A STUDY OF CARBON DIOXIDE ABSORPTION EQUIPMENT FOR CONTROLLED ATMOSPHERE FRUIT STORAGES

Thesis for the Degree of M. S.

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A STUDY OF CARBON DIOXIDE ABSORPTION EQUIPMENT FOR CONTROLLED ATMOSPHERE FRUIT STORAGES

By

Pio Angelini

A THESIS

Submitted jointly to the Schools of Engineering and Agriculture,
Michigan State University of Agriculture and Applied Science
in partial fulfillment of the requirements
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MASTER OF SCIENCE

Department of Agricultural Engineering

1956

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AN ABSTRACT

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Equipment for removal of excess carbon dioxide is an integral part of controlled atmosphere fruit storage. Yet, very little is known about the suitability and operating characteristics of carbon dioxide absorption equipment presently used in controlled atmosphere storages. Studies of this equipment and several of the factors affecting the absorption of carbon dioxide by alkaline solutions are reported in this thesis.

The tests of present installations were conducted in cooperation with operators of controlled atmosphere apple storages in New York and Massachusetts. These operators collected samples of spent or partially spent absorbing fluid from their absorbers under normal operating conditions, according to a specific collection program. These samples were sent to Michigan State University for analysis and study.

An absorber utilizing packed tower was constructed for study of the factors affecting carbon dioxide absorption and operation of methods in comparison to ones used in present controlled atmosphere storages.

The brine spray units show better liquor utilization and greater capacity than the tank type units. A study of the construction and operating conditions shows that the greater interfacial surface area, greater recirculating rate, lower liquor concentration, and larger reservoirs of the brine spray absorbers are responsible for these differences. The once-through method offers a constant rate of carbon dioxide removal and is readily adaptable to automatic operation, but a great deal more surface area would be necessary for comparable liquor utilization to the recirculating method.

TABLE OF CONTENTS

INTRODUCTION

Controlled atmosphere (CA) fruit storage is rapidly gaining significant acceptance throughout the United States. This is largely due to the marked increase in the storage life and quality of some fruits when held in CA storage. Perhaps the best example of this phenomenon is the case of McIntosh apples where the storage-life of the fruit may actually be doubled by maintenance of the proper atmospheric conditions.

CA storage was first used on a commercial scale in England, where it is referred to as gas storage, due to the pioneering efforts of Kidd and West of the Low Temperature Research Station at Cambridge, England about a quarter of a century ago. In England in 1927 there were 3,000,000 cu. ft. of cold storage space utilized for fruit, but no CA storages. In 1937 there were 6,000,000 cu. ft. of cold storage and 29,000,000 cu. ft. of CA storage used for the storage of fruit (Van Doren, 22). In the past decade CA storage has been increasing rapidly in the United States. The International Apple Association Report of November, 1955 states that 812,000 bu. of apples were stored in 1955 in CA storages located mostly in the Hudson Valley. At the present time there are no commercial CA storages in Michigan, but there is great promise that some will be constructed in the near future.

One of the problems of CA storage is the removal of excess carbon dioxide. Equipment presently used in CA storage for carbon dioxide control produces the desired carbon dioxide conditions, but very little is known about the efficiency of this equipment in controlling carbon dioxide. This thesis will attempt to study and compare the existing carbon dioxide absorption equipment and to acquire information that will lead to a more intelligent understanding of carbon dioxide absorption equipment for CA fruit storages. It appears that a better understanding will result in the design of more efficient equipment than is presently used.

LITERATURE REVIEW

In CA storages desired levels of carbon dioxide and oxygen are acquired by allowing the commodity to reduce the oxygen level and increase the carbon dioxide level through the process of respiration. It has been shown that different levels of oxygen and carbon dioxide can be acquired and maintained, in a tight storage room, by controlling ventilation alone. However, since atmospheric air contains approximately 21 percent oxygen and 0.03 percent carbon dioxide, and since it takes one mole of oxygen to produce one mole of carbon dioxide the various combinations of oxygen and carbon dioxide must always total about 21 percent. Smock (17) found that the optimum storage conditions for storing McIntosh apples was an oxygen level of about 3 percent and a carbon dioxide level of about 5 percent. In the ideal storage operation the oxygen level is controlled by ventilating, but all of the excess carbon dioxide cannot be removed by ventilating without also adding an excess of oxygen. Therefore, the excess carbon dioxide is removed by chemical absorption. The excess carbon dioxide is absorbed from the storage atmosphere by either a sodium hydroxide (Smock and Van Doren, 18) or a calcium hydroxide (Kidd and West, 11) solution.

Smock and Van Doren (19) developed a continuously recirculating perforated plate tower apparatus in which the sodium hydroxide is pumped from the reservoir at the bottom to the top of the tower and allowed to flow down through the holes in the plates and back into the reservoir. The storage room air is forced up through the perforations in the plates of the tower by a blower. The carbon dioxide is absorbed from the air in this process. This was the original method used in CA storages in the United States. Another system was developed using the brine spray refrigeration evaporator as the absorption tower (Smock, 17). A sodium hydroxide solution is used in place of the brine; the reservoir and pump for the brine spray evaporator are located outside the CA room. A packed absorption column, developed as part of this project, is also a promising possibility.

A considerable amount of research has been done by previous investigators to understand and evaluate the factors that affect the absorption of carbon dioxide by alkaline solutions. In 1921 Byrne and Carlson (4) absorbed carbon dioxide from carbon dioxide-rich flue gas with a lye solution. The absorption took place in a one-foot diameter, 12-foot high tower packed with three-inch coke. The capacity coefficient was found to be a function of temperature and lye rate.

$$K_L = 0.000074t + 0.0000048L' - 0.0055$$

where

K_L = absorption coefficient, (lb moles of CO_2) $(hr)^{-1}$ $(ft)^{-3}$ (unit driving force)$^{-1}$

t = temperature, °F

L' = lye rate, $(lb)(hr)^{-1}(ft)^{-2}$

This equation was derived from values taken by varying the temperature from 84°F to 138°F, lye rates from 110 to 760 $(lb)(hr)^{-1}(ft)^{-2}$. This equation, as pointed out, should be used only for the range of variables covered. Variation of the gas rate gave no noticeable effect on the capacity coefficient.

The rate of absorption of carbon dioxide by water and solutions of sodium carbonate, sodium bicarbonate, and sodium hydroxide was studied by Payne and Dodge (12) using a small tower packed with glass rings. The results were reported in the form of an over-all gas absorption coefficient (K_Ga), with units of grams absorbed per hour per cubic centimeter of packed volume per atmosphere of mean driving force. In summary Payne and Dodge (12) found that:

1. The average over-all absorption coefficient is independent of the carbon dioxide concentration in the gas.
2. A four-fold increase in gas rate has no effect on the coefficient.
3. An increase in liquid rate increases the coefficient materially.
4. A sixteen-fold variation in sodium carbonate concentration has no significant effect on the coefficient.

5. An increase in temperature causes an increase in the coefficient.
6. The substitution of hydrogen for air has little if any effect on the coefficient.
7. The absorption coefficient is less for sodium carbonate than for water.
8. The addition of small percentages of sucrose or formaldehyde to the sodium carbonate solution appears to increase the coefficient slightly.
9. The addition of sodium bicarbonate to the sodium carbonate solution decreases the absorption coefficient.
10. The coefficient of dilute sodium hydroxide is much greater than that of sodium carbonate solution.
11. The rate of absorption in a dilute sodium bicarbonate solution is appreciably less than in water.
12. The absorption rate is approximately constant throughout the tower and does not diminish as the partial pressure of carbon dioxide decreases.

It was stated that much more experimental data should be assembled before an attempt to give a comprehensive quantitative interpretation could be made. It was pointed out, however, that a pure diffusional theory is probably not adequate to treat the absorption of carbon dioxide in an alkaline media, but that chemical reaction rate should also be considered.

Comstock and Dodge (8) studied further the results obtained by Payne and Dodge and obtained additional information. With respect to the effect of carbonate concentration, Comstock and Dodge found that the coefficient decreased with increase in carbonate concentration. This effect is attributed to the differences in pH and viscosity with different concentrations of carbonate. The coefficient was also found to decrease with the conversion of carbonate to bicarbonate, and increase with pH. The effects of gas velocity, rate of liquor flow and temperature were consistent with those found by Payne and Dodge. A three-inch tower packed with small glass rings was employed for these tests.

Furnas and Bellinger (9) compared 3/8" Raschig rings, 1" Raschig rings, and 1" Berl saddles in a twelve-inch tower and found that absorption varies with the packing material used in the column. From their results a new method of correlating the variables was developed whereby the performance of all three packings is represented in the equation

$$K_0a = 0.37 \times 10^{-6} \quad \frac{L^{1.18}\,A^{0.82}}{H}$$

where

K_oa = the overall absorption coefficient

L = liquor velocity

A = the surface area

H = the liquor holdup

The holdup (H) was found to equal CL^s where C and s were constants determined for each packing. The gas film absorption coefficient was found to be negligible in most applications, as found by other investigators, but it became important for low gas flows, very high liquor rates or large-sized packing. The effect of temperature was found to coincide with results of previous investigators, but it was shown that for the same variation in temperature the coefficient is not affected anywhere near as much by low liquor rates as with high liquor rates.

Sherwood and Holloway (13) discovered that the liquid film coefficient was considerably reduced through the addition of wetting agents to the liquid or by coating the packing with paraffin for desorption of carbon dioxide from water.

Tepe and Dodge (21) carried out an investigation to better understand the absorption of carbon dioxide in aqueous sodium hydroxide, and expressed the results as an over-all absorption coefficient (K_Ga). Their studies showed that the absorption coefficient

1. increases rapidly with increasing sodium hydroxide concentration up to about two

normal and decreases with further increase of concentration above this value,

2. decreases approximately linearly with increasing sodium carbonate concentration,
3. increases approximately as the 0.28 power of the liquor rate, and
4. increases as the sixth power of the absolute temperature.

The effect of gas rate was found to be negligible under the conditions of test. It was concluded that the chief resistance to transfer exists in the liquid phase and that:

$$K_G a = \frac{N}{V\ P^{LM}}$$

where

K_G = overall absorption coefficient in (lb moles) $(hr)^{-1}$ $(ft)^{-2}$ $(atm)^{-1}$

a = effective interfacial area per unit of tower volume in $(ft)^2$ $(ft)^{-3}$

N = moles of carbon dioxide transfer per unit time in (lb moles)$(hr)^{-1}$

V = packed volume of the tower in $(ft)^3$

P^{LM} = log mean partial pressure of carbon dioxide in atmosphere

These studies were pursued further by Spector and Dodge (20) in 1946 whereby carbon dioxide was removed from atmospheric air. They found that $K_G a$ increased with the gas rate as the

0.35 power for flow rates up to 500 $(lb)(hr)^{-1}(ft)^{-2}$; the rate of increase diminishes above this flow rate, being only as the 0.15 power of the gas rate at flow values in the neighborhood of 1000 $(lb)(hr)^{-1}(ft)^{-2}$. Aqueous potassium hydroxide solution gave values of K_Ga 20 to 30 percent greater than those for sodium hydroxide solutions of equal normality and at the same operating conditions. K_Ga was found to decrease as the 0.5 power of absolute tower pressure up to a total of 100 psi gage.

APPARATUS AND PROCEDURES

Previous investigators directed their studies to the acquisition of fundamental data or to problems which, although related to this thesis problem, differ significantly in some respects. The results of the many experimenters show the individual effects of numerous factors affecting carbon dioxide absorption by alkaline solutions. Although very helpful in suggesting the effects of potential variable factors in this study, the total effect of many of these factors acting together is necessary to evaluate and design equipment.

Considerable success has been achieved in the attempt to study the results of these factors acting together. The conditions and purposes of the problems for which these experiments were carried out were different from the aims of this thesis. Previous investigations dealt with the absorption of carbon dioxide from the atmosphere by absorbing with sodium hydroxide-sodium carbonate systems, and sodium carbonate-sodium bicarbonate systems separately in packed towers. Other researchers were primarily interested in the total or near total removal of carbon dioxide from the atmosphere and not necessarily the most efficient utilization of the absorption liquor.

In CA storage operation the maintenance of a constant, relatively high level of carbon dioxide and a high utilization

of the absorbing liquor are desired. This allows a high carbon dioxide driving force over all the absorption area, which in turn permits high utilization of absorbing liquor. The low driving force of carbon dioxide considered by other investigators offers significantly different conditions from those of this study.

This study also differs from previous studies in that some of the equipment investigated does not employ a packed tower for absorption and the total conversion of sodium hydroxide to sodium bicarbonate is considered. Basically, however, many of the findings of previous investigators apply to this study. But, because of the differences, this investigation was carried out differently from previous investigations.

The two types of equipment now used in commercial storages are illustrated schematically in Figures 1 and 2, and the third type, of which the possibilities as carbon dioxide absorption equipment are being investigated, is illustrated in Figure 3.

Brine Spray Type Absorbers - Description and Procedure

The brine spray diffuser in Figure 1 is standard refrigeration equipment. It serves a dual purpose in the newer Hudson Valley CA rooms of evaporator and absorption tower simply by replacing the brine with a caustic soda solution. Absorption takes place when the caustic soda solution is sprayed on the evaporator pipes over which room air is rapidly circulated.

