Fluid calcination of soda ash
by Jerry Dean Mason

A THESIS Submitted to the Graduate Faculty In partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering at Montana State College
Montana State University
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Abstract:
The problem as undertaken here at Montana State College was to develop a process which could remove trace organic matter from a commercially produced soda ash as well as generally maintain or improve other quality features of this ash.

To accomplish this , it was decided to use a fluid calciner using a gas-fired furnace as a heat source and a compressed air system for the fluidizing air stream. Analysis of the calcined ash was made at Green River, Wyoming by the Intermountain Chemical Company, producer of the soda ash. The study involved treatment of both light ash and sodium carbonate monohydrate. Results of the study indicate that a process which meets the objectives is possible.

It was found that the manner of removal of the contaminants in the various types of ash studied was that of mass transfer rather than that of oxidation. Therefore, the variables that affect mass transfer (temperature, stagnant air film, and treatment time) must be considered in determining conditions most favorable for removing the contaminants.

The data indicate that for a given type of ash calcined under similar conditions, an equilibrium level of contaminants is reached after sufficient time, regardless of starting level of the ash.

In general, it was found that the organic contaminant level could be reduced from 60 to 80 per cent depending upon treatment conditions. Further, it was found that the bulk density of the treated light ash was increased some 15 per cent by the fluid treating.

Addition of sodium nitrate in small amounts (2.3 pounds of sodium nitrate per ton of ash) was found to be very effective in maintaining a high reflectance (a quality check) on the treated ash for temperatures above 400°C. Steam mixed, with the air-fluidizing stream has the effect of lowering the contaminant level of the calcined ash.

The economic considerations of setting up operating conditions are not discussed in this paper. These data, along with the necessary economic considerations, however, should be an aid in determining the conditions for manufacture of many grades of high quality soda ash.

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ABSTRACT

The problem as undertaken here at Montana State College was to develop a process which could remove trace organic matter from a commercially produced soda ash as well as generally maintain or improve other quality features of this ash.

To accomplish this, it was decided to use a fluid calciner using a gas-fired furnace as a heat source and a compressed air system for the fluidizing air stream. Analysis of the calcined ash was made at Green River, Wyoming by the Intermountain Chemical Company, producer of the soda ash. The study involved treatment of both light ash and sodium carbonate monohydrate. Results of the study indicate that a process which meets the objectives is possible.

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In general, it was found that the organic contaminant level could be reduced from 60 to 80 per cent depending upon treatment conditions. Further, it was found that the bulk density of the treated light ash was increased some 15 per cent by the fluid treating.

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I. A Brief History of Soda Ash

Soda ash is the common name for technical grades of sodium carbonate (Na_2CO_3). Preparation and uses of soda ash in one or another of its several forms were well known in early historic times. This compound is one of the few currently important chemicals which has been known and used for this length of time. From the time before Christ to the end of the 18th century soda ash was made from deposits of alkaline lakes of the arid regions of Egypt and Armenia and from the ashes of plants. The product was a very impure mixture of sodium and potassium carbonates.

At that time, soda was decidedly the less important and the more expensive of the two alkalies. Potash was readily obtained by leaching wood ashes which were available nearly everywhere. Alkali richer in soda was prepared from the ashes of certain seashore plants. The product of the North African lakes contained principally carbonate of soda. Soda was not practically distinguished from potash until some decades prior to Leblanc's achievement, and all alkalies were mixtures of relatively low quality. The best grades from the ashes of seashore plants, such as Spanish Barilla, contained an alkali equivalent of about 30% sodium carbonate and had nearly 3% insoluble material. The product of the desert lake beds seldom exceeded a sodium carbonate content of 45%.

Nicolas Leblanc (1742-1806) was the first to succeed in changing common salt to soda ash with sodium sulfate as an intermediate product.

The first commercial soda works employing this new source of soda ash was built in France in 1791. By 1810, the production of Leblanc soda ash was sufficient for the national requirements so importation of foreign alkali was prohibited. Commercial production in England started in 1823 but the Leblanc process was never used commercially in America.

