sugar diffusion.

However, the concentration gradient in the sugar was large enough to cause a driving force for the water toward the soil causing a gain in weight of the soil in the test beaker. The values obtained would indicate the advantages to be gained from the added energy for soil removal which the fluid supplies when it is under a higher velocity. Turbulent conditions, while not ideal for this model would be ideal in an industrial cleaning system. These conditions would cause a higher rate of soil removal because of greater energy being available for dislodging the soil particles attached to the glass surface.

Tests were conducted to determine the effect of the variable of time on the rate of removal of sugar soil using distilled water cleaning solutions. An analysis of variance (Table 13) performed on the rate of soil removal data found the rate to be independent of time; however, the amount of soil removed was proportional to the soil solution contact time. The test model is such that for the contact times used the increase in concentration due to soil removal can be considered negligible. This is due to the large amount of solution with respect to the amount of soil removed per unit of time. Since the concentration gradient remains constant, the rate of soil removal is also a constant with the amount of soil removed being proportional to the soil solution contact time. The time factor is important in bottle cleaning because of both the required sterilizing time and the time necessary to remove the soil from the glass surface.

Determination of the soil pick up of cleaning solutions with respect to age and usage were conducted on 11 commercially used cleaning solutions which were provided by the ABCB. These solutions were made up from various proprietary compounds as used by the processing plants. Appendix 1 lists the information which was supplied with each of the cleaning solutions. The cleaning solutions are listed from A to K and for each of these solutions there is given age of solution, compound used, type of washer, number of bottles washed, frequency of make-up, etc. Percent soluble solids and normality was calculated for each solution. The concentration varied from 1.03 to 3.5% soluble solids not caustic as shown in Table 14. There is no apparent correlation between age of solution, number of bottles washed and the percent soluble solids. This result was expected because the conditions encountered in each plant are rarely reproducible. The data of Appendix 1 would indicate that age or use are not criteria for discarding the solution. However, these data do indicate that periodic make up of solution with both water and caustic to maintain the causticity and volume of the solution constant, do not allow a soluble solids to build up to a level where they will substantially affect the rate of soil removal.

The type of washer greatly influences the cleaning of the containers because of the differences in solution contact time, the use of mechanical energy to assist in soil removal, and the temperature of operation. The differences between brands and models of the same brand are great enough so that any study performed on a particular washer will be pertinent only to that model of washer. Thus, because of the dissimilarity between washing operations, this study was performed in a laboratory under ideal conditions with no attempt being made to simulate industrial conditions.

The analytical solution to this problem could not be solved because of the model chosen for this study. The beaker test vessel presents a very difficult system to analyze due to the velocity gradient toward the periphery of the beaker. The velocity is greatest near the sides of the beaker and least in the center. This velocity gradient causes a gradient in the mass transfer film thickness which is proportional to the rate of soil removal. There were several attempts made at trying to determine the thickness of the mass transfer film by analogy with the heat transfer film. These tests were unsuccessful because the equipment at hand was not sensitive enough to measure the very short come up times encountered in the test model. Because of insufficient data the values for the diffusivity of sugar in this system could not be determined, nor was there an available relationship for the mass transfer coefficient of the system under study.

SUMMARY

Studies of the effect of several variables on the rate of soil removal have shown significant differences. The experimental procedure developed in this study allowed for the determination of the rate of soil removal when some of the variables affecting the system were changed. An analysis of variance indicated that the results of tests made using this procedure were reproducible with respect to batches of soil, beaker position in the agitator and experimental procedure.

It was observed that an increase in the sodium hydroxide concentration would cause a marked decrease in the rate of soil removal. The range of caustic concentrations used in the bottling industry (0-5%) were studied extensively. The addition of 5% caustic to a distilled water cleaning solution caused a decrease in the rate of soil removal of 32.5%. The use of higher concentrations of sodium hydroxide further decreased the rate of soil removal. The most effective cleaning agent for removal of soluble solids was observed to be distilled water since this system is controlled by the concentration gradient and distilled water cleaning solutions have the largest concentration gradient of the cleaning solutions used.

The presence of soluble solids in the cleaning solutions lowered substantially the rate of soil removal. However, for all concentrations of soluble solids used in distilled water and alkaline cleaning solutions, distilled water was the most effective cleaning agent at each of the soluble solids concentrations used. Proprietary cleaning compounds were tested and compared to 3% sodium hydroxide cleaning solutions. The rate of soil removal was highest for the 3% sodium hydroxide cleaning solutions; further analysis could not be made because the additive effects in the proprietary cleaning compounds were not known. The rate of soil removal by 3% sodium hydroxide was markedly larger at the highest soluble solids concentrations. Tests using sugar plus milk soil showed that distilled water was again the more efficient cleaning agent as demonstrated by the sugar soil. This soil offered a greater resistance to removal at the high soluble solids cleaning solutions. The high viscosity of the high soluble solids cleaning solutions was evidently a deterrent in the removal of the insoluble soil particles.

The addition of sequestering agents in concentrations of 2.5, 5 and 10% by weight of caustic to 3% sodium hydroxide cleaning solutions was studied to determine any variation in the rate of soil removal. The tests using trisodium phosphate indicated that the addition of this agent lowered the rate of soil removal. The solution containing the highest concentration of trisodium phosphate exhibited the lowest rate of soil removal. The tests with tetrasodium pyrophosphate showed no effect on the rate of soil removal upon the addition of three concentrations of this sequestering agent. The means of the sodium gluconate tests indicated no significant effect for 5 and 10% concentrations of sodium gluconate in the cleaning solution. However, for the 2.5% sodium gluconate cleaning solution there was a decrease in the rate of soil removal when the mean value was compared with that for the 3% sodium hydroxide cleaning solutions. The addition of EDTA sequestering agent in concentrations of 2.5 and 5% to the cleaning solution had no significant effect on the rate of soil removal. Addition of 10% of this sequestering agent enhanced the rate of soil removal by 16%. In conclusion, the experimental data indicate that the sequestering agents used, with the exception of trisodium phosphate, have a very slight effect when used singly, on the rate of soil removal of 3% sodium hydroxide cleaning solutions.

The variables of temperature, agitation, and time were also examined. Studies of distilled water and 3 and 5% sodium hydroxide cleaning solutions mixed with the four concentrations of soluble solids were made at 130, 150, and 170°F. The rate of soil removal was notably enhanced by an increase in the test temperature. The variable of agitation was studied using three agitator speeds. A higher rate of soil removal was demonstrated with the higher agitator speed. The tests were made at low agitation rates to eliminate irregularities caused by turbulence and thus assure reproducibility of the experimental results. The variable of time was found to be proportional to the amount of soil removed, however, due to large solution volumes and a negligible effect on the concentration gradient, the rate of soil removal was constant.