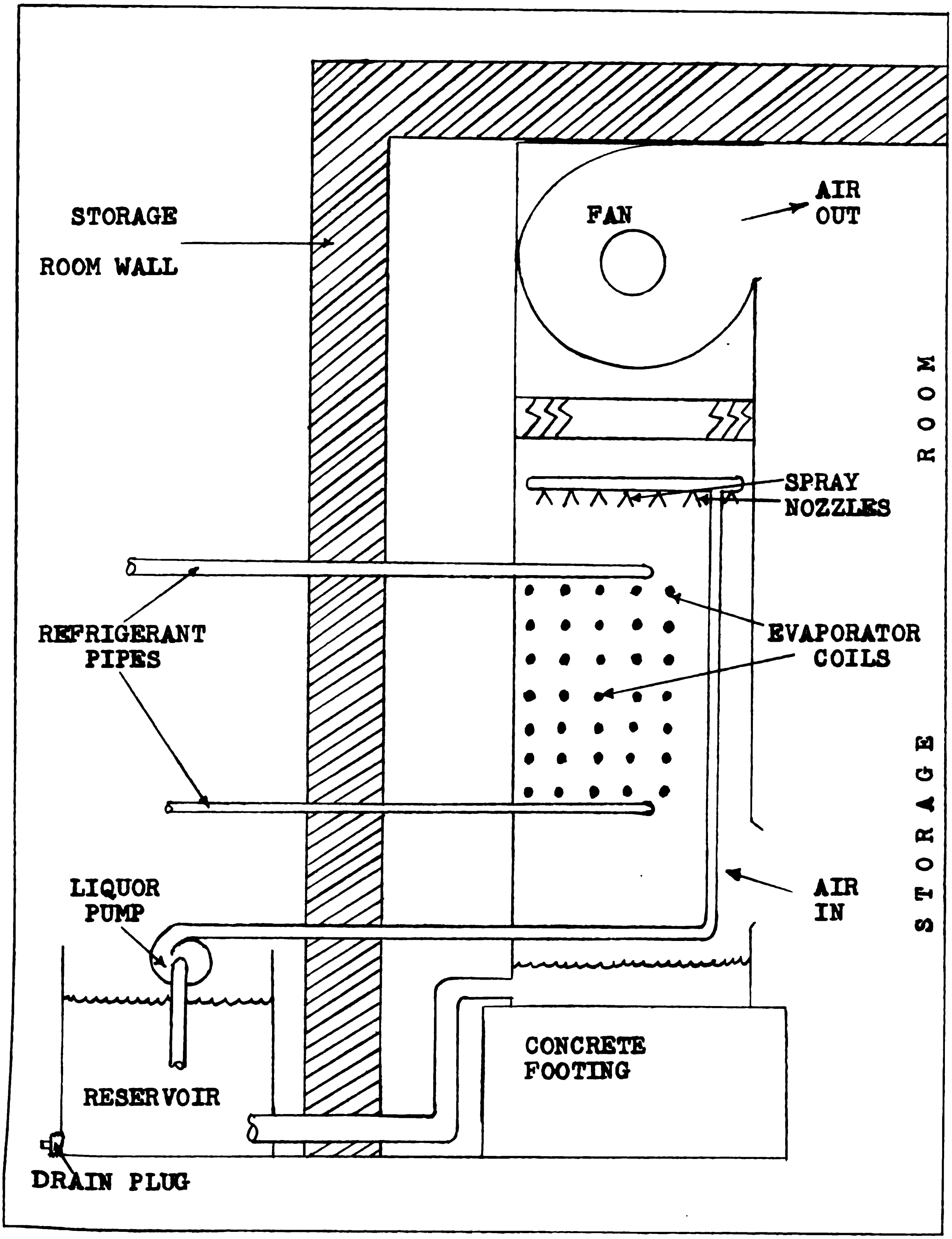

Fig. 1. Brine spray absorption unit.

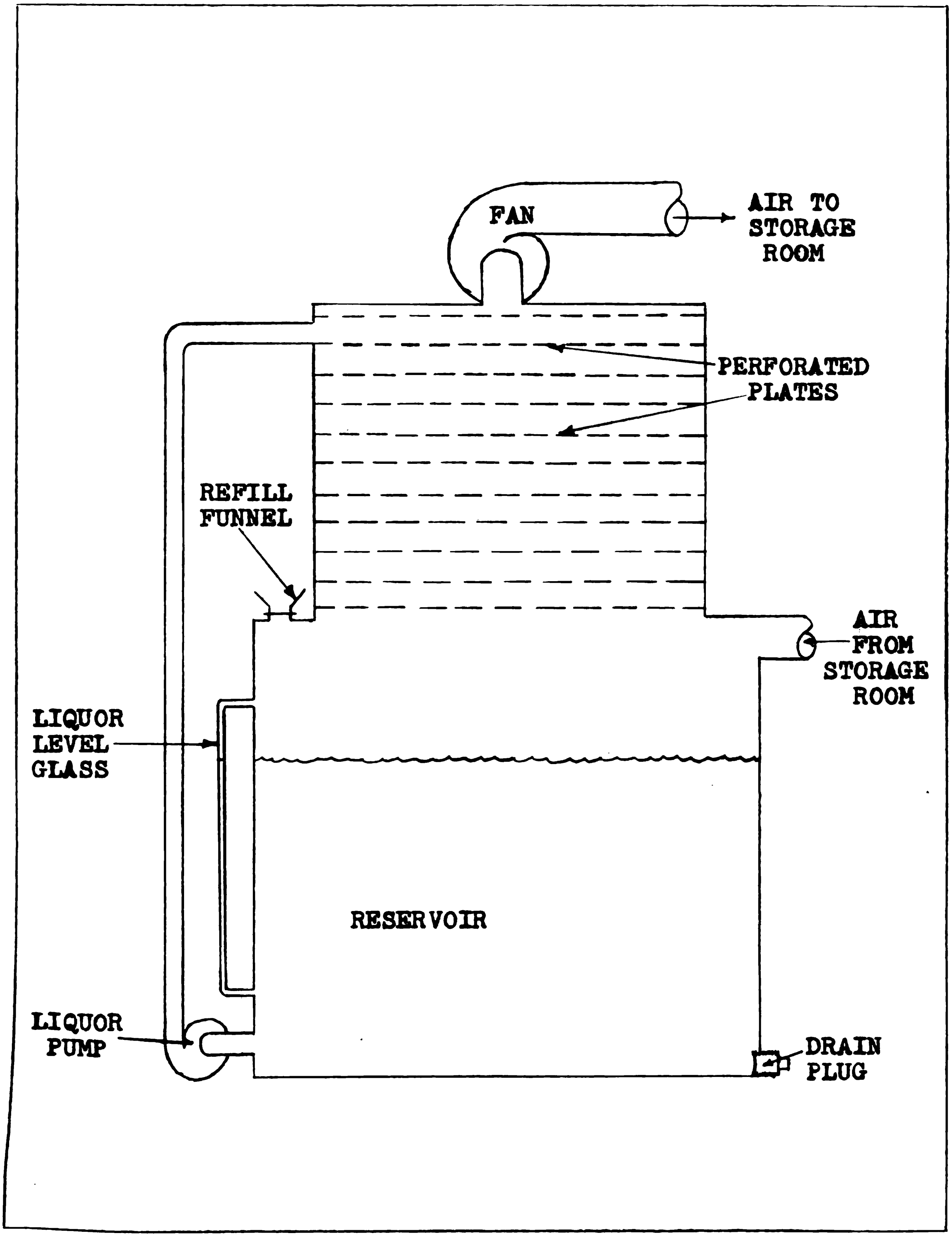

Fig. 2. Tank-type absorption unit.

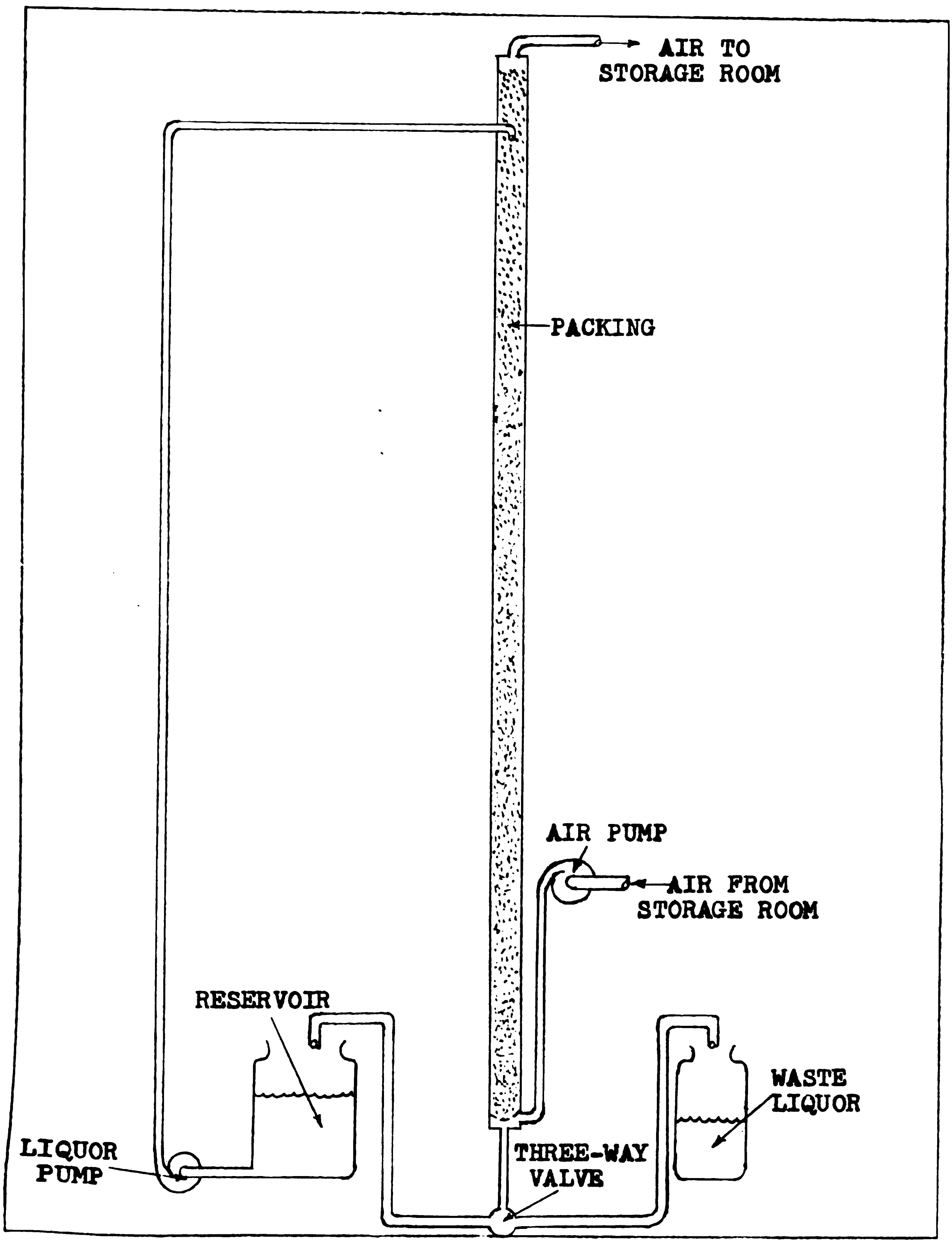

Fig. 3. Packed tower absorption unit.

Three brine spray absorbers were studied. Absorber No. 1 is a Carrier Model 27N5-143 brine spray unit employing a 3/4 H.P. Bell and Gossett pump for liquor recirculation; absorber No. 2 was identical with No. 1 except for a slightly greater air flow rate on No. 2. Both No. 1 and No. 2 have reservoirs of 115 gallons and are located in the Cornell University 1500 bu. experimental CA storage rooms. Absorber No. 3 was operated by P. Calabi. It is a Carrier Model 15B9-149 evaporator unit with a Carrier Model 87W9-184 blower, and a 3/4 H.P. Bell and Gossett pump for liquor recirculation. It has a reservoir of about 100 gallons and is used on a 10,000 bu. room.

Dr. R. M. Smock collected samples from the absorbers at Cornell University in 4-oz. plastic (polyethylene) sample bottles and sent them to MSU for analysis. Two series of samples were taken from each absorber following a prescribed collection program. All samples were collected under normal operating conditions from each absorber. In the first series, samples were collected at intervals over a period of 24 hours. In the second series, samples were collected at intervals over a period of 2 1/2 hours. In both series samples were collected at more frequent intervals near the beginning of the operating period. The time between intervals is shown by the points plotted in Figures 4 and 5. Calabi, of Lagrangeville, New York, collected samples from absorber No. 3 following a similar collection program. Four series of samples were collected; both over a period of 24 hours, but with different amounts of caustic soda per liquor loading.

Tank Type Absorbers - Description and Procedure

Figure 2 shows a tank-type absorption unit using perforated plates in the upper portion or absorption section of the tank while the lower portion is used as a reservoir. The caustic soda solution is pumped from the bottom reservoir to the top of the absorption section and allowed to flow down through the perforations in the plates. The air from the storage room is forced up through the holes in the plates and back into the storage room. The carbon dioxide is removed from the atmosphere when it comes in contact with the caustic soda solution.

G. S. Gay of Three Rivers, Massachusetts, collected samples from his three tank-type absorbers which made possible the evaluation of this type unit. Absorbers No. 1 and No. 2 are used on identical 3300 bu. commercial CA storage rooms, are identical in construction, and were patterned after the original design of Smock and Van Doren (17). Absorber No. 3 has 3" coke packing in the absorption section instead of perforated plates. It is otherwise identical in construction with absorbers No. 1 and No. 2. These absorbers have a reservoir capacity of 45 gallons, a 1/4 H.P. Bell and Gossett pump for liquor recirculation, and a blower capacity of about 400 C.F.M.

Gay collected samples in 4 oz. plastic (polyethylene) sample bottles and sent them to MSU for analysis. During the

1954-1955 storage season Gay experimented with different amounts of caustic soda per loading of absorbing liquor using absorber No. 1. The quantity of caustic soda varied from 15 to 30 pounds per 45 gallons of water. A loading of 20 pounds of caustic soda per 45 gallons of water seemed to fit his operations best so this loading predominates. The procedure followed was to load the absorber and operate keeping account of the number of hours the particular batch of caustic soda was used. A representative sample of the absorbing solution was taken when the absorption solution was discarded. The analysis of the sample determined the final efficiency of the respective loading.

Samples were collected by Gay from absorbers No. 2 and No. 3, during the 1955-1956 storage season, following a procedure similar to that used by Smock, and using 20 pounds of caustic soda per 45 gallons of water for all loadings. Several series were collected from each absorber and the results are summarized in Figures 9, 10 and 11.

Column Type Absorber - Description and Procedures

The third type of absorption unit as shown in Figure 3 is a packed tower through which the caustic soda solution is pumped to the top of the tower and allowed to flow down over the packing. The storage room atmosphere is forced through the packed tower either counter to or parallel to the flow of the caustic soda solution. As the caustic solution drains from the bottom it is discarded as spent solution or it is recirculated continuously through the tower. This tower type absorber was employed to study the more important factors involved in carbon dioxide absorption.

