THE INDUSTRIAL UTILIZATION OF

CARBIDE GENERATOR LIME WASTES

by

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Fulfillment for the Degree of

MASTER OF SCIENCE

in

CHEMICAL ENGINEERING

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I. INTRODUCTION

The disposal of industrial wastes is vital to the healthy growth of industry. Modern concepts of social justice require manufacturers to dispose of their wastes without harm to public welfare. Eventually, every manufacturer, on his own initiative, must solve his disposal problem, otherwise he will be forced by legal means to get rid of his waste.

The manufacturer may meet this problem of waste disposal by several methods. He may utilize the material to produce other saleable materials, or he may develop a market for the waste material. He may discharge it directly into a nearby stream if it is harmless. If the material is harmful he may still process it to render it safe and then discharge it into the stream. Finally, if the previous three methods seem inadvisable, he may impound (or store) his waste, thus marking time until he can find a better disposal method.

The disposal of calcium hydroxide wastes has become a

more acute problem yearly in this country due to the
increasing use of acetylene as a raw material for organic
synthesis. Calcium hydroxide wastes usually can be handled
by any of the first three methods mentioned above. In most
cases, due to favorable locations in regard to other plants,
power, or very large streams, the material can be handled
economically by one of these methods.

The duPont Company's plant at Waynesboro, Virginia,
presents a special case in calcium hydroxide waste disposal.
Due to the pressure of public opinion it seems inadvisable
to discharge the waste slurry from the acetylene generators
into the streams. Here 1350 tons of the slurry, containing
some 95 tons of nearly pure calcium hydroxide daily, at a
concentration of 7 to 10 per cent solids, are discharged from
the generators and collected in ponds as a sludge containing
about 50 per cent water. This material is used at present
in liming the farm lands in the Shenandoah Valley in which
Waynesboro lies. (Shorey[21]). Under the urging of the
government and its payment to lime the land, the farmers
are induced to carry away this waste for use on their lands.
The material is given to them free of charge if they dig it
out of the pond and carry it away. Realizing that the
government bonanza will not last forever, the company is
trying to dry the lime slurry from the generators to a
powder form that can be handled more easily.

To dry the material is not only very costly, but is also unsatisfactory from a technical point of view. The sludge seems to cake up in the driers introducing a considerable handling problem. The great, hard lumps formed are practically useless to the farmer for liming. This drying operation must be carried out at a cost low enough to allow competition with the slaked lime sold for a dollar per ton by a farmers' cooperative near the plant.

The purpose of this investigation was to examine the possibilities of an azeotropic removal of enough water from the sludge to produce an easily dried product for sale as agricultural lime.

II. LITERATURE REVIEW

The disposal of industrial wastes at the Waynesboro, Virginia, plant of the duPont Company presents a special problem in that the material cannot be discharged into the streams. Further, it is not possible to reuse the material in any of the processes at the plant. The material is impounded at present as a sludge containing 50 per cent solids. In order to get the farmers to continue to use it on their lands after the government payments stop, it is proposed to dry the material to an easily handled powdered form. The present sludge is difficult to spread on the land.

Since drying by ordinary means has not proven satisfactory, a means of azeotropic distillation is now to be tried for removal of the water in the sludge. The questions introduced by these problems, to be answered as fully as possible by the literature review, were as follows:

1. What is the physical nature of the calcium hydroxide waste and related materials?

2. What methods have been used or suggested for drying calcium hydroxide wastes or materials of a similiar nature?

3. What methods other than drying have been suggested for disposal of the wastes?

4. What new or untried methods should be examined?

5. What use has been made by previous investigators of azeotropic drying of solids and liquids?

6. What are the physical properties of the azeotropic mixtures that might be used in the drying of calcium hydroxide wastes?

Calcium hydroxide wastes are the byproduct in the production of acetylene by the action of water on calcium carbide, a product of the electric furnace. (Riegel[20])

$$CaC_2 \ + \ 2 \ HOH \longrightarrow C_2H_2 \ + \ Ca(OH)_2$$
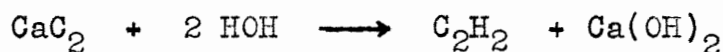
The carbide is charged in at the top of the generator by a screw conveyor. It falls through the water in the lower section of the generator, reacting during this process. Paddles constantly work the calcium hydroxide sludge thus formed to the outlet hole in the bottom of the tank. An excess of water is used to cool the generator and to flush this material in the form of a thin slurry (7 - 10 per cent solids) out to the settling ponds.

Physical Nature of the Wastes. The solids settle rapidly from the 7 - 10 per cent slurry leaving the generators. In the storage ponds the calcium hydroxide finally compacts to a sludge containing about 50 per cent solids. (Knapp[14])

Analysis of the Sludge as it Lays
in the Pond. (Knapp[14])

Calcium Sulphate	1.2 %
Silica	0.8
Calcium Carbonate	2.9
Calcium Hydroxide	45.0
Moisture	50.1 (varies down to 45%)
Total	100.0 %

This material is extremely cohesive and looks something like thick putty. It dries very little. Large cracks develop on the surface of the ponds, extending, however, only three to four feet down. The cracks are about three inches wide at the top and form islands about two or three feet square. These characteristics of the material suggest a colloid nature for the sludge and furnish a partial explanation to previous drying troubles. Aluminum hydroxide, Al_2O_3-3HOH, a similiar material to calcium hydroxide, was found by Damerell, Hovorka, and White [6] to lose water at ordinary temperatures by a surface dehydration in which the lattice structure was not appreciably rearranged. A theory of dehydration was advanced that the vapor pressure of crystals of a hydrate diminish as water molecules leave from the surface until a definite low value is reached. Othmer and Jacobs [16] observed a similiar phenomena in their dehydration of sodium hydroxide. The apparent vapor pressure of the water still left in the hydroxide decreases rapidly as the water is removed.

Previous Methods for Drying Generator Wastes. The
importance of the disposal of generator wastes has led
to a number of attempts to dry this material for sale as
commercial lime. Guttman [10] found it possible to dry the
sludge containing 50 per cent water by adding enough burnt
lime to react with the water present to form dry, slaked
lime. A patent by Whitmore [24] seeks to reduce the size
of the pieces by means of a flexible pickup device carried
by a rotary drum and thus enable quicker drying. Aktiebolaget
Svenska Fläktfabriken [1] patented a process for drying
lime sludge in a thin layer until it had hardened and sub-
stantially lost its adhesive power. The material was
crushed into small pieces or particles and then dried in a
thicker layer than the original one by means of air. Finally,
the material was crushed and bagged. Cohen [5] patented a
process to aerate the sludge to free it from residual
acetylene, separate it from liquid by filtration, and then
dry it just sufficiently to remove mechanically held water
without producing chemical change. The product thus produced
is said to be suitable for commercial use as hydrated lime.

Other Methods for Utilizing Generator Wastes. Since the
attempts to produce marketable lime from the generator wastes
were not very successful, attempts were made to find other
means of disposing of the wastes. Murphy [15], in a review
of disposal methods in use up to 1925, wrote that residues

from acetylene generators have been successfully used
for making lime mortars, causticizing soda liquors, making
bleach, in beet sugar defecation, etc. Only when large
quantities of the residues are available does it pay to
dry and ship the calcium hydroxide to any great distance.
Local markets, however, can usually take all residues
produced. Spence[22] developed methods for the production
of agricultural lime and whiting for building and similar
purposes from paper wastes. These processes are being worked
successfully at many points. The profit is very small in
either case and the market indefinite -- especially so for
agricultural purposes, but for disposal the plans are work-
able. Gutman [10] and Early [8] tried unsuccessfully to
produce satisfactory insecticides at a low cost from calcium
hydroxide slurry. Horner[12] attempted unsuccessfully to
calcine the hydroxide sludge using "Dowtherm A" as a heating
medium. Veller and Mirumyan[23] mixed powdered coke with the
sludge and heated the mixture to $550^{o}C$ to regenerate calcium
carbide. Radcliffe[19] patented a method whereby a portion
of the residue from acetylene generators is removed in over-
flow liquid and the latter is thickened so that it is barely
free flowing. The thickened liquor is ground. Because of the
unusual economic conditions existing in the Waynesboro area,
most of the methods presented above for using the calcium
hydroxide waste have been considered unsuccessful.

Suggested Methods for Utilizing Generator Wastes.

Recent work has suggested the possibilities of new methods of attacking the old problem of drying the generator wastes. Othmer and Jacobs [16] prepared anhydrous caustic soda continuously in a fine, crystalline form from a 50 per cent caustic soda solution by means of steam distillation using kerosene as the diluent in evaporation. The kerosene remaining on the solid particles was removed by centrifuging and washing with a volatile solvent. This solvent was then purified by distillation for reuse. The total heat cost was calculated at about 350 pounds of coal per ton of caustic from the 50 per cent solution, or about one third the present cost in the usual caustic fusion. Practically no corrosion of equipment was noted because of the protective film of kerosene. The authors' comment on partial pressure distillations and on their choice of solvent is worth noting.

"Water is steam-distilled out of a caustic solution with some insoluble hydrocarbon or mixture of hydrocarbons, such as kerosene, as a result of the additive vapor pressures of the water and the oil. -- Kerosene was selected because of its ease of separation from the NaOH and its wide boiling range ($356° - 482°F$). Kerosene was also inactive to NaOH.

"It is necessary to have a wide boiling range because there is a large change in boiling point or vapr pressure between the 50 per cent solution and the anhydrous caustic which may be attributed to normal boiling point

elevation and the fact that the NaOH forms hydrates. The wide variance in vapor pressure of water over caustic solutions of changing concentration requires:

    a. Solvents sufficiently volatile to have a vapor pressure such that it will evaporate with a substantial amount of water at the initial 50 per cent concentration.

    b. Solvents whose volatility at higher temperatures are not much greater than that of water at this temperature.

Since the solvent meeting requirement "a" would remove only a slight amount of water at the higher concentrations and the solvent meeting requirement "b" would be insufficiently volatile at lower temperatures, a mixture of solvents must be chosen to satisfy both requirements; -hence the choice of kerosene.

Othmer and Wentworth [17] used ethyl ether at 100 lbs./sq.in. pressure as an entraining agent in the production of anhydrous ethyl alcohol. In both the alcohol dehydration and the caustic soda dehydration, the solvent entraining agent was separated from the water vaporized along with it decanting the condensed vapors from the still. The entraining agent was recirculated, while the water was discharged.

Physical Properties of Usable Azeotropic Mixtures.