The examination of the used commercial cleaning solutions with respect to soluble soil content did not give any definite criteria on when a cleaning solution becomes inoperative. From the experimental data, a very slight gain in soluble soils can be observed with use. This indicates that restitution of the losses of solution is sufficient to keep the soluble soil content from rising to a significant amount. The highest soluble soil content encountered in this test was 3% which would not affect the rate of soil removal significantly.

CONCLUSIONS AND RECOMMENDATIONS

The variables studied have a marked effect on the rate of soil removal of sugar soil. The results lead to the following conclusions.

1. Distilled water was the most effective soil removal agent tested.

2. An increase in the sodium hydroxide concentration decreases the rate of soil removal.

3. The presence of large concentrations of soluble solids other than caustic in the cleaning solution decrease the rate of soil removal substantially.

4. The three proprietary cleaning compounds tested were approximately the same; however, the 3% sodium hydroxide cleaning solution was a better soil remover.

5. The effect of increasing the concentration of soluble solids not caustic in distilled water and 3% sodium hydroxide cleaning solutions was the same for sugar soil as for the sugar plus milk soil.

6. The addition of trisodium phosphate to the cleaning solution decreased the rate of soil removal. Trisodium phosphate has a greater effect on the rate of soil removal than increasing the sodium hydroxide concentration.

7. The addition of tetrasodium pyrophosphate to the cleaning solution has no effect on the rate of soil removal for the range of 0-10% as percent of caustic.

8. The addition of sodium gluconate sequestering agent has no noticable effect on the rate of soil removal except for the 2.5% as percent of caustic concentration which indicates a slight decrease in the rate of soil removal.

9. The addition of EDTA sequestering agent to the cleaning solution has no effect on the rate of soil removal in concentration of 2.5% and 5% concentrations as percent of caustic. A concentration of 10% EDTA as percent of caustic increases the rate of soil removal significantly.

10. The rate of agitation of the cleaning solution affects the rate of soil removal with the greatest agitation having the largest rate of soil removal.

11. An increase in the test temperature significantly increased the rate of soil removal.

12. The amount of soil removed was proportional to the soil solution contact time; however, the rate of soil removal was constant.

13. The increase in the soluble solids (not caustic) concentration of commercial cleaning solution is negligible.

RECOMMENDATIONS

The bottle washing operation is dependent upon the variables of caustic concentration, temperature, time, agitation and additive or builder concentration. The data obtained in this study suggests that a more efficient cleaning operation than is now in use might be the use of a hot water soak before the bottles are immersed in the caustic solution. The hot water soak would remove the soluble soil in the bottles, and the caustic soak would be used mainly for sterilizing the bottles. To obtain cleaner bottles and insure the free rinsing qualities of the bottles, sequestering agents may be added to the water in the hot water soak tank. The use of this soak would decrease the time necessary for the bottles to remain in the caustic tank because the bottles would then be essentially clean.

The design of a different test model would facilitate obtaining mass transfer coefficients and diffusivities. For this experiment a system where a solution in laminar flow flows over a layer of sugar soil would eliminate the problem of a velocity gradient across the soil thus the mass transfer film thickness would remain constant. The determination of the thickness of the mass transfer film would yield the necessary data for calculating the mass transfer coefficients and diffusivities for the system.

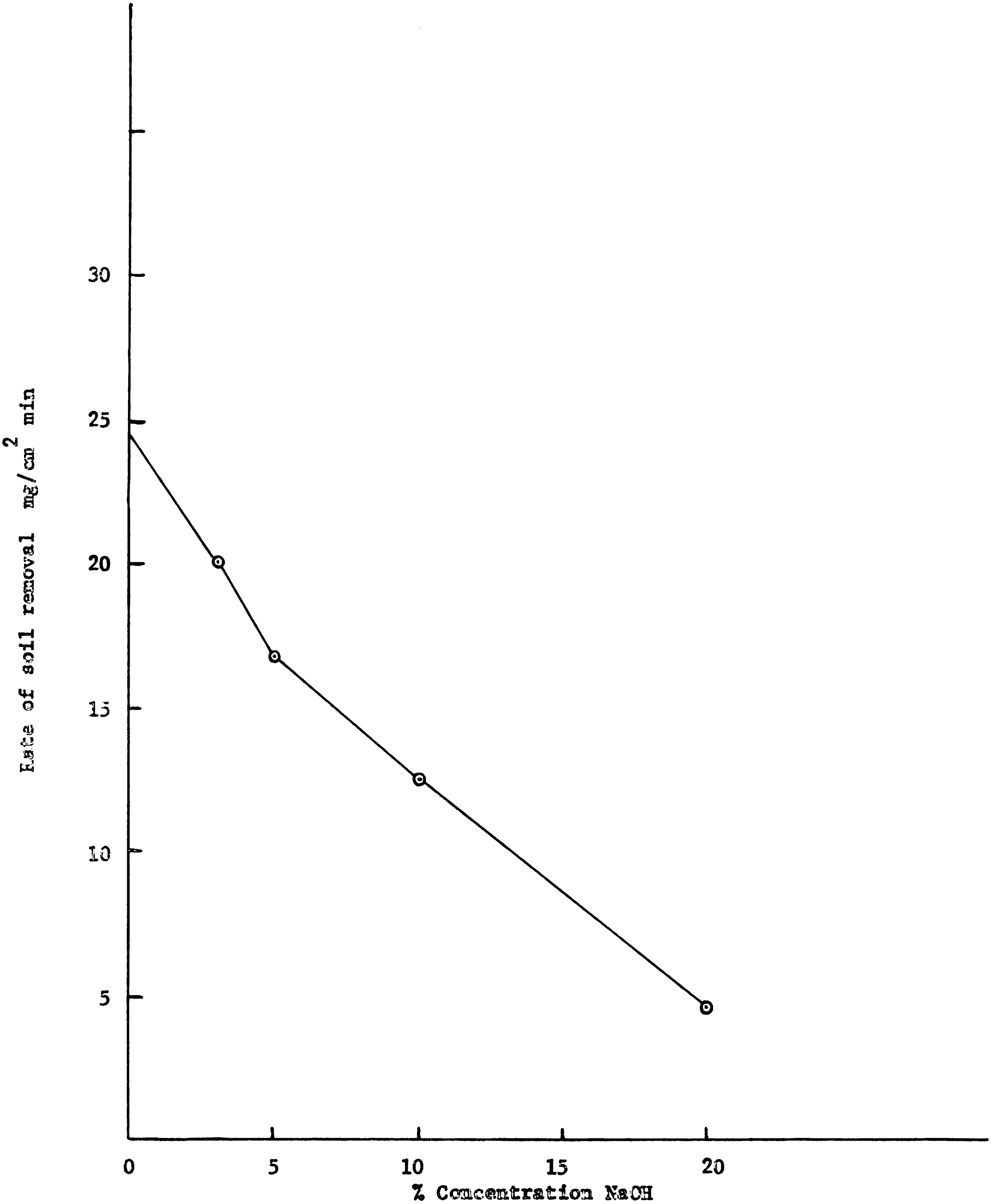

Fig. 3 - Rate of soil removal of sugar soil with increasing NaOH concentration.

