# THE PROGRESS OF THE REACTIONS IN A PORTLAND CEMENT KILN

and

# A METHOD FOR THE PRODUCTION OF ANHYDROUS SODIUM SULFATE

Thesis

by

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In partial fulfillment of the requirements
for the degree of Master of Science
in Chemical Engineering

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California
1931

# PART A

# THE PROGRESS OF THE REACTIONS IN A PORTLAND CEMENT KILN

# The Progress of the Reactions in a Portland Cement Kiln

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The scientific investigation of cement may be said to have begun in 1813 with the work of Collet-Descotils(1) (2) who showed that the burning of the mix converts the silica into a soluble form. Le Chatelier(3) in 1887 was the first to try to classify the definite chemical compounds of importance in Portland Cement. He advanced the theory that Portland Cement is composed essentially of two compounds: $3CaO.Al_2O_3$ and $3CaO.SiO_2$. Using his experimental facts as a basis he calculated the ratio between Lime and Silica-Alumina that would give a good cement. Though Researchers since have shown that his ratio gives too high a Lime content for soundness, most authorities of the present agree that $3CaO.SiO_2$ is the most important single component of Portland Cement.

Other Investigators from time to time rejected old theories and advanced new ones among which may be mentioned the following: Törnbohm (1897)(1) found four distinct mineral constituents in Portland Cement which he called Alit, Belit, Felit, and Celit. He identified these by means of individual color and their refractive power on polarized light. He did not determine their chemical composition. C. Richardson in 1904,(4) (5) through microscopic studies on the clinker, suggested the theory that it was a solid solution composed chiefly of $3CaO.SiO_2$ dissolved in $3CaO.Al_2O_3$. This is not in accord with the present theories. Rankin,(6) in 1915, approached the problem in a different way. Since $SiO_2$, CaO, and $Al_2O_3$ are the most important constituents of Portland Cement, he and his co-workers undertook to study the phase relations of these compounds and to determine the various ratios in which these constituents interacted.

The results of the various investigations may be summed up as follows: The important compounds present in commercial Portland Cement clinker are: MgO, $4CaO.Fe_2O_3.Al_2O_3$, $2CaO.SiO_2$, $3CaO.SiO_2$, $3CaO.Al_2O_3$, and CaO.

Rankin and Wright(6) have identified all these except the Iron Compound by means of their optical properties, even in the presence of impurities such as MgO and $Fe_2O_3$.

In the formation of the clinker, the following reactions are the most important and are assumed to take place roughly in the order given. Undoubtedly they overlap and several may be proceeding at the same time.

1. Removal of free moisture and the dehydration of the combined water in the clay.
2. Decomposition of the $MgCO_3$ and $CaCO_3$ to MgO and CaO.
3. Reaction of CaO with $Al_2O_3$ and $Fe_2O_3$ to give $4CaO.Al_2O_3.Fe_2O_3$.
4. Reaction of CaO with $SiO_2$ to give $2CaO.SiO_2$.

5. Reaction of $Al_2O_3$ and CaO to give $3CaO.Al_2O_3$.

6. Reaction of $2CaO.SiO_2$ and CaO to give $3CaO.SiO_2$.

This order is in accord with the latest findings of the investigators in the Department of Commerce who further find that MgO is present in clinker uncombined. The reaction of Di-Calcium Silicate and Lime to give Tri-Calcium Silicate is slow and the charge must be held at a high temperature for considerable time in order that the reaction may go to completion since the free lime in the finished cement is detrimental to the soundness of the concrete. The $4CaO.Fe_2O_3.Al_2O_3$ acts as a flux for the fusion of the minerals and lowers the temperature at which the reaction takes place.

The present study was undertaken in order to follow the progress of these reactions in a commercially operated Portland Cement Kiln of the rotary type using the dry process. A method has recently been worked out by W. N. Lacey and Hubert Woods(7) at the Riverside Cement Company of Los Angeles whereby samples may be taken from the kiln while it is in continuous operation. Using samples obtained from a kiln of this Company, determinations were made of the water, $CO_2$, and Free Lime (uncombined CaO) content of the charge throughout the length of the kiln. From these Data reactions 1 and 2 of the above list are obtained directly. The progress of 3, 4, 5, and 6 was followed by calculating the utilization of Lime from the $CO_2$ and the

Free Lime data. A close visual examination of the samples was made to determine at what place in the kiln the mix began to "ball up" or form lumps. The specific gravity of the samples was also determined.

While this method has been used in the laboratory for following the reactions, it is the writer's opinion that this is the first time it has ever been applied to a continuously operating kiln. Figure 1 gives the dimensions of the kiln and the locations of the sampling stations. These samples are composites of ones taken every half hour over a five hour period. As they were taken from the kiln they were placed in large tin sample containers provided with tightly fitting covers. After the run these covers were sealed with paraffin until the sample was removed to be ground. After grinding to pass a sixty mesh screen it was well mixed, quartered, and one quarter placed in a small, tightly covered, tin sample can, which, together with the remaining sample, was returned to the large can and again sealed with paraffin. After a sample was withdrawn from the small can for analysis the sample container was again returned to the large can and resealed.

## Experimental Methods

The determinations of water, $CO_2$, and loss on ignition were made in a gas fired combustion tube furnace provided with necessary purifying train and absorbers. The set up is shown in Figure 2.

Figure 1

Locations for Sampling Kiln Charge

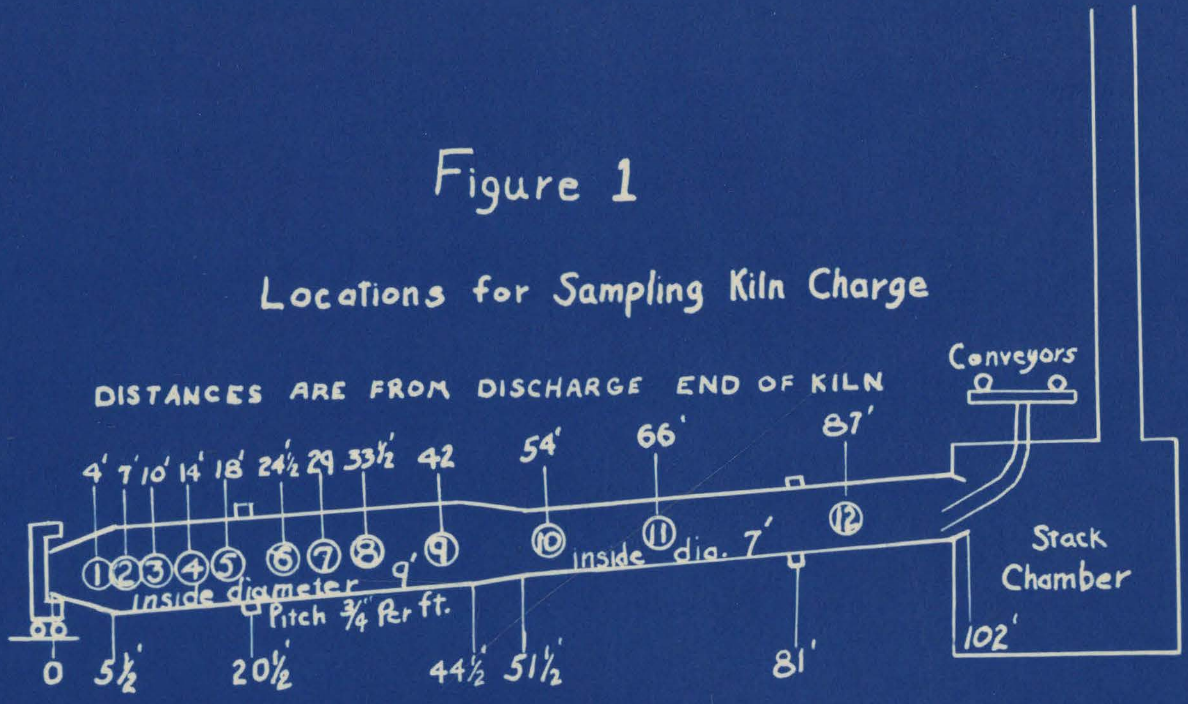


Figure 2

Combustion Train

The combustion tube was of silica, 7/8" inside diameter, 1 & 1/8" outside diameter. It was heated with three Fisher burners using a natural gas and air mixture. This heated zone was 9 inches long. The tube was protected from the direct flame by a closely fitting cover of sheet nickel. However, in spite of this, the tube slowly devitrified and after six months of continuous use was badly crystallized. Desicchlora (anhydrous Barium Perchlorate) was used to absorb the water. Ascarite (asbestos impregnated with NaOH) was the absorbent for $CO_2$. The absorbing train was composed of four Fisher Absorption bottles, the first two filled with desicchlora followed by two more containing a mixture of ascarite and desicchlora. The union between the first absorber and the silica tube was made by pulling down the end of the large tube and sealing a small clear quartz tube to this. The end of the small tube was ground to fit into the side tube of the first absorber. A tight fit was not desired, the union being made air-tight by a piece of pure India rubber tubing. The other end of the silica tube was connected to the purifying train by a long rubber stopper, one end of this fitting the end of the tube, the other end fitting into a piece of large rubber tubing which was taped around the silica tube. Runs made to determine the temperature of the end of the stopper exposed to the radiated heat from the interior of tube showed that it attained a maximum temperature of 40° C.