The tower was constructed from a nominal 1 1/4-inch I.D. Schedule, 40-steel pipe 7 feet long and was packed with 3/8-inch glass Raschig rings. The effective height of the column was 6 1/2 feet and it had 8.2 square feet of effective surface area. The liquor was conducted to the center of the column 1/2 foot from the top by 1/8-inch steel tubing which was brazed in a specially bored hole, 1/2 foot from the top. Reducing connections on the column were made with standard threaded fittings. A refrigeration compressor was used as an air pump to circulate the atmosphere at a constant rate of 0.5 C.F.M. through the absorber. The caustic soda solution was pumped into the absorber with a positive displacement adjustable flow micro-bellows type pump.

Three factors were observed to be important in obtaining desired caustic soda utilization and capacities, and are considered in this report: 1) size of reservoir; 2) concentration of absorbing liquor; and 3) rate of liquor recirculation. Two or three values of each of the three factors were investigated, holding all other variables constant, as designated in Figures 12 through 19. Before each run the column was washed with water and allowed to drain overnight. During each run two one ml. representative samples were taken from the reservoir at definite time intervals shown by points on the respective graphs, transferred to two 200 ml. Erlenmeyer flasks, and analyzed immediately. The amount of liquor removed by sampling was considered insignificant in its effect on the investigation.

The effects of liquor concentration and rate of liquor flow were studied for the once-through method. The column was washed with water before each run and several liquor concentrations were used for each liquor rate studied. The system was allowed to come to equilibrium before sampling. Equilibrium was determined by taking periodic trial samples after the system was started operating. When the analysis of consecutive trial samples yielded identical results the system was considered at equilibrium. After a series of samples at one liquor rate were collected, the liquor rate was changed and another series of samples at varying conceentraionts was taken. The liquor rates and concentrations studied are illustrated by the curves and plotted points on Figure 20.

The factors selected for study are not the only important factors affecting carbon dioxide absorption, but are the factors in which more information would help in designs of carbon dioxide absorption equipment for CA storages. Previous investigations supply adequate information on many other necessary factors while other reported factors would not apply feasibly to carbon dioxide absorption from CA storages.

The study was made with collected samples of the spent or partially spent caustic soda solution from each of the three types of systems under known operating conditions. The samples were analyzed in order to obtain the original concentration of sodium hydroxide, and the percent conversion of total sodium present as sodium hydroxide to sodium bicarbonate. The results of the analyses were then coordinated with the various conditions of operation and are expressed graphically.

The original concentration of sodium hydroxide was calculated from the titration with 0.1 normal hydrochloric acid using methyl orange as the indicator. The percent conversion of total sodium as sodium hydroxide to sodium bicarbonate, referred to as percent efficiency, was calculated from the titration with 0.1 normal hydrochloric acid when the sample was alkaline after the addition of excess barium chloride; or with 0.1 normal sodium hydroxide when the sample was acidic after the addition of barium chloride using phenolphthalein as the indicator.

The procedure for the chemical analysis of the samples was as follows:

A. Titration with methyl orange indicator

1. A one ml. volumetric pipette was used to obtain a one ml. sample which was deposited in a 200 ml. Erlenmeyer flask.
2. The one ml. sample was then diluted with approximately 25 ml. of distilled water.

3. One or two drops of methyl orange indicator were added to the flask.
4. The sample was titrated with approximately 0.1 N standardized hydrochloric acid to the methyl orange end point from a 50 ml. burette with 0.1 ml. graduations.
5. The milliequivalents of hydrochloric acid used in titration are equal to the milliequivalents of sodium hydroxide originally present in the one ml. sample.

B. Titration with phenolphthalein indicator

1. A one ml. volumetric pipette was used to obtain a one ml. sample which was deposited in a 200 ml. Erlenmeyer flask.
2. The one ml. sample was then diluted with approximately 25 ml. of distilled water.
3. Barium chloride was added from a stock solution of approximately 1 M with an excess of 50 percent to that necessary to precipitate all of the carbonate assuming 100 percent efficiency.
4. One or two drops of phenolphthalein indicator were added to the flask.
5. If the phenolphthalein indicator turned pink on addition, the sample was titrated with approximately 0.1 N standardized hydrochloric acid until the indicator was colorless.

6. If the phenolphthalein indicator was colorless on addition, the sample was titrated with approximately 0.1 N standardized sodium hydroxide until the indicator turned pink.

The efficiency of the absorption process was then determined as follows:

$$\text{Percent efficiency} = \frac{\text{me Na (in sample)} + (\text{meNaOH} - \text{meHCl})}{2 \times \text{meNa (in sample)}}$$

RESULTS

The primary interests in this study were the capacity of the system to fully utilize the sodium hydroxide to absorb carbon dioxide and the rate at which the system will remove carbon dioxide from the storage room. The results were analyzed mainly with these two characteristics in mind. Graphical plots of percent efficiency of total utilization of the sodium hydroxide were made on ordinary graph paper, and several selected plots were also made on semi-logarithmic graph paper to point out that the logarithm of one minus the percent efficiency varies nearly linearly with the time of operation for the recirculating method. The capacities of the units expressed in moles of carbon dioxide absorbed per hour were calculated from the slope of the utilization curves and plotted on ordinary graph paper as a function of time. From this information certain conclusions could be drawn concerning the potentialities of these absorption systems.

Evaluation of Brine Spray Absorbers

The information on brine spray diffusers was acquired by analyzing samples collected by R. M. Smock, Cornell University, and P. Calabi, Lagrangeville, New York.

Smock used loadings of four lbs of caustic soda in 115 gallons of water in the brine spray tank which was enough to control the carbon dioxide in a room of 1500 boxes of McIntosh apples for two days.

The results of series 1, illustrated in Figure 4, show that more than 95 percent of the sodium hydroxide was converted to sodium bicarbonate after three hours of operation for both absorbers. The results of series 2 are illustrated in Figure 5. There was a decreasing rate of utilization as operating time increased. This type of behavior was expected. Figure 6 shows that the rate of utilization decreased approximately logarithmically with time. The rate of carbon dioxide absorption varied with operating time as shown in Figure 7. The decreasing rate of carbon dioxide absorption with time indicated that the beginning of the absorption period was the most effective. The high percentage of caustic soda utilization and the high rate of carbon dioxide absorption were two very significant observations.

These data from P. Calabi show that in two hours the sodium hydroxide was more than 95 percent utilized, both in the instances where 5 lbs and where 8 lbs of caustic soda per 100 gal. of water were used. Calabi's diffusers show a slightly higher capacity than do Smock's; but the difference was not significant since both have a great deal more capacity than necessary for the carbon dioxide removal.

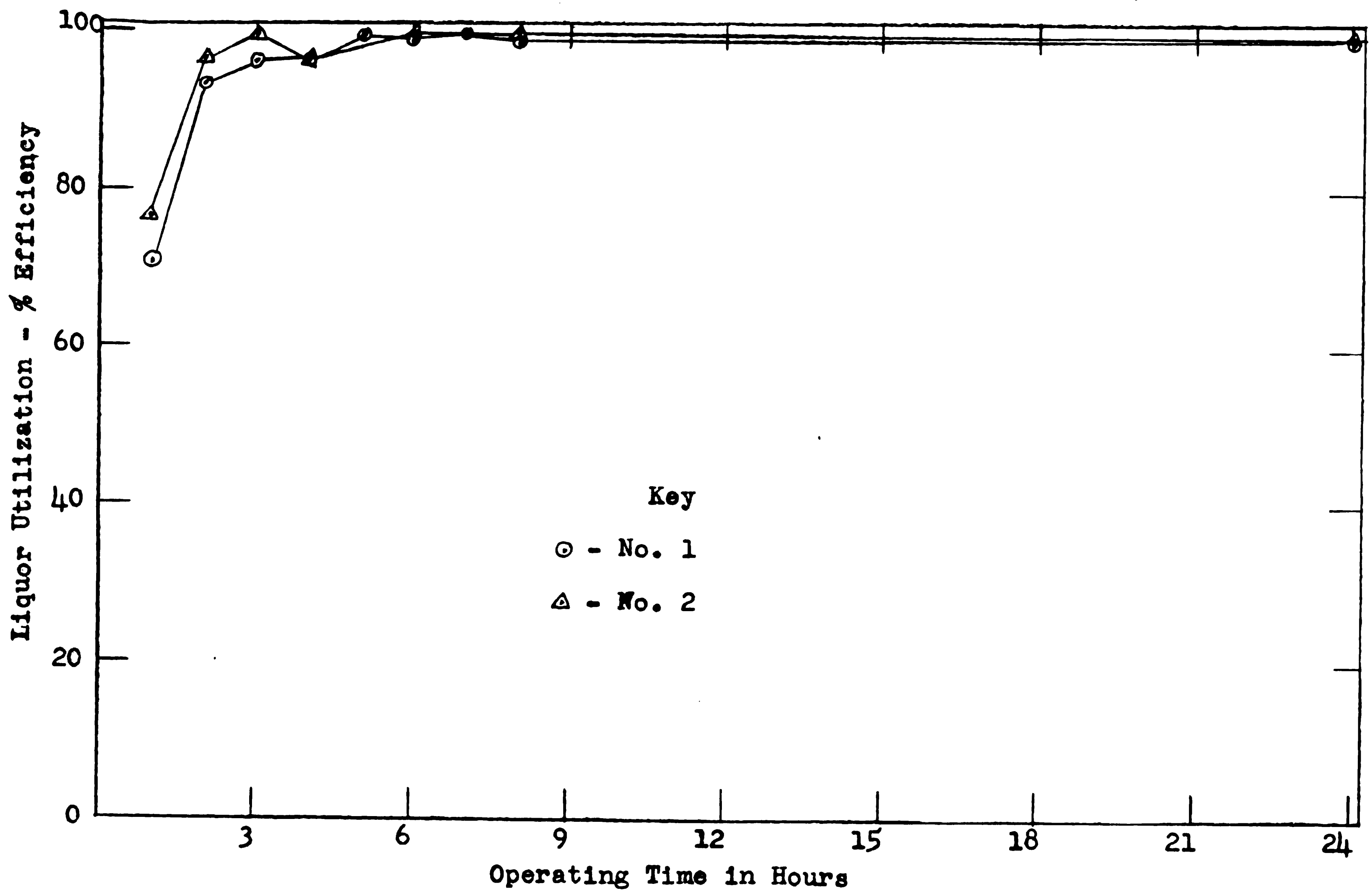

Fig. 4. Absorption liquor utilization vs. operating time of brine spray absorbers No. 1 and No. 2.

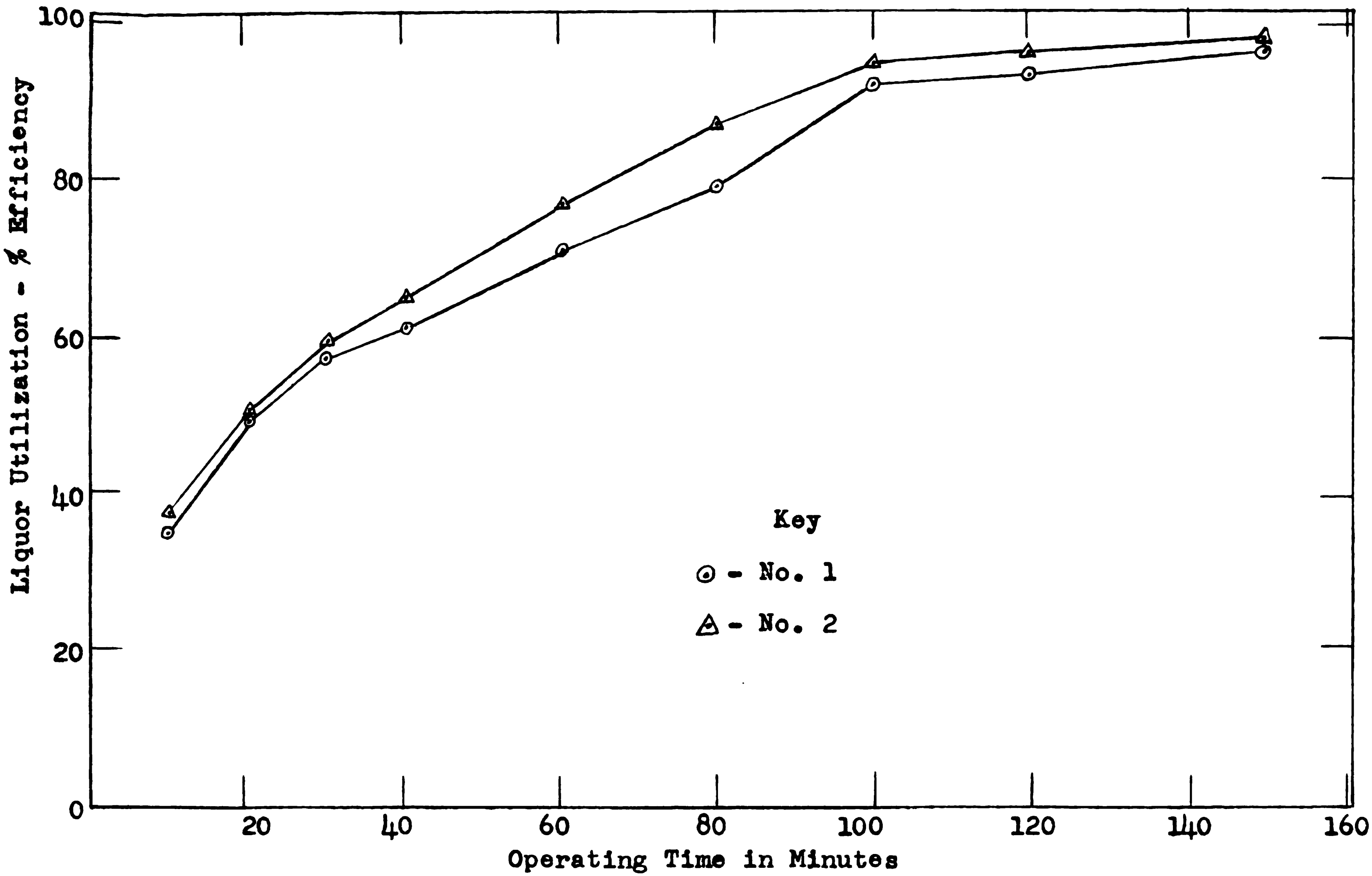

Fig. 5. Absorption liquor utilization vs. operating time of brine spray absorbers No. 1 and No. 2.

