RELEASES DURING CLEANING OF EQUIPMENT

by

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CONTENTS

FIGURES

TABLES

(continued)

TABLES

(continued)

TABLES (continued)

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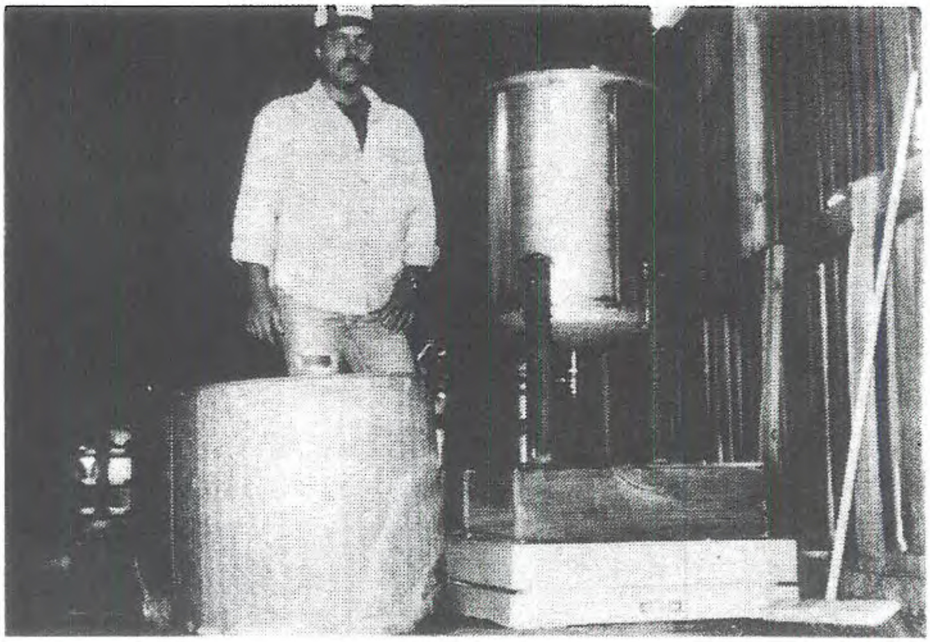

Figure A-1. Dish bottom steel tank atop large scale draining into trough.

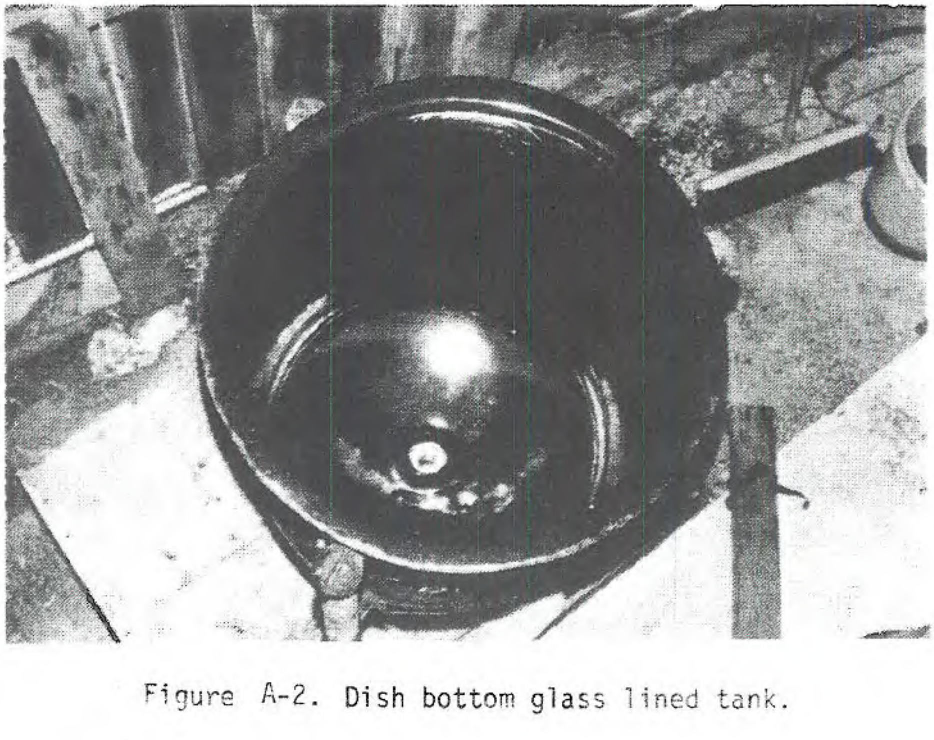

Figure A-2. Dish bottom glass lined tank.

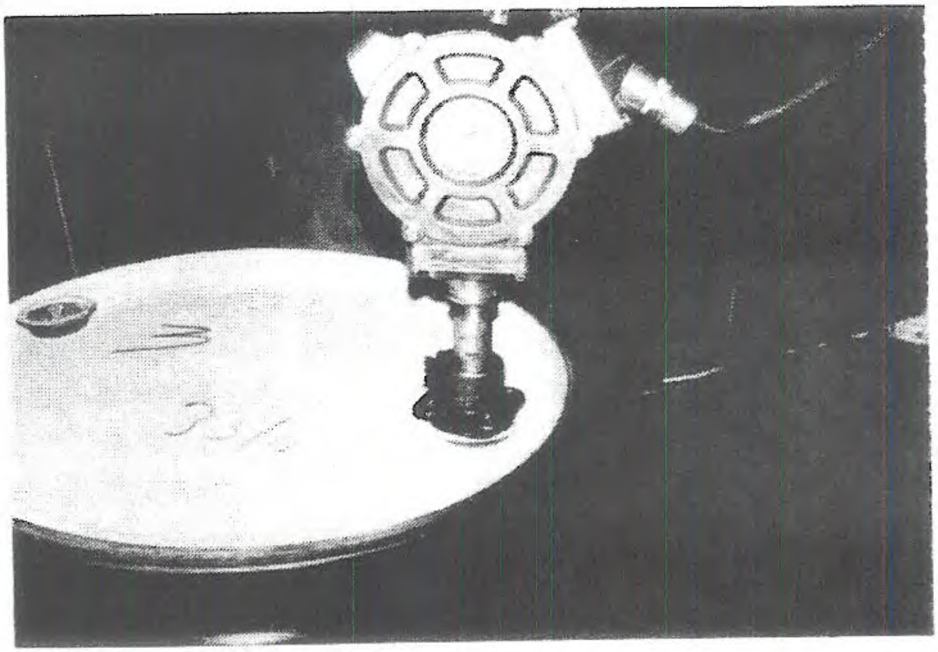

Figure A-3. 55 Gallon (0.21 m^3) steel, bung-top drum with drum pump.

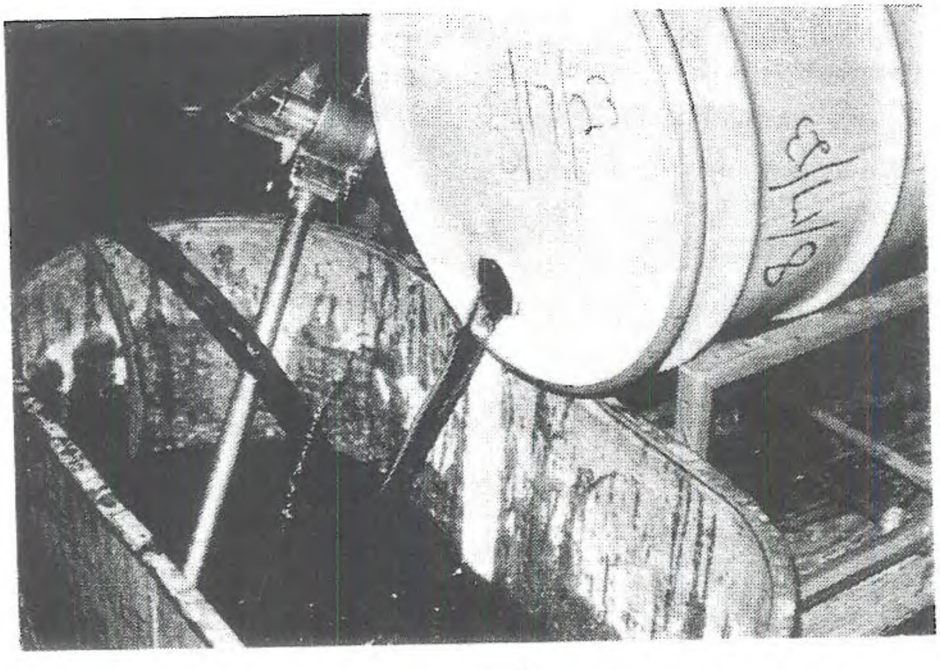

Figure A-4. 55-Gallon, (0.21m^3), steel, open-top drum (lid attached) resting on drum dolly while pouring motor oil into trough.

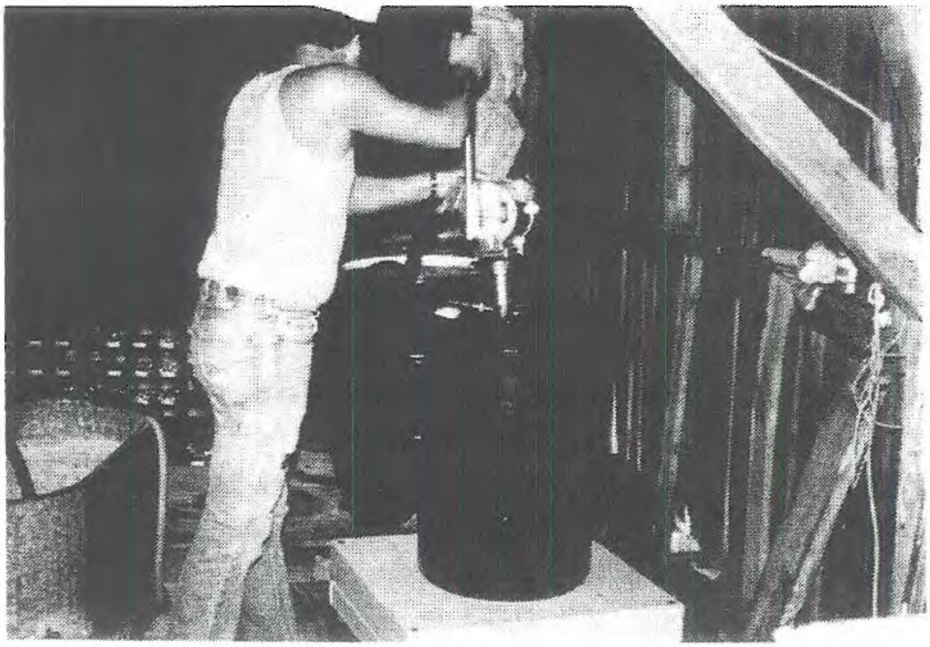

Figure A-5. 30 Gallon (0.11 m^3) polyethylene bung-top drum being pumped empty.

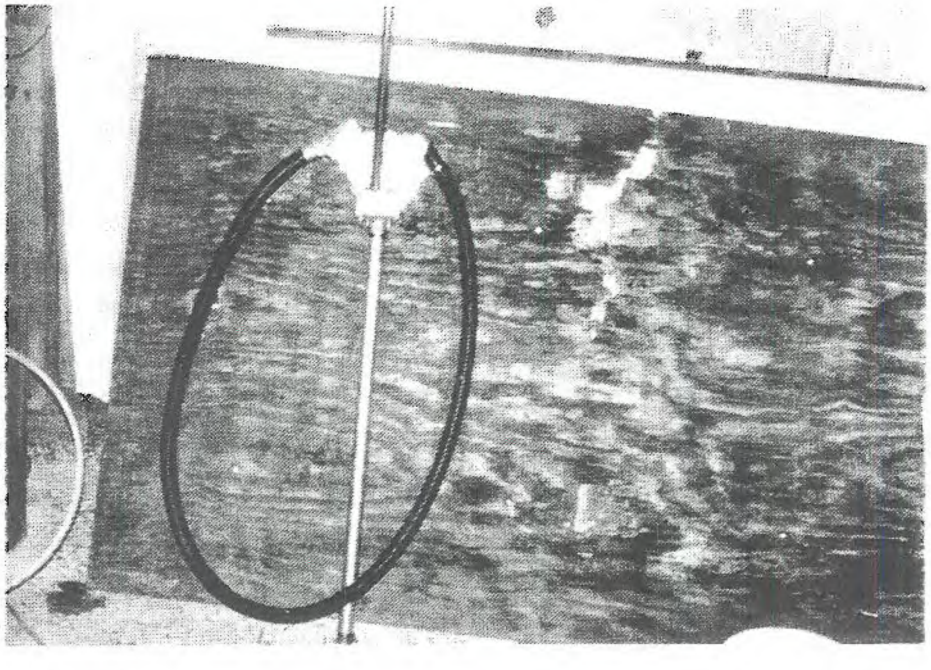

Figure A-6. Drum pump.

SECTION 1

INTRODUCTION

1.1 BACKGROUND

The U.S. Environmental Protection Agency's Office of Toxic Substances (OTS) conducts occupational exposure and environmental release assessments of new chemicals as part of its Premanufacture Notification (PMN) program. Cleaning of process equipment and shipping containers is an activity with potential for release of such chemicals. The frequency of cleaning is especially high for batch processes which require that equipment be cleaned either after every batch or at the end of a campaign. The method of cleaning consists of pumping, pouring, or draining the material out, followed by either rinsing the sides of the vessel or filling it and bottom draining with or without forced air.