The temperature of the air coming from the exit end of the tube was found to be 38° C for the rate of approximately 2 liters per hour used in the determinations. Since this is safely below the decomposition temperature of the Hydrate of Barium Perclorate (120° C) no difficulties were experienced from this source. Blanks were run at frequent intervals and it was found that using a preignited Alundum boat and an occasional shaking of the purifying train to prevent channeling, no corrections were necessary for foreign water or $CO_2$.

The method of making a Determination was as follows: The absorbers were carefully wiped with a clean, dry, lintless towel and weighed. They were then inserted in the ignition train. A sample of the clinker was then weighed into a previously ignited Alundum boat and placed in the heating zone of the combustion tube with the help of a long wire. The tube was closed, stopcocks opened, and the water aspirator adjusted so that air at the rate of approximately 2 liters per hour was pulled through the train. A vacuum of 15mm of Mercury was necessary for this. The tube was then brought up to 1000° C in the course of an hour. Temperatures were measured with a chromel- alumel couple. It was found that four hours were necessary for the $CO_2$ to be completely liberated and swept out of the tube. The Aspirator was then disconnected, the absorbers allowed to come up to atmospheric pressure and then taken down and reweighed, the increase in weight being the $CO_2$ and the $H_2O$. The Boat was allowed to cool in the silica tube. It was then removed, placed in its weighing bottle and weighed. The loss in weight was reported as Loss on Ignition. Specific gravities were determined with a standard Le Chatelier Specific Gravity Bottle. The determinations of the free lime were kindly carried out by the Riverside Cement Company. In order to calculate the Recombination of CaO it was necessary to determine the $CO_2$ which came from $MgCO_3$ . Using a method described by Meade(1), the mean of several determinations gave a value of 3.9% $MgCO_3$ in the feed. The $CO_2$ from this amount of $MgCO_3$ is 1.9%. In the calculations of CaO liberated from the carbonates decomposed, this amount of $CO_2$ has been taken into account as coming from the $MgCO_3$ before any $CaCO_3$ decomposed. Since the relative amount of $CaCO_3$ to $MgCO_3$ is large this assumption causes little error in the calculations.

## Results and Discussion

The experimental results are given in Table I. The Loss on Ignition, $CO_2$ absorbed, and $H_2O$ data were checked to the nearest 0.1%. The check specific gravity determinations agreed to 0.003. Figure 3 shows graphically the changes in these values through the length of the kiln. The $H_2O$ content of the mix is small and this data has been replotted in Figure 3b on a different scale in order that the variations may be more clearly seen.

It is seen that there is a close agreement between the $CO_2$ Absorbed and the Loss on Ignition at all sampling points of the kiln. This is to be expected near the discharge end of the kiln where little water is left, but since it was thought that the ignition loss was merely the sum of the $H_2O$ and $CO_2$ driven off, a greater difference was expected at the head of the kiln. Column 7 of Table I shows how much variation there is between the Ignition loss and the total of the $CO_2$ and $H_2O$. The fact that this difference is negative in the case of the feed and positive elsewhere leads to the supposition that there was some material in the feed taking up Oxygen. A cylinder of Nitrogen was secured and two determinations were made on the feed and on sample eight using Nitrogen instead of Air to sweep out the $CO_2$ and $H_2O$. The results are shown in Table II.

TABLE I

| Sample Number | Description of General Appearance | Specific Gravity | Loss on Ignition % | % $CO_2$ Absorbed | % $H_2O$ Absorbed | Ig. Loss less $CO_2 + H_2O$ | Free Lime % |
|---|---|---|---|---|---|---|---|
| Feed | Light gray, soft, not gritty. | 2.744 | 31.8 | 31.3 | 1.4 | -0.9 | 0.9 |
| 12 | Light gray, soft, fine, not gritty. | 2.744 | 30.7 | 30.3 | 0.4 | 0.0 | 1.4 |
| 11 | Light tan, definite change from 12, not gritty. | 2.772 | 26.3 | 26.1 | 0.2 | 0.0 | 6.7 |
| 10 | Light tan small lumps present, slight tendency to form balls. | 2.793 | 23.1 | 22.7 | 0.1 | 0.3 | 11.7 |
| 9 | Slightly darker than 10. Larger lumps, very slight difference in color between these lumps and mix. | 2.888 | 15.4 | 14.8 | 0.1 | 0.5 | 19.6 |
| 8 | First visible evidence of clinker formation. Large lumps quite dark brown in center. Mix has brown specks. Gritty. | 2.890 | 9.4 | 8.9 | 0.2 | 0.3 | 26.1 |
| 7 | Large lumps of brown, gritty material. No evidence of fusion. Lumps easily broken. Tan color present. | 3.040 | 6.4 | 6.0 | 0.2 | 0.2 | 26.3 |
| 6 | Black specks plentiful. Tan color predominant. Lumps easily broken. Center of lump dark brown. No evidence of fusion. | 3.080 | 3.2 | 2.6 | 0.1 | 0.5 | 28.2 |
| 5 | Definite color change from 6. Mix dark gray. Lumps hard and homogenous. Apparently partially fused. Some tan lumps still present. | 3.202 | 0.4 | 0.2 | - | 0.2 | 5.1 |
| 4 | Slightly darker than 5. Tan particles covering some of the softer lumps. Very few fines. Particles mostly show no evidence of fusion. | 3.202 | 0.3 | 0.1 | - | 0.2 | 4.2 |
| 3 | More fine than 4. Particles crumble under pressure. More evidence of fusion. Slight trace of tan. | 3.178 | 0.3 | 0.1 | - | 0.2 | 2.7 |

Table I (cont)

| Sample Number | Description of General Appearance | Specific Gravity | Loss on Ignition % | $CO_2$ % | $H_2O$ % | Ig. Loss minus $CO_2+H_2O$ | Free Lime |
|---|---|---|---|---|---|---|---|
| 2 | Particles are fused. Fracture on applied pressure. Very hard. Quite dark in color. Fractures present uniform appearance | 3.158 | 0.3 | 0.1 | - | 0.2 | 0.3 |
| 1 | Very hard. Tan particles not present. Particles fracture on applied pressure. Color is greenish gray | 3.187 | 0.2 | - | - | 0.2 | 0.1 |
| Clinker | Particles scratch glass. Fracture shows uniform color. Very small pores present. Color is dark green. | 3.190 | 0.1 | - | - | 0.2 | 0.1 |