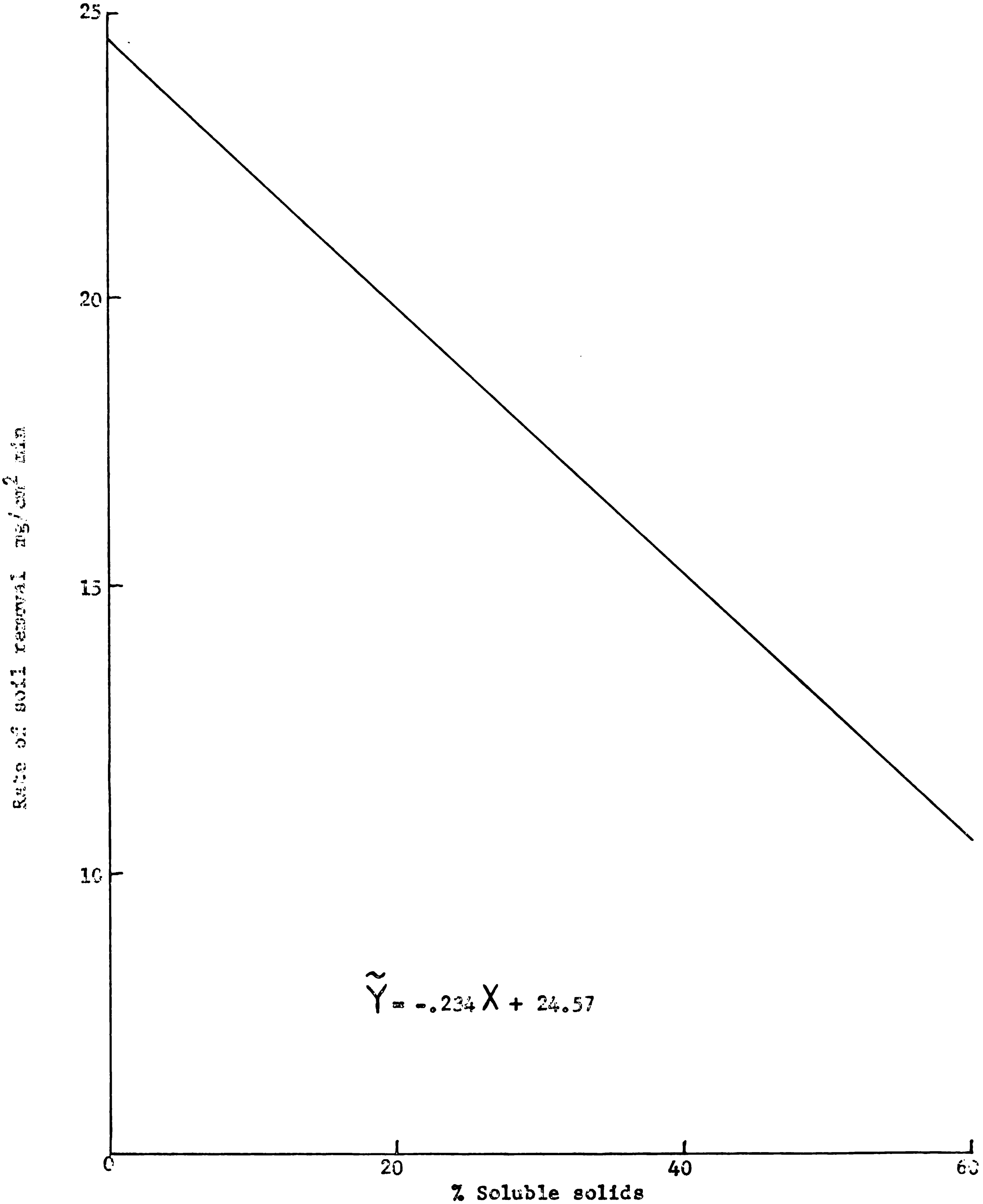

Fig. 4a - Rate of soil removal of H_2O cleaning solution.

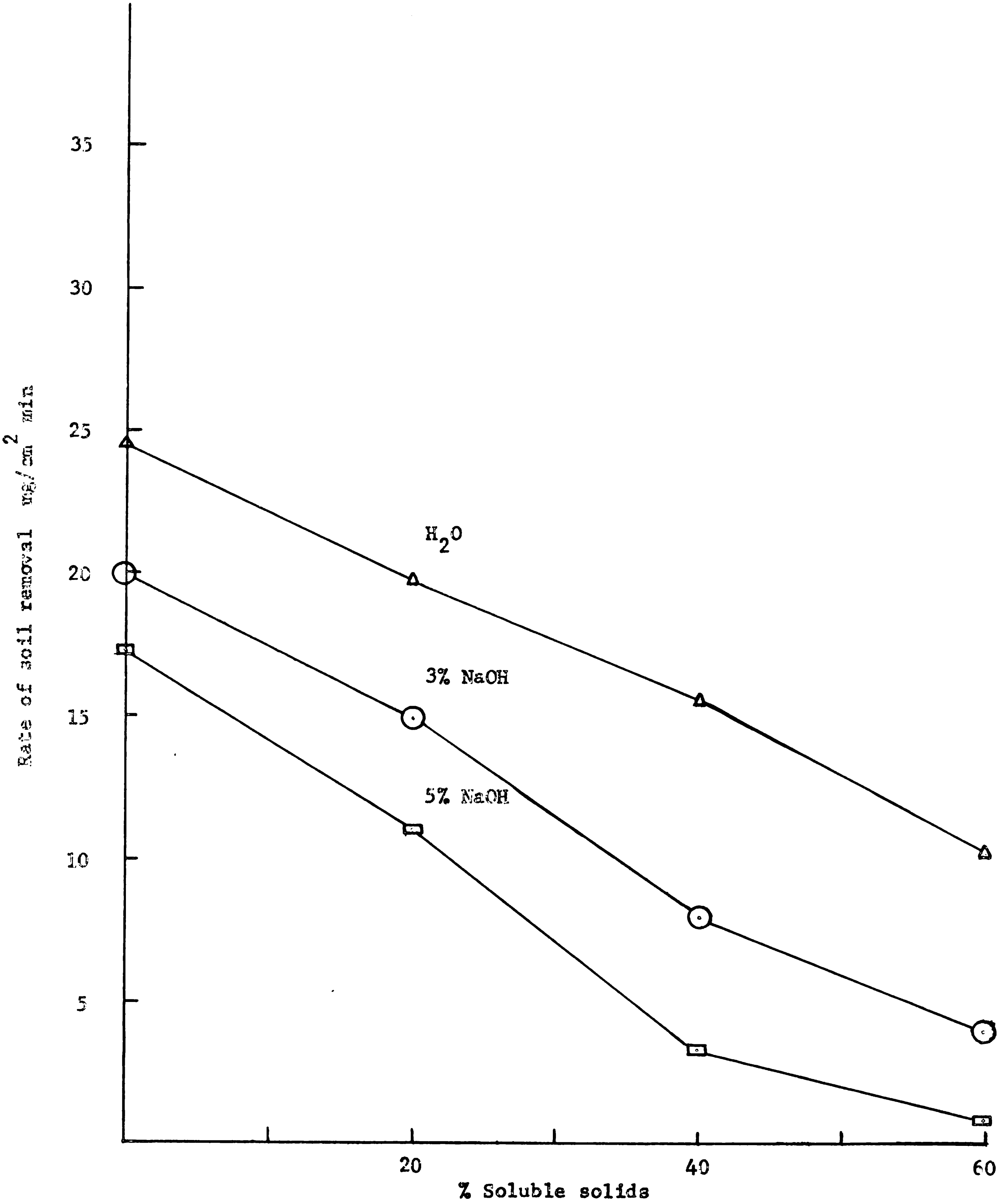

Fig. 4 - Rate of soil removal of H_2O, 3%, 5% NaOH.