Many liquids form azeotropic mixtures with water. Not all
mixtures so formed are usable for drying work because it
must be possible to recover and reuse the liquid chosen.
Further, the azeotrope formed must be easily mixed with
the lime waste introduced and must also be easily removed
from the lime particles after the desired amount of water
has been removed. It is preferable that the azeotropic
liquid mixture be in one phase when in contact with the
sludge. Guinot and Clark [9] in answer to a question from
Underwood state that a separation of the azeotropic liquid
mixture on the upper plates does take place with some
azeotropes. The International Critical Tables [13] list
the properties of various azeotropic mixtures. Suitable
mixtures were chosen from these tables for this investigation.

III. EXPERIMENTAL INVESTIGATION

The calcium hydroxide waste slurry resulting from the production of acetylene from calcium carbide cannot be dried by ordinary means because it cakes up in the equipment. The present mud-like material is used by the farmers in liming their lands. It dries to hard lumps in the fields, thus preventing an even distribution of the lime. A much more useful material would be a powder form which could be spread evenly over the fields or could be used as chemical lime.

In this investigation a drying process will be studied whereby the slurry is first broken up by introducing an azeotrope forming solvent which is partly or wholly miscible with water. After distillation and filtration, the subsequent drying should produce a fine, non-caking powder.

A. CHOICE OF SOLVENT

Purpose and Plan

The most suitable water azeotrope froming solvent or solvent mixture to be used in the drying process should have

the following properties:

(1). The solvent should have a low boiling point.

(2). The solvent should have a high molecular weight, but the azeotrope should contain a high weight per cent of water. (Most of the heat consumption will be used in vaporizing the water and not in vaporizing the recirculating solvent.)

(3). The solvent should be easily separated from water and easily recoverable from its dilute solutions in water. (i.e.,-its recovery should introduce small heat losses and the loss of solvent in the discharge water should be small.)

(4). The solvent should mix easily with the slurry and be interdispersed by means of simple equipment.

(5). The slurry, or slurry-solvent mixture, should not cake or have any tendency to cake during any of the operations.

(6). The resulting mixture of lime wet with solvent should dry as a fine, easily broken up powder.

(7). The solvent chosen must not be unreasonably expensive.

Of these seven requirements, (4), (5), and (6) are essential and must be satisfied before a solvent can be considered. Requirements (1), (2), and (7) can be readily

determined from published data. Most of the information on requirement (3) can also be estimated from published data in the handbooks and technical literature.

A preliminary determination of the mixing characteristics of the solvent and slurry was first made. Upon proof of the solvents mixing ability, a distillation run was made. During this run any tendency of the material to cake could be observed at any time. The condition of the dried product was easily observed by feeling the lime with the fingers and turning it over with a spatula.

Materials

Mixing tests were made on the materials listed in Table I. Important properties of these materials are also shown in this table.

The mixing tests eliminated a large number of these possibilities because the solvent did not mix with the slurry. Distillation tests were finally made on the materials listed in Table II.

Procedure

To make a preliminary determination of the mixing characteristics of the solvent, a small amount of slurry, about 2 cc., was put in a test tube containing 10 to 15 cc. of the solvent to be tested. The contents of the tube were

TABLE I

Materials Used in the Lime Slurry Mixing Tests

Solvent	B.P. $^{\circ}$C	Azeotrope Composition	
		Solvent Mol per cent	Water Mol per cent
Iso-propanol Benzene	66.5	18.6 56.5	24.9
Isopropyl Acetate	75.9	61.3	38.7
Isopropyl Ether	62.2	80.4	19.6
Benzene	69.2	70.4	29.6
Carbon Tetrachloride Ethanol	61.8	57.6 23.0	20.4
Ethanol	78.1	89.4	10.6
n-propanol	87.7	43.2	56.8
iso-propanol	80.4	68.5	31.5
Ethyl Acetate	70.4	76.0	24.0
n-butanol	92.3	29.0	71.0
iso-butanol	89.9	32.9	67.1
sec-butanol	88.5	34.0	66.0
tertiary-butanol	79.9	64.6	35.4
tertiary-pentanol	87.0	35.0	65.0
Toluene	84.1	55.6	44.4
Ethanol Ethyl Acetate	70.3	12.4 60.1	27.5
Propanol Benzene	68.5	8.9 62.8	28.3
Ethyl Ether	34.2	95.0	5.0

TABLE II

Materials Used in Azeotropic Distillation
Studies on Lime Slurry

Solvent	B.P.$^{\circ}$C	M.W.	Water wt. %	Solubility @ 20°C	
				In Water wt. %	Water In wt. %
Isopropanol Benzene	66.5	60.6 78.5	7.5	-	-
Carbon tetrachloride Ethanol	61.8	153.8 46.1	3.4	-	-
Trichloroethylene Ethanol	67.2	131.4 46.1	5.0	-	-
Isopropanol	80.4	60.6	9.0	completely	
Ethyl Acetate	70.4	88.1	6.0	completely	
n-Butanol	92.0	74.1	37.0	7.7	20.1
sec-Butanol	88.5	74.1	32.0	12.5	-

then observed before and after a brief shaking. If the slurry was visibly broken up either before or after the shaking, the solvent was considered satisfactory. No breaking up indicated an unsatisfactory solvent.

During the distillation runs, the slurry-solvent mixture was agitated slowly. Continuous readings of the vapor temperature were made every five minutes. At the same time the volume of the distillate was recorded. If two phases were present in the distillate, both volumes were recorded. Extra solvent was added continuously to the flask to replace that lost in the vapors. The replacing solvent in the case of those azeotropes that formed two phases upon condensation, was the solvent layer of the condensed and recovered vapors.

When the temperature of the vapors started rising, it was concluded that insufficient water remained in the slurry to form an azeotrope with the solvent. The distillations were stopped soon afterward.

As soon as the contents of the distillation flask had cooled enough to allow safe handling, the solvent was twirled quickly around to pick up all the calcium hydroxide particles and dumped into a beaker. After the solids had settled for three or four minutes, the supernatant liquid was carefully poured off, leaving the solvent-wet solids behind. These were then put into an evaporating dish on the top of the drying oven to dry at about $120^\circ - 140^\circ$ F.

Drying usually took from 45 minutes to two hours
depending upon the volatility of the solvent. During the
drying period, the material was continually observed for
signs of any caking tendency. At the end of this time, as
determined by the white appearance of the calcium hydroxide,
the lime was crushed between the fingers and turned over
with a spatula to observe the resulting product. The end
of the drying period was taken as the time beyond which no
further loss in weight of the calcium hydroxide cake could
be detected.

Data and Results

The results of the solvent investigation are outlined
in Tables III and IV, which summarize the observations made
with the different solvents tried.

TABLE III

Summary of Solvent Penetration Tests

Material	Action	Satisfactory
Isopropanol Benzene	solvent got cloudy slurry broke up somewhat	yes
Isopropyl Acetate	no apparent action	no
Isopropyl Ether	no apparent action	no
Benzene	no apparent action	no
Carbon Tetrachloride Ethanol	solvent broke slurry immediately with little shaking	yes
Trichloroethylene Ethanol	solvent broke slurry slowly but effectively	yes
Gasoline	no apparent action	no
Ethanol	immediate dispersion and penetration	yes
Isopropanol	immediate dispersion and penetration	yes
Ethyl Acetate	some penetration, material settled in large particles	yes
n-Butanol	broke up on vigorous shaking. Breaks up better when solvent is hot	yes
sec-Butanol	much better than n-Butanol	yes
tert-Butanol	best of butanols. Slurry broke up immediately	yes
Ethyl Ether	no apparent action	no
Amyl Alcohol	small amount of dispersion	no
Carbon Tetrachloride	no apparent action	no

TABLE IV

Summary of Distillation Studies

Material	Caking Properties during Distillation	Appearance of End Product	Satis-factory
Isopropanol Benzene	Balls up badly	round balls	no
Carbon Tetrachloride Ethanol	Balls up some, caking indicated	small grains, 10 - 20 mesh	no
Trichloroethylene Ethanol	some chemical action appearance of final during drying.	apparent from material. Cakes	no
Isopropanol	no tendency to cake	fine powder	yes
Ethyl Acetate	very bad caking during and after run		no
n-Butanol	no tendency to cake	fine, very easily broken powder	yes
sec-Butanol	no tendency to cake	fine, easily broken powder	yes

B. PILOT PLANT STUDY OF A SOLUTION METHOD
FOR DRYING CALCIUM HYDROXIDE SLUDGES

The study of the different solvents indicated that
n-butanol would be satisfactory. In studying the azeotropic
distillation process for drying the lime sludge, it was
necessary to know the composition of the water and butanol
streams as they left the decanter of the still. Durrans[7]
gives the following solubility table.

TABLE V

Solubilities of n-Butanol-Water

Temperature ^{o}C	n-butanol in water per cent by weight	water in n-butanol per cent by weight
0	10.5	
10	8.9	19.7
20	7.8	20.0
30	7.1	20.6
40	6.6	21.4
50	6.5	22.4
60	6.5	23.6
70	6.7	25.2
80	6.9	26.4
90	7.9	30.1
100	9.2	33.8
110	10.5	37.6
120	16.1	46.0

This data helped explain the observations made during the distillation test studies of the solvents, that the slurry mixed rather slowly with the butanol when the butanol was cold. However, as the butanol was heated to $80^{\circ}C(176^{\circ}F)$ and above, the mixing took place almost immediately upon the introduction of the slurry. Thus, this data suggested the possibility of eliminating the distillation step entirely. That is, the water-lime slurry would be mixed with hot butanol at a temperature of $80^{\circ} - 100^{\circ}$ C. At these temperatures the solubility of water in butanol is 26.4 per cent to 33.8 per cent by weight of solution. The butanol would then be separated from the slurry while still hot. After separation and cooling to 20° to $40^{\circ}C$, the excess water should precipitate out since the solubility of water in butanol at these temperatures is 20.0 to 21.4 per cent by weight of solution. Separating this precipitated water, and recycling the butanol should allow a continual removal of the water from the slurry, without distillation. Figure 1 shows the proposed flow sheet for the process.