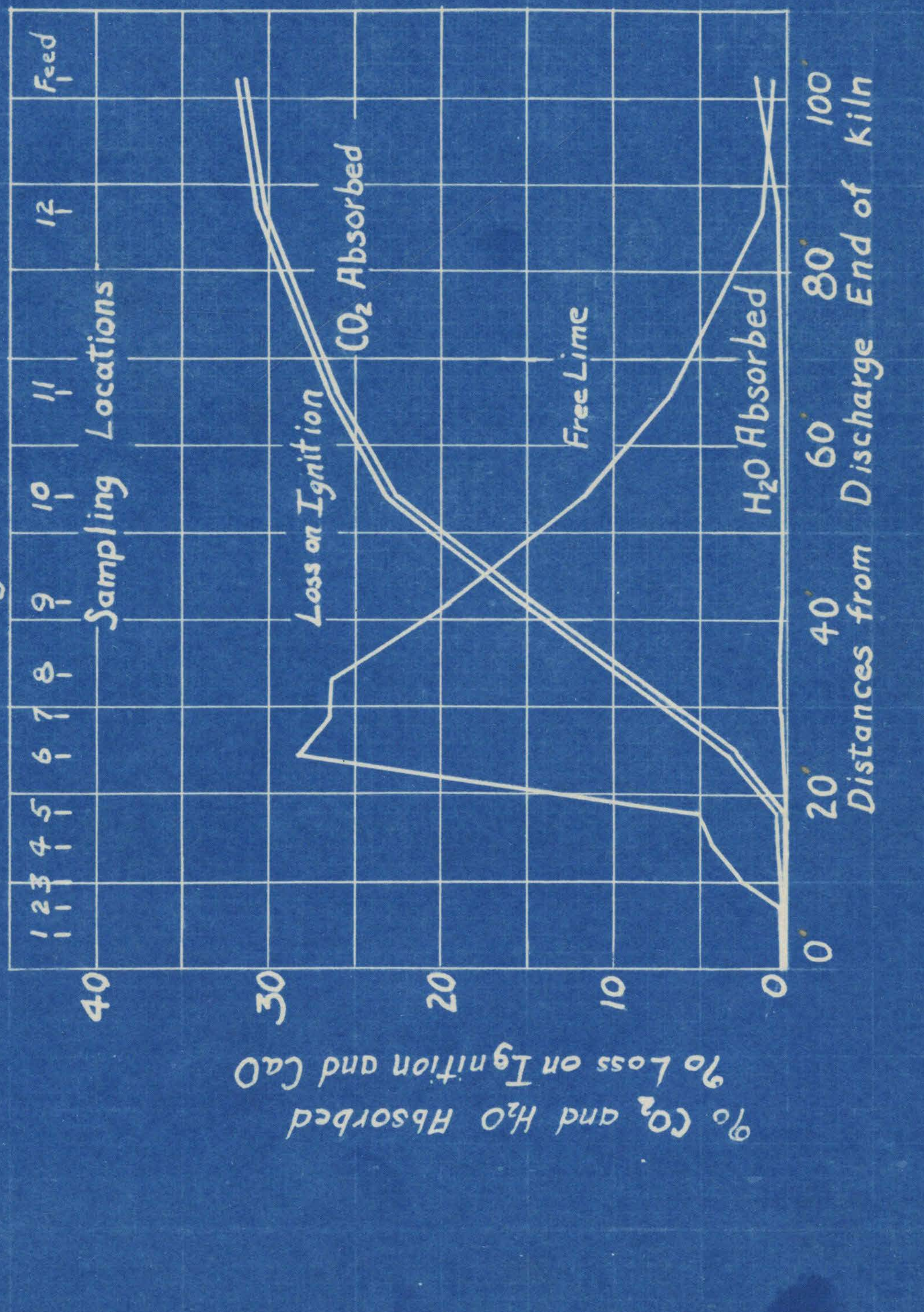
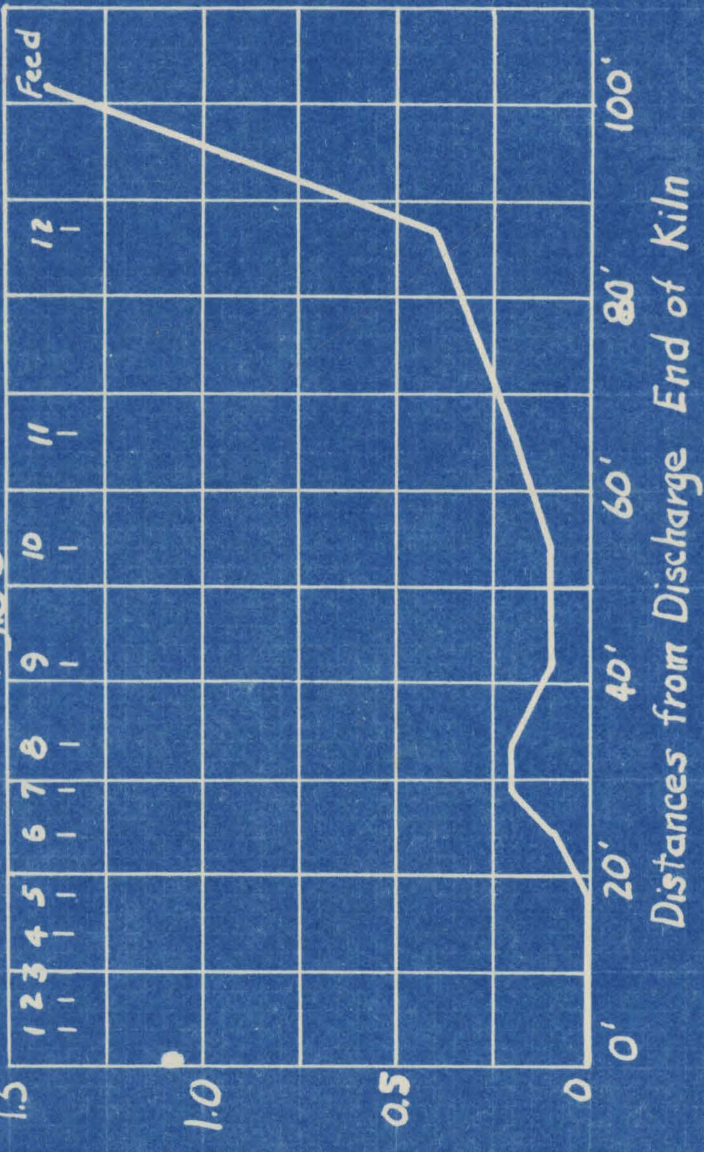


Fig 3

Sampling Locations
1 2 3 4 5 6 7 8 9 10 11 12 Feed
Loss on Ignition
CO₂ Absorbed
Free Lime
H₂O Absorbed
0
20
40
60
80
100
Distances from Discharge End of Kiln
0
10
20
30
40
% CO₂ and H₂O Absorbed
% Loss on Ignition and CaO

Fig. 3b


Feed
1
2
3
4
5
6
7
8
9
10
11
12
0'
20'
40'
60'
80'
100'
Distances from Discharge End of Kiln
1.5
1.0
0.5
0
% $H_2O$ Absorbed

## Table II

| Sample | Ig.Loss in Air | Ig.Loss in Nitrogen | $CO_2$ | $H_2O$ | Difference between Ig. Loss & $CO_2 + H_2O$ |
|---|---|---|---|---|---|
| Feed | 31.7% | 32.2% | 31.3% | 1.1% | -0.2 |
| Feed | 31.8 | 32.2 | 31.2 | 1.2 | -0.2 |
| 8 | 9.4 | 9.3 | 8.9 | 0.2 | 0.2 |
| 8 | 9.4 | 9.2 | 8.8 | 0.2 | 0.2 |

It is seen that using Nitrogen, the difference in the total $CO_2$ and $H_2O$ and the Loss on Ignition for the feed is reduced to -0.2. This tends to strengthen the supposition that Oxygen is absorbed by the feed if the heating is carried out in air. Since the Nitrogen was obtained from liquid air, the negative difference here may be due to some Oxygen present as impurity. The positive difference is again obtained with Sample 8, although less than before. A series of determinations of Ignition Losses were then made in air in order to study the rate of loss over various periods of time. Platinum crucibles were used and the blast burners were not changed after the run was started. The results are given in Table III.

## Table III

| Sample | Time of Heating | Loss in % |
|---|---|---|
| 12 | 12 hours | 31.2 |
| 10 | 12 " | 23.5 |
| 8 | 12 " | 9.9 |
| 6 | 12 " | 4.1 |
| Feed | 20 minutes | 31.3 |
| " | 1 hour | 32.0 |
| " | 2½ hours | 32.2 |
| " | 5½ " | 32.3 |
| " | 16 " | 32.4 |
| 6 | 15 minutes | 2.48 |
| 6 | 30 " | 2.79 |
| 6 | 1 hour | 3.04 |
| 6 | 1½ hours | 3.12 |
| 6 | 2½ " | 3.14 |
| 6 | 4½ " | 3.20 |
| 4 | 15 minutes | 0.215 |
| 4 | 45 " | 0.229 |
| 4 | 1¾ hours | 0.463 |
| 4 | 3¾ " | 0.491 |
| 4 | 4½ " | 0.500 |

These data indicate that the ignition loss may be increased greatly by increasing the time of ignition. Figure 4 gives graphically the rate at which the various samples lose weight on ignition. The loss after 4 and ½ hours is taken as 100% in each case.

The $H_2O$ absorbed curve in figure 3b shows that water is driven out of the mix very rapidly. The material contains very little free moisture; holding a sample of the feed at 105° C for 5 days gave a loss of 0.09%. The slight rise at Stations 8 and 7 is attributed to moisture taken up after the samples had been ground. Work done on samples which had been in tightly covered tin sample cans (not