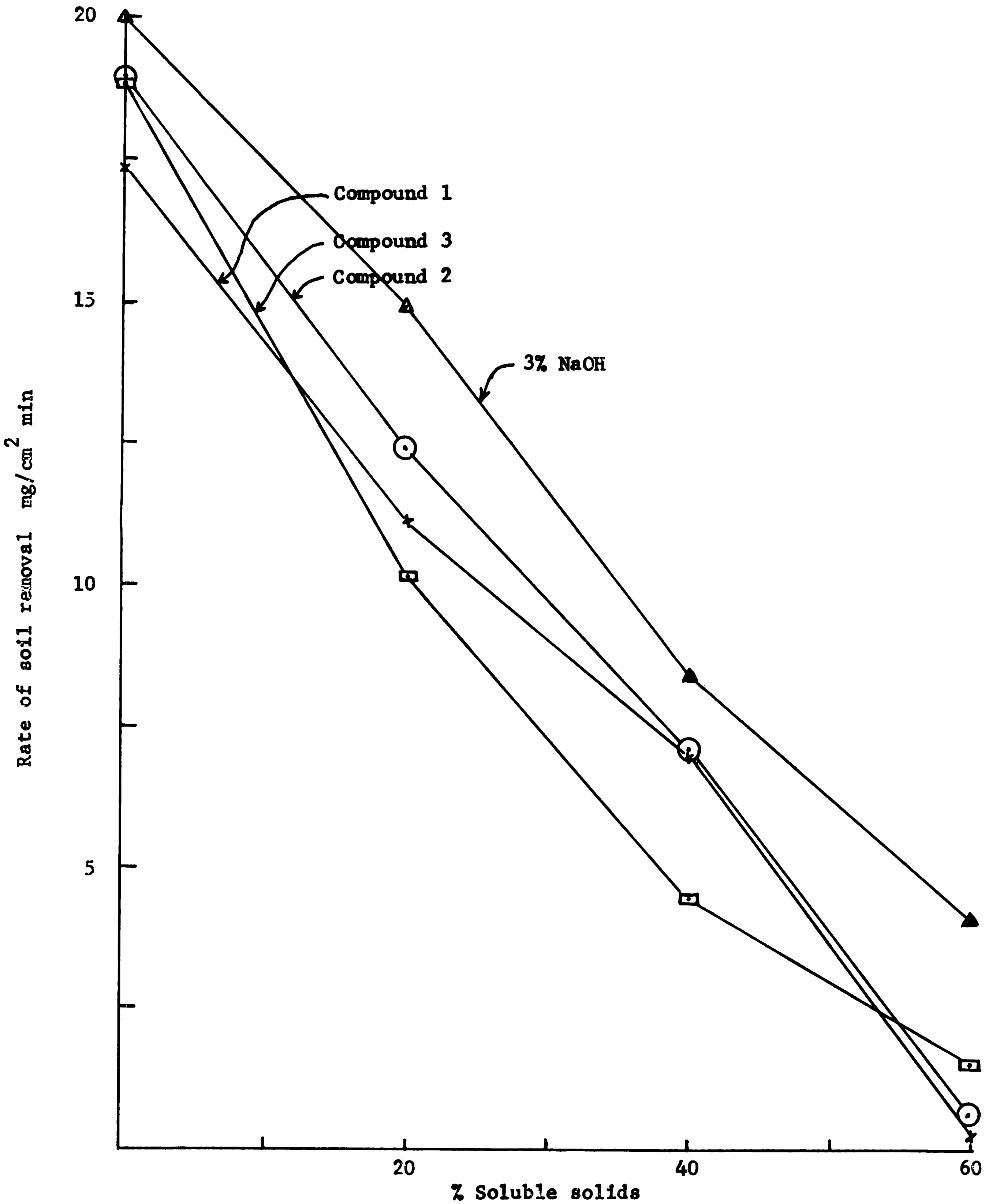

Fig. 5 - Rate of soil removal of 3 proprietary cleaning compounds using sugar soil.