Materials

Waste Lime Slurry. The waste lime slurry used in this investigation was collected as the slurry left the generators and stored in a 50 gallon barrel. Before withdrawing a portion
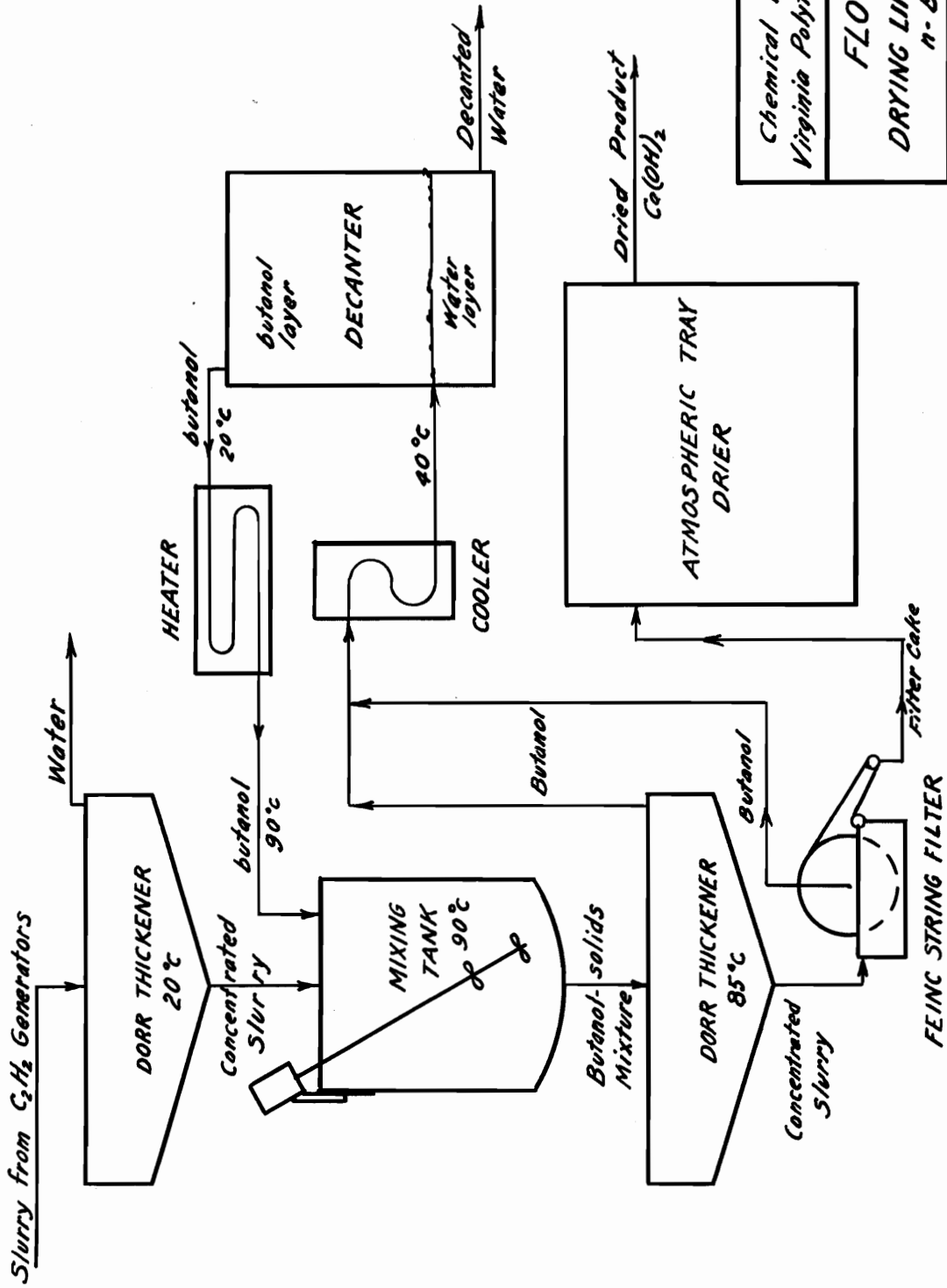
FLOW SHEET

DRYING LIME SLUDGE WITH
n-BUTANOL

Chemical Engineering Department
Virginia Polytechnic Institute, Blacksburg, Va.

Drawn by: Date: 5/15/91
Traced by: H.M.M.   Checked by:
                              Case: Thesis '41

for use, the slurry would be stirred for 20 to 30 minutes
with a $\frac{1}{4}$ H.P. Lightnin' Mixer. The sample needed was with-
drawn from the bottom of the tank during agitation. In this
manner a fairly uniform sample of the slurry could be
obtained. Solid content of the samples withdrawn varied
from 9.9 per cent to 12.4 per cent solids.

n-Butanol. The n-butanol used was obtained from the
Tennessee Eastman Corporation, Kingsport, Tennessee, as
a clean, white, oily like liquid. Its refractive index of
1.3991 at 20°C indicates practically water free n-butanol.
The refractive index of pure n-butanol is 1.3993 at 20°C.

Apparatus

Dorr Thickeners. Due to the small amount of material
on hand compared to the size of the laboratory Dorr Thickener,
a small thickener was simulated in one of the laboratory
crystallizing kettles. As shown in Figure 2, the dilute
slurry was introduced through pipe (D) at the desired rate.
The clear overflow was siphoned off through hose (C), while
the concentrated slurry was bled off the bottom of the tank
through valve (G). The paddle (B) was turned a half revolution
every 30 seconds in order to move the solids to the opening
and prevent caking on the bottom of the vessel. Approximate
capacity of the kettle is ten gallons.

ELEVATION

Grade Level
$\frac{1}{2}$" per 1'-0"

$\frac{1}{2}$" Outlet $\frac{1}{2}$" Water or Steam Inlet

PLAN
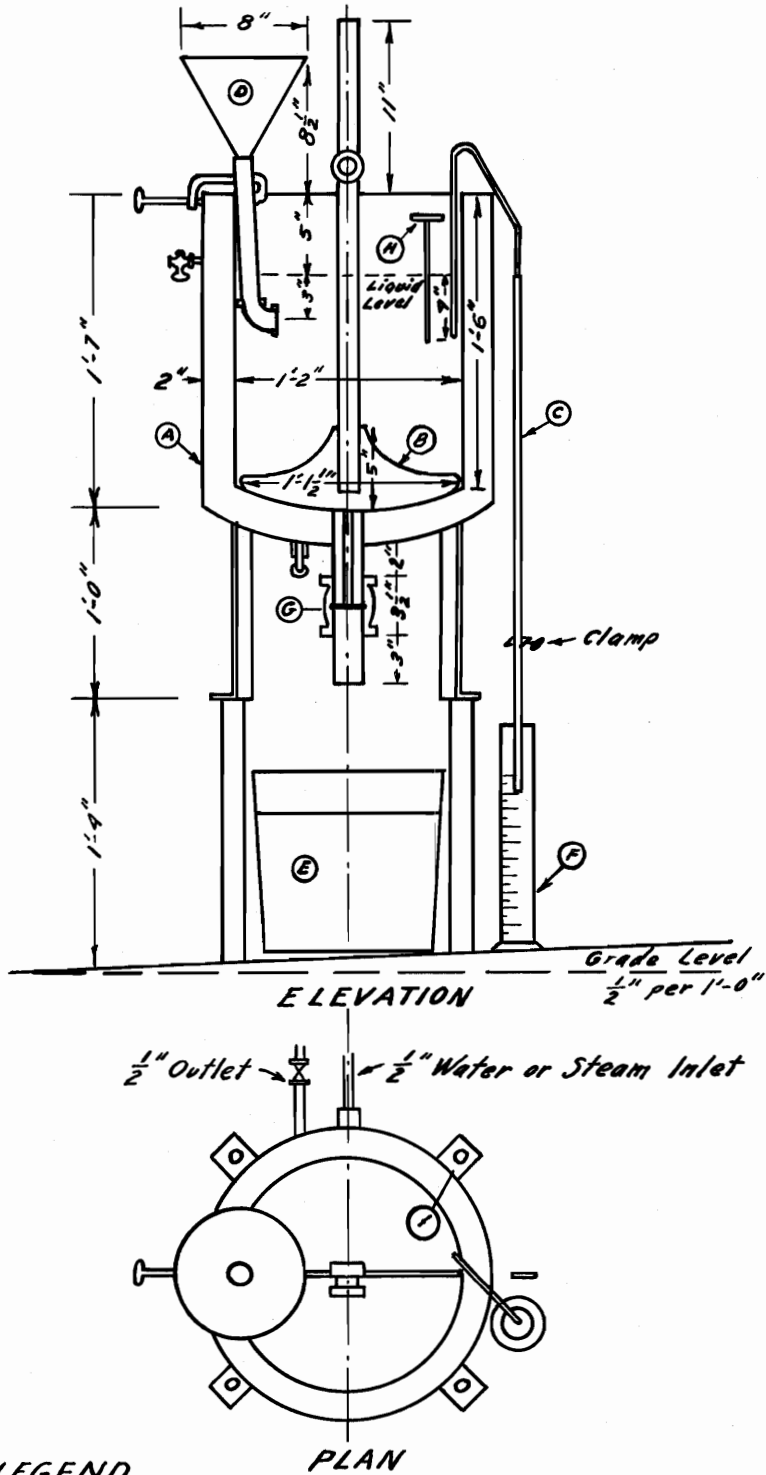
FIGURE 2

LEGEND

Ⓐ Jacketed, Steel Kettle
Ⓑ Oak Stirring Paddle
Ⓒ Glass and Rubber Tubing Siphon
Ⓓ Funnel and 1" Feed Pipe
Ⓔ 3 gal. Bucket
Ⓕ 1000 c.c. Graduate Cylinder
Ⓖ 2" Gate Valve Conc. Discharge
Ⓗ 360°F Metal Thermometer

Chemical Engineering Department Virginia Polytechnic Institute, Blacksburg, Va.	
PILOT PLANT THICKENER	
Scale: 1"=1'-0"	Date: 5/10/41
Drawn by: N.W.W.	Checked by: W.
Traced by: N.W.W.	Case: Thesis '41

Mixing Tank. Figure 3 is a drawing of the mixing tank. The slurry was fed into pipe (B) at the desired rate. It ran into the vortex of the liquid at the same place that the propeller shaft entered the liquid. Fresh butanol was introduced through pipe (C). The mixture of butanol-solids-water was drawn off the bottom through valve (E). A $\frac{1}{4}$ H.P. Lightnin' mixer having two propellers of three blades each on a single shaft was used to furnish the agitation. The approximate capacity of the tank is ten gallons. Temperatures were maintained by means of low pressure , 10 lbs./sq.in., steam.

FEinc Oliver String Filter. The laboratory rotary filter used in these experiments was a 12 inch diameter by 12 inch face FEinc laboratory filter, equipped with both string and blowback discharge, with a variable speed drum drive, and with an oscillating constant speed agitator. 52 strings of ordinary 1/16 inch diameter cord were used. The construction throughout was of stainless steel. Only the string discharge was used. (See Figure 4)

Atmospheric Tray Drier. As shown in Figure 5, the drying equipment used was a Proctor and Schwartz Atmospheric tray drier, containing 12 trays, 17 inches by 32 inches. The blower was powered by a 1 H.P. motor. Only 17 by 28 inches of the trays were used by the fine wire screen used as a holder for the filter cake.