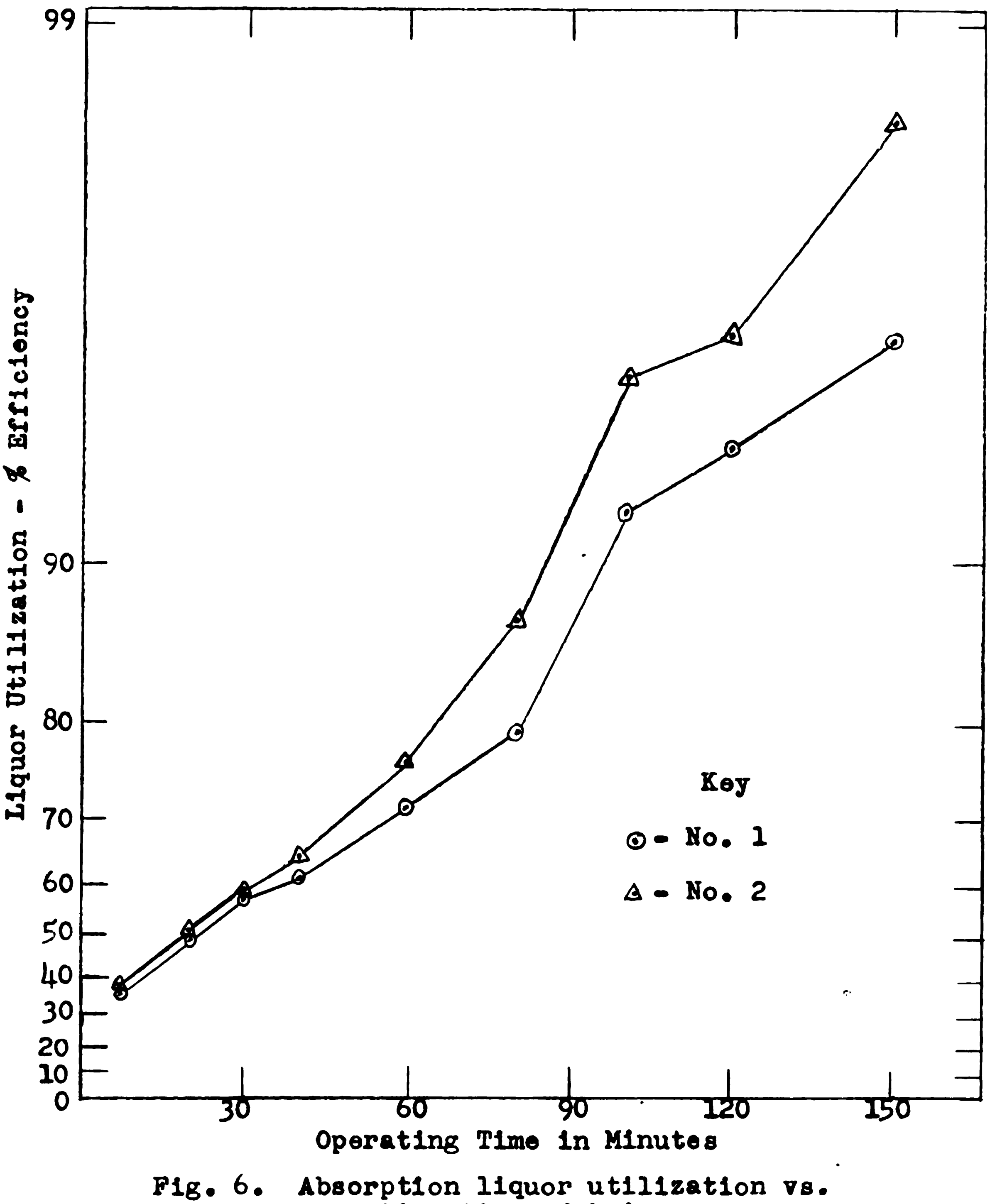

Fig. 6. Absorption liquor utilization vs. operating time of brine spray absorbers No. 1 and No. 2.

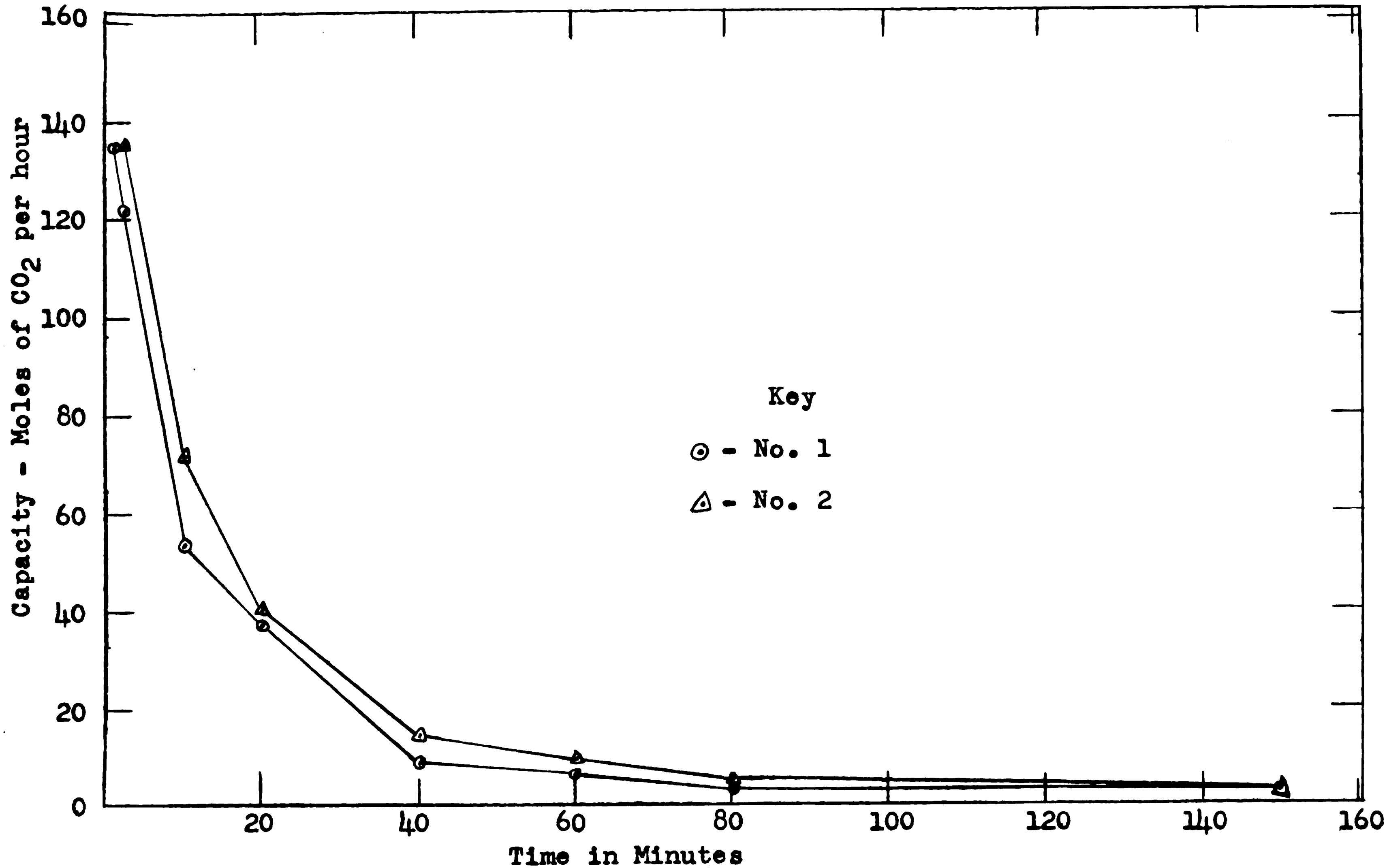

Fig. 7. Capacity vs. operating time of brine spray absorbers No. 1 and No. 2.

Evaluation of the Tank Type Absorber

The tank type absorbers which were investigated were operated by G. S. Gay as described above. The results of samples collected from absorber No. 1 during the 1954-1955 storage season were summarized in Figure 8. The rather wide scattering of points indicates the variation that occurred in the operation of this particular absorber. A curve was plotted to represent an estimated average of the points.

The results of the investigations with absorbers No. 2 and No. 3 are summarized in Figures 9, 10 and 11. The data expressed in Figures 9 and 10 were obtained from several sample series subjected to identical operating conditions from each of the two absorbers. The decreasing rate of utilization of caustic soda as shown in Figure 9 confirms an expected similarity in behavior of this type unit as compared to the brine spray-type unit. It is evident that a much longer period of operating time is required to get comparable caustic soda utilization from the tank-type units studied than from the brine-spray type units studied.

Figure 10 points out that, as in the case of the brine spray-type unit, the decreasing rate of caustic soda utilization with time is nearly logarithmic. Figure 11 illustrates that even though the rate of carbon dioxide removal decreases as time of operation increases, much like the case of the brine spray type unit, the capacities of these tank type units are not as great as the brine spray type units studied.

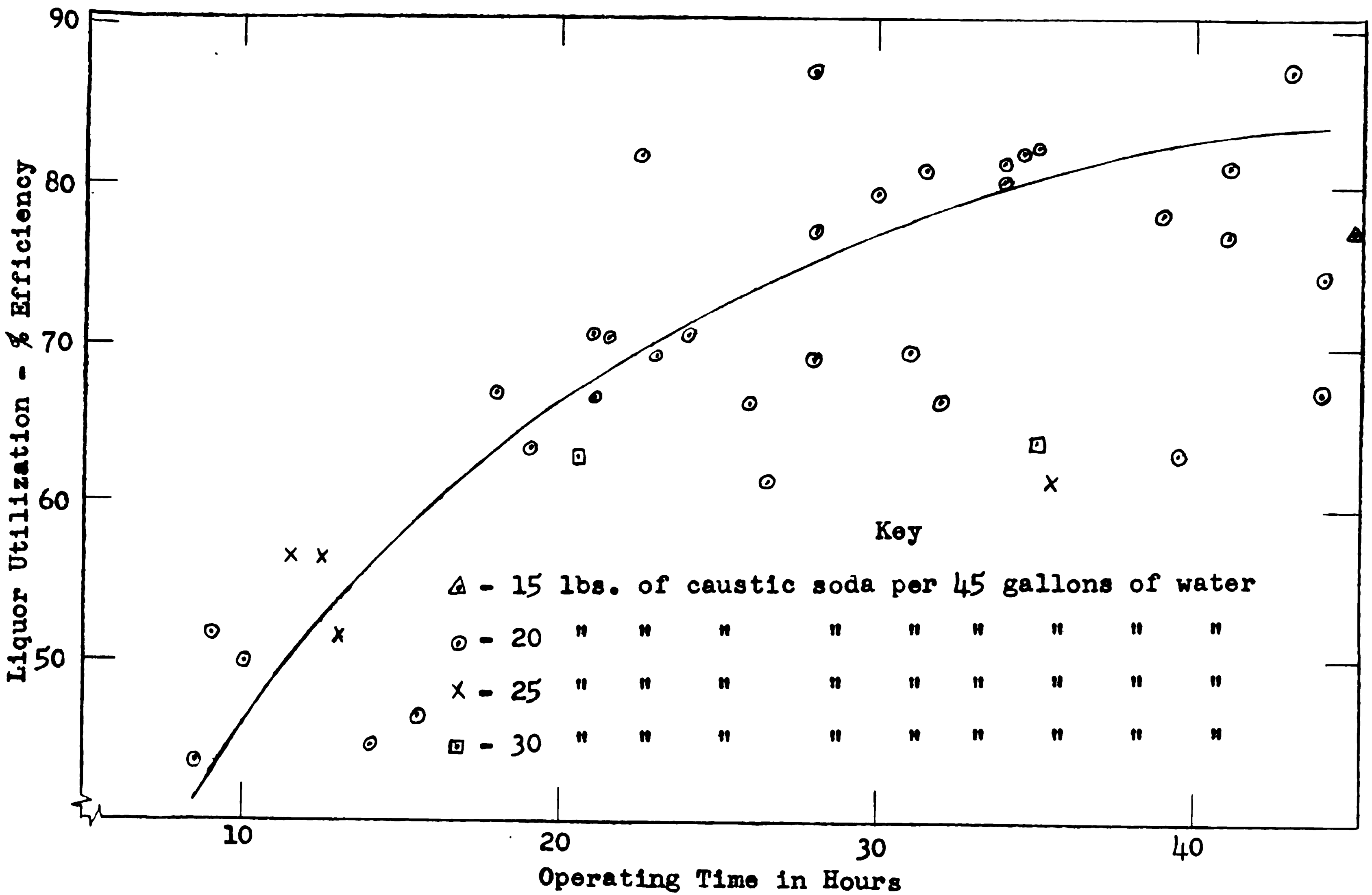

Fig. 8. Absorption liquor utilization vs. operating time of tank-type absorber No. 1.