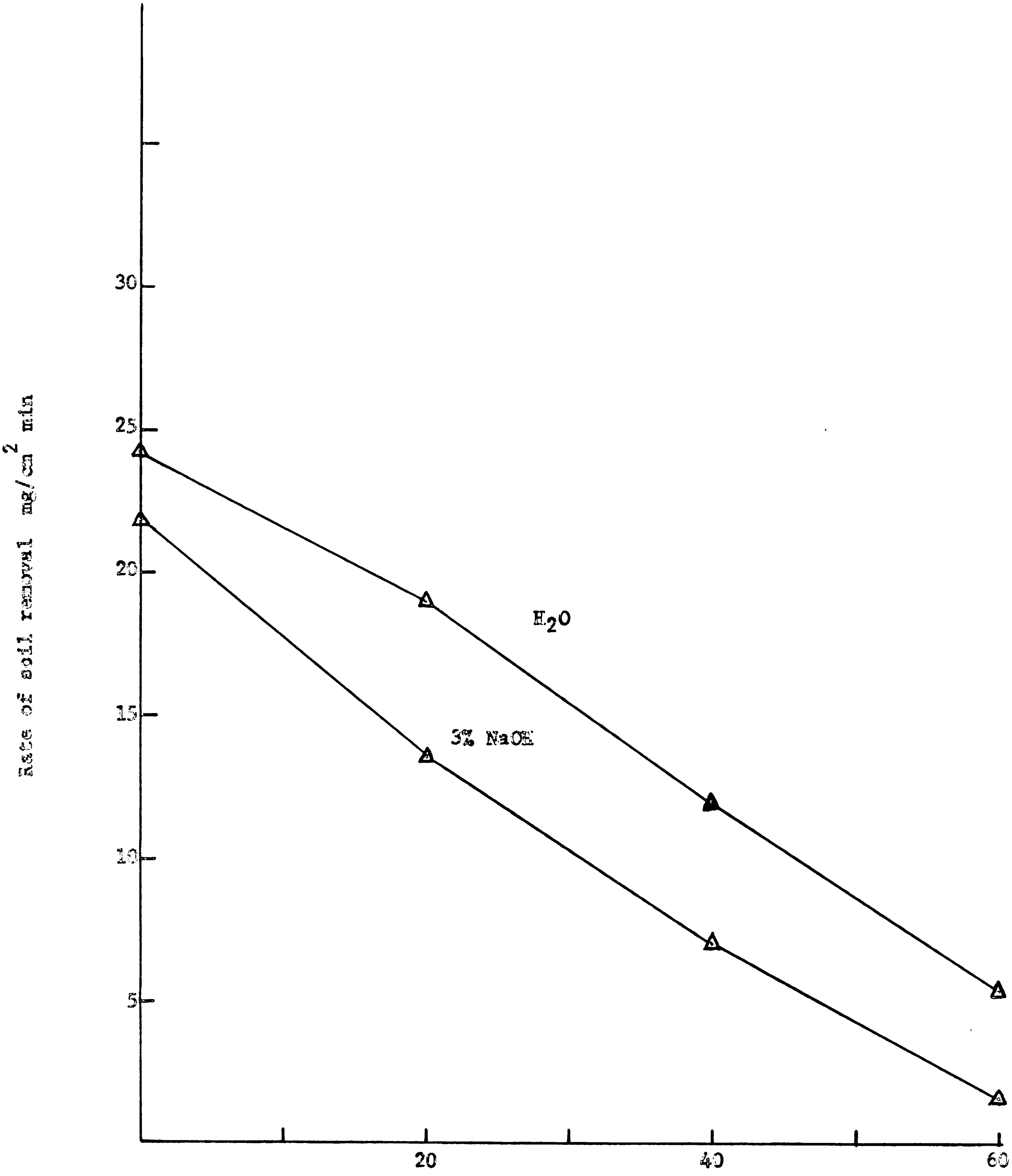

Fig. 6 - Rate of soil removal of milk soil with H_2O and 3% NaOH cleaning solutions vs. sugar concentration.

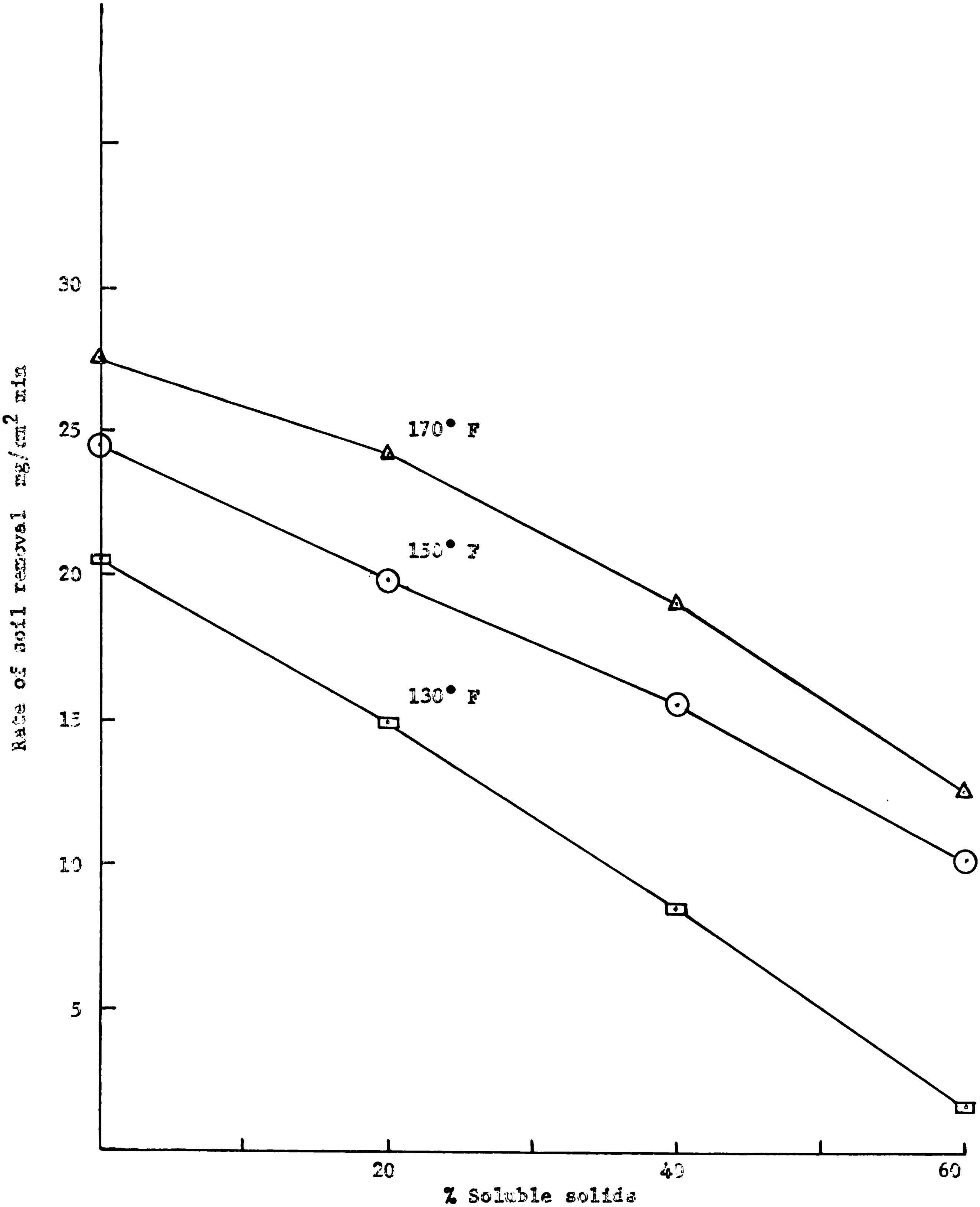

Fig. 7 - Rate of soil removal of sugar soil by distilled water solutions at three temperatures.