ELEVATION
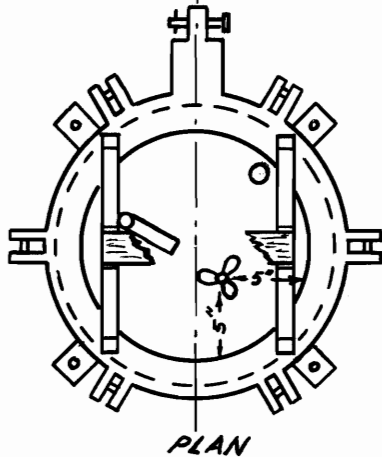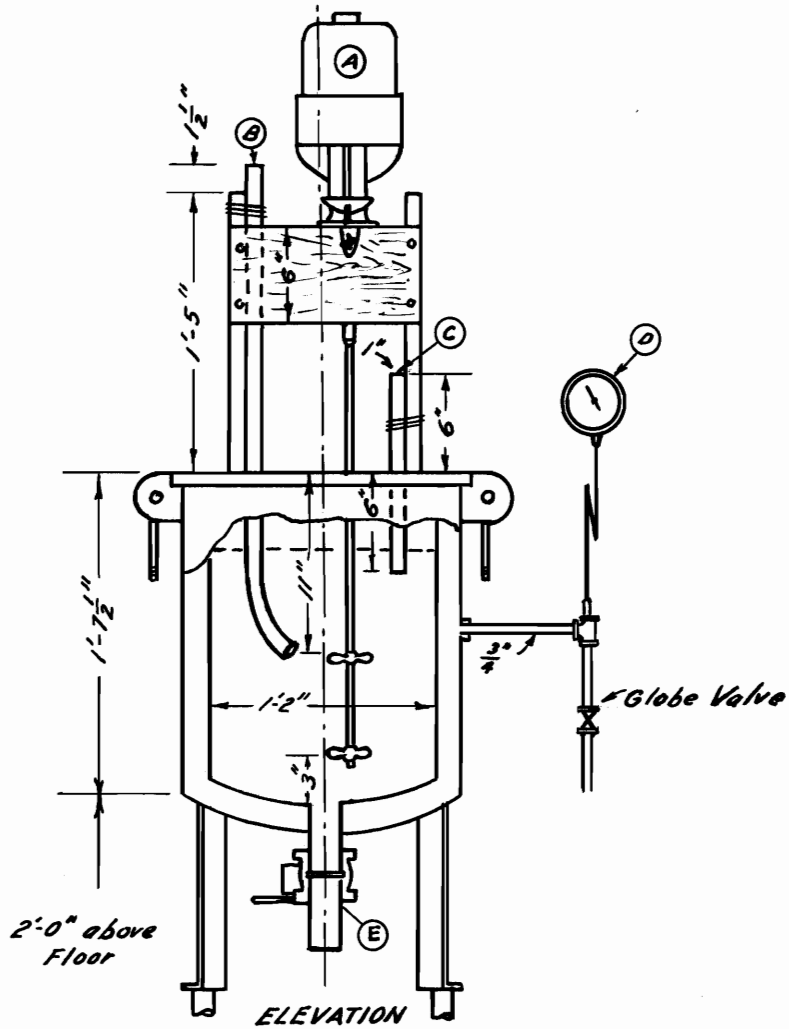
PLAN

FIGURE 3

LEGEND

(A) ¼ H.P. Lightnin Portable Mixer

(B) 1" Slurry Feed Pipe

(C) 1" Butanol Feed Pipe

(D) 100 p.s.i. Steam Gage

(E) 2" Quick Opening Discharge Valve

Chemical Engineering Department
Virginia Polytechnic Institute, Blacksburg, Va.

PILOT PLANT
MIXER

Scale: 1" = 1'-0"   Date: 5/12/41

Drawn by: H.W.W.   Checked by:

Traced by: H.W.W.   Case: Thesis '41

2'-0" above Floor

Globe Valve
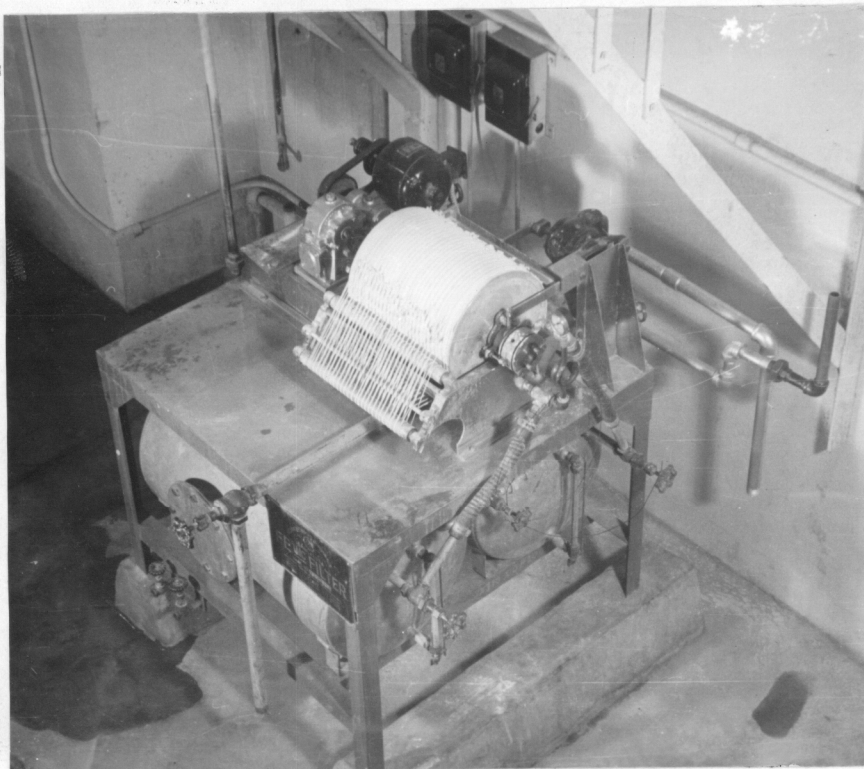
FIGURE 4

FEinc Oliver Rotary Filter

FIGURE 5

Proctor and Schwartz Atmospheric Tray Drier

Butanol Decanter. A decanter tank was simulated in one of the laboratory crystallizing kettles. As shown in Figure 6, the cooled butanol-water suspension was introduced through pipe (D) at the desired rate. The clear overflow was siphoned off through hose (C), while the water was bled off the bottom of the tank through valve (G). The approximate capacity of the vessel was ten gallons.

Procedure

Preliminary Run. A preliminary run was first made in a liter beaker. The n-butanol was brought to 180°F (82°C) and stirred rapidly. The same slurry as was used in the distillation studies was added slowly to the hot butanol. The resulting butanol-solids mixture was allowed to settle, the butanol decanted off, and the solids allowed to dry. The butanol was cooled and the water allowed to settle out. Figure 1 shows a flow sheet of the pilot plant studied.

Dorr Thickener -(Water Slurry). A settling rate determination of the slurry was first made with a 1000 cc. graduate filled with the original slurry as it came from the plant. After mixing the material thoroughly, the distance between the original level of the liquid and the top level of the solids was measured at one minute intervals. The volume of solids suspension was also recorded during the settling period.
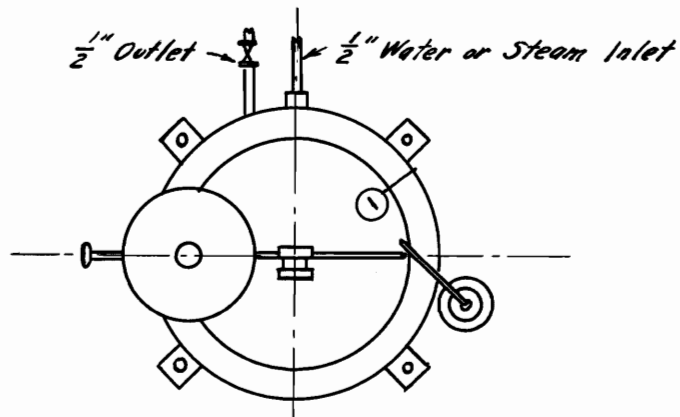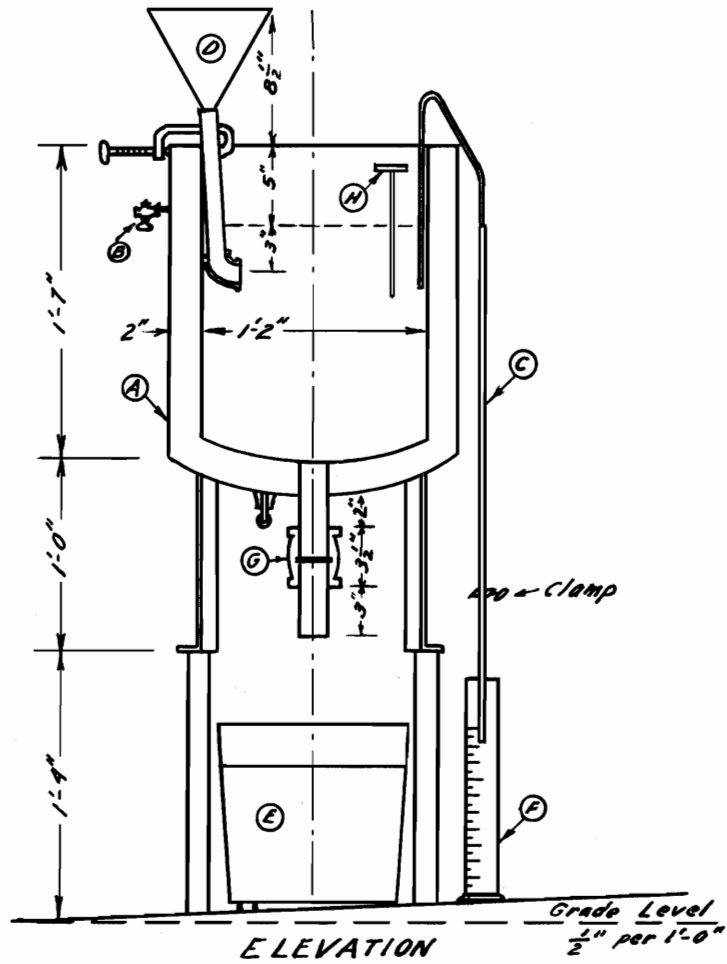
ELEVATION

Grade Level
$\frac{1}{2}$" per 1'-0"

$\frac{1}{2}$" Outlet

$\frac{1}{2}$" Water or Steam Inlet

LEGEND

Ⓐ Jacketed, Steel Kettle

Ⓑ Release Valve

Ⓒ Butanol Siphon

Ⓓ Funnel and 1" Feed Pipe

Ⓔ 3 gal. Bucket

Ⓕ 1000 cc. Graduate Cylinder

Ⓖ 2" Gate Valve, Water Discharge

Ⓗ 360°F Metal Thermometer

Chemical Engineering Department
Virginia Polytechnic Institute, Blacksburg, Va.

n-BUTANOL DECANTER

Scale: 1"= 1'-0"	Date: 5/15/41
Drawn by: N.N.N.	Checked by:
Traced by: N.N.N.	Case: Thesis '41

The solids content of slurry samples was determined by weighing a sample of the slurry in a crucible, evaporating to dryness, and reweighing. Solids content was expressed as the per cent of solids by weight in the slurry.