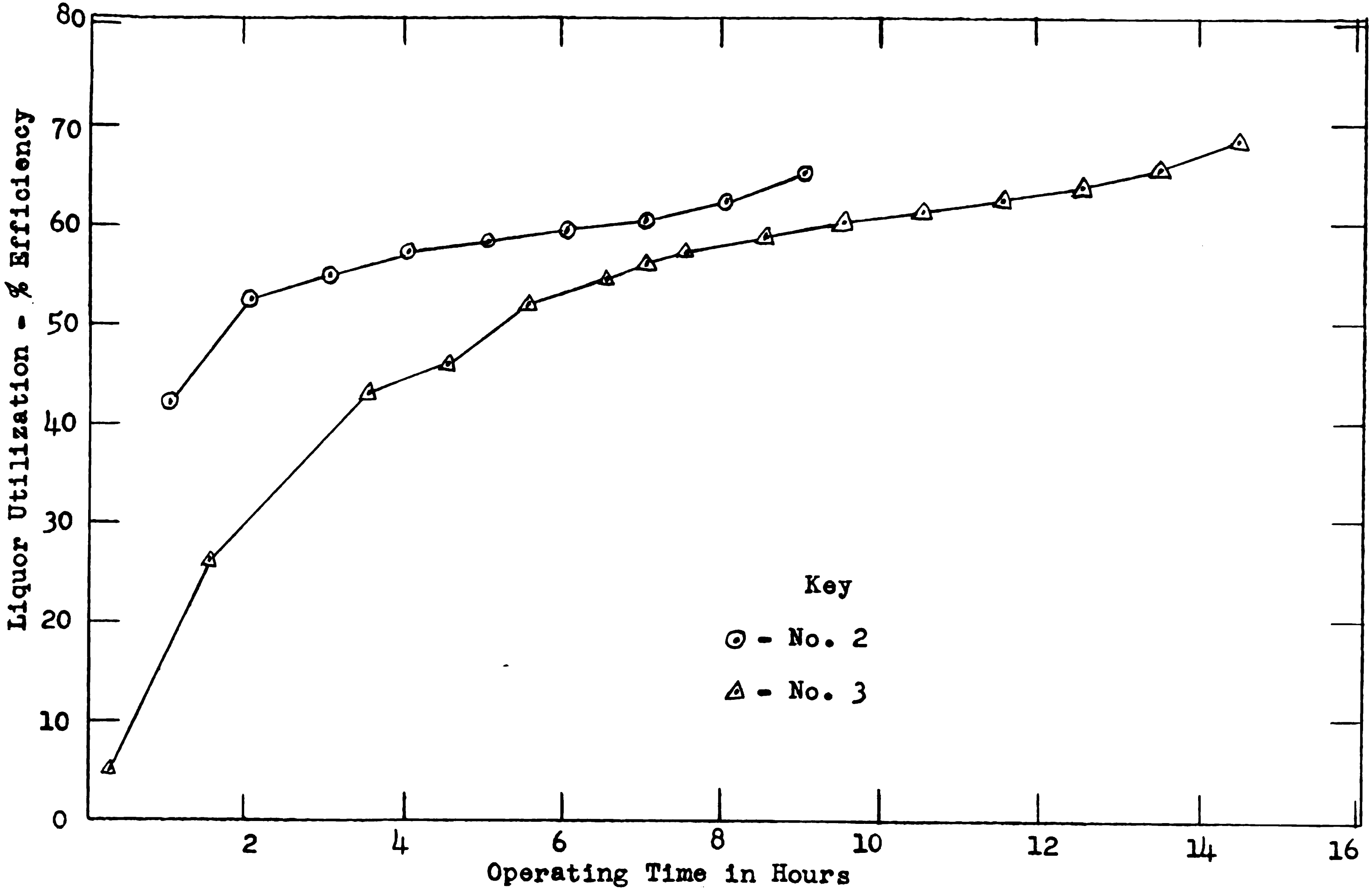

Fig. 9. Absorption liquor utilization vs. operating time of tank-type absorbers No. 2 and No. 3.

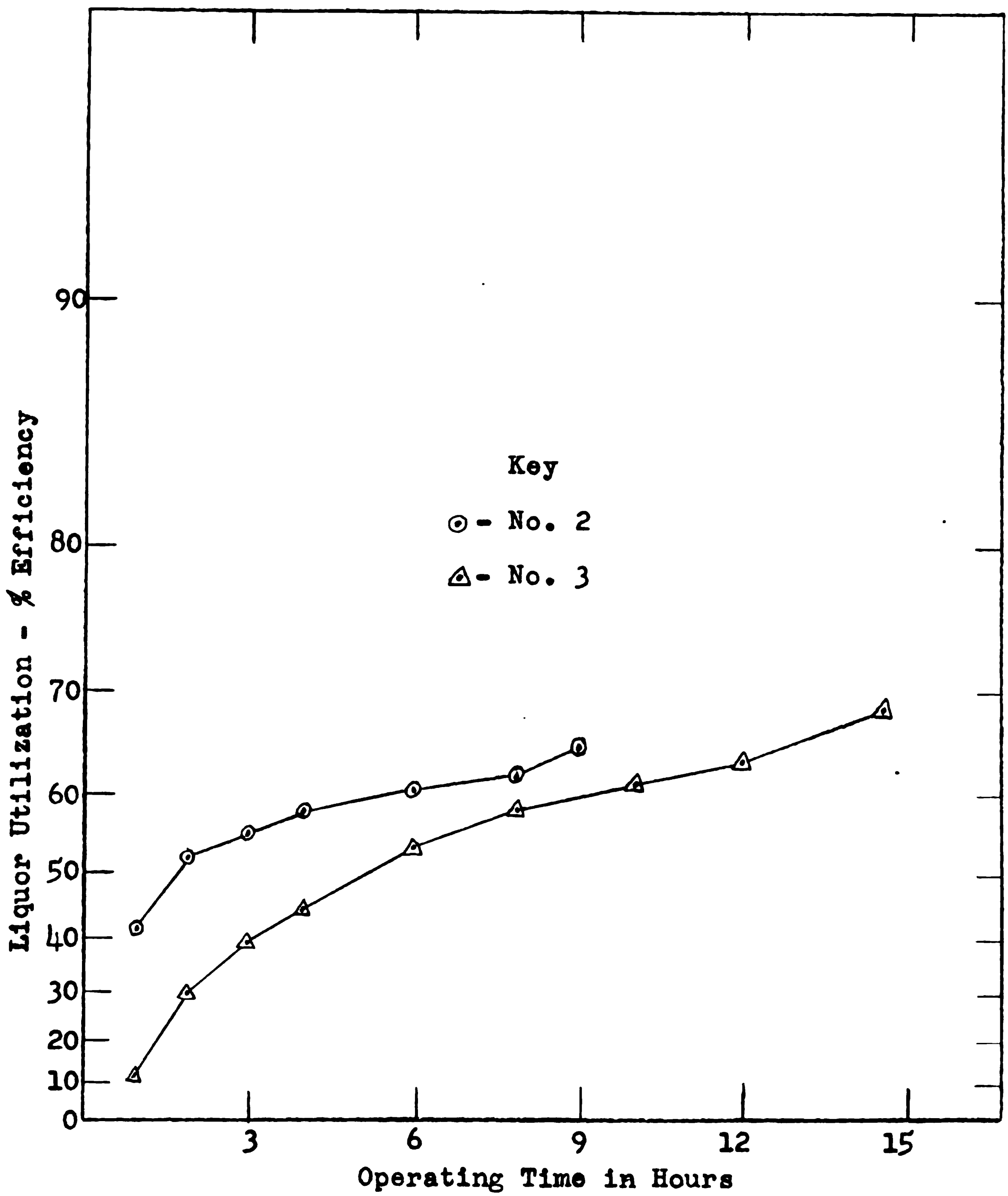

Fig. 10. Absorption liquor utilization vs. operating time of tank-type absorbers No. 2 and No. 3.

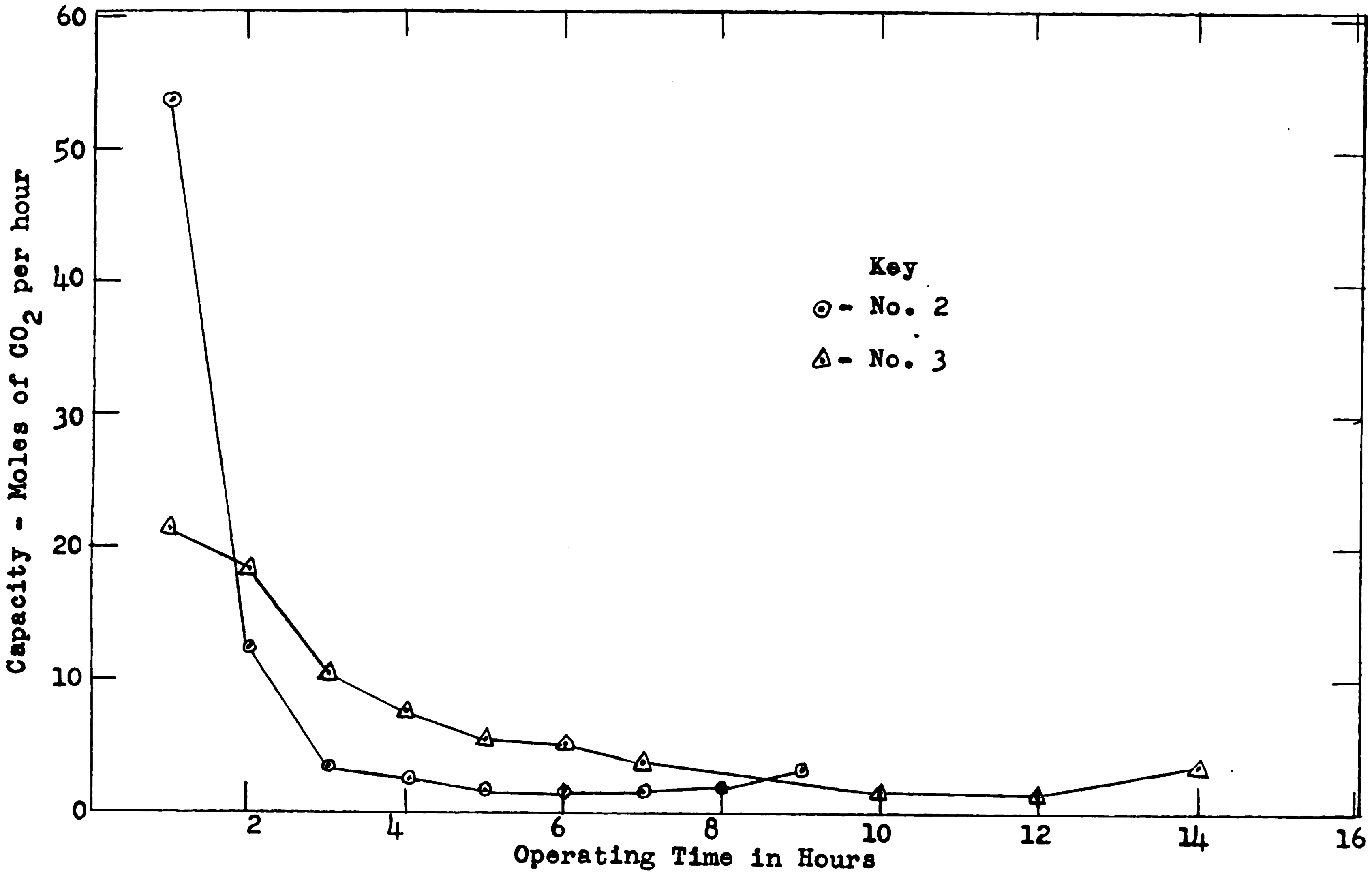

Fig. 11. Capacity vs. operating time of tank-type absorbers No. 2 and No. 3.

The similarities in the behavior of these two types of absorption systems is expected since they both employ the liquor recirculating principle of operation. The differences in the systems is believed to be due to the differences in construction and operating conditions; largely liquor recirculating rate, reservoir size, and liquor concentrations of the two types of systems.

Evaluation of Various Factors Affecting the Performance of Recirculating Method

A consideration of the operating conditions of the recirculating systems studied indicates that there are several conditions materially affecting the performance of such systems which can feasibly be adjusted for CA storages. These factors are: 1) total interfacial surface area, 2) size of reservoir, 3) concentration of absorbing liquor, and 4) rate of liquor recirculation. Previous investigations clearly demonstrate the effects of available interfacial surface area, therefore this factor was not pursued further in this study. The other three factors mentioned above were studied using the packed tower shown in Figure 3 and described above.

The effects of reservoir size are illustrated in Figures 12 and 13. Figure 12 shows that for comparable liquor utilization a longer period of operating time is necessary for the larger reservoir holding other variables constant, because there is more caustic soda to be neutralized in the same

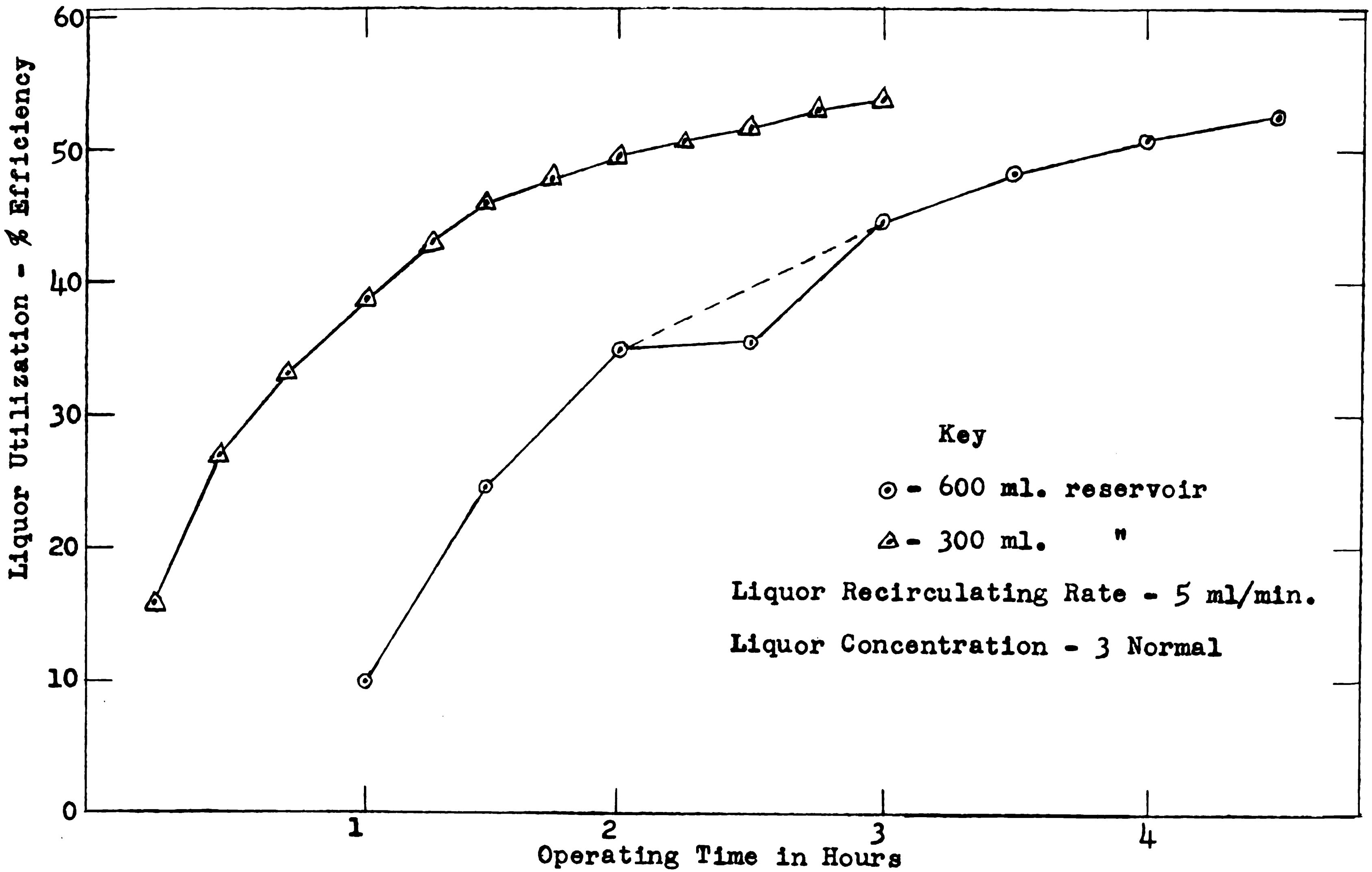

Fig. 12. Absorbing liquor utilization vs. operating time for different size reservoirs.