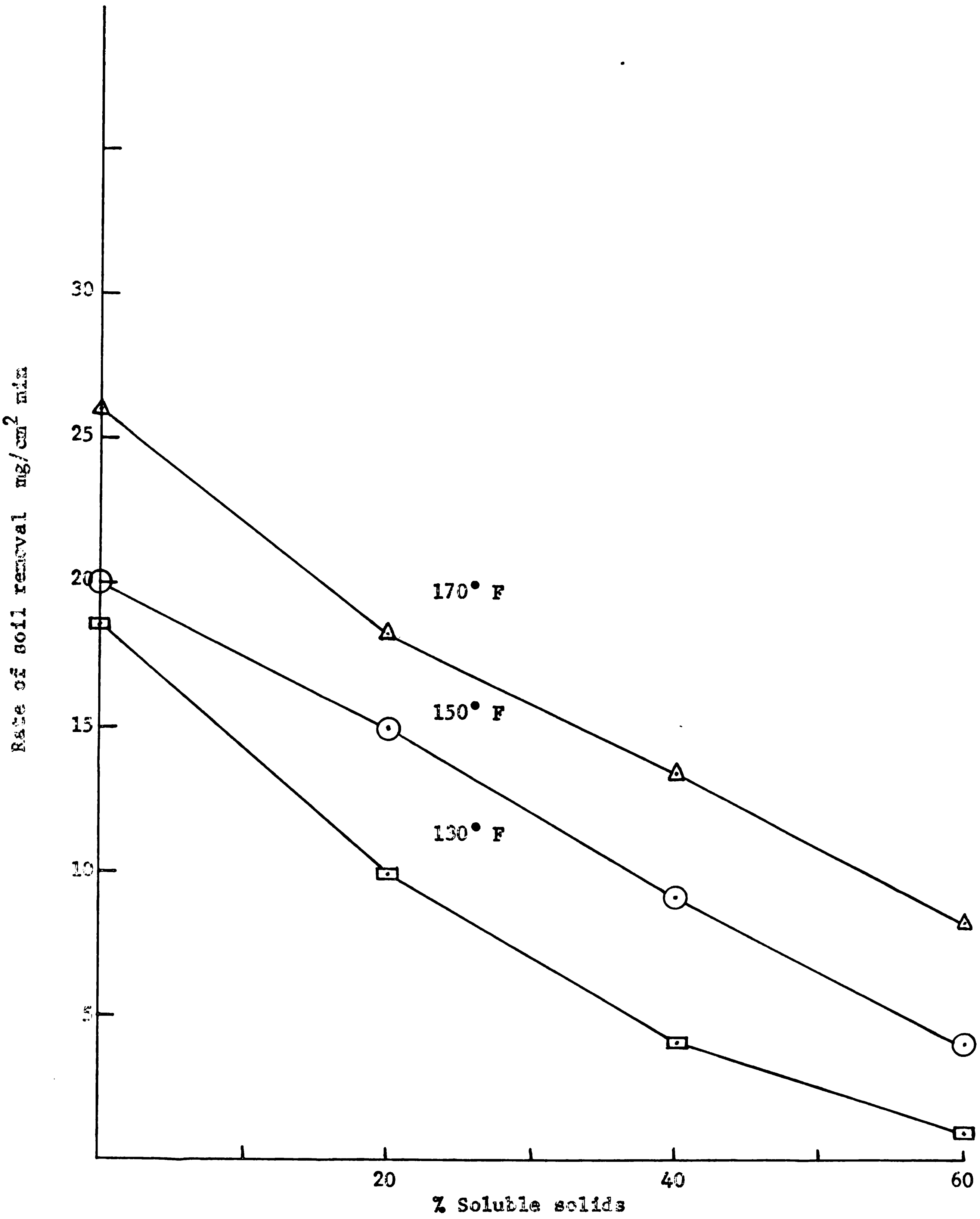

Fig. 8 - Rate of soil removal of sugar soil by 3% NaOH solution at three temperatures.

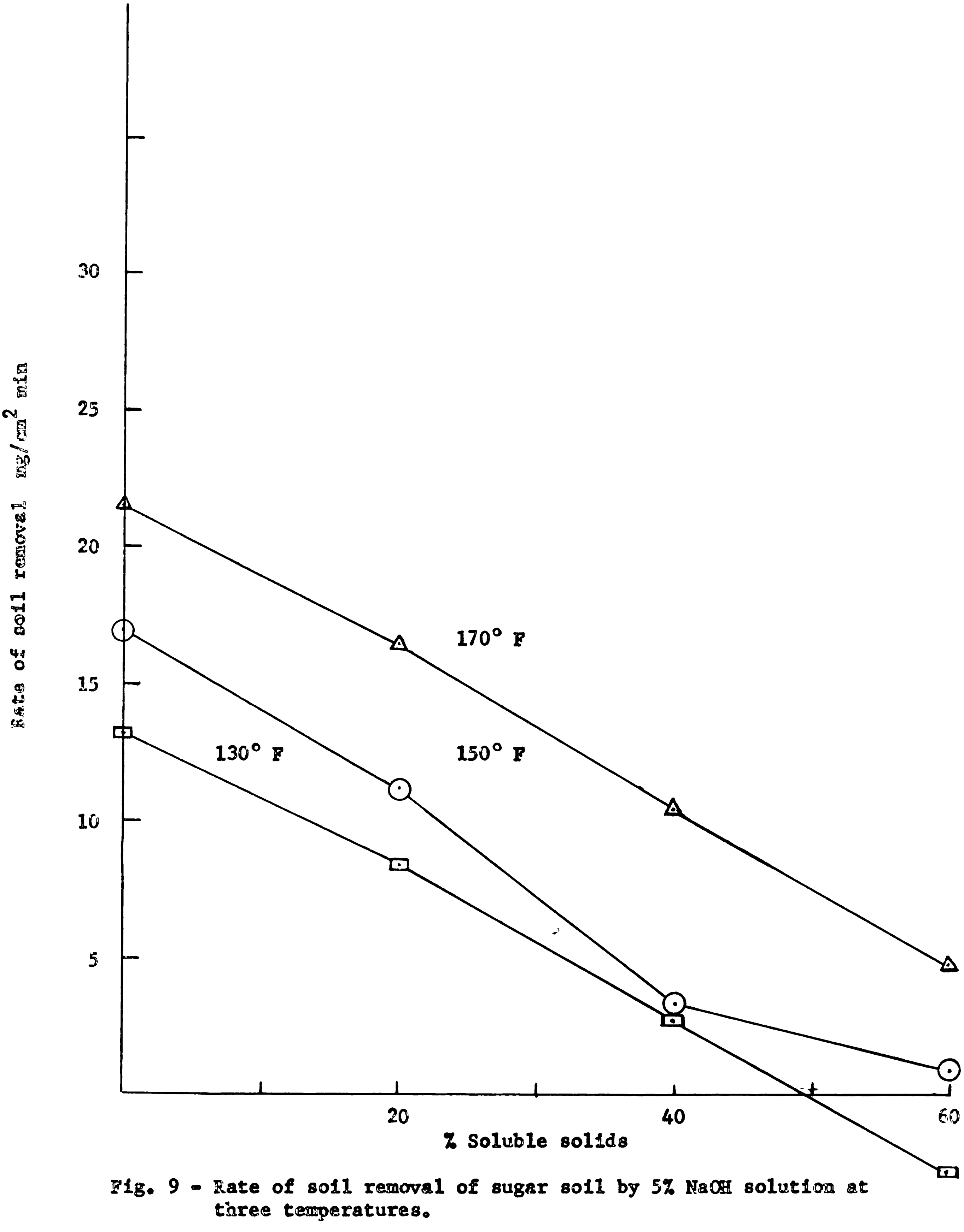

Fig. 9 - Rate of soil removal of sugar soil by 5% NaOH solution at three temperatures.