A drawing of the simulated Dorr thickener used is shown in Figure 2.

The thickener was filled with slurry, thoroughly agitated for 5 to 10 minutes, and then allowed to settle 25 minutes. At the end of this time the addition of a weighed amount of feed slurry was started. Once each minute the predetermined amounts of concentrated slurry and water were drawn off. Every half minute the paddle (B) was twisted very slowly one-half revolution. Fresh slurry was added fast enough to keep the level of the liquid constant. When the feed slurry ran out, the run was stopped, and the weight of concentrate and water recorded. Solids content determinations were made on both the feed and concentrated slurries.

Mixing Tank. The n-butanol was prepared for use in the tank by saturating n-butanol as received, with water at $27^{\circ}C$ ($80^{\circ}F$). This was done by introducing 16 lbs. of water into a tank with 50 lbs. of butanol and stirring vigorously with a $\frac{1}{4}$ H.P. Lighnin' mixer for twenty minutes. From Table V, it can be seen that 16 lbs. of water is more than enough to saturate 50 lbs. of butanol. The contents of the tank were then allowed to settle for 12 to 18 hours. At the end of this

time, the excess water was drawn off the bottom of the tank, leaving water saturated butanol as determined from the refractive index analysis.

The butanol was charged into the mixing tank and brought to $80^\circ C$ ($176^\circ F$) by introducing steam into the steam jacket surrounding the tank. Enough slurry was introduced slowly into the hot butanol to form a water butanol solution that contained 24 per cent by weight water.

In operation, a weighed amount of slurry concentrate was charged into the mixing tank (Figure 3) at a predetermined rate. Slurry was withdrawn from the bottom (valve E), and butanol was charged in at a rate calculated to maintain constant the composition and quantity of the materials in the mixing tank. The temperature of the entering and leaving materials was recorded as well as the temperature of the tank contents. The steam used was collected and weighed.

A satisfactory feed rate was chosen by adding the slurry at an increasing rate until it was observed that the particles leaving the tank had not been thoroughly acted upon. A rate was then chosen that was three fourths of this maximum rate.

By measuring the refractive index of the liquids handled, the concentration of n-butanol could be determined for use in the material accounting on the unit. The refractive index method of analysis offers a quick and simple method for

determining the butanol concentrations. Using an Abbe'
refractometer, a determination was made of the refractive
index at 20°C of n-butanol - water solutions of different
concentrations. Solutions were prepared on a volume basis,
the weight per cent compositions being calculated from the
volume data. Index of refraction was plotted versus weight
per cent butanol.

Thus, by determining the refractive index of the sample
and refering to the figure, the weight per cent butanol in
the sample was determined. In determining those concentrations
expected to lie near the saturation concentrations of water
and butanol in each other, an equal weight of dry butanol
was added to the sample. The resulting concentration as
determined from the index of refraction was multiplied by
two to give the concentration before dilution. This procedure
was also followed for solutions which were single phase when
hot, but became two phase when cooled to 20°C because of the
extra water dissolved in them.

Dorr Thickener -(Butanol Slurry). A settling rate
determination of the solids was made in the same manner as
described under the procedure for the Dorr thickener - water
slurry. A sample was collected from the hot discharge of the
mixing tank, put into the liter graduate, and the fall of
the solids noted at one minute intervals.

After the data on the mixing tank had been collected,

the hot butanol-water-solids mixture was left in the tank
to be used in the Dorr thickener study. The tank temperature
was maintained at $80^{\circ}C$ ($176^{\circ}F$) by means of steam in the steam
jacket. The feed to be thickened was kept at $80^{\circ}C$ ($176^{\circ}F$)
by passing steam through a copper coil immersed in the feed.
As in the water slurry study, feed was added to keep the
liquid level constant. Butanol and concentrated slurry were
drawn off at predetermined rates chosen from a study of the
settling rates. Solids content determinations were made on
both the feed slurry and concentrated slurry.

FEinc Oliver String Filter. The concentrated butanol-
solids slurry was used as feed for the string rotary filter.
A weighed amount of feed was fed to the filter slurry tank
at a fast enough rate to keep the level constant or nearly
constant. The temperature of the slurry in the tank was
considered to be the filtration temperature. Samples of the
filter cake were collected and their dimensions measured.
Solids content determinations were made on both the original
slurry and the filter cake. The filter cake was collected
and weighed on the wire screen used in the drier.

Atmospheric Tray Drier. The filter cake from the rotary
filter was collected on wire screen trays which were weighed
and then put into the driers. The tray below the tray with
the filter cake was covered with paper to catch any fine
material that dusted off and fell through. Periodically the

wire screen and paper with the drying filter cake on them were removed from the drier and weighed. Drying was continued until there was no more loss of weight of the solids on the trays. A final solids content determination of the dried cake was made, and its texture, crumbliness, and color observed.

Butanol Decanter. Upon completion of the Dorr thickener study on the butanol-solids mixture, the hot butanol was decanted and cooled to 25°C (77°F). Previously a settling or separation rate determination had been made.

The water-butanol emulsion that results when the butanol is cooled has a white milky appearance. By measuring at periodic intervals the distance below the surface of the liquid that the top of this milky layer had fallen, a sparation rate or settling rate of the suspension was determined.

A depth of three inches of butanol saturated water was put into the bottom of the decanter tank. The butanol suspension was put in and allowed to settle for the period calculated from the separation rate determination. During this time the feed was cooled down to 25°C (77°F) so that it would be ready at the proper time. At the end of the settling period, the feed was added at the predetermined rate and the water and butanol fractions drawn off at one minute intervals. The water and butanol recovered were weighed, and refractive index readings were made on the feed and products.

Data and Results

Preliminary Run. As the slurry was added to the hot butanol it first formed small droplets as if it had been introduced into gasoline. Then almost immediately the droplets disintegrated and dissolved in the butanol. In the preliminary run stirring was done manually so that the agitation of the solution was not extremely vigorous. When agitation was stopped at the end of the run, the solids settled out in three minutes. The decanted and cooled butanol separated very slowly as shown in Table VI.

TABLE VI

Separation Rate for n-Butanol - Water Suspensions

Time minutes	Observations
16	3 layers exist; a very thin clear top layer, a somewhat cloudy layer down 0.75 inches, and the bottom, generally cloudy layer the rest of the way down.
95	Upper clear portion down 2 inches, a cloudy portion below this 1.62 inches thick, and a bottom, seemingly water layer, 0.38 inches thick and very cloudy.
180	Clear upper layer 2.75 inches from top. Cloudy layer 0.88 inches thick. Bottom layer 0.5 inches thick.
270	Clear upper layer is 3.5 inches from top. No middle layer. Bottom layer is 0.5 inches thick.

The recovered solids, after drying at 140°F (60°C),

powdered almost at touch, and were very fine and white.
Drying took 55 minutes.

Dorr Thickener - (Water Slurry). A settling rate
determination was first made of the particles in the calcium
hydroxide slurry as received from the plant.

TABLE VII

Settling Rate Determination of
Lime Slurry

Temperature 80°F

Time	Volume of solids	Distance -top of solids to top of liquid	Rate of fall
minutes	cc.		inches per minute
0	985	0	
1	910	1.0	1.00
2	850	1.75	0.75
3	795	2.5	0.75
4	740	3.25	0.75
6	635	4.63	0.63
8	540	5.88	0.63
12	410	7.38	0.50
15	345	8.5	0.25
27	290	9.0	0.04

In estimating the feed rate for the settling unit from
the settling rates of Table VII, it was assumed that the feed
should be added at such a rate that the top of the liquid

would be elevated at the same rate that settling proceeds.

The level is not actually raised because the clear water is

removed faste enough to keep it constant. The settling rate

during the last part of the particles fall is 0.25 inches

per minute. The inside diameter of the thickening vessel,

as seen in Figure 2, is 13.5 inches. Thus a volume of

$$(6.7)^2 \pi \text{ x } 3.785/231 \text{ x } 0.25 = 0.575 \text{ liters/ minute}$$

cross	conversion	rate
section	cu. in. to	
area	liters	

should be used as feed. Considering, however, that this rate

exists only at the bottom of the apparatus, it was felt

advisable also to try a feed rate of 1.0 liters per minute.

The volume data from the settling determinations indicate

a draw off rate of 300 cc. per minute for the concentrated

slurry and 700 cc. per minute for the water for a 1000 cc.

per minute feed rate.

Material balances were made on the Dorr thickener for

two different rates of feed. The first material balance

shown was made for the operation at the feed rate calculated

above. (See Tables XIII and XIV in the Materials Balance

section.)

Mixing Tank. In order to analyze the liquid materials

entering and leaving the tank, an index of refraction vs.

composition curve had to be prepared. Data for this curve

was obtained by determining the refractive index of samples

of prepared composition as shown in Table VIII.

TABLE VIII

Refractive Index of n-Butanol - Water Solutions

volume water cc.	volume butanol cc.	wt. water grams	wt. butanol grams	wt. fraction butanol per cent	Refractive Index
0	20	0	16.2	100.0	1.3992
0.5	20	0.5	16.2	97.1	1.3988
1.0	20	1.0	16.2	94.2	1.3983
1.5	20	1.5	16.2	91.5	1.3973
2.0	20	2.0	16.2	89.1	1.3966
2.5	20	2.5	16.2	86.7	1.3961
3.0	20	3.0	16.2	84.5	1.3940
3.5	20	3.5	16.2	82.3	1.3931
4.0	20	4.0	16.2	80.2	1.3927
4.5	20	4.5	16.2	78.3	1.3916
25	0	25	0	0	1.3332
25	0.5	25	0.405	1.59	1.3347
25	1.5	25	1.215	4.64	1.3376
25	2.0	25	1.620	6.09	1.3389
25	2.5	25	2.025	7.50	1.3408

Table VIII is plotted in Figure 7.