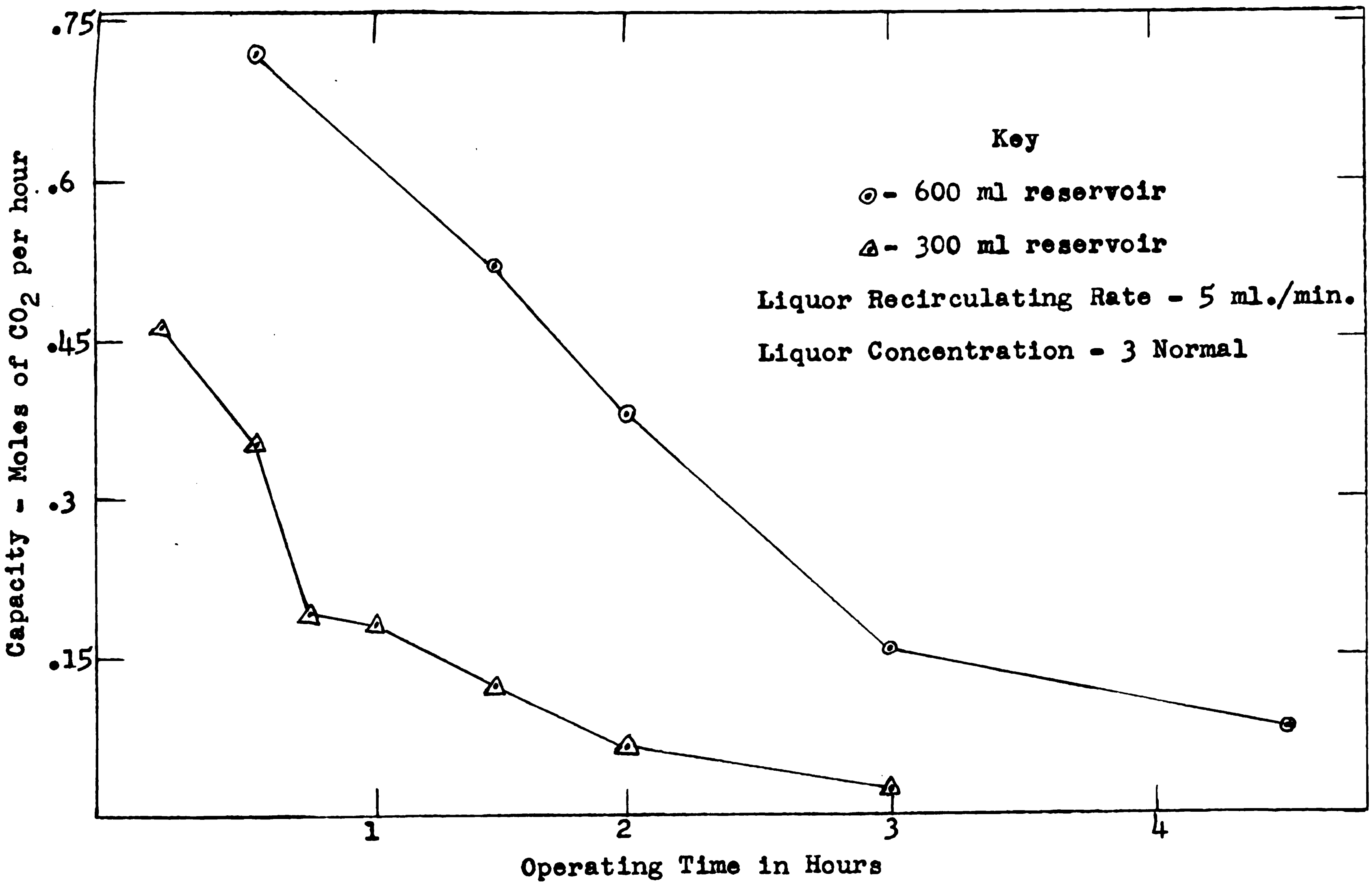

Fig. 13. Capacity vs. operating time for different size reservoirs.

equipment. The rate of sodium hydroxide utilization decreases more rapidly for the smaller reservoir. If a smooth curve were drawn through the series of points, the 600 ml. curve would not intersect the abscissa at 0 time whereas the 300 ml. curve would. This "lag" in time on the 600 ml. curve is believed to have resulted because the column was not moistened with the absorbing liquor before starting this test as was done before starting the test with the 300 ml. reservoir.

The rate of carbon dioxide removal, as shown in Figure 13, proved to be both greater and more constant for the larger reservoir. The greater capacity for the larger reservoir is self-evident since all factors except size are identical. The more constant rate of carbon dioxide removal by the larger reservoir is also expected because the rate of sodium hydroxide utilization is more constant for the larger reservoir as shown in Figure 12.

The effects of sodium hydroxide concentration are illustrated in Figure 14, 15 and 16. The similar "lag" effect for the 1 normal and 3 normal curves, as mentioned above, is very likely due to the fact that the column was not moistened before these two tests. It is observed that for the more concentrated liquor, there is a greater initial rate of sodium hydroxide utilization but it decreases at a faster rate with operating time, than for the less concentrated liquor. It is also evident that a considerably longer operating time is necessary to acquire comparable sodium

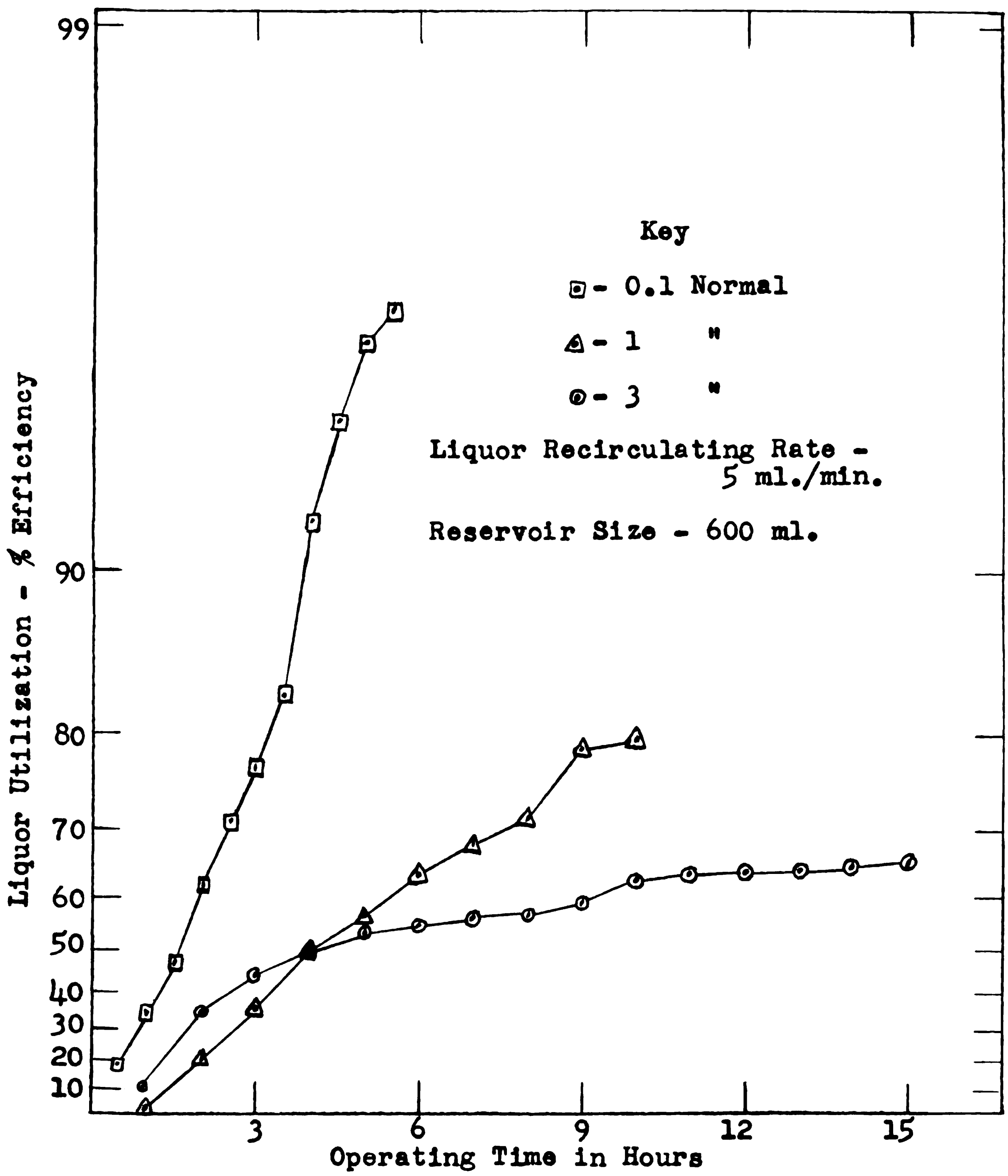

Fig. 15. Absorption liquor utilization vs. operating time for different liquor concentrations.

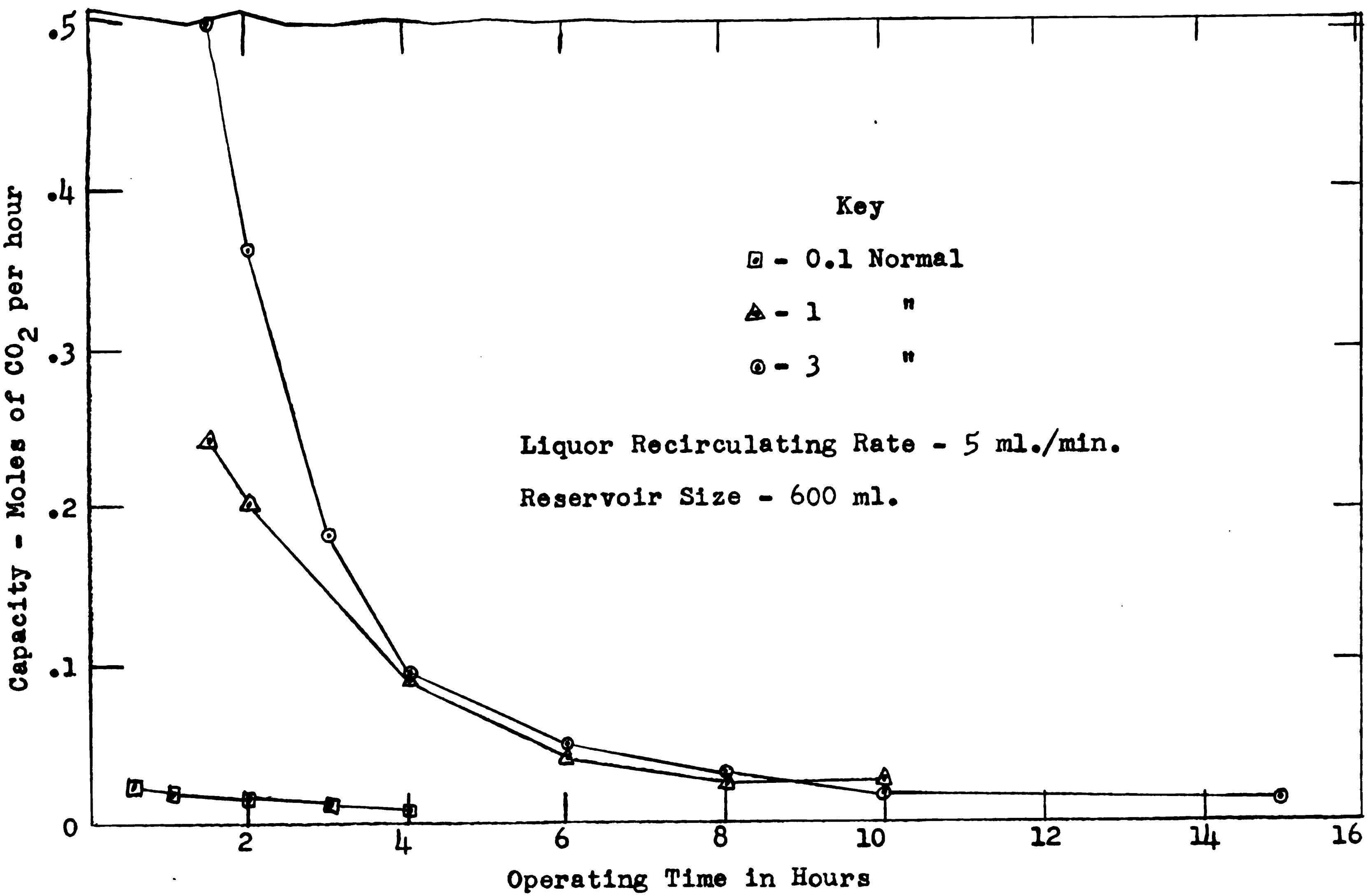

Fig. 16. Capacity vs. operating time for different liquor concentrations.

hydroxide utilization for the more concentrated solutions than for less concentrated solutions. The rate of caustic soda utilization approaches a logarithmic function as less concentrated solutions are used as illustrated in Figure 15. The slopes of the curves in Figure 15 are indicative of the rates of liquor utilization.

Figure 16 illustrates the effects of liquor concentration on the capacity of the system. The total capacity, assuming all other factors to be identical, varies directly as the concentration. The removal of carbon dioxide with operating time was more variable with the more concentrated liquor than with the less concentrated liquor. However, the 3 normal liquor removed carbon dioxide at a greater rate after 8 hours of operation than the 0.1 normal after 3 hours of operation.