During PMN reviews, for cases where there is concern for potential ecotoxicity or exposures to workers involved in cleaning, OTS must estimate the amount of material released during cleaning of vessels. Very limited data exist on the quantities of such releases. When data are not available, OTS postulates that 0.1 to 1 percent of the vessel batch size is released per occurrence. Other factors also considered include the type of equipment cleaned, the cleaning medium or solvent used, and the frequency of cleaning. The purpose of this study was to obtain rough estimates of potential releases of chemicals during cleaning of process equipment and shipping containers through: 1) a review of available information on vessel design, cleaning practices, and release data; and 2) a laboratory pilot-scale experimental program to determine the quantities of residue material left in vessels and therefore available for loss during cleaning. OTS could use the results of the experiments to develop a model that will enable the prediction of amounts of material released during cleaning as a function of different parameters.

1.2 APPROACH

The first source of information for this study was the open literature; the references used are cited at the end of this report. Literature sources which were reviewed included reports and publications by other divisions of the EPA, American Petroleum Institute (API), National Barrel and Drum Association (NABADA) and the Department of Transportation (DOT), as well as science and engineering journals. PEI also conducted a search of computer data bases to identify additional information sources. In addition, PEI obtained further information on releases from cleaning via telephone contact with knowledgeable personnel at EPA, API, DOT, NABADA, chemical companies, and commercial companies engaged in the business of cleaning and reconditioning drums, tanks (and associated product transfer lines), and other types of vessels.

As the second phase of this study, PEI prepared a detailed proposal for a laboratory pilot-scale experimental program to obtain estimates of residue materials left in vessels prior to cleaning. In addition to quantifying residues (which was the primary goal of the study), the pilot-scale experiments were designed to investigate the influence of various parameters, such as type of unloading method and bulk liquid viscosity, on the amounts of residue left in the vessels. It was decided that the pilot-scale study would focus on drums and tanks of different design configurations in the 30- to 55-gallon (0.11 to 0.21 m^3) size range. Three materials of construction were considered: steel, plastic, and glass-lined. Unloading methods included pouring, pumping, and bottom draining by gravity. Liquid materials studied consisted of water, kerosene, motor oil and a surfactant to investigate the effects of viscosity, density, and surface tension of the chemicals on the amount of residue. Upon review and approval of the proposed pilot-scale experimental program by OTS, PEI procured the necessary equipment and conducted the experiments in accordance with the proposed experimental design.

1.3 CONTENTS

Section 2 presents the results of the literature review. It provides a description of the cleaning methods employed in industry for different types of vessels, and characterizes available release data. It presents estimates of residue quantities reported in the literature for different types of vessels as well as for process piping. Section 3 addresses the objectives of the laboratory pilot-scale study, and describes the experimental design, equipment, and experimental procedures. Section 4 presents the results of the pilot-scale experiments. It discusses the effects of different parameters on the amount of residue materials retained in the vessels. It also includes a comparison of the results of the pilot-scale study with published information in the literature. Section 5 summarizes the principal conclusions of this effort, and presents our recommendations for future activities to comprehensively assess the potential for release of chemicals during cleaning of equipment. Appendix A presents photographs of the different types of vessels and ancillary equipment used for the pilot-scale experiments.

SECTION 2

LITERATURE REVIEW

The purpose of conducting a literature review for this study was to gather available information characterizing vessel cleaning practices and amounts of residue left for potential release during cleaning. This section briefly describes vessel cleaning methods, presents estimates of residue quantities reported in the literature, and addresses factors that influence the amount of residue materials and hence the potential for release of such chemicals during cleaning.

For the purpose of this study, it is convenient to divide vessels into two categories, stationary and mobile. Stationary vessels include, but are not limited to, storage tanks and reaction vessels. Mobile sources include barges, railroad tank cars, tank trucks, and drums.

2.1 METHODS OF VESSEL CLEANING

2.1.1 General

The need for vessel cleaning arises in an infinitely wide variety of situations. In general, however, vessel cleaning corresponds to changes in the type of material contained in the vessel or to situations where adverse conditions could develop when a material is exposed to impurities (e.g., in food processing, pharmaceuticals manufacturing). Vessels are also cleaned as part of routine maintenance operations. Vessels repeatedly used for the same purpose with the same material, however, rarely need cleaning.

Even though there are a wide variety of vessel types, the cleaning methods are generally similar. Very large vessels sometimes require non-typical cleaning methods (e.g., vessel entry and maintenance). Vessel cleaning is usually performed using one or more of the following methods and cleaning materials:[1-12]

Methods

- Fill and flush
- High pressure steam nozzles
- Orbiting or rotating spray nozzles
- Sludge removal by vacuum truck or dissolution
- Scraping of vessel walls

Cleaning materials

- Water
- Steam
- Detergents
- Caustic/acid solutions
- Organic solvents

2.1.2 Stationary Vessels

Storage Tanks--

Storage tanks are not normally cleaned because they usually handle the same material. Cleaning is necessary when there is a change in stored material, contamination of the stored material, or when a sludge/sediment build-up interferes with the operation and capacity of the tank.[1,2]

The methods involved in cleaning a storage tank depend on its size. For smaller tanks, the general aforementioned methods of cleaning will usually sufice.[3] For large storage tanks, however, cleaning can be much more labor intensive because of the need to enter the vessel and/or remove sludge and sediment.[1,4] In either instance, safety precautions must be followed (as specified under the Occupational Safety and Health Administration's confined space entry requirement). The vessel must be made free from explosion hazards and toxic working environments. It is often necessary that a storage tank be freed of vapors by mechanical, natural, or steam ventilation or simply by filling the vessel with water.[3,4]

Reaction Vessels--

Reaction vessels and other process equipment that operate on a continuous or semi-continuous basis usually need cleaning during maintenance operations only. Exceptions include the food, pharmaceutical, and some dye processing operations; equipment in the food processing industry is cleaned, after every shift or at least daily.[5,6] Furthermore, polymerization reactors usually need to be cleaned after every batch.

For the most part, cleaning on a maintenance basis also holds true for batch reactors. Batch reactors used for processing different grades of chemicals, however, require cleaning after each batch or at the end of a campaign.

Cleaning of reactors and processing vessels on a maintenance basis is performed to remove formations of scales, sludges, and corrosive materials that interfere with equipment performance.[7,8] The difficulty in removing these materials necessitates the use of high strength detergents, solvents, or caustic/acid solutions. Methods of applying the cleaning solution must be tailored to the particular process equipment being cleaned. Methods range from flooding the vessel with cleaning solution for smaller vessels to applying the solution in foam or vapor form when the vessel is large.[8]

When reaction vessels and associated equipment require frequent cleaning, cleaning devices (e.g., spray nozzles) can be built into the vessels to eliminate the need to open the equipment.[6,7] These systems are referred to as "clean-in-place" operations and are used widely in the food processing industry.[6]

2.1.2 Mobile Vessels

All rail tank cars, tank trucks, and most barges are generally used in dedicated service (i.e., they are used repeatedly to transport one type of material).[9,13] In this service they are rarely or never cleaned unless they become contaminated. Some materials require periodic cleaning even with dedicated service. For example, styrene cars and trucks must be cleaned after every fifth trip because of the slight polymerization of the styrene on the sides of the container.[9]

Barges, tank trucks, and drums not in dedicated service must be cleaned after each trip before another material can be put into them for shipping. These shipping containers must also be cleaned prior to repairs or testing.[9,13]

In 1978 an estimated 37,200 rail tank cars, 5,010,000 tank trucks, and 24,680,000 drums were cleaned.[9] For 1986, an estimate for the number of drums reconditioned (cleaned) in the United States is 50,000,000.[14]

When a mobile vessel is cleaned, it is generally brought to a centralized location dedicated to cleaning a particular type of vessel. Often in the case of barges, railroad tank cars, and tank trucks, cleaning is performed at shipping and receiving terminals. However, there are also many independent service and maintenance stations that perform interior cleaning.[9] Drums on the other hand, are either reconditioned by independent companies for reuse or destroyed.[9]

For the most part, cleaning depots for barges, tank cars, and tank trucks utilize the general cleaning methods listed earlier.[9-12] Drum reconditioners usually perform additional draining of received drums followed by rinsing and either submerging in a caustic bath or incineration in a furnace.[9,15,16] Most open-top drums are cleaned by incineration.

2.2 RESIDUE QUANTITIES

During the cleaning process, residue material contained in a vessel is released either as a liquid mixture with the cleaning solution, a gas, a sludge, or any combination of the three. It is helpful to know the amount of material left as residue in a vessel, especially if the material is expensive or toxic. Studies and estimates of residue quantities are presented for both stationary and mobile vessels.

2.2.1 Stationary Vessels

Tanks--

In searching the literature, two laboratory studies were found in which residue quantities were directly measured for stationary vessels. In the first study, dairy products of various viscosities were drained by gravity from a 200 gallon (0.76 m^3), stainless steel, sloped bottom tank.[17,18] After the bulk of material had been emptied, the tank drain was left open for an additional two minutes.[18] Results of this study are presented in Table 2-1.

In a study of cleaning a milk storage tank,[19] the average thickness of milk remaining in a 690 gallon (2.61 m^3), sloped bottom test vessel after bottom draining by gravity was found to be 20 μm. This corresponds to 0.006 percent of the volume of the test vessel. Also noted in this study was the inverse effect of drain time on the amount of residue. At a drain time of 2 to 5 minutes, the film thickness was calculated to be to 20 to 24 μm. At a drain time of 8 minutes, the residue milk film thickness decreased to 17 μm. When the drain time exceeded one hour, the milk film thickness decreased further to 10 to 12 μm.[19] The degree of the inverse relationship that is apparent between drain time and film thickness is likely a function of the properties of the bulk material (e.g., viscosity).

TABLE 2-1. EFFECT OF PRODUCT VISCOSITY ON THE QUANTITY OF RESIDUAL MATERIAL LEFT IN A 200 GALLON (0.76 m^3) STAINLESS STEEL, SLOPED BOTTOM TANK.*[17]

Product	Viscosity, cp	Percent remaining on surface
Milk, skim	1.4	0.10
Milk, whole	2.0	0.26
Chocolate milk	21.0	0.47
Half-and-half	15.6	0.39
Cream, 18% fat	45	0.73
Cream, 40% fat	91	0.95
Cultured buttermilk	500	2.3
Sour cream	9000	3.5
Ice-cream mix	121	0.86

* Values obtained following two minutes of draining (i.e., tank was left to drain for two minutes after the bulk of material had drained). Test run at 20°C.

Product Transfer Lines--

One factor which should be taken into consideration when estimating residue amounts in reaction vessels and process equipment is the material retained in product transfer lines. Relative to the residue left in the reactor vessel itself, there may be a substantial amount of material retained in undrained process piping.[5,6]

Factors which will influence the amount of residue left in process piping include 1) the physical properties of the material (e.g., viscosity), 2) method of emptying the line (i.e., pumping or gravity drain), 3) surface area of piping, 4) slope or levelness of the line and 5) "dead spots" in the transfer lines.[5,18,20,21,22] A poorly-designed or installed piping system could have a variety of "dead spots" in the lines where sections of the pipe are filled with process material.[5,20,21] Dead spots may also occur at valves and sampling and instrument ports.[5,20,21]

In the search of the literature, no information from laboratory or pilot studies was found from which the quantity of residue left in a pipe could be determined. PEI, however, obtained pertinent information from three firms involved in the manufacture or use of "pigs" used widely for cleaning product transfer lines.[5,20,21,22] The first firm indicated that a residual of 1 to 2 percent of the pipe volume was left in most instances, and as much as 5 percent was retained when heavy oils are involved.[20] The second firm estimated that a residual of approximately 1 percent of the pipe volume would be left before using a pigging device, and 0.5 to 1 percent after one run of the pigging device.[21] The third firm estimated that a residual of 1 to 2 percent of the bulk material would be obtained.[22] They also cited an estimate of a 0.51 m diameter line containing a 0.8 to 1.6 mm residue lining.[22] This translates to 0.6 to 1.25 percent of the pipe volume.

It is often the case that the quantity of residue retained in process piping is greater than that left behind in the process vessels.[5,20] While all vessel/piping systems will be unique, we can compare the relative amounts of residue left in vessels and process piping by using the percent residue estimates for two vessel/ piping scenarios.

For an example of a small system, a 1000 gallon (3.79 m^3) tank is chosen with 30.5 m of 0.1 m diameter pipe. The volume of the pipe is 65.3 gallons (0.25 m^3). Assuming that the percent residue of 0.1 percent from Table 2-1 for skim milk is applicable for this example, the residue in the tank equals 1 gallon (0.0038 m^3). Using an estimate of 1.5 percent residue in the piping, the piping residue would be 0.98 gallons (0.0037 m^3), indicating that the residue quantities are similar for the tank and process piping for this example.

For an example of a large system, a 10,000 gallon (37.9 m^3) tank is postulated with 91.5 m of 0.2 m diameter pipe. The volume of the piping is 783 gallons (2.96 m^3). Using the same percent residues as in the previous example, the vessel would yield 10 gallons (0.04 m^3) of residue as compared to 11.7 gallons (0.05 m^3) for the piping. The quantity of residue in the product transfer line is, again, comparable to that in the vessel.

2.2.2 Mobile Vessels

Residue Studies and Estimates--

The literature revealed a greater volume of information on residue quantities for this category; this is probably because mobile vessels can be classified according to similar vessel designs.

Table 2-2 presents a summary of study results and estimates of residue materials remaining after unloading mobile vessels. It is stressed that the items addressed as "estimates" are based solely upon experience with the particular types of vessels, and not on laboratory studies.