A material balance was prepared from the weights and compositions of the materials entering and leaving the mixing tank. The tank was operated at 80°C (176°F). The material

FIGURE 7a

REFRACTIVE INDEX
OF n-BUTANOL — WATER SOLUTIONS

20° C

(High n-Butanol Concentrations)

BUTANOL — weight per cent

REFRACTIVE INDEX at 20°C
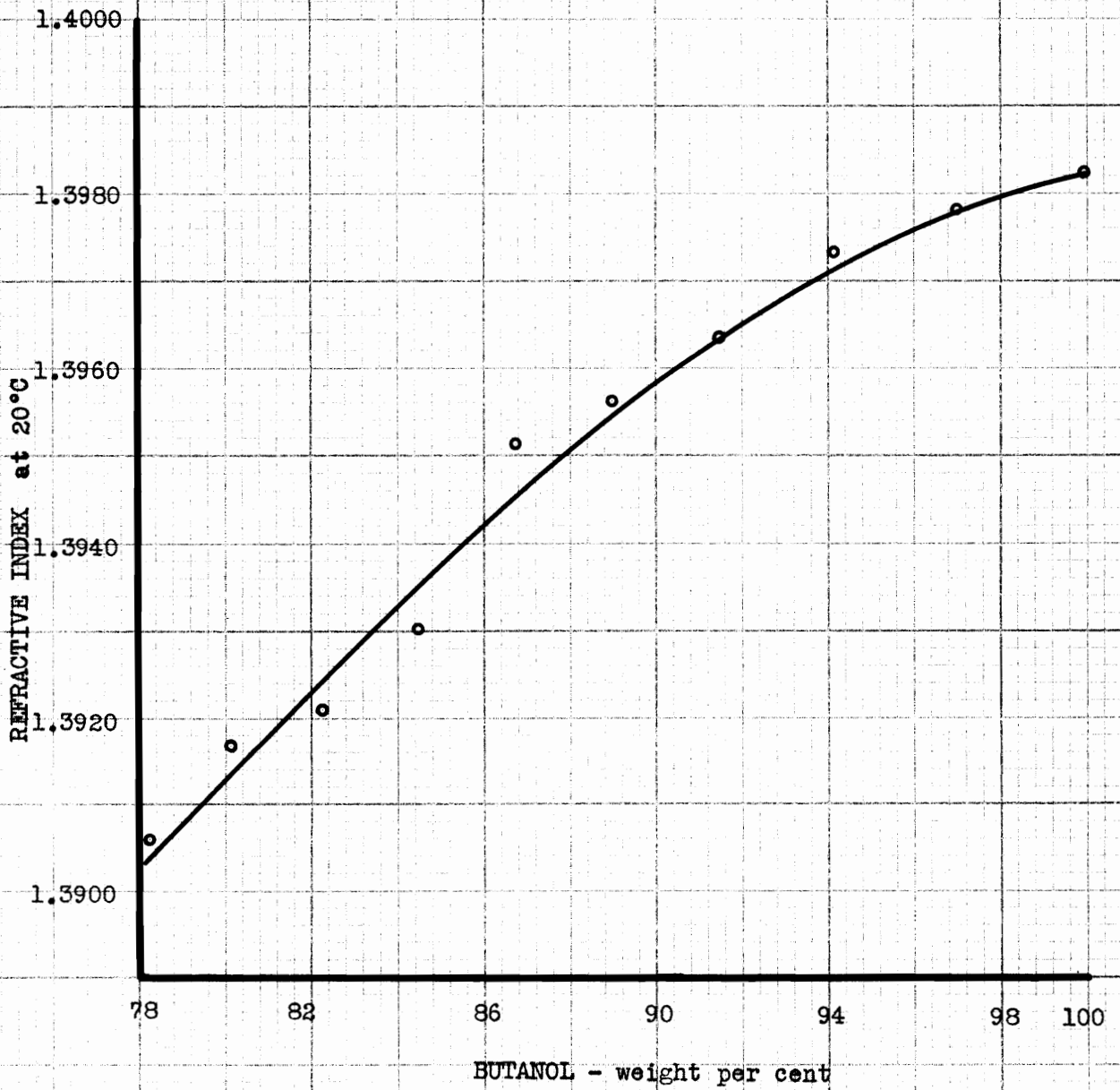
R.L.T.
5/13/41

FIGURE 7b

REFRACTIVE INDEX
OF n-BUTANOL - WATER SOLUTIONS

20° C

(Low n-Butanol Concentrations)

BUTANOL - weight per cent

REFRACTIVE INDEX - 20° C
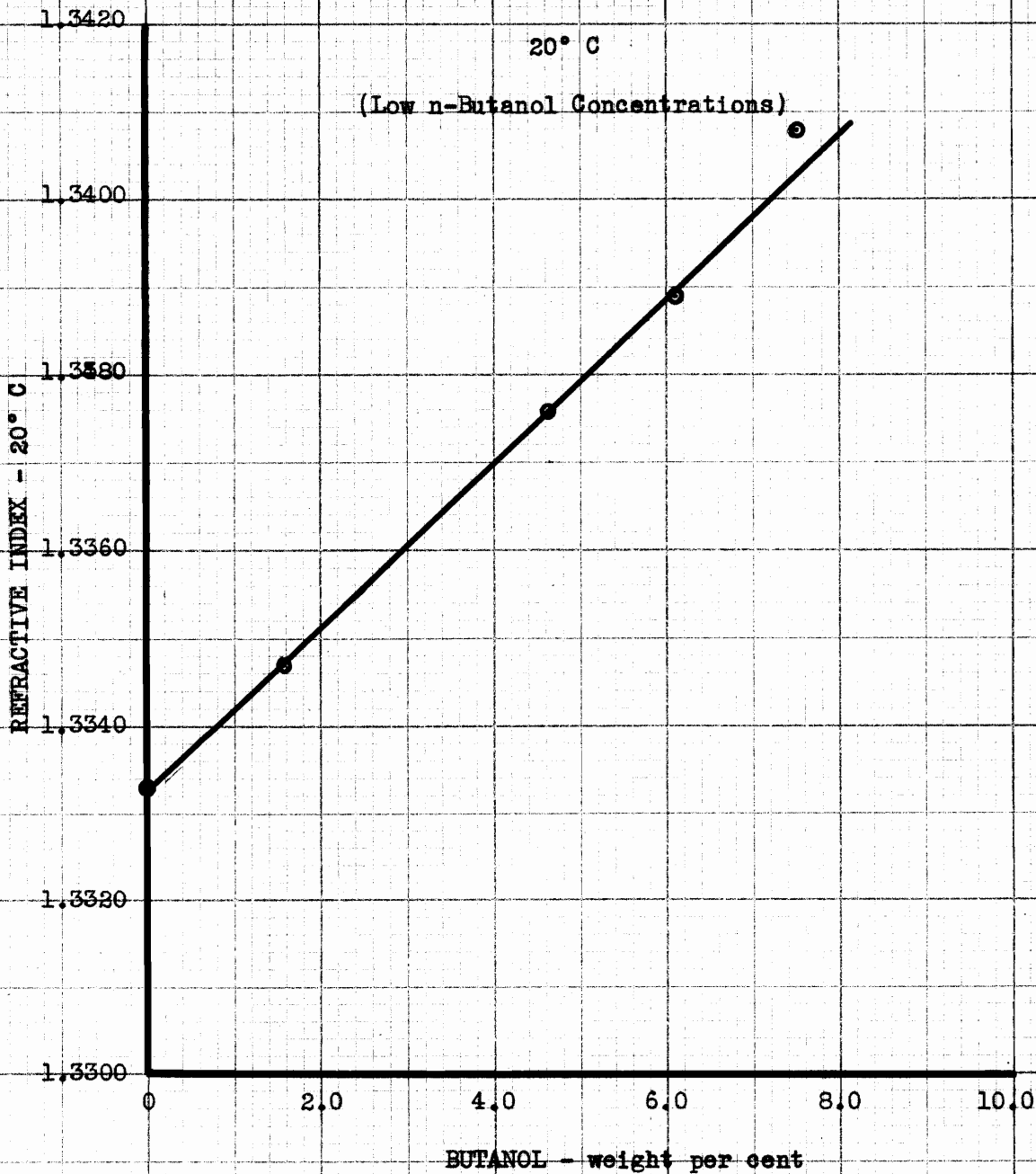
R.L.T.
4/14/41

balance shown in Table XV is for the maximum successful addition rate tried.

Steam consumption both during operation of the tank and during the time when no materials were being added or withdrawn was determined. From this information the heat balance shown in Table XX was prepared.

The ability of the hot butanol to break up the slurry was so great that extreme difficulty was experienced in adding the fresh butanol and concentrated slurry fast enough.

Dorr Thickener - (Butanol Slurry). A settling rate determination was first made of the particles in the hot butanol slurry as it was withdrawn from the mixing tank. This data is presented in Table IX.

TABLE IX

Settling Rate Determination of Lime-Butanol Slurry

Time minutes	Volume of Solids cc.	Distance-top of solids to top of liquid in inches	Rate of fall inches per minute
0	950	0	
0.5	720	3.0	6.0
1.0	575	5.0	4.0
1.5	385	7.5	5.0
2.0	200	10.0	5.0
2.5	70	11.5	3.0
3.0	65	11.62	0.25

The feed rate for the butanol slurry was calculated in the same manner as for the water slurry. Previous experience with the water slurry had indicated that the settling rate determined during the early part of the settling should be used in the calculations. Using the same tank for thickening, a settling rate of 6 inches per minute thus indicates a feed rate of 15.0 liters per minute. The volume data of the settling rates indicate a concentrate draw off of 1000 cc. per minute and a butanol draw off of 14,000 cc. per minute.

Material balances as shown in Table XVI were made on the Dorr thickener using the calculated rate of feed. The operating temperature of the thickener was 165°F (74°C).

FEinc String Filter. Immediately after concentration, the hot butanol slurry was filtered. Some cooling resulted because the slurry had to be carried in buckets from the thickener to the filter. The filter cake broke off the string discharge system readily, giving a cake that was light colored in appearance, non-cohesive and easily broken up, with a somewhat dry texture. The cake was 0.12 inches thick on the filter, and broke into pieces about 0.40 by 0.25 inches as it discharged from the strings. A material balance was prepared from data taken during the operation of the filter and is shown in Table XVII. Table X lists the conditions under which filtration took place.

TABLE X

Operating Conditions of the FEinc String Filter
for Filtering Butanol-Lime Slurry

Drum Speed:	1/3	r.p.m.
Agitator speed:	12	cycles/min.
Temperature of slurry in unit	135°F	(57°C)
Vacuum	10	lbs./sq. in.
Feed rate (24.7% solids)	1.37	lbs. slurry/min.
Discharge rate (68.0% solids)	0.49	lbs. cake/min.