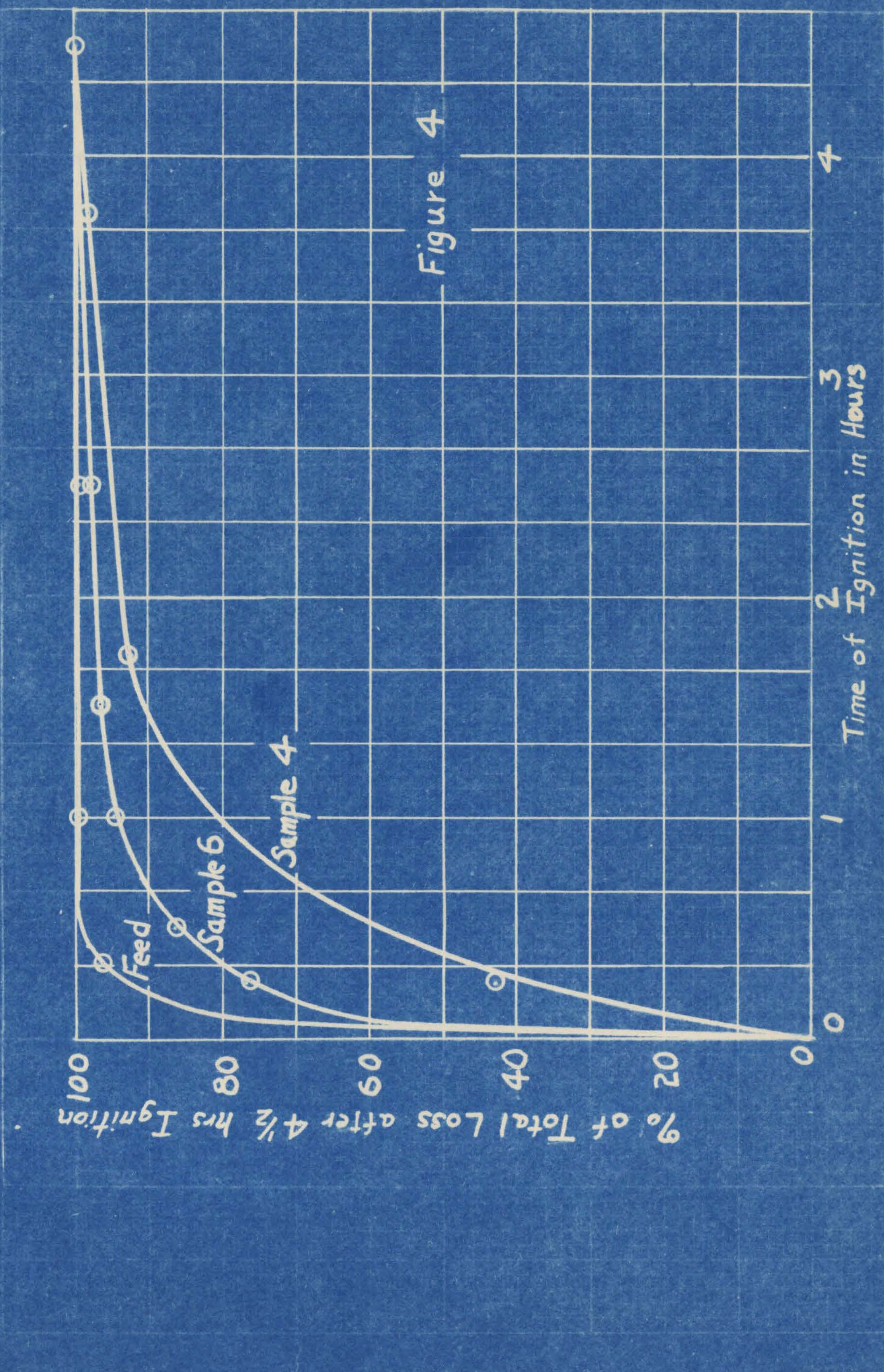


Figure 4

% of Total Loss after 4½ hrs Ignition
100
80
60
40
20
0
Time of Ignition in Hours
0
1
2
3
4
Feed
Sample 6
Sample 4

sealed) for a year show that in this region of the kiln the samples have a water content of around 9.0% while the feed runs only 1.5%. The data in Table IV indicate that the charge is highly hygroscopic throughout the length of the kiln.

## Table IV

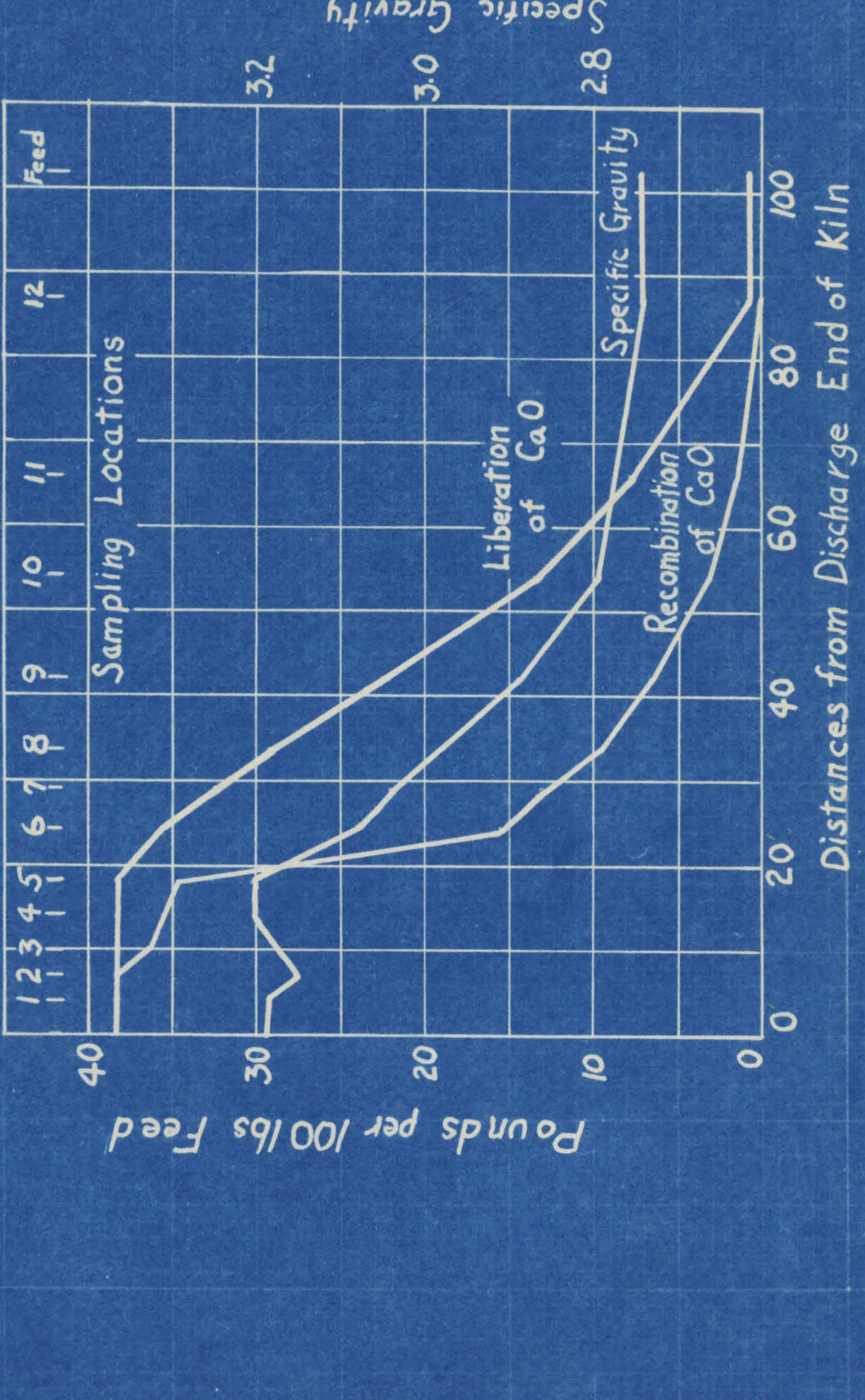
| Sample | Initial Loss on Ignition<br>% | Loss on Ignition 4 months later<br>% | Difference | Free Lime Content<br>% |
|---|---|---|---|---|
| Feed | 31.8 | 31.7% | -0.1 | 0.9 |
| 10 | 23.1 | 23.4 | 0.3 | 11.7 |
| 9 | 15.4 | 17.2 | 1.8 | 19.6 |
| 8 | 9.4 | 12.0 | 2.6 | 26.1 |
| 7 | 6.4 | 10.3 | 3.9 | 26.3 |
| 6 | 3.2 | 8.2 | 5.0 | 28.2 |
| 4 | 0.3 | 1.7 | 1.4 | 4.2 |
| 2 | 0.3 | 0.4 | 0.1 | 0.3 |
| Clinker | 0.1 | 0.6 | 0.5 | 0.1 |

Table V gives the experimental data converted into pounds of material at the different stations of the kiln based on 100 pounds of feed. This conversion is made on the assumption that the non-volatile material, as determined in the feed, travels through the kiln with practically no loss or gain in weight. Thus, the weight of the original 100 pound charge of feed at any point in the kiln can be calculated from the ignition loss at that point and the ignition loss of the feed. Direct multiplication of this weight by the percentage of the $CO_2$ and the CaO present gives the quantities of these compounds present at the various stations. The decrease in $CO_2$ content between the feed and the charges at the stations corrected for the 1.9 pounds attributed to the MgCO is converted into CaO and this quantity plus the initial CaO determined in the feed is tabulated as "CaO Liberated". The difference between this figure and the "CaO Determined" at that station is given as "CaO Recombined". The last three columns of the table give the per cent of the total CaO from Carbonates that has been liberated, the per cent of the CaO liberated that has recombined and the per cent total CaO from Carbonate that has recombined. In Figure 5 and 6 these results have been plotted against length of kiln. It is seen from Figure 5 that the rate of CaO liberation is rapid and practically constant until it is completed about twenty feet from the discharge end of the kiln. The recom-

## TABLE V

| Sample Number | Basis - 100 pounds Feed | | | | | % of Total CaO Liberated | % of CaO Liberated Recombined | % of Total CaO Recombined |
|---|---|---|---|---|---|---|---|---|
| | Total Weight Present | Weight $CO_2$ Present | Initial CaO and CaO Liberated | CaO Determined | CaO Recombined | | | |
| Feed | 100 | 31.3 | 0.9 | 0.9 | - | 2.3 | - | |
| 12 | 98.5 | 29.8 | 0.9 | 1.4 | - | 2.3 | - | |
| 11 | 92.7 | 24.2 | 7.8 | 6.2 | 1.6 | 20.4 | 20.5 | 4.2 |
| 10 | 88.8 | 20.5 | 13.5 | 10.4 | 3.1 | 35.2 | 22.9 | 8.1 |
| 9 | 80.7 | 12.4 | 22.5 | 15.8 | 6.7 | 58.8 | 29.8 | 17.5 |
| 8 | 75.4 | 7.1 | 29.3 | 19.7 | 9.6 | 76.5 | 32.8 | 25.1 |
| 7 | 73.0 | 4.7 | 32.3 | 19.2 | 13.1 | 84.4 | 40.7 | 34.2 |
| 6 | 70.6 | 2.3 | 35.4 | 19.9 | 15.5 | 92.5 | 43.8 | 40.5 |
| 5 | 68.6 | 0.14 | 38.1 | 3.5 | 34.6 | 99.5 | 90.7 | 90.4 |
| 4 | 68.5 | 0.1 | 38.2 | 2.9 | 35.3 | 99.7 | 92.5 | 92.1 |
| 3 | 68.5 | 0.1 | 38.2 | 1.8 | 36.4 | 99.7 | 95.3 | 95.0 |
| 2 | 68.5 | - | 38.3 | 0.2 | 38.1 | 100.0 | 99.5 | 99.5 |
| 1 | 68.4 | - | 38.3 | 0.1 | 38.2 | 100.0 | 99.8 | 99.8 |
| Clinker | 68.3 | - | 38.3 | 0.1 | 38.2 | 100.0 | 99.8 | 99.8 |