Concerning the estimates for drums, the estimate of 0.65 gallons (0.0025 m^3) or 1.2 percent residue is based upon the most substantial set of information. It was based upon a compilation of estimates of residue left in drums received at drum reconditioning plants from experts in the reconditioning field and a survey conducted in 1980 of NABADA members. This estimate, however, was made prior to strict enforcement of the "1 inch rule" for drums which formerly contained hazardous materials. It is presumed that the quantity of residue in drums received at reconditioning plants would now be lower.[27] Since most of the data in the literature was collected prior to 1980, it should be noted that these results do not necessarily reflect industry practice today.

The study which found an average of 0.15 percent milk residue in tank trucks (Table 2-2) was performed by sampling the wastewater from individual trucks for biological and chemical oxygen demand (BOD and COD).[25] Sampling

TABLE 2-2. RESIDUE QUANTITIES FOR MOBILE VESSELS

Type of vessel	Bulk material	Unloading method	Residue quantity	Estimate or study results	Reference	Percentage residue computed from estimate
Barge	Oil	NA[a]	Average: 0.3% Range: 0.1 - 0.9%	Estimate	(10)	0.3 0.1 - 0.9
	Oil	NA	0.1%	Estimate	(10)	0.1
Rail tank cars	NA	NA	250 kg	Estimate	(9)	0.2 - 0.7
	NA	NA	55 gal (0.21 m³)	Estimate	(23)	0.2 - 0.6
	NA	Pumping	<1%	Estimate	(24)	<1
	NA	Bottom draining	10 gal (0.04 m³)	Estimate	(24)	0.03 - 0.10
Tank trucks	Milk	NA	0.15%	Study	(25)	0.15
	NA	NA	100 kg	Estimate	(9)	0.5
	NA	NA	10 - 500 gal (0.04 - 1.90 m³)	Estimate	(11)	0.2 - 9
Drums	Milk[b]	Open-top pour	0.093%	Study	(17)	0.093
	NA	NA	2 kg	Estimate	(9)	1.0
	NA	NA	0.65 gal (0.0025 m³)	Estimate	(15)	1.2
	Grease	NA	10%	Estimate	(26)	10
	Oil	NA	0.1%	Estimate	(26)	0.1

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[a] Not available.

[b] 10 gallon (0.04 m³) milk cans.

[c] Based on estimates compiled from survey results.

results were used to calculate the amount of milk residue using known values of BOD and COD for pure milk and the amount of wash water used.[25] A total of 18 tank trucks were tested and the highest residue value was found to be 0.56 percent.[25]

In Table 2-2, the study which found an average of 0.093 percent milk residue in 10 gallon (0.04 m³), open-top milk cans was performed to determine the effect on product losses of the method of feeding the cans to a washer.[17] The cans were emptied and then placed upside down on a rack for one to two minutes before entering the washer.[18] The total amount of unrecovered milk (residue) for 1000 cans was calculated by difference between the amount of milk measured before and after emptying of the cans.[17] In a related study, the amount of milk residue left in 10 gallon (0.04 m³) cans after different periods of draining was measured.[18] Results of this experiment are given in Table 2-3. Again, an inverse relationship between drain time and residue quantity is apparent.

TABLE 2-3. MILK REMAINING IN A 10 GALLON (0.04 m³) MILK CAN AFTER DRAINAGE FOR VARIOUS PERIODS OF TIME.[17]

Period of draining (seconds)	Percent of product remaining
10	0.20
23	0.14
30	0.13
60	0.09
90	0.06

Two other studies involving residue in mobile vessels were found in the search of the literature. One study involved measurement of emissions of pollutants to the atmosphere during steam cleaning of tank cars and trucks at railroad and highway cleaning depots, and characterized the bulk materials cleaned by their viscosities and vapor pressures.[9] Table 2-4 summarizes the results from this study. Because these results are for atmospheric emissions of the test materials during cleaning, it is not possible to relate them to residue quantities. Examples of low, medium, and high vapor pressures, respectively, at ambient temperature are 1 mm Hg for o-dichlorobenzene, 10 mm

TABLE 2-4. MEASURED EMISSIONS TO THE ATMOSPHERE FROM TANK CAR AND TANK TRUCK STEAM CLEANING[9]

Compound	Chemical class: Vapor pressure	Chemical class: Viscosity	Total emissions (grams)[a]	Measured emission concentration (mg/m³)
Acetone	High	Low	311/truck	654
Perchloroethylene	High	Low	215/truck	426
Methyl methacrylate	Medium	Medium	32.4/truck	79.1
Phenol	Low	Low	5.5/truck	14.0
Propylene glycol	Low	High	1.07/truck	4.3
Ethylene glycol	Low	High	<0.32/car	<0.2
Chlorobenzene	Medium	Medium	15.7/car	8.8
o-Dichlorobenzene	Low	Medium	75.4/car	94.3
Creosote	Low	High	2,350/car	118

[a] Total emissions = (emission rate) x (emission volume).

Hg for chlorobenzene, and 200 mm Hg for acetone.[28,29] Examples of low, medium and high viscosities, respectively, at ambient temperature are 0.3 cp for acetone, 0.8 cp for chlorobenzene, and 12 cp for creosote.[28,29]

The other study was conducted to determine the effectiveness of a typical drum reconditioning caustic washing process in removing residue from empty pesticide containers. Drums were tested for pesticide content as received, after triple rinsing with water and after reconditioning plant processing. Since the drums used were as received at a reconditioning plant, the method of unloading the drums is unknown. Pesticide content of the drums was determined by sampling wedge sections cut from the drums and multiplying by an appropriate proportionality factor.[30]

Average results for processing 55 gallon (0.21 m³) drums formerly containing phorate and disulfoton are shown in Table 2-5. The formulations of bulk pesticide solutions originally contained in the drums was not stated, hence a percent residue could not be derived.

TABLE 2-5. PESTICIDE RESIDUE RESULTS.[30]

	55 gallon (0.21 m^3) drum residue quantity, grams		
	Unprocessed	After triple rinsing with water	After reconditioning plant processing
Phorate	39.0	8.63	1.266
Disulfoton	18.8	0.741	0.249

Regulatory Definitions--

For drums and railroad cars which have contained hazardous materials, regulatory definitions of "empty" have been adopted. Implementation of the empty container rule in 40 CFR 261.7 at the beginning of EPA's Resource Conservation and Recovery Act (RCRA) program in 1980 revolutionized the emptying of containers. The regulations for hazardous materials define an empty drum as one containing not more than 25.4 mm (1 inch) of residue on the bottom or inner liner.[14] An examination of the "1 inch rule" as well as EPA's discussion of it in relevant preambles shows that a container must be as empty as it can be, and that only for very viscous materials is 1 inch an upper bound. To quote the preamble to the final rule, "1 inch of waste material is an overriding constraint and may remain in an empty container only if it cannot be removed by normal means. The rationale for this provision is that there are certain tars and other extremely viscous materials that will remain in the container even after the container is emptied by normal means." For a 55 gallon (0.21 m^3) drum, one inch of residue represents 2.9 percent of capacity. Currently, NABADA has developed an "empty drum certification" program which will combine educational efforts with a form for reconditioners' clients to sign certifying that their drums are in compliance with the "1 inch rule."[31] Another requirement under EPA's RCRA regulations is the necessity for triple rinsing of drums formerly containing pesticides;[32] the drums are otherwise considered hazardous waste.

DOT, in 49 CFR 173.29, declares that every drum containing the residue of a hazardous material, regardless of amount, is regulated as if it were full. All closures, marking, labels, and the like must be present. In March 1985, the DOT Research and Special Programs Administration proposed changes to their definition of "residue" for railroad tank cars. Originally the rule defined a tank car carrying residue as containing a quantity of material not greater than 3 percent of the car's volumetric capacity. The proposed change would increase this quantity to 4 percent, plus or minus 1 percent.[33] The basis for the original 3 percent definition was a regulation from the "Uniform Freight Classification, 6000C, Rule 35, Section 7."[23] This requires that any tank car not unloaded below 3 percent of its capacity be charged freight proportional to the amount of material remaining. If unloaded under 3 percent of capacity, the car is considered empty and no such freight charge is applied.[34]

For tank trucks and barges, no definition of "empty" has been adopted; however, it is expected that MARPOL (International Convention on Marine Pollution) regulations will be adopted in early 1987 for ocean-going vessels. These regulations will address the issue of "emptyness" in consideration of washwater disposal from sea vessels.[13,35]

2.3 FACTORS AFFECTING RESIDUE QUANTITIES

The amount of material left in a vessel as residue after unloading is a function of many variables. These include:

- Type of vessel;
- Specific design configuration of the vessel;
- Material of construction or lining of vessel;
- Method of removing the bulk of material from the vessel; and
- Physical properties of the bulk material.

These variables were later used for the partial factorial design of the pilot-scale experiments.

2.3.1 Type of Vessel

The type of vessel cleaned can influence residue quantities. As discussed previously, vessels can be divided into two categories - stationary and mobile- with sub-types of storage tanks, reaction vessels, barges, tank cars, tank trucks, and drums.

2.3.2 Specific Design Configuration of the Vessel

Within each type or category of vessel, there may be several distinct modifications to the basic vessel design or configuration. For example, drums may have closed, sealed tops (bung-top), or detachable lids (open-top). It should be noted, however, that open-top drums are frequently used for shipping greases and adhesives as opposed to liquids. Tanks can be designed with dish bottoms or sloped (hopper) bottoms. Although there are other examples of vessel configurations, (e.g., flat bottom) these two are the more common types.

In the comparison of sloped bottom to dish bottom tanks, the present school of thought favors sloped bottom when attempting to minimize residue.[5,24,36] Because of the elevated concern in the past decade to reduce pollutant loadings to tank car and tank truck cleaning depots, newer vessels of these types tend to use sloped bottoms.[24,35] When unloading a barge, the separate compartments are pumped at different rates so that the barge will be tilting to one side in the water near the end of the process.[13]

2.3.3 Material of Construction or Lining for Vessel

Another aspect of vessel design affecting residue quantity is the material of construction or type of lining that the bulk material comes in contact with. There are numerous types of vessel linings, the selection of which is based upon the compatibility with the bulk material and not the effect on vessel residue.[5] Some examples of vessel linings are stainless steel, aluminum, glass, plastic, rubber, acrylic, epoxy, and latex.[5,13,35,36] Stationary vessels can use a wide variety of linings; mobile vessels are predominantly steel.[13,19,35,36]

2.3.4 Method of Removing Bulk Material From Vessel

Unloading methods primarily used are pumping, pouring, and bottom gravity draining. Pressurizing the vessel is another method used by barges, tank cars, and tank trucks for unloading gaseous material, to expedite gravity draining, or as an alternative to pumping.[13,24,34,36]

The method of unloading a vessel is largely dependent of the specific application involved. Storage tanks, reaction vessels, tank cars, and tank trucks are either pumped empty or bottom drained by gravity .[5,6,23,24,36] Because barges are submerged, pumping is the predominant method of unloading for this type of vessel.[13,35] Drums, on the other hand, can be emptied either by pumping or pouring.

It would be expected that, in general, pumping a vessel empty would leave more residue than either pouring or bottom draining by gravity. Table 2-2 presented earlier supports this conjecture for rail tank cars. The depth of the pump suction pipe inside the vessel could also affect the amount of residue.

2.3.5 Properties of Bulk Material

Some of the physical properties of the material expected to influence the residual mass are viscosity, surface tension, density, and vapor pressure. Temperature of operation must also be taken into consideration for these properties. A material with a high viscosity will leave a larger amount of residue in a vessel than a material with a lower viscosity. Also, a material with a high vapor pressure will generate a larger amount of material in vapor form than a material with a lower vapor pressure. The degree to which these properties affect residue quantities, however, was not found in the literature.

SECTION 3

DESCRIPTION OF PILOT-SCALE TEST PROGRAM

3.1 OBJECTIVES

The primary objective of the pilot study was to quantify the amounts of residue material left in vessels which can potentially be lost during cleaning. A secondary objective was to investigate the effects of the following parameters on the amount of material retained in the vessel:

- Type of vessel - drums, tanks.
- Design configuration - open top vs. closed top, dish bottom vs. slope bottom.
- Materials of construction - steel, glass lining, plastic lining.
- Method of removing the bulk of the material from the vessel - pouring, pumping, bottom draining by gravity.
- Physical properties of the bulk material - viscosity, surface tension, density.

3.2 EXPERIMENTAL DESIGN

The experiments conducted in the laboratory pilot scale study were divided into two groups corresponding to the types of vessels used: drums and tanks. Within each group, variations were made of the vessel design configuration, material of construction and unloading method. The sizes of all vessels used were in the 30 to 55 gallon (0.11 to 0.21 m^3) capacity range. A total of seven different equipment design/unloading method arrangements were studied in the experimental program, as shown in Table 3-1.

Data from all seven equipment configurations were used to evaluate the impact of the physical/chemical properties of the liquid materials tested. Specifically, these evaluations focused on the impact of viscosity, surface tension, and density of the liquid materials on the quantity of residue left

TABLE 3-1. EQUIPMENT ARRANGEMENTS FOR PILOT-SCALE EXPERIMENTS

Vessel type	Material of construction	Size	Unloading method
Drums			
Open top	Lined steel	55 gallon (0.21 m^3)	Pour
Bung top	Lined steel	55 gallon (0.21 m^3)	Pour
	Lined steel	55 gallon (0.21 m^3)	Drum pump
	Plastic	30 gallon (0.21 m^3)	Drum pump
Tanks			
Slope bottom	Stainless steel	30 gallon (0.11 m^3)	Gravity
Dish bottom	Stainless steel	30 gallon (0.11 m^3)	Gravity
	Glass lined	30 gallon (0.11 m^3)	Gravity

in the vessel. The test liquids comprised kerosene, water, motor oil, and a surfactant solution. Samples of the liquids were analyzed for viscosity, surface tension, and density at room temperature.