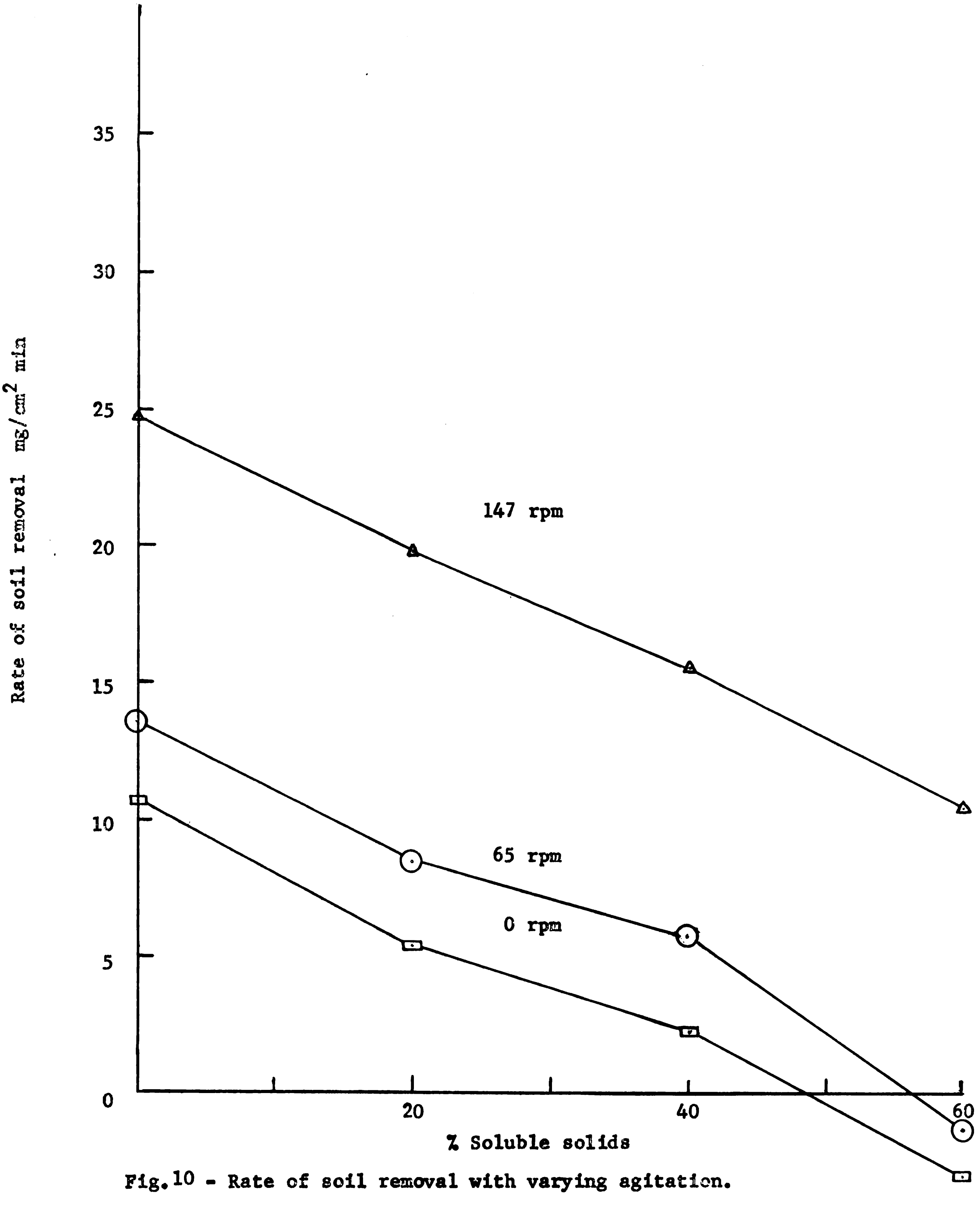

Fig. 10 - Rate of soil removal with varying agitation.

APPENDIX 1

Description of Commercially Used Cleaning Solutions

Sample No. - A

Age of solution Six (6) months

Name of compound used Diversey Rely-On

Type of washer used Heil - 8 wide

Number of bottles washed to date 1,872,000

Frequency of make-up Weekly

Amount of Caustic added at make-up

Number of bottles washed between make-up 84,000

Type of labels used on bottles ACL *

Capacity in gallons of Caustic Compartment

Normality .276

% Caustic 1.1%

% Soluble solids 1.03%

* - Applied Color Label

Sample No. - B

Age of solution Two (2) weeks (from No. 1 tank of washer)

Name of compound used Solvay - 76% Flake Caustic Soda

Type of washer used Meyer Dumore - 16 wide

Number of bottles washed to date 480,000

Frequency of make-up Daily

Amount of Caustic added at make-up Made up with Caustic from No. 2 and No. 3 tanks

Number of bottles washed between make-up 48,000

Type of labels used on bottles   Paper

Capacity in gallons of Caustic Compartment   951

Normality   .84

% Caustic   3.30

% Soluble solids   2.4%

Sample No. - C

Age of solution   Four (4) months

Name of compound used   Economics Laboratory, Inc. BW - 61 - 1

Type of washer used   Ladewig - 28 wide

Number of bottles washed to date   64,000,000

Frequency of make-up   Every other bottling day

Amount of Caustic added at make-up   200 - 300 lbs.

Number of bottles washed between make-up   2,000,000

Type of labels used on bottles   ACL *

Capacity in gallons of Caustic Compartment   3,500

Normality   .97

% Caustic   3.90%

% Soluble solids   2.5%

*- Applied Color Label

Sample No. - D

Age of solution   Five (5) months (taken from No. 2 compartment of washer)

Name of compound used   Diversey - Glo-Tak

Type of washer used   Barry-Wehmiller - 40 wide

Number of bottles washed to date 29,160,000

Frequency of make-up Automatic make-up equipment used

Amount of Caustic added at make-up

Number of bottles washed between make-up 1400-1500 bottles washed for each pound of make-up, Caustic

Type of labels used on bottles ACL *

Capacity in gallons of Caustic Compartment

Normality .80

% Caustic 2.80%

% Soluble solids 3.2%

* - Applied Color Label

Sample No. - E

Age of solution Five (5) months (taken from No. 2 compartment of washer)

Name of compound used Diversey - Glo-Tak

Type of washer used Barry-Wehmiller - 28 wide

Number of bottles washed to date 22,680,000

Frequency of make-up Automatic caustic strength control system

Amount of Caustic added at make-up One pound/1400-1500 bottles

Number of bottles washed between make-up

Type of labels used on bottles ACL *

Capacity in gallons of Caustic Compartment

Normality 1.03

% Caustic 4.10%

% Soluble solids 2.0%

* - Applied Color Label

Sample No. - F

Age of solution Eleven (11) months

Name of compound used Diversey Spec-Tak-1000

Type of washer used Ladewig - 24 wide

Number of bottles washed to date 10,500,000

Frequency of make-up Daily

Amount of Caustic added at make-up 30 lbs.