Fig. 5

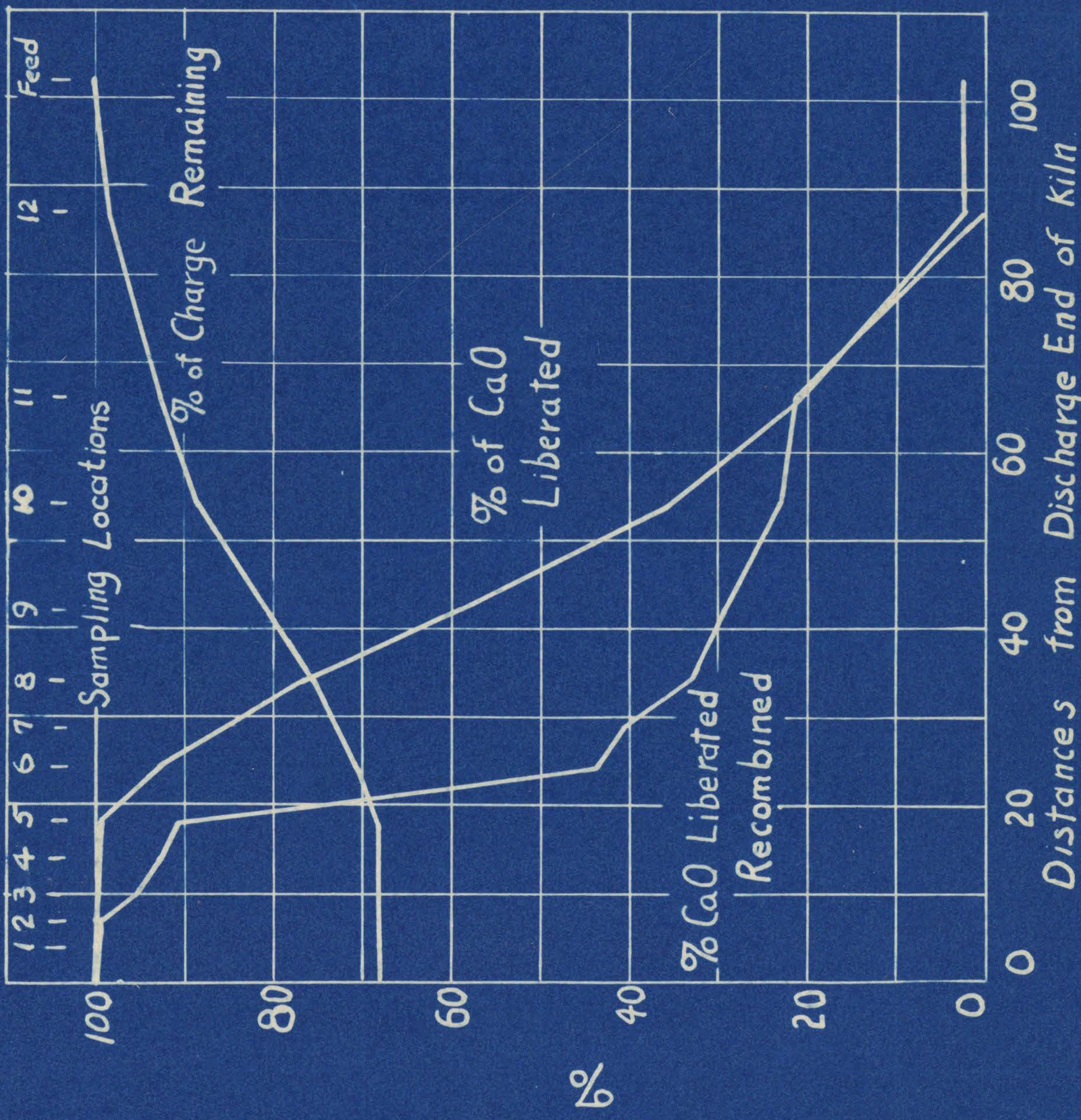

Sampling Locations
1 2 3 4 5 6 7 8 9 10 11 12 Feed
Specific Gravity
3.2
3.0
2.8
Liberation of CaO
Recombination of CaO
Specific Gravity
40
30
20
10
0
Pounds per 100 lbs Feed
0
20
40
60
80
100
Distances from Discharge End of Kiln

bination of the lime is slower at the start but the reaction increases more rapidly, much like an autocatalytic one. It slows down after about 91% of the CaO has reacted but continues at an appreciable rate until within seven feet of the mouth of the kiln. This final twenty feet is evidently the portion of the kiln in which most of the reaction between $2CaO.SiO_2$ and CaO takes place.

The specific gravity changes of the charge are also shown in Figure 5. The curve follows the Liberation of CaO, reaching a maximum at the point where the CaO is a maximum. The following sharp and decided fall in the curve has not been explained. It may be due to the conversion of the "$\beta$" $2CaO.SiO_2$ into the "$\gamma$" $2CaO.SiO_2$ when the sample cooled after being withdrawn from the kiln. This change is accompanied by an increase in volume of about 10%.

In Figure 6, the per cent of the total CaO liberated from $CaCO_3$ and the per cent of this quantity to have recombined is shown. As in figure 5 the amount of CaO formed is seen to vary as a straight line function of the distance the charge has traveled down the kiln. The "per cent CaO Liberated Recombined" curve emphasizes the fact that the initial recombination of the free Lime is rapid. The recombination then follows much the same course as shown in Figure 5 for the remaining length of the kiln. The "% of Charge Remaining" curve is the Loss on Ignition curve of Figure 3 shown on a flattened scale. It is seen that the clinker comprises 68% of the original charge.

Fig. 6


Sampling Locations
1 2 3 4 5 6 7 8 9 10 11 12 Feed
% of Charge Remaining
% of CaO Liberated
% CaO Liberated Recombined
%
100
80
60
40
20
0
0
20
40
60
80
100
Distances from Discharge End of Kiln

## Summary

In summarizing it is seen that during the first fifteen feet of the kiln, most of the free and combined water has been driven off. Evidence is given that indicates an oxidation takes place in this portion of the kiln. The decomposition of the carbonate then progresses practically linearly with respect to the distance travelled down the kiln until the reaction is completed about 20 feet from the discharge end. The recombination of the lime formed is slow at first but increases rapidly to within 18 feet of the kiln discharge where 90% of the reaction has taken place, 50% of it occurring in the last third of this distance. The reaction then proceeds more slowly and is complete about 7 ft. from the discharge point. The charge is hygroscopic throughout the length of the kiln and the samples must be hermetically sealed if they are to be preserved. Due to the presence of volatile materials (presumably largely $K_2O$) in addition to $CO_2$ and $H_2O$, loss on ignition should be made under carefully controlled conditions as to temperature and time of heating if the results are to be comparable.

These data in themselves are too meager to warrant any change in kiln design or firing conditions in the production of Portland Cement. It was the plan of this research to study the effect of various changes in the raw mix and firing conditions, but owing to the impossibility of securing samples this procedure had to be abandoned. The data given can only be taken as representative of the conditions prevailing at the time of sampling, namely of normal conditions of production as to firing, rate of burning, and composition of the raw mix.

Acknowledgment:

Acknowledgment is due the Riverside Cement Company for their coöperation in securing these samples and for making certain determinations which this laboratory was not equipped to carry out and to Dr. W. N. Lacey for his assistance and suggestions during the course of these investigations.

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# PART B

# A METHOD FOR THE PRODUCTION OF ANHYDROUS SODIUM SULFATE

## A Method for the Production of Anhydrous Sodium Sulfate

A chemical that is becoming of increasing importance for commercial use is Anhydrous Sodium Sulfate. Laury (1) gives a survey of the amounts used by various industries in 1925 as follows:

| | |
|---|---|
| Glauber's Salt ($Na_2SO_4.10H_2O$) | 57,000 tons |
| Sodium Sulfite (from $NaHSO_3$) | 18,660 " |
| Wood pulp requirement in U.S. | 22,000 to 56,000 tons |
| Glass manufacture | 60,000 tons |

In addition Canada requires about 50,000 tons annually and is constantly increasing the demand.

At the present time this demand is almost entirely supplied by salt cake obtained as the by-product in the manufacture of hydrochloric acid by sulfuric acid and sodium chloride. In 1925, 139,000 tons of salt cake were sold at an average price of $17.00 per ton. This does not, however, represent the potential market for $Na_2SO_4$. The product obtained as salt cake is very impure and not suitable as a source of $Na_2O$ for many of processes in glass and paper manufacture. These industries need an anhydrous sodium sulfate of approximately 96% purity with certain foreign constituents, such as chloride, below definite limits. The sale of the salt of this grade in 1925 amounted to

2,100 tons at an average price of $61.00 per ton. Obviously at this price it cannot compete with Sodium Carbonate as the source of $Na_2O$.