The effect of viscosity on the amount of residue was evaluated by comparing the two different petroleum fractions, kerosene and motor oil. Surface tension evaluations were conducted by comparing water with the surfactant solution. The effect of density was evaluated by comparing the data for kerosene with that for the surfactant solution.

A partial factorial experimental design was adopted for the experiments. Table 3-2 presents a complete matrix of the experimental evaluations performed in the pilot-scale study. For all runs except those for the surfactant solution, a minimum of three replicate runs was performed for each equipment arrangement. The first block of experiments involved quantifying the residue material left in various drum configurations. Four different equipment configurations were used to compare the relative influence of unloading method (pouring vs. pumping), design configuration (open top vs. closed top), and material of construction (steel vs. plastic), on the amount of residue left in drums.

In the second block of experiments three different equipment configurations were used to quantify residue in tanks. Two different tank bottom designs, sloped and dish, were evaluated using similar, stainless steel tanks

TABLE 3-2. MATRIX OF EXPERIMENTS FOR PILOT-SCALE TEST PROGRAM

Vessel type	Material of construction	Unloading method	Kerosene	Motor oil	Water	Surfactant
Block I						
Drums						
55 Gallon (0.21 m^3) open top	Lined steel	Pour	X	X	X	X
55 Gallon (0.21 m^3) bung top	Lined steel	Pour	X	X	X	X
55 Gallon (0.11 m^3) bung top	Lined steel	Pump	X	X	X	X
30 Gallon (0.11 m^3) bung top	Polyethylene	Pump	X	X	X	X
Block II						
Tanks						
Slop bottom	Stainless steel	Gravity	X	X	X	X
Dish bottom	Stainless steel	Gravity	X	X	X	X
Dish bottom	Glass lined	Gravity	X	X	X	X

of identical capacities. In addition a 30 gallon (0.11 m^3), glass-lined, dish bottom tank was evaluated to determine the impact of material of construction on the quantity of residue.

3.3 EQUIPMENT SPECIFICATIONS

Electronic Scales--

Two electronic scales were used in the pilot-scale test study. A "small scale" was used to weigh the vessels before the loading and after the emptying of the test liquid. A "large scale" was used to weigh the vessels when loaded with the test liquid.

The "small scale" was a "Pennsylvania, Base 100" floor scale, accurate to ±0.01 pounds (0.0045 kg) with a capacity of 45.4 kg. The large scale was a "Pennsylvania PAB 3030 Flexure Deck Scale" accurate to ±0.2 pounds (0.09 kg) with a capacity of 454 kg. Both scales were connected to a "Pennsylvania Model 5400" Electronic display meter. When conducting experiments with the glass-lined tank, it was necessary to increase the accuracy of the large scale because the excessive weight of the glass-lined vessel prohibited the use of the small scale for measuring its weight while empty. The supplier of the scales provided instrumentation such that the large scale was accurate to ±0.05 pounds (0.02 kg) and could be used for weighing the vessel empty as well as full.

Vessels--

Two types of vessels were used in the pilot study, tanks and drums. Photographs of the different types of vessels used for the tests are presented in Appendix A. Three different tanks were used as described below:

- 30 Gallon (0.11 m^3), sloped bottom, stainless steel tank: This vertical tank measured 0.81 m from drain-hole to brim with a 0.45 m inside diameter. The conical bottom started 0.13 m above the 0.03 m drain hole. The angle of the sloped bottom was 30 degrees.
- 30 Gallon (0.11 m^3), dish bottom, stainless steel tank: This vertical tank measured 0.69 m from drain-hole to brim with a 0.45 m inside diameter. This dish bottom started 0.08 m above the 0.03 m drain hole.
- 30 Gallon (0.11 m^3), dish bottom, glass-lined tank: This vertical tank measured 0.63 m from drain-hole to brim with a 0.51 m inside diameter. The drain-hole was 0.05 m in diameter.

Each tank was fitted with a 0.03 m drain valve.

Three different types of drums were used: 55 gallon (0.21 m³), steel, bung-top drums (17-H); 55 gallon (0.21 m³), steel, open-top drums (17-E); and 30 gallon (0.11 m³), polyethylene, bung-top drums. All bung-top drums were used only once, while the open-top drums were cleaned, dried, and reused.

Test Liquids--

Four different test liquids were used in the pilot study: kerosene, water, motor oil, and a surfactant solution. The kerosene was grade "K-1" while the motor oil was "10W-30". Water was drawn from a well at the site of the experiments. The surfactant solution was made by mixing 0.45 kg of powdered detergent ("Tide") in 55 gallons (0.21 m³) of water.

Miscellaneous--

- Drum Pump: A manual drum pump ("Great Plains Industries; Model #HP-100") was used in unloading drums via pumping.
- A "Drum-Dolly" was used for transporting and tipping loaded drums for pouring tests.
- An 80 gallon (0.30 m³) metal trough was used as a receptacle for test liquids unloaded by pouring and bottom gravity draining.
- An electric transfer pump was used to load the vessels with test liquid from supply drums and the trough.

3.4 EXPERIMENTAL PROCEDURES

The experiments consisted of measuring the weight gained by the vessel as a result of filling it with the test liquid and subsequently unloading it. A total of three weights were taken for each run: the weight before loading, the weight of the full vessel, and the unloaded weight.

The mass of residue left in the vessel was quantified in the pilot-scale study using the following procedures:

1. The clean, dry vessel was weighed on the small electronic scale.
2. The vessel was then transferred to the large electronic scale and filled to its stated capacity (i.e., 55 gallons (0.21 m³) or 30 gallons (0.11 m³) based upon the approximate density of the material) with the test liquid.
3. The vessel was then emptied by either pumping, pouring, or gravity draining. In general, the vessel was emptied as long as a steady stream of liquid was observed.

4. The vessel was then transferred back to the small scale and weighed.

5. The residual weight was the difference between the final weight of the emptied vessel and the initial weight of the clean, dry vessel. The percentage residual was calculated by dividing the residual weight by the difference between the full-loaded weight of the vessel and the weight of the clean, dry vessel, and multiplying the result by 100.

6. For each run the ambient temperature and the drain times were recorded.

Samples were taken of each of the four test liquids and tested at room temperature for viscosity, surface tension and density. Viscosity was measured using a Brookfield viscometer (ASTM 2983), density was measured using a Bingham Pycnometer (ASTM 1217), and surface tension was measured by the "ring method" in accordance with ASTM D1590.

3.4.1 Block I: Drums

Pouring--

Evaluations of residue material left in drums after pouring were performed using open- and bung-top 55 gallon (0.21 m^3) steel drums. The procedure consisted of weighing a cleaned and dried drum with a removable lid on the small scale and transferring it to a tared drum dolly resting on the large scale. With the lid securely in place, the test liquid was pumped into the drum through the bung opening. The drum was then filled to 55 gallons (0.21 m^3) based upon approximate densities of the test liquids (obtained through the literature). Once full, the weight was recorded, the bung cap was screwed securely into place, and the drum tilted to a horizontal position with the dolly. The bung cap was then removed and the test liquid allowed to drain into a trough. When the flow stopped, the drum was tilted approximately 45 degrees and allowed to drain until a steady stream was no longer evident. For the runs performed with motor oil, the tilt time was measured and ranged between 51 and 58 seconds. Tilt time was not measured for water, kerosene or the surfactant solution. Because of the lower viscosity of these materials relative to motor oil, tilt times were undoubtedly lower and are estimated to be between 10 and 20 seconds. The drum was then transferred to the small scale and its weight recorded. This weight corresponded to the final weight of the drum for closed-top (or bung opening) pouring.

The drum lid was then removed and the drum placed back on the horizontal dolly and allowed to drain further (with a 45-degree tilt) until the steady stream of flow ceased. The tilt time for the motor oil runs were measured and ranged between 26 and 35 seconds. Again, tilt times for the other liquids were not measured, and are estimated to be less than 10 seconds. The drum (with lid) was again transferred to the small scale and weighed. This weight corresponded to the final weight of the drum for open-top pouring.

Pumping--

Evaluations of residue material left in drums after pumping were performed with both bung-top, steel drums, and bung-top, polyethylene drums. The first step in the experimental procedure consisted of weighing a clean and dry drum on the small scale and transferring to the large scale for loading. Once filled to its respective capacity and the loaded weight recorded, an emptied drum pump with a dip-pipe was placed in the bung opening of the drum. The center of the bung opening was approximately 75 mm from the nearest edge of the drum. The drum pump was secured to the drum with an adapter which allowed the depth of the dip-pipe to be adjusted. The dip-pipe was allowed to drop to the very bottom of the drum, then raised to a distance of 38 mm and secured. This distance of 38 mm between the end of the dip-pipe and the bottom of the drum was chosen based upon a discussion with the pump manufacturer who indicated that they recommend a depth of 25 to 50 mm to their customers.[37]

After the drum pump was secured, the drum was emptied until a loss in resistance to pumping was noticed signifying that air was being pumped. At this point the drum was tilted approximately 4 degrees upon a strip of wood so that the liquid would accumulate underneath the bung hole in this position. Pumping was then resumed. Pumping was stopped when further pumpstrokes did not produce any surges of material from the pump hose outlet and only a trickle of material was being discharged. An effort was made to keep the number of pumpstrokes after tilting consistent corresponding to our judgement regarding a reasonable endpoint. After pumping, the drum pump was removed, the drum transferred to the small scale, and the final weight recorded.

The drum pump originally came with a collar to secure it to the drum which did not allow the depth of the dip-pipe to be adjusted. An adjustable adapter was fabricated (as is available with other types of drum pumps) and a dip-pipe capable of reaching the bottom of any drum was attached to the pump. The pumping runs were completed using a dip-pipe clearance of 38 mm. Towards the conclusion of the experiments, one pumping run for each test liquid was performed letting the dip-pipe sit on the bottom of the drum during pumping. Although this is probably not typical industry practice, this method would result in the maximum removal of liquid.

3.4.2 Block II: Tanks

Evaluations of residual material left in tanks after bottom draining by gravity were performed using 30 gallon (0.11 m^3), dish bottom and slope bottom, stainless steel tanks and a 30 gallon (0.11 m^3), dish bottom, glass-lined tank. Each tank was fitted with a 25 mm gate valve to facilitate loading and draining.

After the initial weight of the cleaned dried tank had been recorded, the tank would be transferred to the large scale where it was filled to its 30 gallon (0.11 m^3) capacity. When filled, the weight was recorded, a 25 mm hose connection was attached to the valve, and the tank was drained into a trough. Draining continued until a steady stream was no longer apparent. The time of draining was recorded. The drain hose was disconnected and the tank transferred to the small scale for final weighing.

In the initial portion of the pilot-scale study, the two stainless steel tanks were fitted with a 6.3 mm drain valve and a 9.5 mm discharge hose. This worked well for runs with kerosene and water; however, when using motor oil, the tanks took over 5 hours to drain. In order to expedite the process and also better simulate industry draining practices, these valves were replaced with 25 mm valves as noted earlier in this section. The kerosene and water runs were repeated with the 25 mm valves in order to assure consistency of equipment.

The empty weight of the glass-lined tank (~91 kg) exceeded the capacity of the small scale. Experience with the other tanks indicated that the large scale was not sensitive enough to measure residuals. Fortunately, the supplier of the scales was able to change the instrumentation in the large scale to make it sensitive to ±0.05 pounds (0.02 kg) up to a load of 114 kg, while still capable of measuring its capacity of 454 kg.

3.5 QUALITY ASSURANCE

All of the experiments described in this plan were conducted in accordance with PEI's corporate quality assurance program. The technical approach and apparatus assembles were reviewed by the project director and PEI's quality assurance manager prior to the collection of data. There were three areas of particular concern relative to quality assurance in this study. These included the consistency of the overall experiments, the accuracy of the bulk material property data, and the scale reliability and calibration.

Regarding the consistency of the actual experiments, three replicates were conducted for each experiment outlined in Table 3-2 except for those involving the surfactant solution in order to check the variability of the measurements. An effort was made to strictly define the endpoint of each drain procedure and record pertinent drain times. Also, efforts were made to insure that each vessel was cleaned and dried thoroughly before each run.

Samples were collected of each of the four test liquids and tested for density, surface tension, and viscosity. The samples were tested by a certified contract laboratory using approved ASTM procedures. Replicates were performed on each of the surface tension tests. Results of all replicate testing were reported identical to their respective original values.

Two scales were rented for this project as previously described. These scales were set up and calibrated by the supplier at the test site two days before commencement of the experiments. The scales were not recalibrated during the test period of 25 days following the original calibration.

SECTION 4

TEST RESULTS

4.1 OVERVIEW OF RESULTS

PEI conducted a total of 95 experimental runs in the pilot-scale experimental program. The initial goal of the pilot-scale study was to perform three runs on each equipment configuration using water, kerosene, and motor oil. At the completion of these experiments, one additional run on each equipment configuration (except pumping from the plastic drum) was also performed using a surfactant solution.

Table 4-1 summarizes the results for all the equipment configurations investigated in the pilot-scale study. The main goal of the study was to obtain such quantitative estimates for residue materials. Figure 4-1 provides a graphical representation of the residue quantities for each of the seven vessel design configurations and four test liquids. Figures 4-2 through 4-4 present the results separately for each of the three unloading methods employed in the study.