Thus, in a very short time, an entirely new source of alkali had been developed and the primitive or crude methods which had been used for some 1800 years were replaced by this revolutionary process. This not only made soda ash cheaper than potash but also of a quality far surpassing hitherto known alkalies and much more readily available from abundant common salt. This product, Leblanc soda ash, contained 96.5% sodium carbonate, about 1% insoluble material, and the remainder about equal parts of sodium chloride and sodium sulfate.

In these few short years great progress had been made but this process had several undesirable points. High consumption of fuel and labor, undesirable by-products, and disagreeable waste materials were characteristics of the Leblanc process. If this process did nothing else, it did encourage the search for simpler methods. It was not until 1863, however, that the conversion of common salt into the carbonate by a process using lower temperatures than those used by Leblanc and without intermediate formation of sulfate was successfully achieved. In that year, Ernest and Alfred Solvay erected their first soda ash works in Couillet, Belgium for the manufacture of soda ash through their ammonia soda process.

In about 1915 the Leblanc process completely succumbed to the ammonia soda process and in its last years was sustained only by its by-product, hydrochloric acid, which was used as a source for chlorine gas during the early part of the first World War.

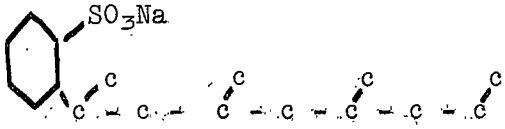
The ammonia soda process was successfully introduced into England in 1874 and in the United States the first ammonia soda ash plant was erected near Syracuse, New York in 1881.

In more recent times, deposits of a naturally occuring mineral, trona, have been found in the United States. Trona is an impure form of the chemical sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). One of the major deposits of interest is an extensive deposit near Green River, Wyoming which was discovered in the search for oil in that area. The trona bed extends over several square miles and is located approximately 1500 feet below the surface between two layers of oil shale. This deposit is currently being mined and converted to high grade soda ash by the Westvaco Chemical Company, and this report involves certain studies made with this ash.

II Manufacture of Westvaco Ash

Because of the type of raw material available in the production of Westvaco Soda Ash, the process is quite simple considering the purity of the final product. To illustrate this manufacturing scheme, Figure 1 (see appendix) is presented showing the basic elements in the process.

The mining is done in a modern manner making full use of belt conveyors, mechanical loaders, drillers, etc. Because of the structural

strength of the overburden, almost no timbering is required. After the ore is removed from the trona bed, it is conveyed to a central ore shaft where it is taken to the surface in a skip hoist and placed in ore storage. From here, the ore is put through a screening and crushing operation and charged to the dissolver. At this point, all of the soluble material is taken into solution with hot water. The resulting slurry from the dissolver is then charged to the clarifier where most of the insoluble matter is removed as a heavy sludge. Liquor from the top of this clarifier is sent to a surge tank, then to a filter operation for the removal of the residual solids, and then to a storage tank. From the storage tank, the feed liquor is charged to a crystallizer where water is removed and sodium sesquicarbonate crystals are formed. Particle size is influenced by the addition of D-40, a synthetic detergent  , and carefully measured amounts are added to obtain the desired particle size from the crystallizer. Following the crystallization, the sesquicarbonate and liquor are separated by settling and by a centrifugal separator. The solids from this operation are fed to a steam heated calciner and the liquor is recycled to the dissolver. In the calciner the charge is dried and converted into soda ash. The reaction here can be given by the equation:

$$2\left[Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O\right] \rightarrow 3Na_2CO_3 + 5H_2O + CO_2.$$

The discharge from the calciner is at a temperature of 240°C. From here, the soda ash is cooled by water jacketed conveyors and sent to

product storage as light ash or to retreatment in the production of dense ash.

III Properties of Westvaco Soda Ash

Table I (see appendix) gives a summary of some of the basic chemical and physical data on grade 100 light ash as published by the Westvaco-Chlor-Alkali Division of the Westvaco Chemical Company.