The rate of liquor recirculation effected the rate of sodium hydroxide utilization and the rate of carbon dioxide removal. Figure 17 illustrates that the greater the recirculating rate, the greater the rate and rate of change of sodium hydroxide utilization. Consequently, less time was required to achieve desired utilizations for the faster than for the slower recirculation rates. Figure 18 illustrates that the faster recirculating rate had the steepest slope when plotted on semi-logarithmic graph paper, consequently, the rate of liquor utilization was greater than the slower recirculating rate. Figure 19 points out that the faster

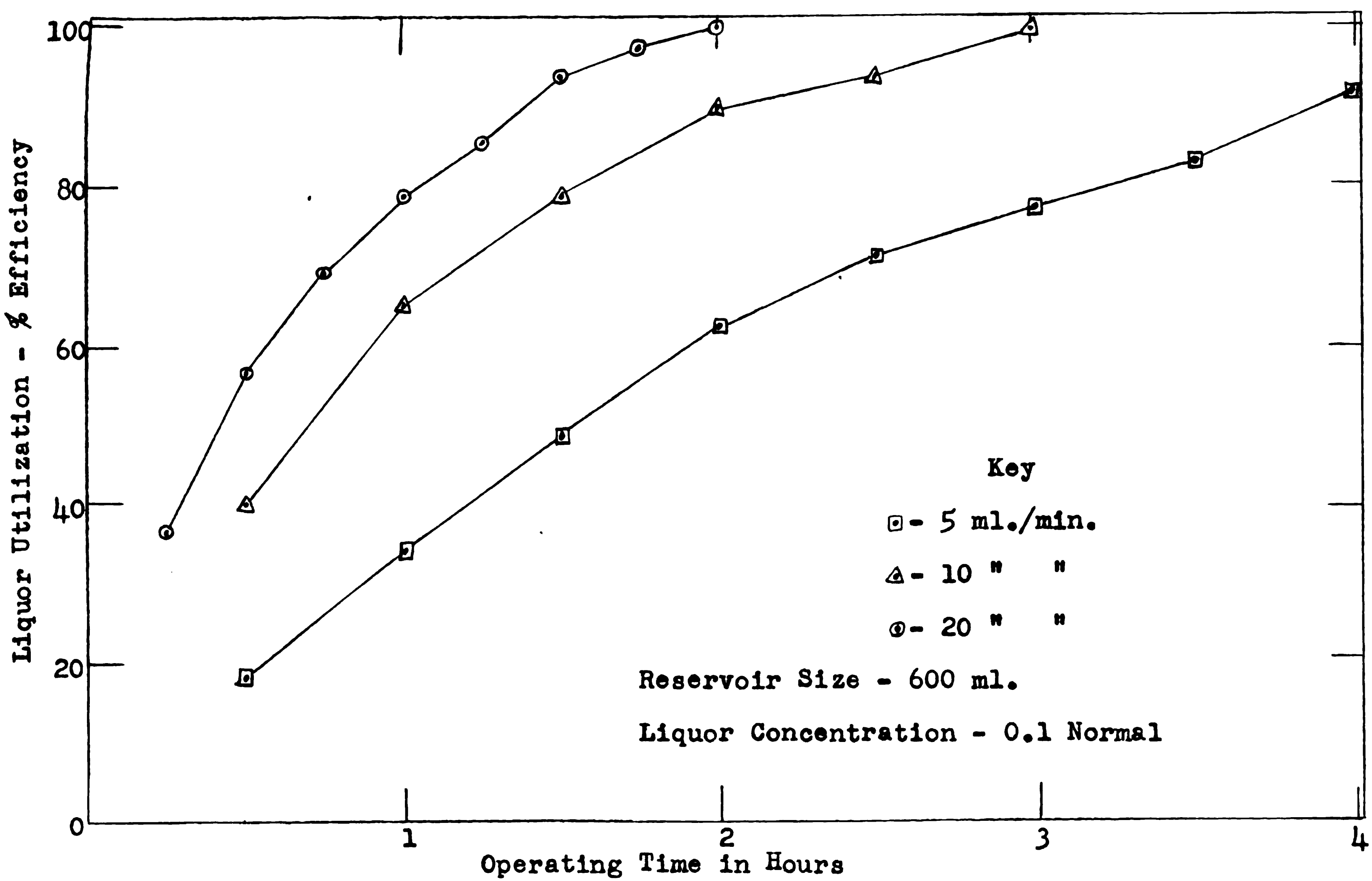

Fig. 17. Absorption liquor utilization vs. operating time for different rates of liquor recirculation.

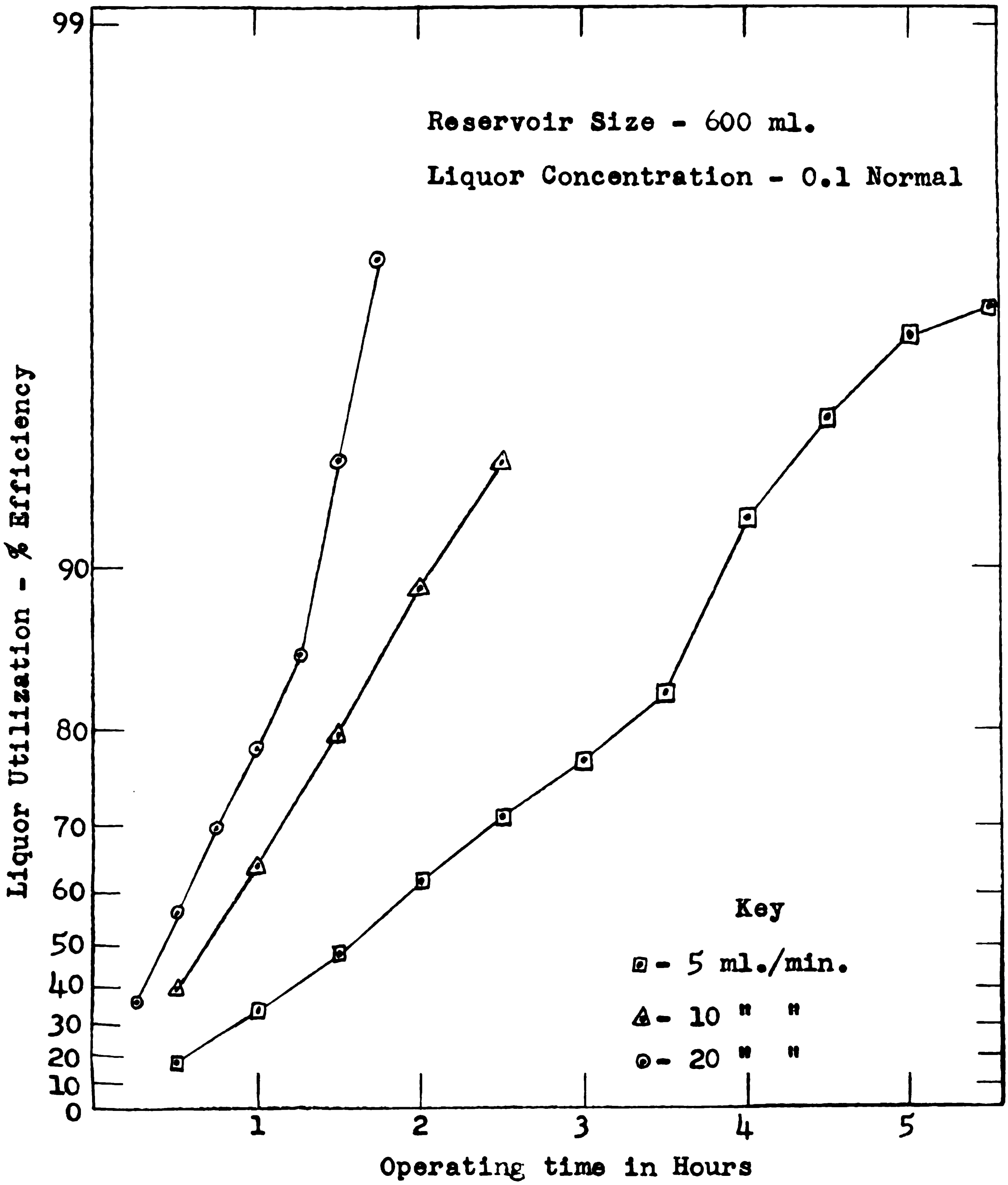

Fig. 18. Absorption liquor utilization vs. operating time for different rates of liquor recirculation.

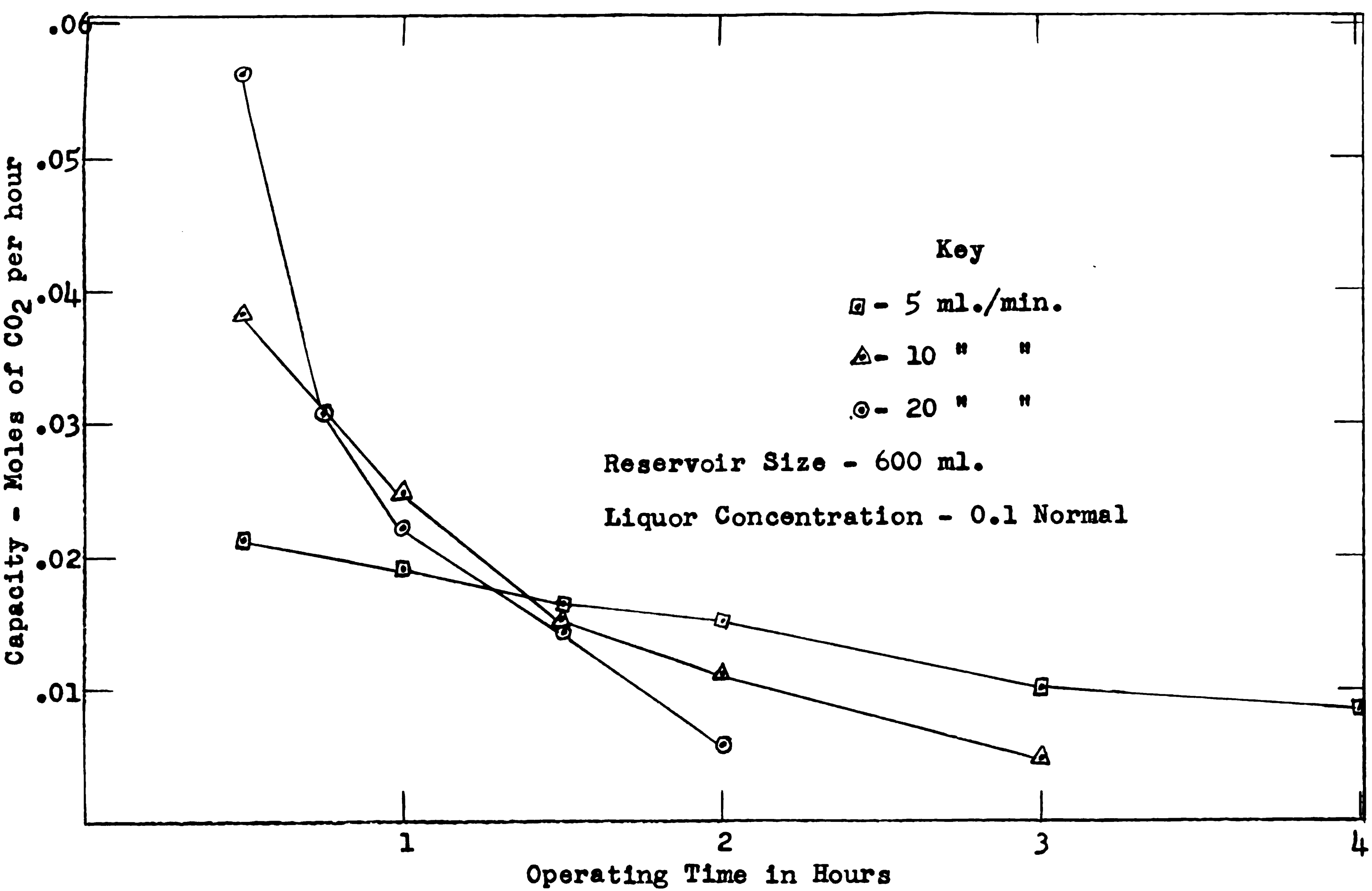

Fig. 19. Capacity vs. operating time for different rates of liquor recirculation.

rates of recirculation remove carbon dioxide at a greater rate at the beginning of the absorption period than the slower recirculating rates; but the slower recirculating rates remove carbon dioxide at a more constant rate.

Upon comparing the brine spray type units and the tank type units it is evident that the brine spray type units were operated with larger reservoirs, greater recirculating rates, lower liquor concentration, and greater interfacial surface areas, than the tank type units investigated. It is concluded that the greater capacities and better sodium hydroxide utilizations of the brine spray type units studied than the tank type units studied resulted from these differences.