A synopsis of each individual experimental comparison performed in the pilot-scale study is provided in this section. The data used in each individual comparison was taken from those vessel/material configurations which isolated the subject comparison while identical in all other aspects.

A statistical analysis was performed using a two-way analysis of variance (ANOVA) and confidence intervals of 95 and 99 percent to determine the significance of the comparisons. All replicates of the test runs for kerosene, water, and motor oil were used for the analysis. Because the runs involving the surfactant solution were not replicated, they were not used in the statistical analysis.

TABLE 4-1. SUMMARY OF RESIDUE QUANTITIES FROM PILOT-SCALE EXPERIMENTAL STUDY

Unloading method	Vessel type	Value	Material, (wt. %)			
			Kerosene	Water	Motor oil	Surfactant
Pumping	Steel drum	Range	1.93 - 3.08	1.84 - 2.61	1.97 - 2.23	3.06
		Mean	2.48	2.29	2.06	3.06
Pumping	Plastic drum	Range	1.69 - 4.08	2.54 - 4.67	1.70 - 3.48	Did not perform
		Mean	2.61	3.28	2.30	
Pouring	Bung-top steel drum	Range	0.244 - 0.472	0.266 - 0.458	0.677 - 0.787	0.485
		Mean	0.404	0.403	0.737	0.485
Pouring	Open-top steel drum	Range	0.032 - 0.080	0.026 - 0.039	0.328 - 0.368	0.089
		Mean	0.054	0.034	0.350	0.089
Gravity drain	Slope-bottom steel tank	Range	0.020 - 0.039	0.016 - 0.024	0.100 - 0.121	0.048
		Mean	0.033	0.019	0.111	0.048
Gravity drain	Dish-bottom steel tank	Range	0.031 - 0.042	0.033 - 0.034	0.133 - 0.191	0.058
		Mean	0.038	0.034	0.161	0.058
Gravity drain	Dish-bottom glass-lined tank	Range	0.024 - 0.049	0.020 - 0.040	0.112 - 0.134	0.040
		Mean	0.040	0.033	0.127	0.040

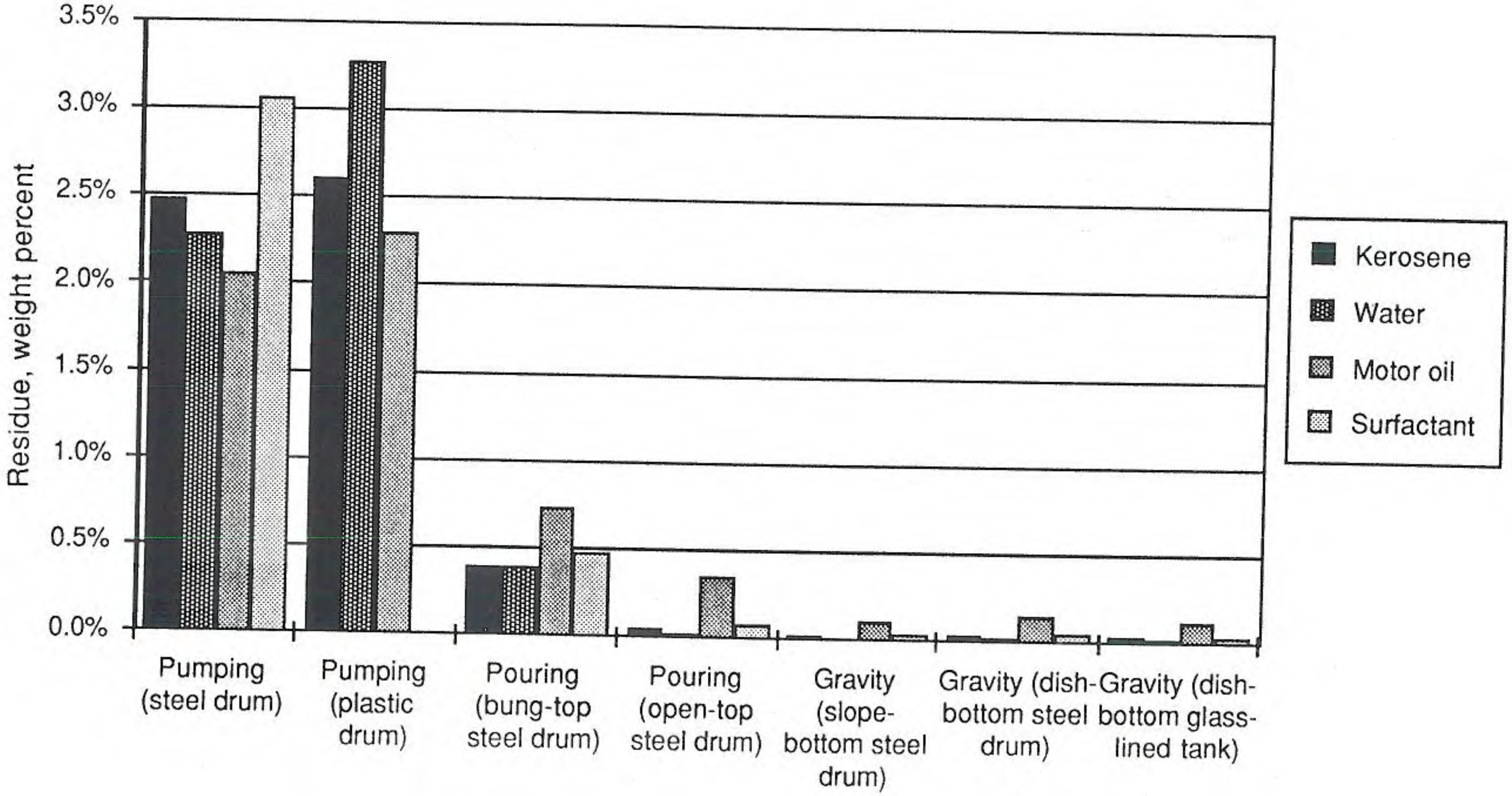

Figure 4-1. Residue quantities (weight percent) from all experimental configurations.

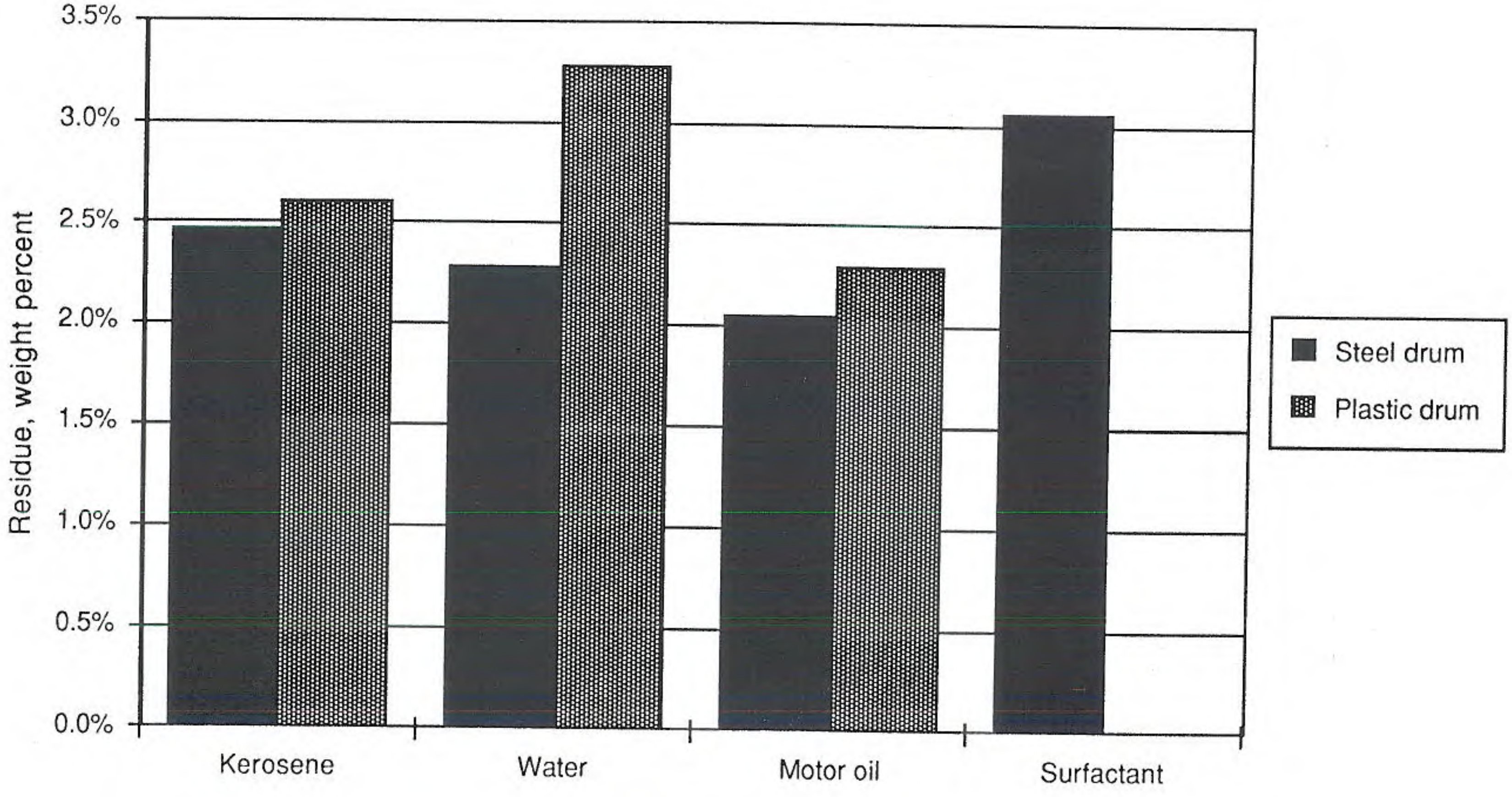

Figure 4-2. Residue quantities from drum pumping tests as a function of material of construction of the drum and type of test liquid.

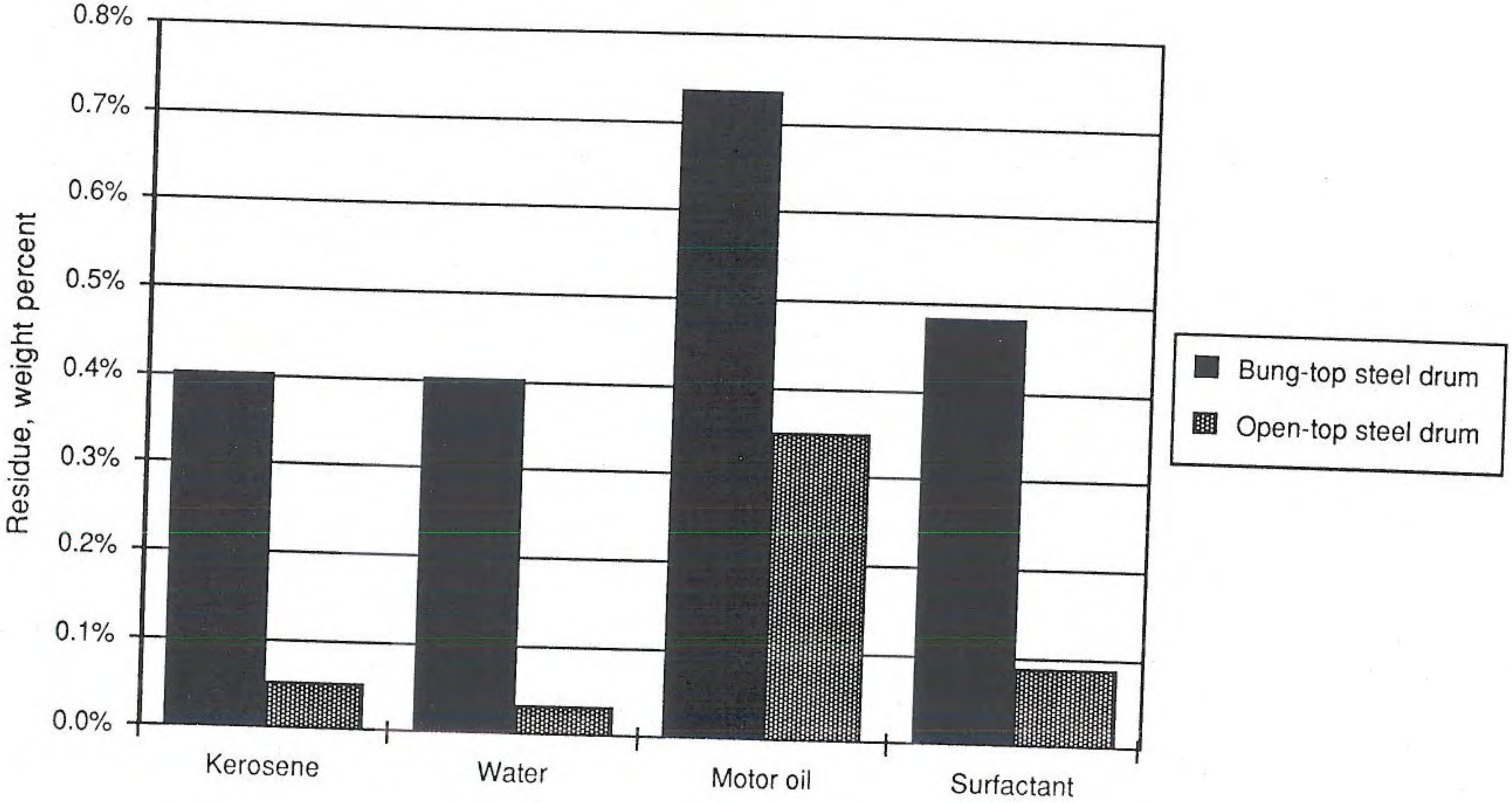

Figure 4-3. Residue quantities from drum pouring tests as a function of drum configuration and type of test liquid.