IV Uses of Soda Ash

Soda ash is one of the most important chemicals and the most widely used fixed alkali in the manufacture of other alkali products, sodium salts, glass, soap, pulp and paper, iron and steel, aluminum, cleaning compounds, water softening compounds, textiles, drugs, clay and brick, beet sugar, and many others. Figure 2 (see appendix) shows the distribtion of use of soda ash for the year 1950. Total consumption in 1950 was almost 4.3 million tons of soda ash.

V Purpose of the Project

As mentioned above, the trona deposit used in the manufacture of "Westvaco Ash" is located between two layers of oil-bearing shale. Because of its proximity to the shale, the trona contains small amounts of organic material. Some of these materials are water soluble and, because of the method of manufacture of soda ash, find their way into the final product. The chemical oxygen demand (COD), indicative of organic content, will run from 300 to 500 ppm for a typical ash made in the manner described earlier in this report. For many of Westvaco's

customers, this trace of organic material is objectionable. In addition, the foaming characteristics of Westvaco Ash was in some cases found objectionable. For this reason the project was undertaken here at Montana State College to devise a method of reducing the organic content of the ash and, in general, improve the quality of the ash.

To accomplish the reduction of the organic material, it was decided to calcine soda ash in a fluidized state and study the effects of residence time, temperature, bed density, and starting material. In addition to the effects of these variables on reduction of organic content, a study was also made to determine the effects of these variables on other physical and chemical characteristics of soda ash. These characteristics are:

1. COD (an indication of organic content)
2. Bulk density
3. Iron content
4. Foam height
5. D-40 content
6. Ash reflectance.

As the project progressed, several different types of soda ash were charged to the fluid calciner. These can be divided into three major groups: 1) sodium carbonate (grade 100 light ash), 2) sodium carbonate monohydrate, and 3) sodium carbonate monohydrate with trace amounts of sodium nitrate added to the carbonate.

VI Equipment Used in the Project

As originally conceived, the fluid calciner was to use a natural gas heat source and the products of combustion as the fluidizing medium. In the event that the process developed into a practical situation, the

choice of natural gas for heating was logical since it is an abundant and cheap heat source in the Wyoming area. The first calciner was constructed with this in mind. Because the products of combustion were to be used as the fluidizing medium, it was necessary to construct a furnace that could operate under a small positive pressure. Figure 3 (see appendix) shows the flow diagram of the first calcining unit. The furnace was built of firebrick inside a steel framework and supplied with compressed air and natural gas. A gas duct from the furnace to the reactor carried the combustion gases and picked up the fresh charge of soda ash. This charge was regulated by use of a gate valve. The combustion gases and charge entered the bottom of the reactor where the fluid bed was held. As fresh charge entered the bottom of the reactor, some of the fluidized bed was forced to spill over into the discharge tube along with the fluidizing medium. The hot gases separated from the bulk of the ash in the dust eliminator and were then vented to an off-gas stack through a cyclone. A water cooler was placed around the discharge tube to cool the exit calcined ash. The furnace that was constructed was cubical in shape, about 20 inches on a side. A hole was placed on the top to permit lighting of the burner and was fitted with a high temperature ceramic plug to provide a pressure seal. Both the heat duct and charge tube were 1-inch standard black iron pipe. The reactor was fabricated from type 316 stainless steel and was conical in shape. Its overall height was 36 inches and measured 1 inch at the bottom or entry point. Across the top, it measured 6 inches and at the discharge point,

2 feet from the bottom, the diameter was almost 4 inches. The discharge tube sloped down 45° from the horizontal and emptied into the dust eliminator. This latter unit, the dust eliminator, was a pyramid 1 foot square at the top and tapered down to fit a 2-inch discharge pipe at the bottom. From the top of the dust eliminator, 1-1/2-inch pipe was used to vent the off-gas into the cyclone. A 6-inch steel pipe was used as the outer shell of the cyclone and the riser inside the cyclone was, again, a 1-1/2-inch pipe. Wherever possible, the unit was covered with a 1-inch thickness of magnesia mud insulation. After several test operations, it was decided to alter the system because of difficulty in maintaining the necessary pressure, and because of operational hazard.