In view of the fact that there are numerous natural salt deposits in the United States, particularly in the western section, that run high in $Na_2SO_4$, the present study was undertaken in order to determine a feasible way of manufacturing anhydrous sodium sulfate of suitable purity from this source of raw material. These deposits sometimes run as high as 98% $Na_2SO_4$ (1) with the chief impurities consisting of sodium carbonate, sodium chloride, and dirt with some organic matter. Usually, however, the Sodium Sulfate is present in these deposits as the decahydrate $Na_2SO_4.10H_2O$ and this form, known as Glauber's Salt, was chosen as the raw material for this work.

Figure 1 gives the equilibrium relations between Sodium Sulfate and Water over the temperature range from the freezing point to the boiling point of the saturated solution. It is seen that a transition occurs near 33° C where the hydrated form changes into the anhydrous, and that the solubility curve reverses. It is this reverse solubility that makes the preparation of the anhydrous phase by evaporation of a saturated solution very difficult. At the point of contact of the solution and the heating surfaces in an evaporator, a higher temperature

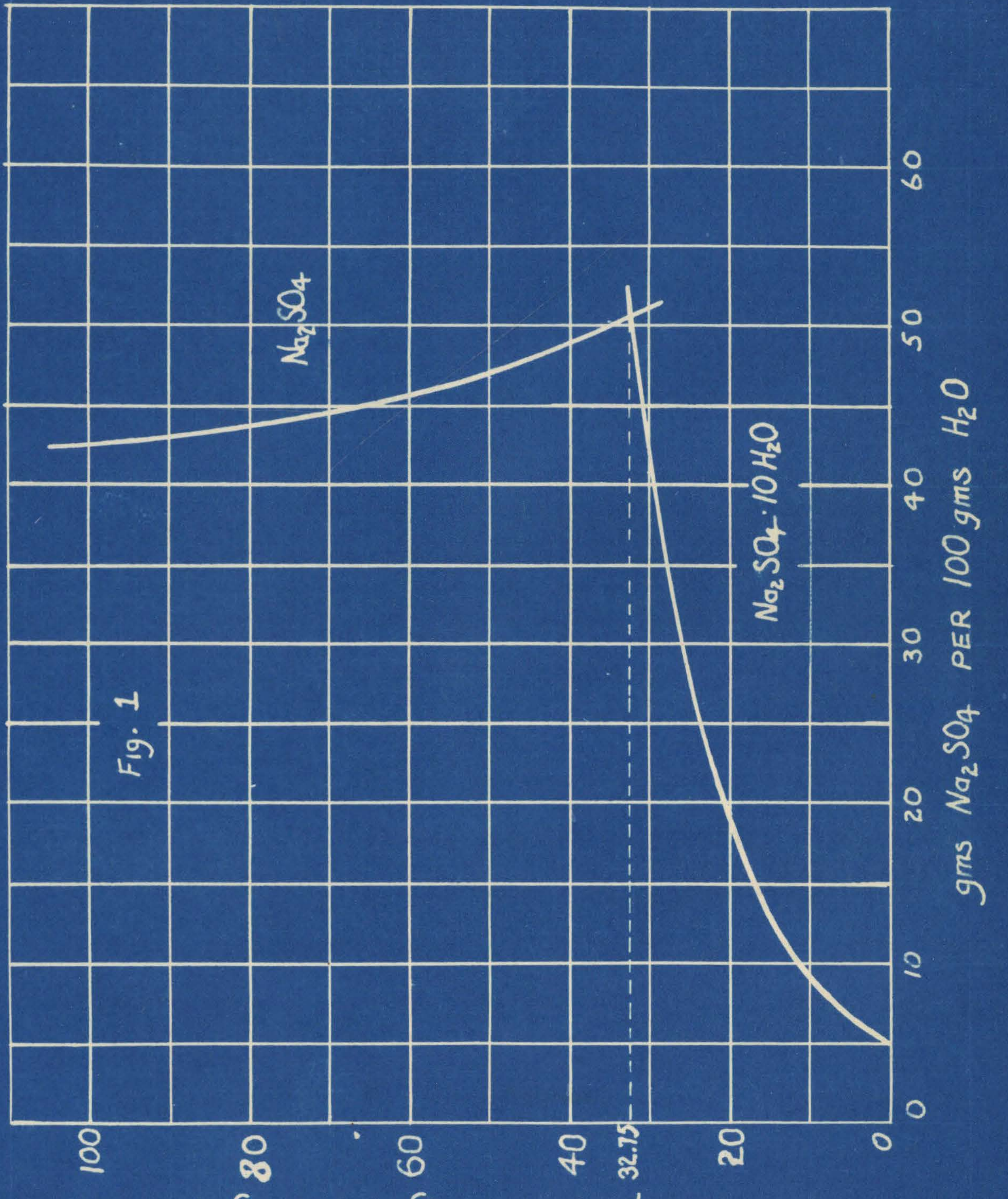


Fig. 1
$Na_2SO_4$
$Na_2SO_4 \cdot 10H_2O$
0
10
20
30
40
50
60
gms $Na_2SO_4$ PER 100 gms $H_2O$
0
20
32.75
40
60
80
100
Temperature Degrees Centigrade

is maintained than in the main body of the liquor. If this liquor is saturated with $Na_2SO_4$ above the transition temperature, Sodium sulfate is precipitated as a hard scale on the heating surfaces and this scale greatly diminishes the rate of heat transfer to the main body of the solution. Obviously, unless scrapers are provided for the surface, this scale will continually increase in thickness as evaporation proceeds. Badger, (2) in the development of apparatus for the evaporation of solutions of salts with reverse solubility curves, found that the rate of heat transfer dropped in a few hours to a value that was much too low for economical production. He succeeded in designing equipment for the evaporation of such solution by using a tubular preheater and then flashing this heated liquor in a double effect evaporator heated by a steam basket. It was necessary to provide two preheaters for each effect because scale formation was so rapid that the tubes had to be washed out every hour. The double effect evaporator was washed out every twelve hours.

As it was desired to study various possibilities for the production of Sodium sulfate, the set-up used in these experiments included a single effect Vacuum evaporator provided with closely scraped, machined, heating surfaces, a centrifugal pump to circulate the liquor and sludge between the evaporator and settling vat, a melting vat provided with steam coils, and a centrifugal separator for the separation of the sludge and liquor. It is seen from the solubility curve that the anhydrous salt may be obtained by melting the decahydrate and separating the liquid and solid phases above 33° C. This method was used in Run 1. Three hundred and fifty pounds of technical Glauber's salt were added in the melting vat to a system containing a saturated solution of sodium sulfate contaminated with sodium carbonate and chloride. This resulting sludge and liquor were drawn into the vacuum evaporator and circulated to the settling vat by means of the pump. The liquor was then returned to the melting vat while the solid was recovered by means of the centrifugal separator. The run lasted about six hours; samples of the product were taken from the centrifugal at intervals during this time. Analysis of these are given in Table I.

Table I

| Sample No. | Sodium Carbonate | Sodium Chloride |
|---|---|---|
| 1. | 0.16% | 0.024% |
| 2. | 0.14% | 0.016% |
| 3. | 0.28% | 0.055% |
| 4. | 0.22% | 0.032% |

It is seen that the samples are of about the same composition throughout the run. The product was good from a physical standpoint; 85% of the crystals were retained on an 80 mesh screen. There was no tendency for them to dust. There was a slight brown color which probably was due to iron picked up in the system.

Very little water was evaporated in this run; the purpose of the evaporator was to keep the liquor well above the transition temperature. A temperature of 90° C was maintained in the settling vat. The temperature of the liquor dropped about 10° through the separator and was returned to the evaporator at about 70°C. A hard scale deposited on all heating surfaces. The scrapers were binding badly in the evaporator by the time the run was concluded.

Fifteen pounds of impure sodium carbonate were added to the solution obtained from Run I which had increased considerable in volume due to the water from the Glauber's salt. The solution was quite dark in color and foamed badly in the evaporator. Sodium Sulfate was produced by evaporation of the water from this solution. The evaporation was slow; the deposited scale very effectively reduced heat transfer and the tendency of the solution to foam made it necessary to keep the temperature of the solution low so that the froth could be controlled by breaking vacuum. The samples taken and their analyses are given in Table II. (Sample six is the unwashed product as it came from the centrifugal. Number seven was thoroughly washed with hot water.)

Table II

| Sample No. | Identification | Sodium Carbonate | Sodium Chloride |
|---|---|---|---|
| 5 | Solution in settling vat at beginning of run | 1.2% | 0.07% |
| 6 | Unwashed product | 0.5% | 0.04% |
| 7 | Hot water washed product | 0.5% | 0.02% |
| 8 | Solution from settling vat at end of run | 1.7% | 0.08% |

The product obtained by evaporation was composed of larger crystals than that made by melting Glauber's salt. Washing with hot water improved the handling properties of the crystals in that the cake was not so tightly packed in the centrifugal or so hard to get loose from the sides as it was when not washed. As in Run I the scrapers rubbed quite hard against the deposited scale, the entire evaporator vibrating from the violence of the action at times.

As a final run a Sodium Sulfate solution was nearly saturated with Sodium Chloride and this solution circulated through the system. The $Na_2SO_4$ was precipitated entirely by evaporation. The solution did not foam so badly as in Run II. The results are given in Table III. The samples are from successive centrifugal loads.