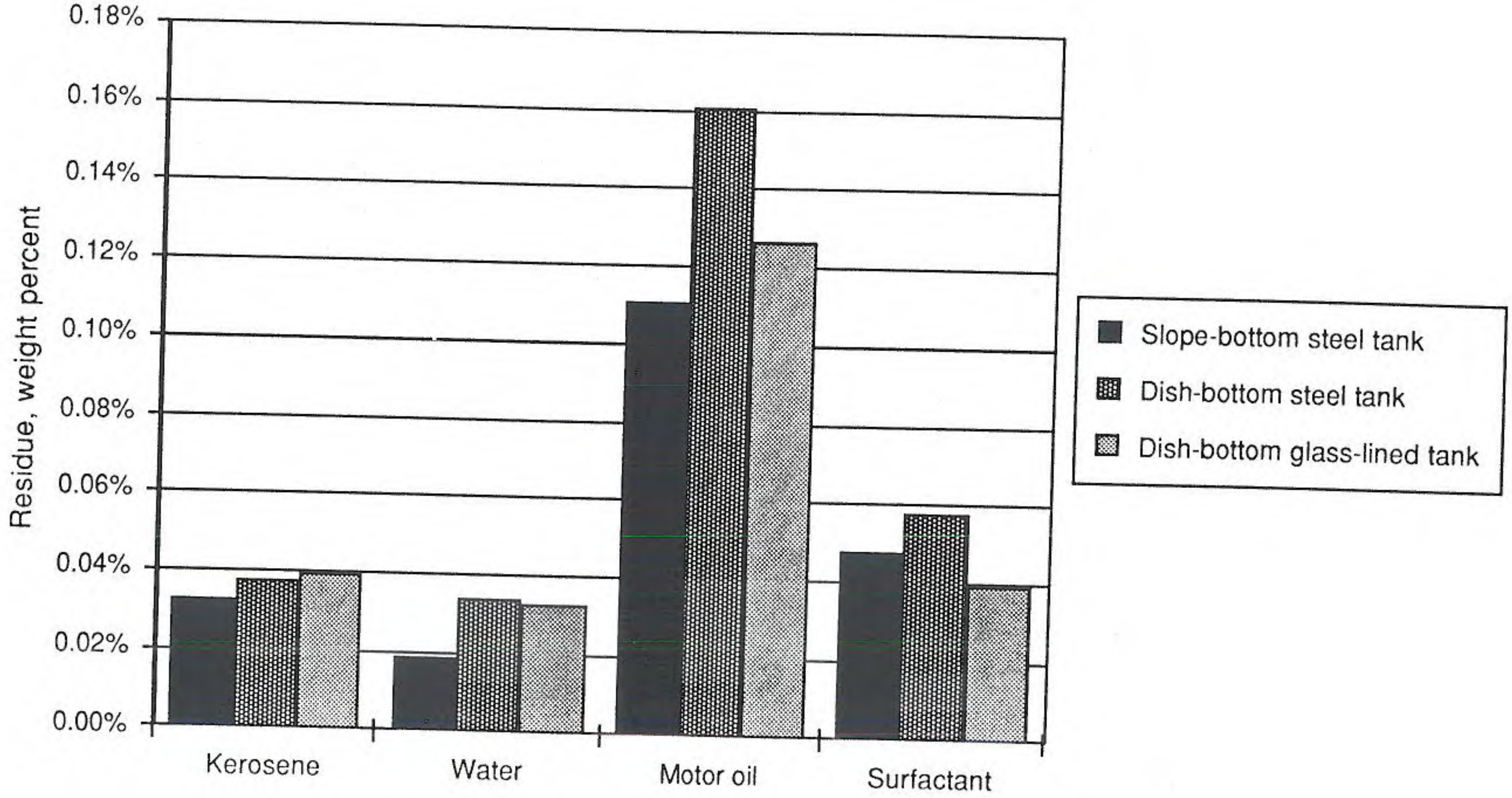

Figure 4-4. Residue quantities from tank bottom gravity tests as a function of material of construction and configuration of the tanks and type of test liquid.

4.2 SPECIFIC COMPARISONS

4.2.1 Type of Vessel

The two types of vessels used in the pilot-scale study were tanks and drums. Because the unloading methods used for these vessel types were not the same in the partial factorial experimental design, no experimental comparisons can be made; however, the unloading methods used in the experiments were felt to be representative of unloading methods used in industry for these types of vessels. As such differences in vessel type would be reflected in the comparison of unloading methods.

4.2.2 Effect of Unloading Method

Only one true comparison was made of unloading method in the experiments. This was between the pumping and pouring of the bung-top, 55 gallon (0.21 m^3) steel drums. To compare bottom gravity draining to pumping and pouring, a bottom draining 55 gallon (0.21 m^3) drum would have been needed. The closest alternative used was the gravity draining of the 30 gallon (0.11 m^3) stainless steel, dish-bottom tank.

Table 4-2 gives the results of the comparison of unloading methods including data for the 30 gallon (0.11 m^3), dish-bottom, steel tank. As in all of the comparisons, only data from pumping runs using the 38 mm depth for the dip-pipe and tank runs using the 25 mm valve were used.

For each of the four test liquids, pumping left substantially higher amounts of residue than either pouring or gravity draining. Pouring, on the other hand, also left substantially higher residues when compared to gravity draining. A statistical analysis was performed with the data from the pumping and pouring runs. This analysis showed a strong, significant difference between the two unloading methods and no significant effect from the different test liquids used. Also, there were no significant interaction effects between the unloading methods and the liquids.

As mentioned in Section 3.4.1 (Experimental Procedures, Drum Pumping), the depth of the dip-pipe in the drum was suspected of influencing residue quantities. Using data from the early 55 gallon (0.21 m^3), kerosene pumping runs (where the distance from the dip-pipe end to drum bottom varied), the 55 gallon (0.21 m^3) kerosene pumping runs used in the experimental comparisons (dip pipe end to drum bottom distance of 38 mm), and one final kerosene

TABLE 4-2. PERCENT RESIDUE: UNLOADING METHOD COMPARISON

		55 gallon (0.21 m³) steel, closed top drums		30 gallon (0.11 m³) stainless steel dish bottom tank
Bulk material		Pump	Pour	Gravity drain
Kerosene:	Range	1.93 - 3.08	0.244 - 0.472	0.031 - 0.042
	Mean	2.48	0.404	0.038
Water:	Range	1.84 - 2.61	0.266 - 0.458	0.033 - 0.034
	Mean	2.29	0.403	0.034
Motor oil:	Range	1.97 - 2.23	0.677 - 0.787	0.133 - 0.191
	Mean	2.06	0.737	0.101
Surfactant:	Range	3.06	0.485	0.058
	Mean	3.06	0.485	0.058

pumping run with the dip pipe sitting on the bottom of the 55 gallon (0.21 m³) drum, a direct relationship between dip pipe depth and residue quantity was established as displayed in Figure 4-5. Towards the end of the study one run was performed for each of the test liquids with the dip pipe sitting on the bottom of the 55 gallon (0.21 m³) drum during pumping. It was felt that this would represent the maximum amount of material (or minimum amount of residue) pumpable from the drum. Table 4-3 shows the results of these runs.

TABLE 4-3. PERCENT RESIDUE: 55 GALLON (0.21m³) PUMPING RUNS WITH DIP PIPE AT BOTTOM OF DRUM

Material	Wt. percent residue
Kerosene	0.19
Water	0.22
Motor oil	0.35
Surfactant	0.17

These residue results are lower than those obtained with bung-top pouring of the drums for each test liquid. This points out the large variability that the unloading method (especially pumping) can have on residue quantities.

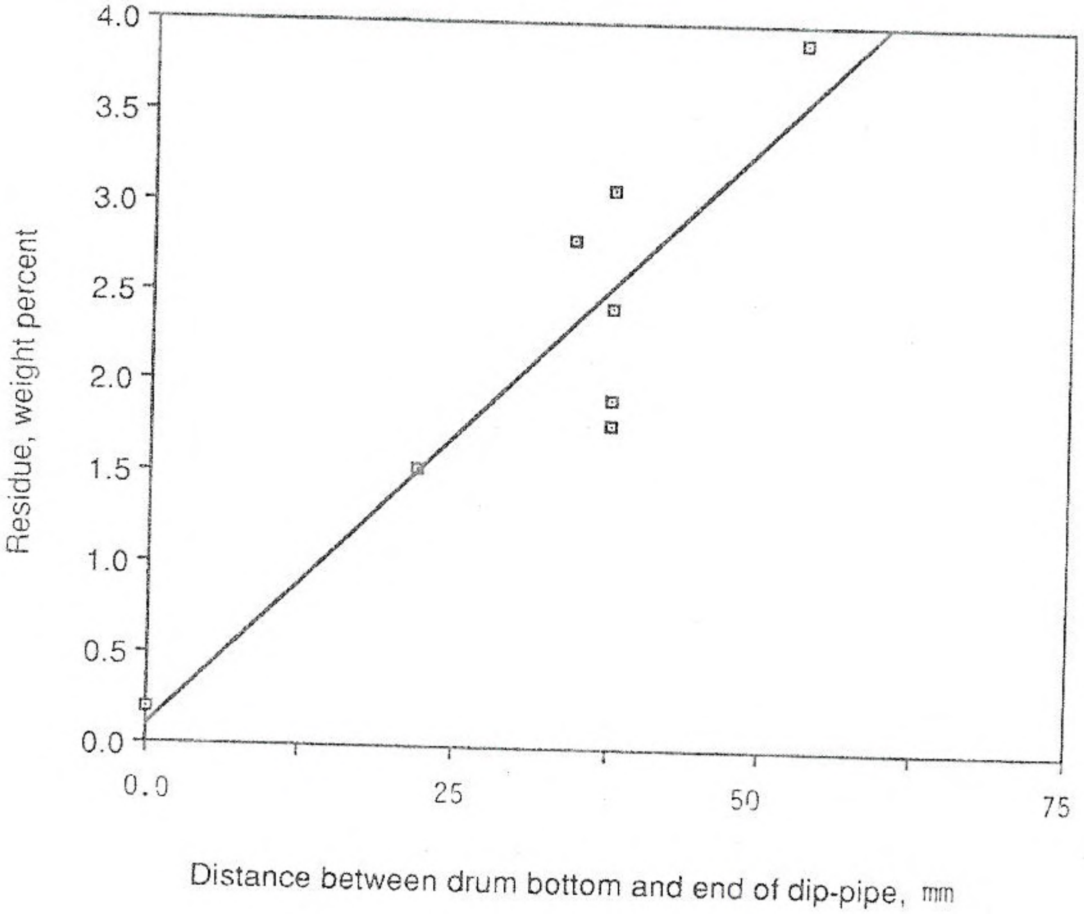

Figure 4-5. Effect of clearance between drum bottom and dip-pipe on residue quantity for kerosene pumping experiments.

TABLE 4-4. PERCENT RESIDUE: OPEN-TOP VS BUNG-TOP DRUMS

Test liquid		Pouring of 55 gallon (0.21 m³) steel drums: Open-top	Pouring of 55 gallon (0.21 m³) steel drums: Closed-top (Bung-top)
Kerosene:	Range	0.032 - 0.080	0.244 - 0.472
	Mean	0.054	0.404
Water:	Range	0.026 - 0.039	0.266 - 0.458
	Mean	0.034	0.403
Motor oil:	Range	0.328 - 0.368	0.677 - 0.787
	Mean	0.350	0.737
Surfactant:	Range	0.089	0.485
	Mean	0.089	0.485

Slope Bottom vs. Dish Bottom Tanks--

An evaluation was made between residue quantities for slope-bottom and dish-bottom tanks using the 30 gallon (0.11 m³) stainless steel tanks with bottom gravity draining. Results of this evaluation are shown in Table 4-5. The results show that for each test liquid, the slope-bottom tank left less residue than the dish bottom tank. The significance of these differences seems minimal, however. The difference in motor oil residue was the greatest for the four test liquids. Increasing the slope on the slope bottom tank (above 30 degrees) would potentially increase the difference in residue between the dish and slope bottom tanks.

TABLE 4-5. PERCENT RESIDUE: SLOPE BOTTOM VS DISH BOTTOM TANKS

Test liquid		Gravity draining with stainless steel tanks: Sloped bottom	Gravity draining with stainless steel tanks: Dish bottom
Kerosene:	Range	0.020 - 0.039	0.031 - 0.042
	Mean	0.033	0.038
Water:	Range	0.016 - 0.024	0.033 - 0.034
	Mean	0.019	0.034
Motor oil:	Range	0.100 - 0.121	0.133 - 0.191
	Mean	0.111	0.161
Surfactant:	Range	0.048	0.058
	Mean	0.048	0.058

A statistical analysis of these sets of data show a significant difference between the dish bottom and slope bottom configurations and a significant difference between the test liquids because of the higher residue quantities when using motor oil. Also significant vessel configuration/test liquid interaction effects are indicated.

As noted in the experimental procedures, a number of test runs were performed using a 6.3 mm drain valve rather than the 25 mm drain valve used to obtain the data in Table 4-5. By comparing the runs using the two different valves, the effect of drain time was investigated, as shown in Table 4-6. For each type of tank and test liquid, an increase in drain time yields a decrease in percent residue. In the extreme case of motor oil, a large increase in drain time yielded a substantial decrease in residue.