Number of bottles washed between make-up 48,000

Type of labels used on bottles ACL *

Capacity in gallons of Caustic Compartment 2140

Normality 1.21

% Caustic 4.8%

% Soluble solids 3.5%

* - Applied Color Label

Sample No. - G

Age of solution Twenty (20) months (taken from No. 3 tank of 6 tank washers)

Name of compound used Diversey - Spec-Tak-1000

Type of washer used Meyer-Dumore - 24 wide

Number of bottles washed to date 73,920,000 (40% are non-returnable bottles)

Frequency of make-up Made up with Caustic from No. 1 compartment

Amount of Caustic added at make-up

Number of bottles washed between make-up 168,000

Type of labels used on bottles ACL *

Capacity in gallons of Caustic Compartment 922

Normality 1.38

% Caustic 5.50%

% Soluble solids 3.5%

* - Applied Color Label

Sample No. - H

Age of solution Twenty (20) months (taken from No. 3 tank of 5 tank washer)

Name of compound used Diversey - Spec-Tak-1000

Type of washer used Meyer-Dumore - 40 wide

Number of bottles washed to date 126,000,000

Frequency of make-up Made up with Caustic from No. 1 compartment

Amount of Caustic added at make-up

Number of bottles washed between make-up 288,000

Type of labels used on bottles ACL *

Capacity in gallons of Caustic Compartment 1490

Normality 1.04

% Caustic 4.20%

% Soluble solids 2.2%

* - Applied Color Label

Sample No. - I

Age of solution One (1) day

Name of compound used Diamond Alkali Hi-Test Alkali No. 3

Type of washer used Meyer-Dumore - 24 wide

Number of bottles washed to date 56,000 (all non-returnable bottles)

Frequency of make-up

Amount of Caustic added at make-up

Number of bottles washed between make-up

Type of labels used on bottles   Paper

Capacity in gallons of Caustic Compartment   1200

Normality   .93

% Caustic   3.7%

% Soluble solids   2.3%

Sample No. - J

Age of solution   Three (3) months

Name of compound used   Maryland Chemical Co. - Utopia

Type of washer used   Ladewig - 28 wide

Number of bottles washed to date   5,702,400

Frequency of make-up   Daily

Amount of Caustic added at make-up   8 lbs.

Number of bottles washed between make-up   86,400

Type of labels used on bottles   ACL *

Capacity in gallons of Caustic Compartment   3,500

Normality   .60

% Caustic   2.40%

% Soluble solids   2.20%

* - Applied Color Label

Sample No. - K

Age of solution Three (3) months

Name of compound used Sterling Chemical Co. CH-100

Type of washer used Ladewig - 24 wide

Number of bottles washed to date 5,602,400

Frequency of make-up Daily

Amount of Caustic added at make-up 8 lbs.

Number of bottles washed between make-up 85,400

Type of labels used on bottles ACL *

Capacity in gallons of Caustic Compartment 2140

Normality .61

% Caustic 2.40%

% Soluble solids 1.7%

* - Applied Color Label

BIBLIOGRAPHY

Benson, W. F. 1956. The polyphosphate story. Proc. Third Ann. Meeting Soc. Soft Drink Technol., Washington, D. C.

Bottle Washing Bulletin, 1893. Nordberg Manufacturing Co. Milwaukee, Wisconsin.

Buchanan, J. H., and M. Levine. 1939. Bottle washing and its control. Beverage Production and Plant Operation. 1958. American Bottlers of Carbonated Beverages. Washington, D. C.

Carpenter, P. L. 1961. Microbiology. W. B. Saunders and Co. Philadelphia. p. 432.

Chaberek, J. and A. E. Martell. 1959. Organic sequestering agents. John Wiley and Sons. New York. p. 616.

Dixon, W. J. and F. J. Massey, Jr. 1957. Introduction to statistical analysis. McGraw Hill Co., Inc., New York. p. 488.

Dormuth, L. C. 1956. Discussion of the longevity of bottle washing solutions including make up and caustic reclamation. Proc. Third Ann. Meeting Soft Drink Technol. Washington, D. C.

Dungfelder, C. C. 1957. Importance of efficient rinsing in bottle washing equipment. Proc. Fourth Ann. Meeting Soc. Soft Drink Technol. Washington, D. C.

Jennings, W. G. 1959. Circulation cleaning III. The kinetics of a simple detergent system. J. Dairy Sci., 42, 1763.

Jennings, W. G. 1963. Detergency. J. Food Tech. 17 (7): 53.

Jensen, J. M. 1946. Measuring detergency functions as affected by various detergents and procedures against milk films by application of a mechanical washing apparatus. J. Dairy Sci. 29, 453.

Kaufmann, O. W., T. I. Hedrick, I. J. Pflug, C. G. Pheil and R. A. Keppeler. 1960a. Relative cleanability of various stainless steel finishes after soiling with innoculated milk solids. J. Dairy Sci. 43, 28.

Kaufmann, O. W., T. I. Hedrick, I. J. Pflug and C. G. Pheil. 1960b. Relative cleanability of various finishes of stainless steel in farm bulk tanks. J. Milk Food Tech. 23, 377.

Korab, H. E. 1964. Private communication. American Bottlers of Carbonated Beverages. Washington, D. C.

Ladewig, A. 1955. Report of the bottle washing committee. Proc. Second Ann. Meeting Soc. Soft Drink Technol. Washington, D. C.

Martell, A. E. and M. Calvin. 1953. Chemistry of the metal chelate compounds. Prentice Hall. New York.

McCalleon, J. J. 1961. Some chemical factors involved in bottle washing. Proc. Eighth Ann. Meeting Soc. Soft Drink Technol., Washington, D. C.

Mehltretter, C. L., B. H. Alexander, and C. E. Rist. 1953. Sequestration by sugar acids. Ind. Eng. Chem., 45, 2782.

Overman, O. 1964. Private Communication. Cowles Chemical Co. Cleveland, Ohio.

Parker, R. B., P. R. Elliken, G. T. Nelson, G. A. Richardson and G. H. Wilster. 1953. Cleaning pipelines in place. Food Eng. 25 (1), 82.

Pflug, I. J., T. I. Hedrick, O. W. Kaufmann, R. A. Keppeler and C. G. Pheil. 1961. Studies on the deposition and removal of radioactive soil. J. Milk Food Tech. 24, 390.

Ruff, D. G. and K. Becker. 1955. Bottling and canning of beef. Siebel Publishing Co. Chicago, Illinois.

Schwartz, A. M., J. W. Perry and J. Berch. 1958. Surface active agents and detergents. Interscience Publishers, Inc. New York. p. 839.

Shand, E. B. 1958. Glass Engineering Handbook. McGraw Hill Co., Inc. New York. p. 482.

Technical Bulletin No. 99. 1959. Pfizer gluconates in caustic bottle washing. Charles Pfizer and Co. New York.