Table III

| Sample No. | Centrifugal Load | Sodium Carbonate | Sodium Chloride |
|---|---|---|---|
| 9 | first | 0.6% | 0.2% |
| 10 | second | 0.6% | 0.4% |
| 11 | third | 0.6% | 0.7% |
| 12 | fourth | 0.6% | 0.8% |
| 13 | fifth | 0.6% | 1.6% |

All these samples were well washed with hot water. The crystals differed little from those obtained in Run II. As usual, evaporation was slow, about six hours being required to collect the five centrifugal loads of product.

A survey of these runs gives the following results: Sodium Carbonate is the hardest to get out of the finished product. Even in a nearly saturated solution of Sodium Chloride, Sodium Sulfate will precipitate with little sodium chloride impurity; but a solution containing only 2% Sodium Carbonate will give a product with about 0.5% of the Carbonate present. This is thought to be due to the similarity in the solubility curves of the two salts, Sodium Carbonate and Sodium Sulfate, and the fact that a double salt crystalizes from a solution of the two when concentrated above 35° C. The data agree with the findings of other workers in regard to the salting out of the sulfate on the heating surfaces. The success of the evaporation in these runs is attributed to the scrapers in the evaporator. However a commercial size evaporator with machined heating surfaces scraped to within a sixteenth of an inch would be prohibitive in cost. The very satisfactory results obtained by melting the Glauber's Salt in a hot saturated solution of Sodium Sulfate indicate that the most satisfactory way to manufacture the anhydrous material is to heat a saturated solution by direct means and to use this liquid as the medium in which to melt the solid Glauber's Salt.

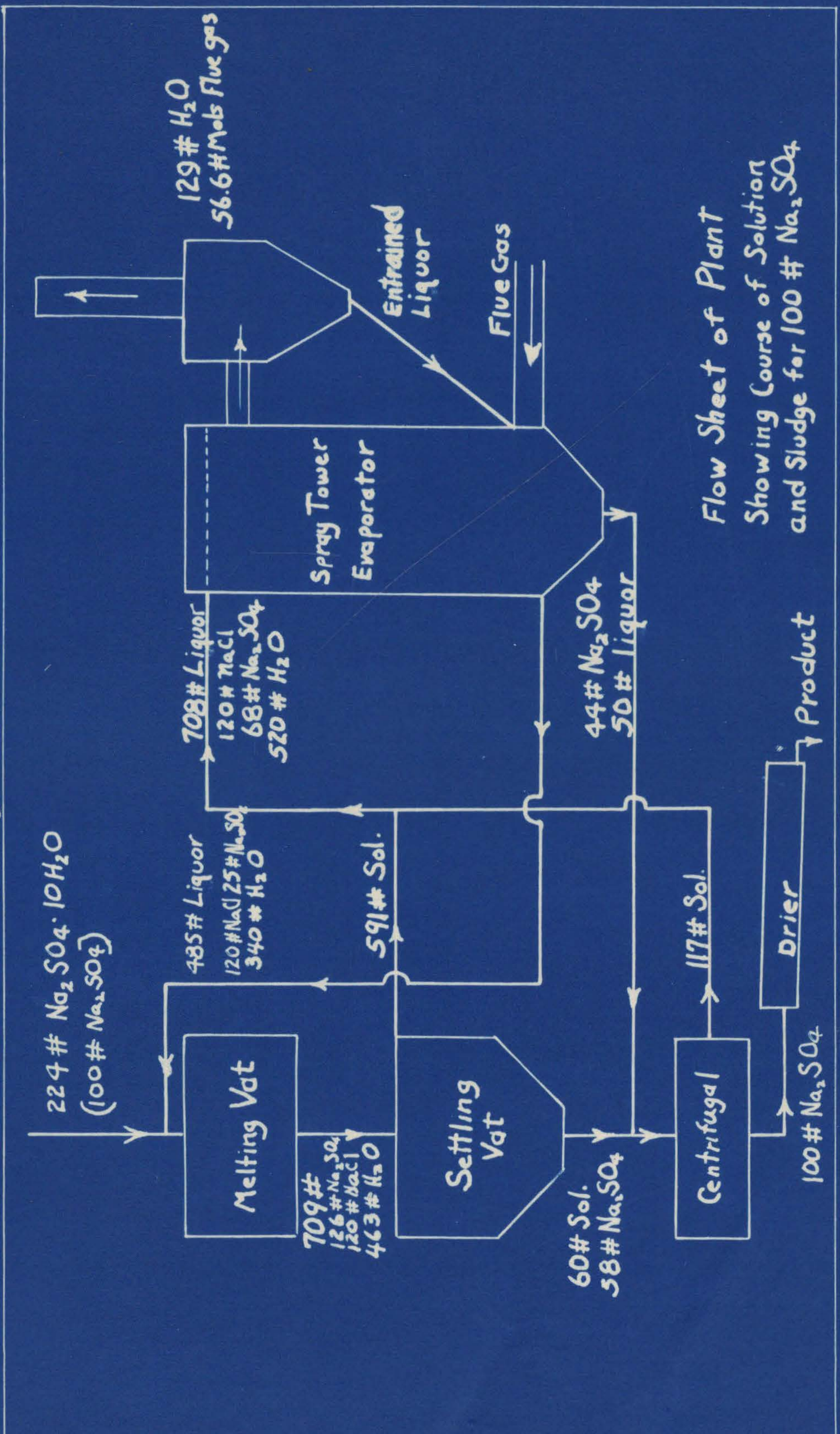
The use of live steam as a means of direct heating has several disadvantages, among which are:

The steam must be made entirely from make-up water.

Extra water is added to the solution.

The use of hot, permanent gases as the source of heat eliminates the above mentioned difficulties and also offers a means of using effectively the waste heat in flue gas. Likewise this method has its disadvantages, among which the inefficiency and the large volume of gas necessary to handle are the most important. However the latter method was thought to offer the best possibilities and the following plant was designed on this basis.

Figure 2



Flow Sheet of Plant
Showing Course of Solution
and Sludge for 100 # $Na_2SO_4$

Figure II is a schematic flow sheet of the plant showing the course of the sludge and liquor in the process. It is based on 100 pounds of Sodium Sulfate fed into the melting vat. The process consists essentially of circulating enough liquor at a sufficiently high temperature to melt the Glauber's Salt and then evaporating the water carried in as water of crystalization in a spray tower evaporator. If Sodium Chloride is present in the raw material, then the system will eventually become saturated with it and a small amount of the liquor will need to be discarded continually so that no Sodium Chloride will be precipitated in the tower. This flow sheet assumes a saturated solution of Sodium Chloride circulated to the melting vat, but since the amount discarded will depend on the analysis of the raw materials no attempt has been made to estimate this quantity. Likewise the free moisture coming in with the Glauber's Salt has been considered as balancing the water carried out by the $Na_2SO_4$ to the drier.

<u>Data and Assumptions:</u>

Heat of fusion of $Na_2SO_4\ 10H_2O$ 92.3 B.T.U./#
Specific Heat of Sol. 0.8
Ave. Specific Gravity of Sol. 1.3
Assume flue gases into tower at 800° F and out at 300° F
Circulate liquor into tower at 100° F

Liquor withdrawn from tower at 215° F

Temperature of Raw Material 50° F

Circulating liquor for melting, working between 215° and 130° F

Liquor Sat. at 215° F with NaCl + $Na_2SO_4$ contains 24.7% NaCl and 5.1% $Na_2SO_4$

Liquor at 130° F with 18% NaCl contains 10.6% Na SO

**Basis:**

100 # $Na_2SO_4$ (equivalent to 224 # $Na_2SO_4$ $10H_2O$)

Heat required to melt the Glauber's Salt and bring it to 130° F

224 x 92.3 = 20,700 B.T.U. (melting)

0.8 x 224 (130-50) = 14,300 B.T.U. for heating

Liquor necessary to circulate to supply this heat:

$$\frac{35,000}{(215-130) \times .8} = 485 \text{ \# required}$$

## BALANCES ON SYSTEM

### Melting Vat

| In | | Out | |
|---|---|---|---|
| 485# liquor (circulating) | 120# NaCl<br>25# $Na_2SO_4$<br>340# $H_2O$ | 58# $Na_2SO_4$ (Sludge) | |
| 224# Glauber's Salt | | 651# liquor | 463# $H_2O$<br>120# NaCl<br>68# $Na_2SO_4$ |
| 709# total | | 709# total | |

### Settling Vat

| In | | Out | |
|---|---|---|---|
| 651# liquor | 463# $H_2O$<br>120# NaCl<br>68# $Na_2SO_4$ | 60# liquor to centrifugal | |
| | | 58# $Na_2SO_4$ " " | |
| 58# $Na_2SO_4$ | | 591# to tower | 110# NaCl<br>63# $Na_2SO_4$<br>418# $H_2O$ |
| 709# | | 709# | |

### Centrifugal

| In | | | Out | |
|---|---|---|---|---|
| 60# liquor | 11# NaCl<br>5# $Na_2SO_4$<br>44# $H_2O$ | from settling vat | 100# $Na_2SO_4$ to drier | |
| 58# $Na_2SO_4$ | | | | |
| 50# liquor | 12# NaCl<br>3# $Na_2SO_4$<br>35# $H_2O$ | from tower | 117# liquor to tower | 23# NaCl<br>10# $Na_2SO_4$<br>84# $H_2O$ |
| 44# $Na_2SO_4$ | | | | |
| 5# wash water | | | | |
| 217# | | | 217# | |

### Tower

| In | | Out | | |
|---|---|---|---|---|
| 591# liquor from settling vat | 110# NaCl<br>63# $Na_2SO_4$<br>418# $H_2O$ | 485# liquor recirculated | 120# NaCl<br>25# $Na_2SO_4$<br>340# $H_2O$ | |
| | | 44# $Na_2SO_4$ | | to centrifugal |
| 117# liquor from centrifugal | 23# NaCl<br>10# $Na_2SO_4$<br>84# $H_2O$ | 50# liquor | 12# NaCl<br>3# $Na_2SO_4$<br>35# $H_2O$ | |
| | | 129# $H_2O$ evaporated | | |
| 708# | | 708# | | |

## TOWER DESIGN

Basis: 5 ton per hr.