TABLE 4-6. EFFECT ON RESIDUE QUANTITY FOR BOTTOM, GRAVITY DRAINING FROM 30 GALLON (0.11 m^3) DISH AND SLOPE BOTTOM TANKS WITH 25 mm AND 6.3 mm DRAIN VALVES

Test liquid	Type of tank	Valve size, mm	Number of runs	Average drain time, minutes	Average residue, wt. percent
Kerosene	Slope bottom	25	3	2.3	0.033
Kerosene	Slope bottom	6.3	3	23.1	0.013
Kerosene	Dish bottom	25	3	2.2	0.038
Kerosene	Dish bottom	6.3	3	22.0	0.018
Water	Slope bottom	25	3	1.8	0.019
Water	Slope bottom	6.3	3	22.4	0.011
Water	Dish bottom	25	3	2.0	0.034
Water	Dish bottom	6.3	3	21.2	0.019
Motor oil	Slope bottom	25	3	19.2	0.111
Motor oil	Slope bottom	6.3	1	309.0	0.028
Motor oil	Dish bottom	25	3	15.5	0.161
Motor oil	Dish bottom	6.3	1	342.0	0.057

4.2.4 Vessel Material of Construction

Plastic Lining vs. Steel Lining--

An evaluation was made of residue quantities from plastic lined and steel lined drums. For this purpose 30 and 55 gallon (0.11 and 0.21 m^3) plastic and steel, bung-top drums, respectively, were tested using pumping as an unloading method. The results of these runs are summarized in Table 4-7.

TABLE 4-7. PERCENT RESIDUE: PLASTIC VS STEEL DRUMS

Test liquid		Drum pumping	
		Plastic	Steel
Kerosene:	Range	1.69 - 4.08	1.93 - 3.08
	Mean	2.61	2.48
Water:	Range	2.54 - 4.67	1.84 - 2.61
	Mean	3.28	2.29
Motor oil:	Range	1.70 - 3.48	1.97 - 2.23
	Mean	2.30	2.06
Surfactant:	Range	-	3.06
	Mean	-	3.06

For each run the drum with plastic lining held slightly more residue than the steel lining. The significance of this is clouded, however, in the high variability of the pumping runs and the fact that different size drums were used. A statistical analysis of these two sets of data indicate no significant effect from the type of lining (plastic or steel), test liquid, or lining/test liquid interaction.

For runs involving water, a large difference in residue was observed between the steel and plastic drums. This could potentially be due to the high surface tension of the water relative to the other liquids although this effect is not shown to be significant in the statistical analysis. It is likely that the difference is due to the high variability of the data generated when using pumping as the unloading method.

Glass Lining vs. Steel Lining--

The effect of glass lining vs. steel lining on residue quantity was evaluated using two, 30 gallon (0.11 m^3), dish bottom tanks and unloading them via bottom gravity draining. Table 4-8 shows the results of this comparison.

The data shows that there seems to be no difference between the runs involving glass and steel lining. The kerosene and water runs are nearly identical for the two linings, while the motor oil and kerosene runs had slightly higher residues with the steel lined tank.

TABLE 4-8. PERCENT RESIDUE: GLASS LINING VS STEEL LINING

Test liquid		Bottom gravity draining 30 gallon (0.11 m^3) dish bottom tanks	
		Glass-lined	Steel-lined
Kerosene:	Range	0.024 - 0.049	0.031 - 0.042
	Mean	0.040	0.038
Water:	Range	0.020 - 0.040	0.033 - 0.034
	Mean	0.033	0.034
Motor oil:	Range	0.112 - 0.134	0.133 - 0.191
	Mean	0.127	0.161
Surfactant:	Range	0.040	0.058
	Mean	0.040	0.058

A statistical analysis of these two sets of data indicate no significant difference for the glass and steel linings; however, there was a significant effect from the test liquids because of higher viscosity of the the motor oil. There were no significant lining/test liquid interaction effects.

4.2.5 Effect of Bulk Material Properties

The test liquids used in this study--kerosene, water, motor oil, and a surfactant solution--were all tested for viscosity, surface tension and density. Table 4-9 presents the results of these analyses.

TABLE 4-9. RESULTS FOR PHYSICAL PROPERTIES OF TEST LIQUIDS AT 20°C

Test liquid	Density (g/cm^3)	Surface tension (dynes/cm)	Viscosity (centipoise)
Kerosene	0.800	29.3	5
Water	1.000	77.3	4
Motor oil	0.875	34.5	97
Surfactant	0.996	31.4	3

In order to evaluate the relative impact of these three properties, comparisons of results obtained from pairings of test liquids were made. For each property, two test liquids were chosen such that they would differ significantly in the property of interest but still have similar values of the other two properties. For viscosity, kerosene data was compared to motor oil data (Table 4-10); for surface tension, results from water and surfactant runs were compared (Table 4-11); and for density, results for kerosene and surfactant runs were compared (Table 4-12).

From these data it can be seen that viscosity has the the most substantial impact of the three properties on residue quantity. In all the equipment configurations, except the pumping runs, motor oil left significantly more residue than kerosene.

Surface tension and density both seem to have little effect on the amount of residue. In each equipment configuration comparing water to surfactant, a slight inverse relationship between surface tension and residue is apparent. In each equipment configuration comparing kerosene to surfactant, a slight direct relationship between density and residue is seen. The differences in residue quantities observed between the surfactant solution as compared to both water and kerosene may also be due to foam adhering to the walls of the vessels in surfactant runs. The presence of foam can increase the amount of residue left in vessels.[19] The high value for surfactant residue in pumping is probably due to the high variability of the pumping data.

Because replicate data for the surfactant solution was not available, statistical analyses were not performed for the material property evaluations. A statistical analysis of three test liquids and all seven equipment configurations was performed however, which showed no significant effects on the residue between the water, kerosene, and motor oil. Significant effects were indicated between the seven equipment configurations, whereas no significant equipment configuration/test liquid interaction effects were shown.

Although the overall statistical analysis showed no significant difference between the test liquids, this result is misleading. In several of the individual experimental comparisons (open top vs. closed top drums, glass vs. steel lining and dish bottom vs. slope bottom tanks) statistically significant differences were noted between the test liquids primarily because of the

TABLE 4-10. PERCENT RESIDUE: VISCOSITY COMPARISON (KEROSENE VS MOTOR OIL)

Unloading method	Vessel type	Value	Material Kerosene	 Motor oil
Pumping	Steel drum	Range	1.93 - 3.08	1.97 - 2.23
		Mean	2.48	2.06
Pumping	Plastic drum	Range	1.69 - 4.08	1.70 - 3.48
		Mean	2.61	2.30
Pouring	Bung-top steel drum	Range	0.244 - 0.472	0.677 - 0.787
		Mean	0.404	0.737
Pouring	Open-top steel drum	Range	0.032 - 0.080	0.328 - 0.368
		Mean	0.054	0.350
Gravity drain	Slope-bottom steel tank	Range	0.020 - 0.039	0.100 - 0.121
		Mean	0.033	0.111
Gravity drain	Dish-bottom steel tank	Range	0.031 - 0.042	0.133 - 0.191
		Mean	0.038	0.161
Gravity drain	Dish-bottom glass-lined tank	Range	0.024 - 0.049	0.112 - 0.134
		Mean	0.040	0.127

TABLE 4-11. PERCENT RESIDUE: SURFACE TENSION COMPARISON (WATER VS SURFACTANT)

Unloading method	Vessel type	Value	Material	
			Water	Surfactant
Pumping	Steel drum	Range	1.84 - 2.61	3.06
		Mean	2.29	3.06
Pumping	Plastic drum	Range	2.54 - 4.67	Did not perform
		Mean	3.28	
Pouring	Bung-top steel drum	Range	0.266 - 0.458	0.485
		Mean	0.403	0.485
Pouring	Open-top steel drum	Range	0.026 - 0.039	0.089
		Mean	0.034	0.089
Gravity drain	Slope-bottom steel tank	Range	0.016 - 0.024	0.048
		Mean	0.019	0.048
Gravity drain	Dish-bottom steel tank	Range	0.033 - 0.034	0.058
		Mean	0.034	0.058
Gravity drain	Dish-bottom glass-lined tank	Range	0.020 - 0.040	0.040
		Mean	0.033	0.040

TABLE 4-12. PERCENT RESIDUE: DENSITY COMPARISON (KEROSENE VS SURFACTANT)

Unloading method	Vessel type	Value	Material	
			Kerosene	Surfactant
Pumping	Steel drum	Range	1.93 - 3.08	3.06
		Mean	2.48	3.06
Pumping	Plastic drum	Range	1.69 - 4.08	Did not perform
		Mean	2.61	
Pouring	Bung-top steel drum	Range	0.244 - 0.472	0.485
		Mean	0.404	0.485
Pouring	Open-top steel drum	Range	0.032 - 0.080	0.089
		Mean	0.054	0.089
Gravity drain	Slope-bottom steel tank	Range	0.020 - 0.039	0.048
		Mean	0.033	0.048
Gravity drain	Dish-bottom steel tank	Range	0.031 - 0.042	0.058
		Mean	0.038	0.058
Gravity drain	Dish-bottom glass-line tank	Range	0.024 - 0.049	0.040
		Mean	0.040	0.040

higher viscosity of motor oil. Only in the experimental comparisons involving pumping (pumping vs. pouring, plastic lined drums vs. steel drums) were no significant effects noted between the test liquids.

This implies that motor oil has a significant effect on residue in non-pumping applications. The effect of motor oil (viscosity) however, is not apparent when pumping is involved. While viscosity will have an effect on residue quantities, the effect will be overshadowed by unloading method. For bottom gravity draining, viscosity will have the greatest influence on residue.

It should be noted, however, that vessels containing products of similar viscosity or similar surface tension may not necessarily be emptied to the same extent. The economic value of the product and the relative hazard of the residue are two other important factors affecting the emptying process. The higher each of these factors is, the more thoroughly the vessel is emptied.

4.3 EXPERIMENTAL CONCLUSIONS

4.3.1 Comparison of Experimental Data With Literature Review Estimates

Drums--

In the pilot-scale study, residue quantities for drums ranged between 0.026 and 4.87 percent. This range can be broken down into three ranges based upon unloading methods and type of drum.

- Pumped drums, 1.69 - 4.67% residue
- Poured, bung-top drums, 0.244-0.787% residue
- Poured open top drums, 0.026-0.368% residue

The literature review estimates of residue quantity for drums ranged between 0.1 and 10 percent; the estimate based upon the most substantial set of information was 1.2 percent.[15] This number falls between the pilot-scale study ranges for pumping and pouring bung-top drums. The literature estimate of 1.2 percent was derived from information from the drum reconditioning industry (i.e., residue amounts as received at reconditioning operations) without any specific mention of the unloading method. As noted in Section 2.2.2, the literature estimates predate the "1 inch rule" and may not be necessarily representative of industry practice today.

In the study on emptying 10 gallon (0.04 m^3) milk cans, the average amount of milk left unrecovered was 0.093 percent.[17] Emptying of the milk cans most closely resembles pouring from open-top 55 gallon (0.21 m^3) drums in the pilot-scale study. Milk on the average has a viscosity of 1.5 centipoise,[38] a surface tension of 44 dynes per centimeter,[19] and a density of 1.03 grams per cubic centimeter.[38] This most closely resembles the surfactant solution used in the pilot-scale study. The residue value measured for open-top drum pouring for surfactant (0.089 percent) was in close agreement to the literature value. Another similarity between milk and the surfactant solution is their tendency to foam. This foam which adheres to the sidewalls during draining contributes to increased residue.[19]

Tanks--

In the pilot-scale study, residue quantities for tank runs ranged between 0.016 and 0.191 percent. When evaluating these numbers, it must be kept in mind that the unloading method in each run was bottom gravity draining. As with the drums, pumping a tank empty could leave significantly more residue.

For barges, tank cars, and tank trucks, literature residue estimates range from 0.1 to 9.0 percent with the median around 0.5 percent.[9,10,11] These estimates are higher than what was found in the pilot-scale study; however, the literature estimates make no distinction as to unloading method. As such, it is difficult to compare how well the pilot-scale study and literature review estimates match. It is apparent however, based upon the experimental results and literature estimates, that, the defining of "3 percent" as "empty" for railroad tank cars is significantly higher than what would be expected for residue quantities.