Atmospheric Tray Drier. Table XI gives the data taken
during the drying of the filter cake. Also included in Table
XI are the calculations from which the drying rate curve,
shown in Figure 9, was determined. From the data of Table
XI, the material balance shown in Table XVIII was prepared.
The drier was operated at 180°F (82°C).

The dried product was finely divided and white. Small
lumps of it crumbled immediately between the fingers and
dusted upon impact when falling three or four feet. No
tendency to cake was noted at any time during the entire
filtering and drying operations. Analysis showed the dried
product to contain 95.0 per cent solids by weight.

Butanol Decanter. After drawing off the excess butanol
from the slurry in the Dorr thickener, the butanol was cooled
to 25°C (77° F) and fed to the decanter. Previous to this a

TABLE XI

Operating Data and Rate of Drying Calculations for
the Drying of Butanol-Lime Filter Cake in the
Proctor and Schwartz Atmospheric Tray Drier

Time Elapsed min.	Time Increment min.	Sample Weight grams	Change in Weight grams	Change in Weight grams per minute	Liquid Content of Cake grams	Grams Butanol per gram of solid
0		630			163	0.349
3.0	3.0	608	22	7.35	141	0.302
5.0	2.0	591	17	8.50	124	0.266
7.25	2.25	566	25	11.10	99	0.212
10.5	3.25	541	25	7.70	74	0.158
13.5	3.0	524	17	5.65	57	0.122
17.0	3.5	507	17	4.85	40	0.086
19.5	2.5	497	10	4.00	30	0.064
23.5	4.0	491	6	1.50	24	0.054

(Bone dry weight taken as 467 grams since a solids
content analysis showed the final material to have
95.0% solids, 5.0% butanol in it.)

FIGURE 8

RATE OF DRYING OF BUTANOL-LIME FILTER CAKE

Proctor and Schwartz Atmospheric Tray Drier
Operating Temperature 180°F

FREE BUTANOL - Grams per Gram of Solid

DRYING RATE - Grams Butanol Evaporated per Minute
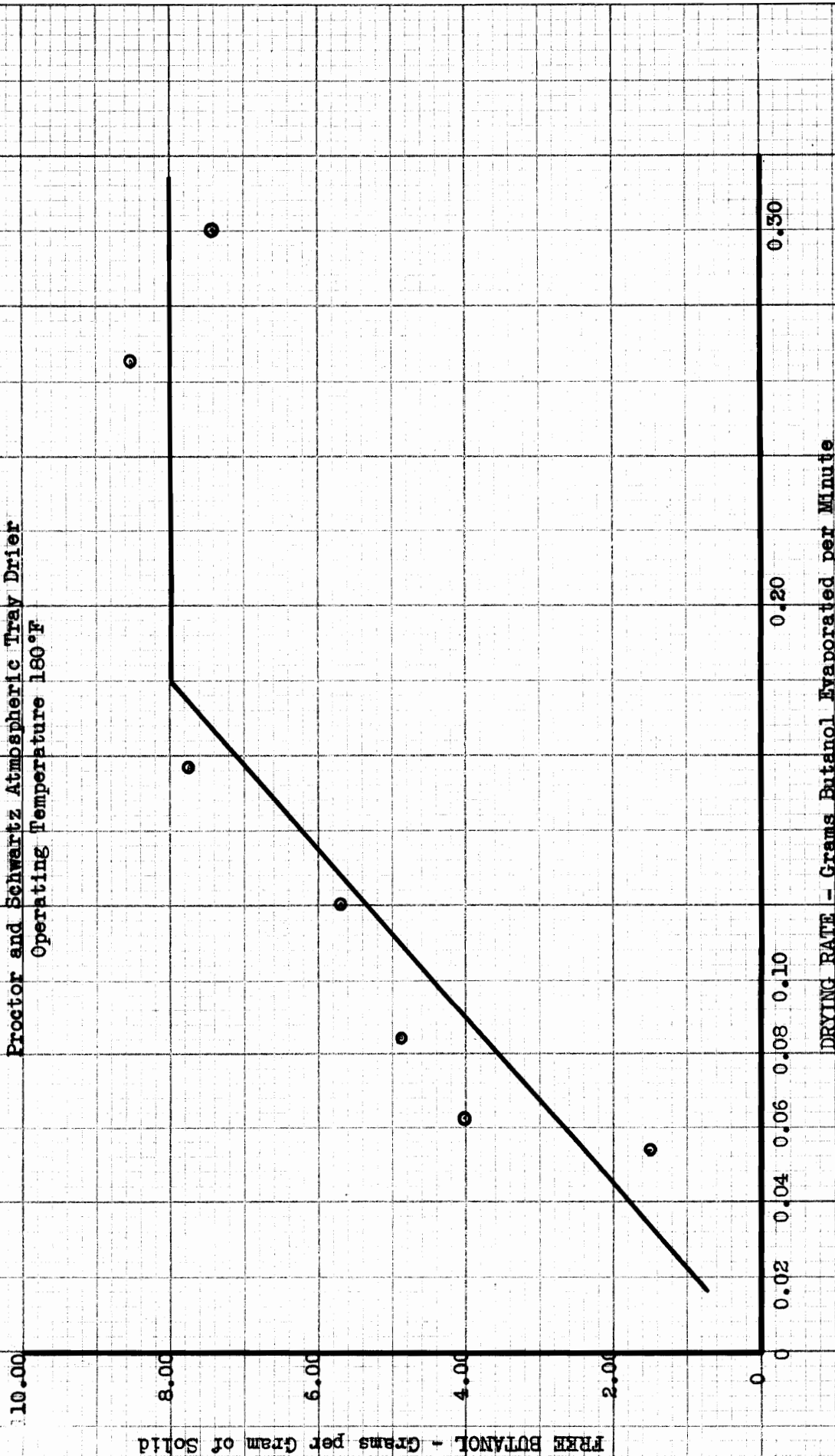
R:L:T.
5/13/41

separation rate determination had been made as shown in Table
XII.

TABLE XII

Separation Rate of Saturated Water-in-Butanol Suspensions at 25°C (77°F)

Time	Distance (depth of clear top) solution	Settling Rate
minutes	inches	inches/minute
90	2.0	0.0210
180	3.2	0.0132
480	7.2	0.0135

As previously explained for settling rate calculations,
in estimating the feed rate for the decanter unit from the
settling rates of Table XII, it was assumed that the feed
should be added at such a rate that the top of the liquid
would be elevated at the same rate that settling proceeded.
The level does not actually rise because the butanol is
siphoned off fast enough to keep this level constant. The
settling rate determined was 0.0135 inches per minute. The
same vessel as was used before in the thickener studies was
used, so that this settling rate would correspond to a feed
rate of 31.5 cc. per minute. The composition of the feed was
75.5 per cent butanol by weight, indicating that 30.0 cc.
78.8 per cent butanol by weight should be drawn off the top
and 1.5 cc. water (8.0 per cent butanol by weight) should be
drawn off the bottom.

After determining the quantities and compositions of the feed introduced and water and butanol drawn off, the material balance shown in Table XIX was made. The operating temperature of the decanter was 25°C (77° F).

Material Balances: -

TABLE XIII

Operation of the Dorr Thickener Using Lime-Water Slurry

Feed rate   2.19 lbs./min., 1000 cc./min.
Concentrate   .69 lbs./min., 300 cc./min.
Clear water 1.42 lbs./min., 700 cc./min.

IN: OUT:

Fresh Slurry (9.9 % solids)	26.3 lbs.	Concentrated Slurry (32.8 % solids)	8.2 lbs.
		Clear Water	17.0 lbs.
		Loss -(water)	1.1 lbs.
Total In	26.3 lbs.	Total Out	26.3 lbs.

TABLE XIV

Operation of the Dorr Thickener Using Lime-Water Slurry

Feed rate   1.18 lbs./min., 500 cc./min.
Concentrate   .42 lbs./min., 150 cc./min.
Clear Water   .74 lbs./min., 350 cc./min.

IN: OUT:

Fresh Slurry (12.4% solids)	22.5 lbs.	Concentrated Slurry (38.0% solids)	8.0 lbs.
		Clear Water	14.0 lbs.
		Loss	0.5 lbs.
Total In	22.5 lbs.	Total Out	22.5 lbs.

TABLE XV

Operation of the Water Slurry - Butanol Mixing Tank
(Time - one minute)

IN:		OUT:	
Slurry from thickener (30.2% solids)	1.00 lbs.	Butanol-water-solids (2.07% solids, 75.5% butanol)	16.00 lbs.
Butanol (77.5% butanol)	15.00 lbs.		
Total In	16.00 lbs.	Total Out	16.00 lbs.

TABLE XVI

Operation of the Dorr Thickener Using Lime - Butanol Slurry.

IN:		OUT:	
Slurry from mixing tank (2.07% solids)	13.0 lbs.	Concentrated Slurry (22.9% solids)	1.0 lbs.
		Butanol	12.0 lbs.
Total In	13.0 lbs.	Total Out	13.0 lbs.

TABLE XVII

Filtration of the Butanol - Solids Slurry on the FEinc Oliver String Filter

(3.5 minutes operation)

IN:		OUT:	
Concentrated Slurry (24.7% solids)	4.8 lbs.	Filter cake (68.0% solids)	1.7 lbs.
		Butanol	3.0 lbs.
		Losses	.1 lbs.
Total In	4.8 lbs.	Total Out	4.8 lbs.

TABLE XVIII

Drying of the Filter Cake from the FEinc String Filter
in the Proctor and Schwartz Atmospheric Tray Drier

IN:		OUT:	
Filter Cake (68.0% solids) solids 0.94 lbs. butanol 0.45 lbs.	1.39 lbs.	Dried Product (95.0% solids) solids 1.03 lbs. butanol 0.05 lbs.	1.08 lbs.
		Butanol Evaporated (by difference)	0.40 lbs.
		Gain of Material (error in work)	(-0.09 lbs.
Total In	1.39 lbs.	Total Out	1.39 lbs.

TABLE XIX

Operation of the Butanol - Water Separating Decanter

IN:		OUT:	
Water-Butanol Suspension (75.5% butanol)	0.600 lbs.	Butanol (78.8% butanol)	0.560 lbs.
		Water (8.0% butanol)	0.028 lbs.
		Losses	0.012 lbs.
Total In	0.600 lbs.	Total Out	0.600 lbs.