Liquor in at 100°F out at 215°F

Liquor required 708 x 20 x 5 = $\frac{\text{70,800\# liquor to tower}}{\text{hr.}}$

70,800 x 8 x 115 = 6,810,000 B.T.U. per hr. to heat liquor

12,900 x 965 = 12,450,000 B.T.U. per hr. to evaporate $H_2O$

Total B.T.U. supplied in tower per hr. 19,260,000

Flu gases in at 800°F out at 300°F

Circulating liquor out at $\frac{215}{585}$ in at $\frac{100}{200}$

$$\Delta t = \frac{585 - 200}{2.3 \log \frac{580}{200}} = \frac{385}{2.3\ (.463)} = 357^{\circ}$$

h (H) (from W.L.& Mc.) = 1.5 B.T.U. /min/F /$ft^3$

= 90 B.T.U. /hr./F /$ft^3$

90 x 357 = 32,100 B.T.U. /hr./$ft^3$

$\frac{19,260,000}{32,100}$ = 600 cubic ft. required in tower

Assume factor of 3 giving 1800 cu ft.

Assume gas velocity through tower as 5 ft/sec.

From W.L. & Mc. MCp 800° = 5200 B.T.U.

MCp 300° = 1800 B.T.U.

3400 B.T.U.

$\frac{19,260,000}{3400}$ = 5660 # Mols /hr. = 1.57 # Mol/Sec.

$\frac{1.57 \times 359 \times 1010}{492 \times 5}$ = 232 sq. ft. area of tower cross section

Thus a 17' tower with an effective height of 15 ft. provides an ample safety factor.

Assuming waste heat is utilized from boilers, which absorb 25% of the heat derived from the fuel oil and 60% efficiency is secured in the tower:

$$\frac{19,260,000}{17,000 \times .75 \times .6 \times 10,000} = .25 \text{ \# oil/\#}Na_2SO_4 \text{ Produced}$$

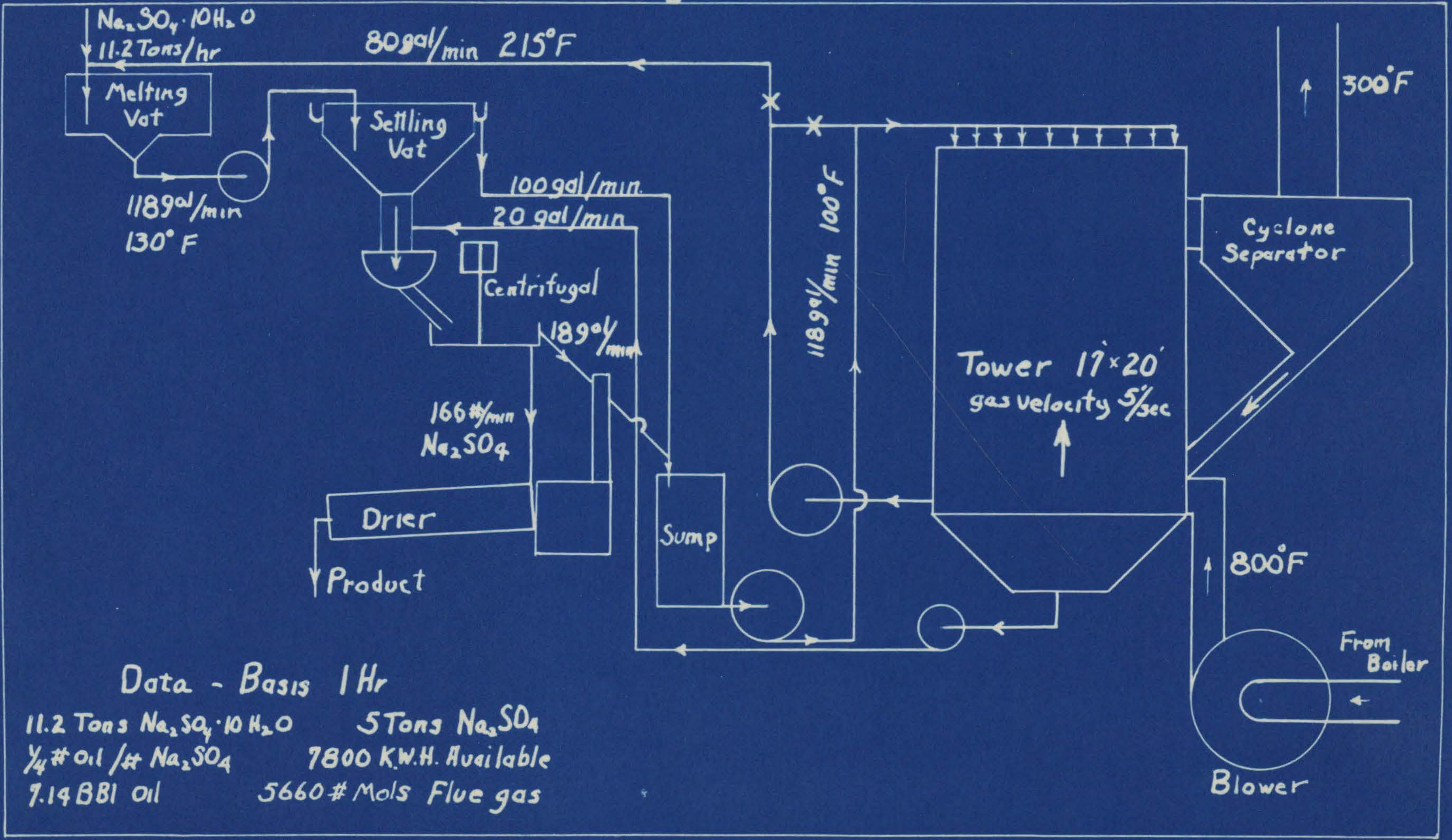
A plant producing 5 tons of $Na_2SO_4$ per hr. would then require 2500 # oil/hr or $\frac{2500}{350} = 7.14 \frac{BBl}{hr}$

at $1.50 per BBl the fuel cost per ton of $Na_2SO_4$ would be $\frac{7.14 \times 1.5}{5} = \$2.12$

The power plant would have available (assuming 25% efficiency)

$$\frac{2500 \times .25 \times .25 \times 17,000}{3411} = 7800 \text{ K.W. Hours.}$$

Figure 3



Data - Basis 1 Hr

11.2 Tons $Na_2SO_4 \cdot 10H_2O$ 5 Tons $Na_2SO_4$
1/4 # oil /# $Na_2SO_4$ 7800 K.W.H. Available
7.14 BBl oil 5660 # Mols Flue gas

General Discussion.

Figure III is a flow sheet of a plant capable of producing five tons of Anhydrous Sodium Sulfate per hour. Centrifugal pumps are recommended for handling the sludge and liquor. Badger (2) found that the $Na_2SO_4$ crystals were hard on the impellers and packing glands of the pump. He designed a centrifugal pump with extra large impellers and a liquid sealed packing gland and experiences no further difficulties from this course.

This process is capable of several variations. If large quantities of Sodium Chloride are available, the tower may be used as a heat interchanger and the $Na_2SO_4$ salted out of the melted solution by the addition of Sodium Chloride to saturation. The main part of the liquid can then be run to solar ponds, while only that necessary to furnish heat for the melting of the Glauber's Salt need be circulated. If the Sodium Sulfate is to be obtained by evaporation there is no advantage in having a saturated solution of NaCl, since its presence only changes the quantities that precipitate in the melting vat and the tower and not the total amount precipitated. Naturally the chance of contamination of the product will be less, the lower the concentration of the foreign salts.

$Na_2SO_4$ has a specific gravity of 2.67 and settles very rapidly. This would facilitate the separation of the sludge and liquor in the melting vat in case the latter had to be filtered to remove suspended matter. A Sweetland filter press is suggested as suitable for this filtration. It is noted that a circulating system is shown in figure 3 for the tower. Due to lack of time no data was obtained on the efficiency of this means of evaporation. However recent works (3) by R. H. Newton and T. C. Lloyd on evaporation of water by hot, dry air indicate that by circulating sufficient quantities of liquor the exit air approaches 100% relative humidity. While this degree of efficiency is not expected with flue gas working between 800° F and 300°F the figure of 60% used in these calculations is thought to be conservative. Large scale experiments in a pilot plant using this procedure of manufacture would give the desired information and such a study must necessarily be the first step if this method were to be developed commercially.

## Acknowledgments:

Grateful acknowledgment is accorded Dr. W. N. Lacey for his suggestions and interest in this study and to Bruce H. Sage for his very material aid in the development of the method.

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