Comparing the results of the pilot-scale study with those given in the study of dairy food residue obtained after draining a 200 gallon (0.76 m^3) stainless steel, sloped bottom tank, it is apparent that significantly higher results were found in the dairy food study.[17] Figure 4-6 presents a graphical comparison of the results from runs with the sloped bottom stainless steel tank to those cited in the dairy food residue study. Only limited information concerning details of the dairy food residue study are available. No measure of drain time was given except that the vessel was drained for two minutes after the bulk of material had been emptied. An explanation for the differences in percent residue between the two studies may lie in the nature

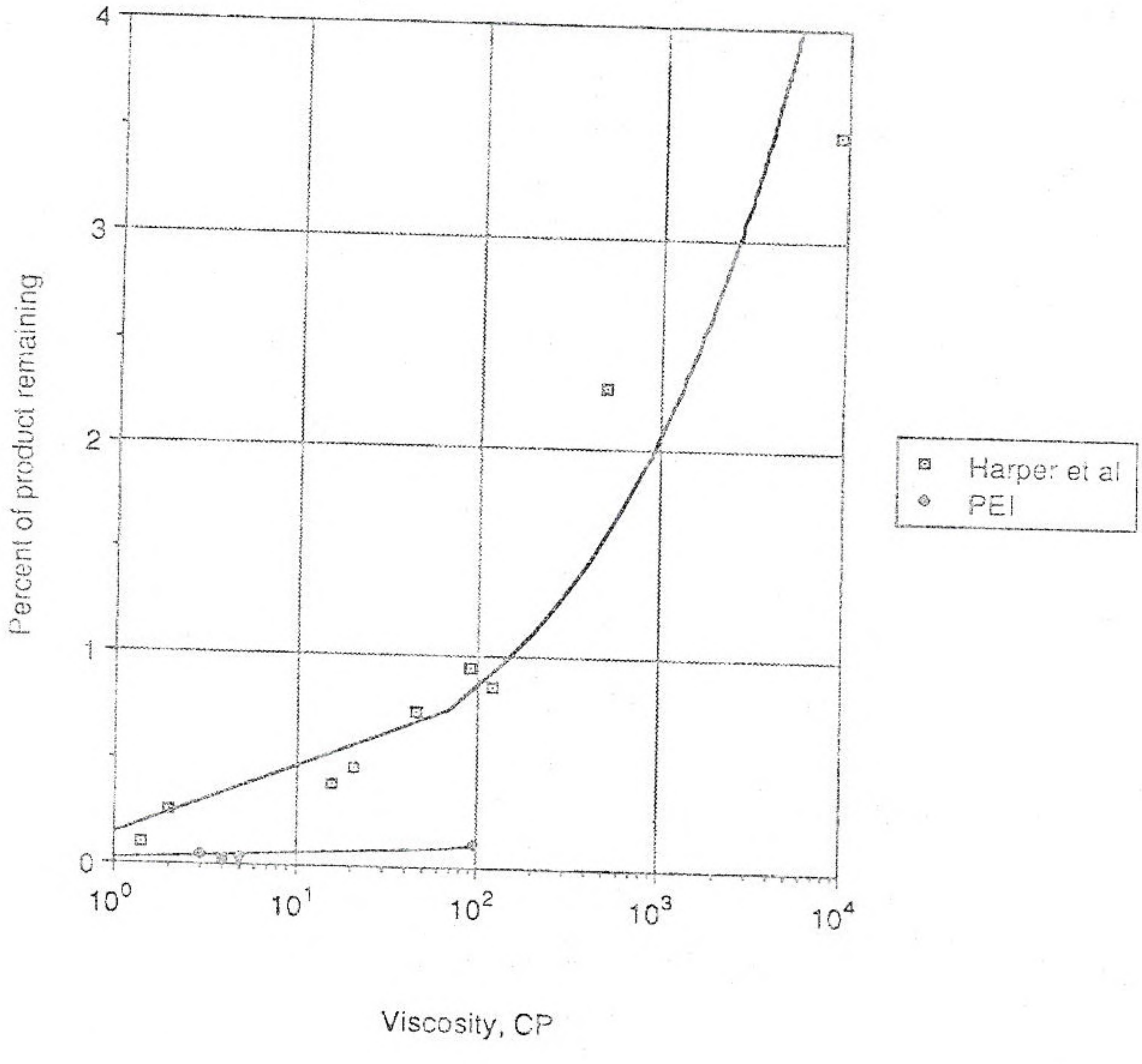

Figure 4-6. Percent residue vs viscosity data from the dairy food residue study (Harper et.al.[17]) and the pilot-scale experiment using the sloped bottom tank.

of the dairy food products. In the dairy food residue report, the bulk materials are identified as "fluid dairy products" while the residue left after draining is referred to as "residual solids".[17] The greater percent residue quantities may therefore be due to the deposition of solid material on the vessel sidewalls and bottom. Only liquid residue was noticed in the pilot-scale study.

Comparing the results of the pilot-scale study to those given in a study of cleaning a milk storage tank, the pilot-scale study results were slightly higher: 0.016 - 0.191% as compared to 0.006%.[19] Table 4-13 shows approximations on the average residue film thickness for the test liquids and the three tanks. In both the pilot-scale study and the milk storage tank study, results for residue thickness make no distinction between residue on the vertical wall and lower cone of the tank.

TABLE 4-13 . APPROXIMATE RESIDUE FILM THICKNESS LEFT DURING TANK DRAINING* (μm)

Test Liquid	30 gallon (0.11 m³), steel slope bottom tank	30 gallon (0.11 m³), steel dish bottom tank	30 gallon, (0.11 m³) glass-lined dish bottom tank
Kerosene	35	39	45
Water	20	35	36
Motor oil	109	171	145
Surfactant	48	62	45

* Calculated using approximate surface area of tanks and average residue quantities found in pilot study using 25 mm drain valve and hose.

In the milk storage tank study, a 690 gallon (2.61 m³) stainless steel sloped bottom tank was used and an average calculated residue of 20 μm of milk was found.[19] As mentioned previously, of the test liquids used in the pilot-scale study, the surfactant solution most closely resembles milk. The calculated surfactant residue thickness in the pilot-scale study using the sloped bottom tank was 48 μm or 0.048 percent.

One theory which may explain the difference in results between the pilot-scale study and the milk storage tank study (beyond the difference in test liquids) is the differences in vessel size. The 30 gallon (0.11 m³) slope bottom tank used in the pilot-scale study had a liquid-metal interfacial area of 1.15 m², while the 690 gallon (2.61 m³) tank used in the milk study had an interfacial area of 8.31 m². The ratio of the liquid-metal interfacial area to volume in the pilot-scale study and milk study were 10.4 m²/m³ and 3.2 m²/m³, respectively. Intuitively it would be expected that the vessel with the higher interfacial area to volume ratio would have a higher percentage residue. This explanation, however, is contradicted by results from the dairy food residue study in which a greater percentage residue was found from tests with a vessel of greater volume and presumably with a lower liquid-metal interfacial area to volume ratio.

In the pilot-scale study, the percent residue was found to be inversely proportional to drain time, as was observed in the milk storage tank and the 10 gallon (0.04 m³) milk can studies.[17,19] The degree of the inverse relationship is likely influenced by the viscosity of the bulk material. An increase in drain time would increase the time available to overcome the resistance to flow of the material (i.e., viscosity) down the sides of a vessel and thus reduce the quantity of residue.

4.3.2 Analysis of Individual Comparisons

The following is a summary of the results from the experimental comparisons performed in the pilot-scale study.

- Unloading Method: Strong significant differences in residue quantities were found between pumping, pouring, and bottom gravity draining a vessel. Pumping left the largest quantities of residue (1.69 to 4.67 percent), followed by pouring (0.026 to 0.787 percent), and bottom gravity draining (0.016 to 0.191 percent).

- Specific vessel design configuration: Open-top vs. bung top drums. A strong, significant difference in residue quantity was found between the open-top and bung-top configurations of drums. Bung-top drums left 0.244 to 0.787 percent residue, while open-top drums left 0.026 to 0.368 percent residue after pouring empty. Slope bottom vs. dish bottom tanks. A slight but significant difference was found between a slope bottom and dish bottom tank when unloaded by bottom gravity draining. The dish bottom steel tank left between 0.031 and 0.191 percent residue while the sloped bottom steel tank left 0.016 to 0.121 percent residue.

- Material of construction of vessel: No significant differences in residue quantities were found in comparisons of plastic, steel and glass linings.

- Properties of bulk materials: <u>Viscosity vs. surface tension vs. density</u>. In a statistical analysis of all seven equipment configurations and three of the four test liquids, no significant difference was found between the test liquids. However, it is obvious that viscosity has a large, direct impact in all situations except those involving pumping. Surface tension and density have slight inverse and direct relationships respectively on residue quantities, but not nearly to the degree of that of viscosity.

Of the parameters examined in the experimentation, unloading method has the primary influence on residue quantity. Special vessel design configurations and properties of the bulk material (namely viscosity) have a secondary influence, while the vessel lining material has no detectable influence on residue quantity. The variability in the residue quantity values from replicate runs is low except for the pumping experiments.

A direct influence on residue quantity when unloading a vessel via pumping is the distance between the end of the suction pipe and the bottom of the vessel. A direct but less pronounced influence on the quantity of residue left in a tank after bottom gravity draining is the time of draining; the longer the draining time, the lesser is the quantity of residue.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

Cleaning of process equipment and shipping containers is an activity with potential for release of chemicals handled in such vessels. The quantity of residue material left in vessels after unloading and prior to cleaning can be used to provide estimates of potential releases during cleaning.

Vessels can be categorized as stationary or mobile. There is considerable information in the literature on cleaning methods used for different types of vessels. Limited information, however, is available on estimates of residue materials left in vessels prior to cleaning. Residue estimates for stationary vessels are reported to range from less than 0.1 percent to 3.5 percent, increasing with the viscosity of the bulk material. Residues retained in product transfer lines are estimated to be comparable to that left in process vessels. Residue estimates for mobile vessels (e.g., tank cars, tank trucks, drums) range from 0.1 to 10 percent. Details regarding the unloading practices and bulk materials associated with these estimates are often not fully characterized. Factors which influence the quantity of residue material left in vessels include the type of vessel (e.g., drums, tanks), its design configuration (e.g., open top vs. bung top, dish bottoms vs. slope bottom), its material of construction (e.g., steel, plastic, glass-lined), the method used for unloading the bulk of the material from the vessel (e.g., pouring, pumping, bottom draining by gravity), and the physical properties of the bulk material (e.g., viscosity, surface tension, density).

PEI designed a laboratory pilot-scale experimental program using equipment in the 30 to 55 gallon (0.11 to 0.21 m^3) range to obtain quantitative estimates of the amount of residue left in vessels and, therefore, potentially available for release during cleaning. Experimentation was conducted in a manner that also allowed the investigation of the relative effects of several factors on residue quantities. The experimental design consisted of an evaluation of four liquid materials (kerosene, motor oil, water, a surfactant solution) for seven vessel type/unloading method arrangements. Mean residue quantities measured in the tests ranged from 0.02 to 3.3 weight percent of the vessel batch size. Table 4-1 provides a complete summary of residue quantities measured. The results from the experiments clearly showed that the amount of residue is influenced more significantly by the unloading method (e.g., pumping, pouring, gravity draining) than by other variables. Specifically, the mean residue quantities from pumping of both steel and plastic drums were the highest among all configurations studied, ranging from 2.1 to 3.3 weight percent for all four liquid materials investigated. The variability among the replicate measurements was also higher for the pumping configuration than for the other equipment arrangements. The viscosity of the bulk material was another variable that affected the amount of residue to a significant degree for the gravity draining and pouring experiments, but not for the pumping experiments. Residue quantities for motor oil (which has a viscosity about 20 to 30 times that of the other liquid test materials) were about 4 to 5 times higher as compared to the other materials for the tank draining configuration; residue amounts for open-top drum pouring were 7 to 10 times higher for motor oil. The size of the drain valve (and, hence, drain time), was another factor that influenced the residue quantity for the tank-draining arrangement. The overall mean residue quantities for all four liquid test materials were lower than 0.8 weight percent for both the pouring and gravity draining configurations. It should be noted that the test program did not include parameters to characterize equipment such as reactors and totes, horizontal design vessel configurations, and bulk material properties such as volatility; these factors could possibly influence the resiaue estimates in a different fashion.

Based on the findings that the residue quantities are more significantly influenced by the unloading method, we believe that the focus of immediate further research should be directed towards a comprehensive characterization of industry practices followed by field measurements. This would provide reliable information on residue estimates for PMN reviews. The need for characterization of industry practices is further supported by the dearth of data on residue quantities currently generated in industry and the existence of regulations for hazardous materials that define precisely the maximum quantity an "empty" drum or railroad tank car may contain. The need for agencies to define "empty" through regulations suggests that, in industry, vessels may not be unloaded or drained as thoroughly as was defined for the pilot-scale experimental study, i.e., the "reasonable end point" for unloading and draining a vessel will likely vary in industry.

Specifically, the following activities are recommended for obtaining both a thorough understanding of operations in industry and more representative estimates of industrial residue quantities.

- Review of Regulations - A comprehensive review of Federal, State, local and industry regulations pertaining to draining and cleaning of different types of vessels and chemicals will provide guidelines on residue estimates.

- Contact With Industry Sources - Initiating contacts with industry associations (e.g., CMA, SOCMA, NABADA, API), drum reconditioners, chemical plants, and transportation (e.g., rail car, truck, barge) facilities will aid in assessing industry unloading practices. Contact should also be made with makers and users of emptying equipment to identify and evaluate the range of available emptying equipment and techniques, and to examine how variations in equipment and/or techniques can affect residual volume. Such information could stimulate the selection of more effective mechanisms for emptying, and also define potential design changes in containers, equipment and techniques to improve emptying.

- Development of Questionnaire - A comprehensive questionnaire should be developed to assess draining as well as cleaning practices employed in industry as a function of type of vessel, materials of construction, chemicals used, etc. The questionnaire should cover both chemical plants and drum reconditioning facilities and mailed to a number of such facilities for input.

- Conduct of Walkthrough Surveys - Walkthrough surveys at several candidate facilities should provide further insight on unloading and cleaning practices. Any estimates of residues and/or releases available from the plant could be obtained during such surveys. Plants selected for surveys should be representative of the pharmaceutical, chemical, food processing, drum reconditioning and transportation industries. Residue quantities and their variability may depend on the personnel involved in emptying the drums or tanks, in addition to the actual techniques employed for emptying. The surveys should provide additional information in this area.

- Conduct of Field Study Programs - The information from the walkthrough surveys could be used to initially determine the feasibility and subsequently design field study programs of approximately one-week duration each at candidate plants to characterize and obtain field data on residue quantities actually obtained in industry.