Heat Balances: -

TABLE XX

Operation of the Water Slurry - Butanol Mixing Tank
(Time - one minute)
(Base Temperature - 80°F (27°C)

HEAT IN:

    in butanol - 15 lbs. at 80°F   0   BTU

    in slurry - 1 lbs. at 80°F   0   BTU

    in steam to maintain the temperature
       and to heat the materials added -   1850 BTU
       (to maintain temperature 0.31 lbs., 360 BTU
        to heat materials   1.3 lbs.,1490 BTU
       1155 BTU/lb. , Total   1.61 lbs,1850 BTU

                     Total Heat In   1850 BTU

HEAT OUT:

    in slurry discharged - 176°F (80°C)   1262 BTU
      (16 lbs., sp. heat 0.79)

    in condensate - 1.6 lbs., 193 BTU/lb.   309 BTU

    Unaccounted for Losses   279 BTU

                     Total Heat Out   1850 BTU

IV. DISCUSSION OF RESULTS

Choice of Solvent

The choice or rejection of a solvent under consideration
will depend upon the degree to which it fulfilled the seven
requirements previously listed in part A of the experimental
investigation. No one material can be expected to meet all
the requirements completely, so that a compromise among the
less important requirements must be made in order to choose
a satisfactory material.

Elimination of Unsatisfactory Solvents. From Table III
it can be seen that a great number of the solvents must be
discarded because they will not mix with the slurry and break
it up. Of those that do mix, some of them tend to cake during
the operations and thus must also be eliminated as shown in
Table IV. Three materials eventually remain as satisfactory
for use in the proposed azeotropic process; n-butanol, sec.-
butanol, and iso-propanol. However, iso-propanol does not
form a two phase mixture when the condensed vapors of the
azeotrope are cooled, and the two phase mixture formed with
sec.-butanol contains more butanol in the water layer and
more water in the butanol layer than does n-butanol. Iso-
propanol must be reconcentrated by special processes of

ternary azeotropic distillation which are expensive and call for expensive equipment.

Choice of n-Butanol. n-Butanol, however, does form a two phase system upon cooling of its azeotrope vapors. The azeotrope contains 37 per cent water by weight, whereas the butanol fraction of the two phase condensed vapor system contains only 20.1 per cent water. Thus the butanol layer can be recirculated without further concentration if it is so desired. A great amount of recovery cost is thereby eliminated, the only cost being that of recovering the butanol lost in the water discharged from the decantation system. n-Butanol is readily available commercially at a satisfactory price (about $0.03 per pound in quantity). Its azeotrope is high boiling compared to the other solvents, (198°F), but it is believed that this is a very minor consideration.

The distillation tests were not tried on ethanol and tert.-butanol because, like iso-propanol, it is difficult to separate the pure material from the water azeotrope for recirculation.

Pilot Plant Study of a Solution Method for Drying Calcium Hydroxide Waste Sludges

In studying the azeotropic distillation process for drying the lime sludge, it was necessary to know the composition of the water and butanol streams as they left the

decanter of the still. The solubility data given in Table V was found during the decanter study and helped explain the observations made during the distillation test studies of the solvents, that the slurry mixed rather slowly with the butanol when the butanol was cold. However, as the butanol was heated to $80^{\circ}C(176^{\circ}F)$ and above, the mixing took place almost immediately upon the introduction of the slurry. Thus, this data suggested the possibility of eliminating the distillation step entirely. That is, the water-lime slurry would be mixed with hot butanol at a temperature of $80^{\circ}C$. At these temperatures the solubility of water in butanol is 26.4 per cent by weight of solution. The butanol would then be separated from the slurry while still hot. After separation and cooling to $20^{\circ}C$, the excess water should precipitate out since the solubility of water in butanol at $20^{\circ}C$ is 20.0 per cent by weight of solution. Separating this precipitated water, and recycling the butanol should allow a continual removal of the water from the slurry without distillation.

Preliminary Run. Two troubles were encountered in the preliminary run. First, the agitation had to be rapid when the slurry was added to the hot butanol. If it was not, the slurry settled to the bottom and tried to cake up. Second, the settling or separation rates of the cooled butanol-water suspensions were very low.

It should be noted that the solids were not filtered

during the preliminary run, so that some of the drying time was used in evaporating the excess butanol.

Dorr Thickeners. Theoretically, a concentration of 985 cc. of 10 per cent solids slurry to 290 cc. would yield a slurry containing 30 per cent solids by weight. A slurry containing 32.8 per cent solids was obtained in the experimental equipment. This was considered to be within the range of expected accuracy.

It was not possible to attempt a concentration to greater than 38 per cent solids because the slurry had to stay fluid enough to flow through the tiny opening of the cracked gate valve. In an actual large size thickener, using a slurry pump, and having much larger openings, greater concentration could be attempted. In the small equipment the valve clogged and would not stay o pen when the higher concentrations were tried.

Mixing Tank. Special technique in making the refractive index analysis was necessary because most of the compositions encountered fell in the saturation regions. For this reason great care had to be excersized to be sure that a reading was not being made on a two phase system. It was believed simpler and more reliable to dilute all the samples and be sure that they would be single phase solutions at 20°C.

The losses shown in the material balance are due mainly to the evaporation of the butanol since it is near its boiling point and in an open vessel. Other errors undoubtedly occured

due to spillage and inaccuracies in weighing.

Much discomfort to the workers resulted from the butanol vapors arising from the kettle. Some provision should certainly be made in an actual plant to keep these vapors under control.

Atmospheric Tray Drier. In practice, a plant using the solution method of drying would use a continuous drier. The data obtained in the tray drier used, however, represents the conditions existing in the various sections of a continuous drier as the particles travel through.

The capacity of the tray drier used is much greater than was needed. For this reason the data for this piece of equipment should not be considered as completely representative of the conditions in a normally operating drier.

The results taken do serve, however, to indicate the results to be expected in actual plant operation and as such give valuable information.

Butanol Decanter. The very low separation rate of the water from the cooled butanol may cause this operation to be the bottle neck of the process. However, separation takes place at ordinary temperatures (20°- 40°C) so that large settling tanks are not impractical.

A centrifuge was suggested to replace the settling tank. It might prove to be economical in that it would replace the item of a large butanol storage. Since butanol is worth $0.08

per pound, the reduction in capital investment might be an item worthy of consideration.

Summation of Factors Affecting the Process. The solution process of drying offers possibilities of use on other materials than lime wastes from acetylene generation. The process has the advantage of simplicity and low heat consumption. The elimination of the distillation step offers a decided advantage in simplification of the equipment.

Heat economies could be realized by using the hot butanol leaving the butanol-slurry thickener to heat the cold butanol entering the mixing tank.

Greater concentration of the water slurry would favorably affect the entire water removal system. By reducing the water content of the slurry, the butanol throughput to the mixing tank would be reduced. Further, the amount of solids carried by each pound of butanol leaving the mixing tank would be increased. This is because the butanol leaving the mixing tank is governed by the amount added. The butanol needed per pound of slurry is proportional to the water content of the slurry and independent of the amount of solids. The resulting increase in solids content of the butanol slurry would result in a corresponding increase in solids content of the concentrated butanol slurry with a resulting improvement in filter operation.

Further study on the mixing tank conditions might uncover distinct advantages in operating under slight pressure and using

higher temperatures. The solubility of water in butanol increases rapidly with increasing temperature above $80^{\circ}C$ ($176^{\circ}F$) as was shown in Table V. This greatly increased solubility of water in butanol would materially reduce the throughput of butanol in the mixing tank and at the same time increase its capacity or reduce the power needed for agitation. This power reduction would be due to increased speed with which the slurry would be attacked and broken up by the hot butanol.

V. <u>CONCLUSIONS</u>

1. The weak carbide generator calcium hydroxide waste slurry discharged from the acetylene generators at the duPont Company plant at Waynesboro, Virginia, can be concentrated in a Dorr thickener from 9.9 per cent solids by weight to a slurry containing 38.0 per cent solids by weight.

2. The water contained in the concentrated slurry containing 38.0 per cent solids by weight can be dissolved in n-butanol containing 77.5 per cent butanol by weight, 22.5 per cent water by weight, if an amount of the concentrated slurry containing not more than enough water to saturate the butanol at 80°C (176°F) be vigorously mixed with the n-butanol, and the temperature of the n-butanol be maintained at 82°C (180°F).

3. The slurry mixture of solids and butanol containing dissolved water that is discharged from the mixing tank can be concentrated in a Dorr thickener from 2.07 per cent solids by weight to a slurry containing 22.9 per cent solids by weight.

4. Using 10 lbs. vacuum, n-butanol - calcium hydroxide slurry containing 24.7 per cent solids by weight can be filtered on a FEinc Oliver rotary string filter giving a resulting filter cake whose solids content is 68.0 per cent solids by weight.

5. Filter cake containing butanol and calcium hydroxide can be satisfactorily dried from a solids content of 68.0 per cent by weight to 95.0 per cent solids by weight in an atmospheric air drier operated at 180°F (82°C).

6. Excess water may be removed from the n-butanol used in the process and separated from the solids, and the butanol made available for reuse, by first chilling the water-in-butanol solution containing 75.5 per cent butanol by weight to 25°C (77°F) and then decanting the drier butanol containing 78.5 per cent butanol by weight.

7. The calcium hydroxide lime wastes resulting from acetylene generation from calcium carbide can be satisfactorily dried by the solution method, using n-butanol as the solvent, under the conditions of operation outlined in the previous conclusions.

VI. SUMMARY

The disposal of calcium hydroxide wastes resulting
from the production of acetylene from calcium carbide and
water presents a special problem since the resulting slurry
cannot be flushed into the streams. The slurry cannot be
dried by ordinary means because it cakes up in the equipment.
At present the solids in the slurry are allowed to settle
in great ponds, the excess liquid flowing off to the streams.
The settled material is putty-like and dries only on the
surface. Farmers of the vicinity carry away the calcium
hydroxide "mud" for use in liming their lands, but the hard
lumps formed as the "mud" dries in the field prevent even
distribution. A much more useful material would be a powder
form which could be spread evenly over the fields or could
be used as chemical lime.

A drying process has been investigated in which the
slurry is first concentrated by settling. This concentrated
slurry in then introduced with rapid agitation into a mixing
tank containing butanol at $82^{\circ}C$ ($180^{\circ}F$). Here the water in
the slurry is dissolved by the butanol. The mixture of water

dissolved in butanol and solids is drawn from the mixing tank and the resulting slurry concentrated. The concentrated slurry is filtered on a rotary filter, and the filter cake dried in an atmospheric air drier. Water is **separated** from the recovered butanol by chilling the butanol to $25^{\circ}C$ ($77^{\circ}F$). The water that precipitates out is removed in a decanter. The butanol is reheated to $82^{\circ}C$ ($180^{\circ}F$) and returned to the mixing tank.

A fine, non-caking powder is produced which can be used for either chemical or agricultural purposes. The material is easily handled in simple equipment by this process.

VII. <u>BIBLIOGRAPHY</u>

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VIII. ACKNOWLEDGEMENT