Evaluation of the Effects of Liquor Concentration and Flow Rates for the Once-Through Method

The study was performed using the packed column shown in Figure 3 and described above. The results of this study are summarized in Figures 20 and 21. In Figure 20 it is seen that both sodium hydroxide concentration and rate of liquor flow effect the sodium hydroxide utilization. The greatest effect on utilization seems to be due to changes in sodium hydroxide concentration in the more dilute range. The curves for the higher rates of liquor flow have a sharp break and continue, assuming a straight-line, at a decreasing

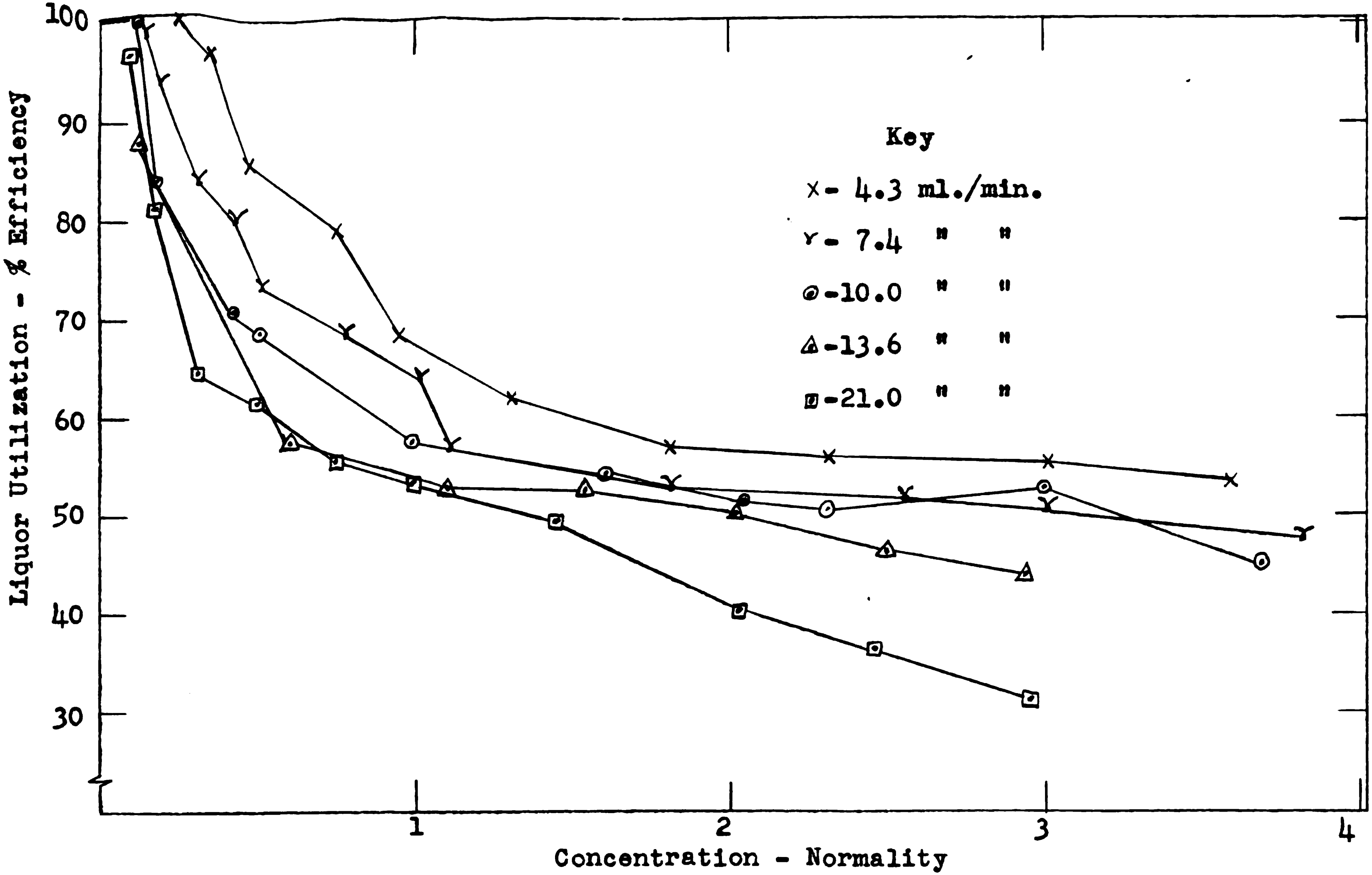

Fig. 20. Absorption liquor utilization vs. liquor concentration.

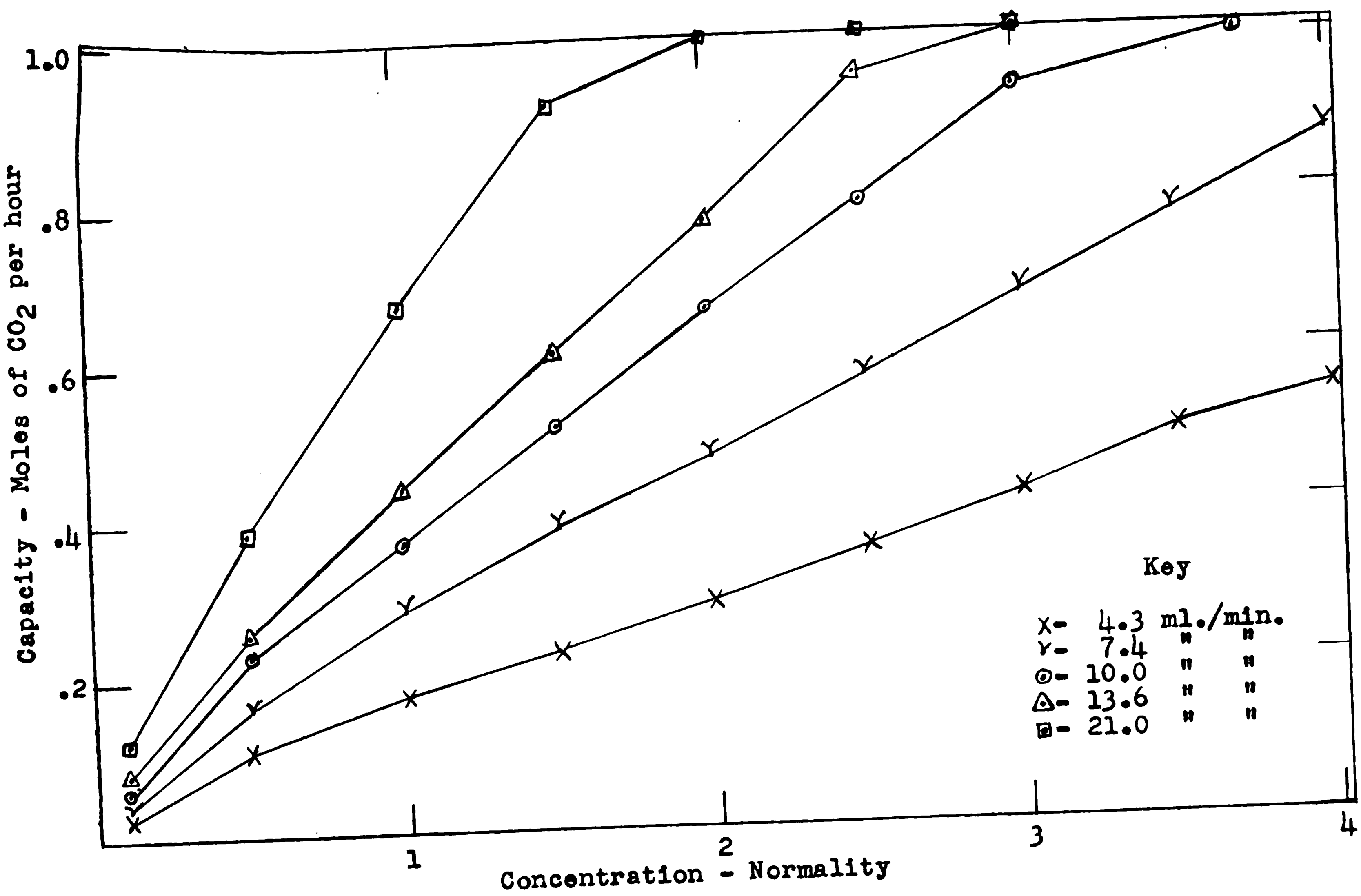

Fig. 21. Capacity vs. concentration.

utilization as concentration increases. This is due to the fact that an insufficient amount of carbon dioxide was being passed through the column.

The rate of carbon dioxide removal, as shown in Figure 21, is effected both by liquor flow rate and concentration. The rate of carbon dioxide removal increases linearly with an increase in sodium hydroxide concentration for any given liquor rate. An increase in liquor rate increases the slope of the straight line which results from plotting moles of carbon dioxide removed per unit length of time on the ordinate against liquor concentration on the abscissa. The breaks in the curves representing the higher liquor rates, once again, are due to the insufficient supply of carbon dioxide.

From the foregoing it seems desirable to use as great a liquor flow rate as possible to get the most capacity. In considering the liquor concentration to be used, capacity must be weighed against utilization.

DISCUSSION OF RESULTS

Two basic methods of absorbing carbon dioxide have been studied: (1) the liquor recirculating method, and (2) the once-through method. The brine spray diffuser system and the tank type system are of the liquor recirculating type now used in commercial CA storage, whereas the tower type system has been developed and studied as part of this thesis project.

Since information on these different absorbers with identical operating conditions has not been available, it is extremely difficult to compare them. In the operation of the brine spray diffusers the only controllable factor which will cause a significant change in the performance is the concentration of the sodium hydroxide solution; since the rest of the controllable factors are predetermined by the refrigeration requirements. However, from the information available, we find that with the operating conditions required for proper refrigeration, the brine spray diffusers have a much greater capacity than is necessary for the control of carbon dioxide in the storage room. This enables the use of very dilute solutions making possible extremely high efficiencies of sodium hydroxide utilization.

The tank type and packed tower systems are separate from other storage equipment and may thus be operated independently. All of the factors which are mentioned above are controllable in these two systems for each individual absorber. Another pertinent factor which can be adjusted in the construction of the tank type and the packed tower systems, and which is also predetermined in the brine spray diffusers is the effective interfacial surface area. The information available on the specific tank type absorbers, shows them to be quite efficient in utilizing the sodium hydroxide but not as efficient as the brine spray diffusers under the particular operating condition employed. The utilization of the sodium hydroxide in the tank type absorbers can be improved by increasing the operating time or decreasing the concentration if desired, and does not interfere with proper control of carbon dioxide.

It may seem that the only consideration to be made on recirculating systems is whether one will have one unit doing two jobs and give up flexibility in storage operation, or whether one will provide separate systems for each job and thereby gain flexibility and better control of each factor in storage operations. The author would like to point out that there may be many other factors concerned, which are beyond the scope of this thesis, and that thorough consideration taking into account all factors, should be given the problem.

In comparing the recirculating method with the once-through method, it was found that each has advantages and disadvantages. The recirculating systems have exceptionally high capacities and are capable of achieving high rates of sodium hydroxide utilization. On the other hand, the recirculating method does not have a constant rate of carbon dioxide removal. For the once-through method it appears that a larger interfacial surface area would be necessary to achieve the capacity and efficiency obtainable by some recirculating systems. However, the constant rate of carbon dioxide absorption feature of the once-through method lends itself very nicely to automation, thus reducing labor cost.

In considering the construction of a carbon dioxide absorber for CA storages, it is recognized that it would consist of several parts regardless of the type. The parts would be a liquor pump, an air pump or blower, a liquor reservoir, and an absorption bed. Since the principle of operation of a recirculating system is different from that of a once-through system, the best design for a recirculating type absorber would not be the best design for a once-through type absorber and vice-versa. Commercially it seems feasible to use low concentrations of sodium hydroxide and thereby achieve high utilization efficiencies. However, the possibility of using higher concentrations with lower sodium hydroxide utilization, in a smaller absorber automatically controlled must be considered.

Previous investigations seem to indicate that near flooding conditions produce the most efficient all-around operating conditions for absorption in a packed tower.

Flooding conditions are a function of the packing used and the liquor rate-gas rate ratio per unit cross section area. The gas rate should be of such a magnitude as to supply sufficient carbon dioxide for absorption over the total height of the absorption bed.

Considering a recirculating type system, for any given sodium hydroxide concentration the capacity of the unit will be largely determined by the rate of liquor recirculation and the effective interfacial surface area. The most important factor affecting the efficiency of utilization for a single concentration is the number of total reservoir volume recirculations. Since high efficiency of utilization is expected, low concentrations of sodium hydroxide would be used.

It appears, therefore, maximum capacity and efficiency for recirculating unit might be obtained by increasing the cross sectional area of the bed and using a correspondingly higher liquor recirculating rate which would both increase capacity and obtain the desired efficiency sooner.

A consideration of the factors influencing efficiency of sodium hydroxide utilization of a once-through system points to the fact that the efficiency of utilization of this type system would be determined by the height of the column for any one concentration and packing assuming near flooding conditions are always maintained. The maximum height for any column would therefore, be the height producing 100 percent efficiency of sodium hydroxide utilization. The capacity would then be a function of the cross section area of the column.

In the design of an absorption system for a CA storage, a unit should be designed which would be most practicable for the particular job which it must perform. The practicability would depend upon many things, such as size of storage room, area provided for absorption system, cost of installation, and many other factors which are beyond the scope of this thesis.

CONCLUSIONS

In this project, carbon dioxide absorption equipment in use in commercial CA storages was studied along with laboratory equipment of a design that may be used in commercial CA storages. The following conclusions can be drawn from the results of the work in this project.

1. The liquor recirculating systems in use commercially show very high efficiencies of sodium hydroxide utilization and large capacities.
2. The rate of carbon dioxide absorption in the recirculating systems is not constant, but decreases as the amount of carbon dioxide absorbed increases.
3. The brine spray diffuser absorbers investigated had capacities of such magnitude that total utilization of the caustic soda required for controlling the carbon dioxide in the CA storage room for one day took place within six hours.
4. The separate absorption systems, such as the tank-type or the packed tower are more versatile in their use than the brine spray diffusers.
5. The carbon dioxide absorption rate is not constant when using recirculating systems.
6. The once-through method has a constant rate of carbon dioxide absorption and perhaps is the most versatile of all the systems studied.

7. The once-through method is readily adaptable to automatic operation which could maintain levels of carbon dioxide in the storage room as constant as desired.
8. Perhaps the most obvious and outstanding conclusion of this work is that a great deal more information would be helpful in making suggestions for carbon dioxide absorption equipment, especially concerning the once-through method.

SUMMARY

The lack of knowledge about and dissatisfaction with the performance of present carbon dioxide absorption equipment used in CA storages initiated this study.

A selected review of literature concerning carbon dioxide absorption in general and carbon dioxide absorption equipment was set up which provides a description of the equipment, a record of the operating conditions of the equipment, outlines of liquor sampling procedures, and the results of the sample analyses; all of which are reported in this thesis.

A packed column was constructed to study the effects of several major factors influencing the performance of the liquor recirculating method and to investigate the possibilities of a liquor once-through method. The factors concerning the recirculating method are: size of reservoir, liquor recirculating rate, and liquor concentration. The factors studied concerning the once-through method are liquor concentration and liquor flow. All of the factors studied for both methods greatly effect the performance of the equipment.

The conclusions drawn from the results of this study show the brine spray units to have greater capacity and efficiency of utilization than the tank-type units due to the greater interfacial surface area, greater recirculating rate, lower

liquor concentration and larger reservoir of the brine spray units. The once-through method offers constant carbon dioxide removal and is readily adaptable to automation but requires more surface area than the recirculating method for comparable efficiencies of liquor utilization.

In view of information gathered from literature and the results of this thesis the major design features for both recirculating and once-through carbon dioxide absorption equipment for CA storages are discussed.

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