It was decided to run steel pipes through the furnace and heat compressed air. This hot compressed air was used as the fluidizing medium rather than the combustion products from the furnace. Other than this change, the flow was the same as before. The calculations indicated that the rather small quantities of air required for fluidizing would have to be in the neighborhood of 2000°C in order to maintain a 1000-gram bed of ash at 400°C. Since it was impossible to preheat the air to this temperature, additional heat was obtained by building a jacket around the reactor through which the hot combustion gases could be passed before venting.

To facilitate repairs to the unit, which were occasionally necessary, the magnesia was eventually replaced by a 3-inch layer of rock wool batting which could be removed and applied with much less difficulty.

The rock wool was in turn wrapped with sheets of aluminum foil to minimize heat loss by radiation. This combination provided effective insulation and temperatures in the region of 560°C could be attained within the bed.

Further troubles showed up in the flow pattern, however, as frequent clogging occurred at the point where the fresh charge entered the hot fluidizing gas stream. This often caused shutdown of the unit to clear this obstruction. A further change in flow pattern had to be made to to avoid this point of frequent clogging. The fresh charge was added directly to the top surface of the fluid bed and a much smoother operation resulted.

One additional difficulty came as a result of tube failure in the furnace. To correct this point, stainless steel pipes were used in the furnace. This was found to be very effective as only one replacement of the stainless steel pipes was required in two years of service. One further change was made on the unit and this was done because the air compressor in the laboratory did not have sufficient capacity to supply the requirements of both the fluid bed and the natural gas burner. A Spencer four-stage blower was used as an air supply for the burner. The capacity of this blower was 12 CFM at 35 ounces.

Figure 4 (see appendix) shows the flow pattern of the calcining unit as it finally developed. The soda ash flow through the unit is quite simple. From the hopper labeled 'charge' in Figure 4 it is dropped by gravity onto the surface of the fluidized bed. Here, because of the

bed movement, the fresh charge is immediately dragged downward and mixed throughout the bed. The product or overflow from the reactor is discharged into porcelain-lined buckets. The flow of the fluidizing medium through the unit starts at the furnace where it is heated to about 800 or 900°C. From the furnace, it enters the bottom of the reactor where it mixes with the bed. The hot combustion gases exiting from the furnace after passing through the jacket surrounding the reactor are exhausted to the stack. The exchanger, of course, serves a dual purpose, 1) it makes use of what otherwise might go as waste heat, and 2) it cools the combustion products from the furnace and allows the handling of a much cooler off-gas stream.

The dust eliminator was found to be sufficient and the cyclone was seldom used, as the dust problem was not serious at this point. Regulation of the rate at which new ash was added to the bed was done by use of a standard glass stopcock. With this arrangement the feed rate could be varied from about 25 grams per minute to over 100 grams per minute and by controlling the bed density at the proper level, a residence or retention time of from 1 to 35 minutes could be attained. By controlling the amount of gas and air fed to the furnace, the temperature could be controlled.

VII Collection of Data

In general, three types of starting material have been used in this study. These have been mentioned above but for review they are, 1) light ash, 2) monohydrate, and 3) monohydrate with added amounts of sodium

nitrate. Although procedure was similar for all types of materials calcined, the monohydrates required a predrying step before the actual calcining was carried out.

The drying step was effected in the calciner at temperatures in the range of 100 to 150°C. Because the starting material is a monohydrate, treatment at this temperature results in the discharge of steam. Usually the bed was fed at rates of over 100 grams of the monohydrate per minute, resulting in the formation of about 15 grams of steam per minute. For this reason, the normal feeding mechanism could not be used as the steam discharge caused caking of the cold ash at the feed entrance. The ash was poured by hand through the top of the reactor onto the surface of the fluid bed at such a rate that the temperature could be maintained somewhere between the limits of 100 to 150°C. This process was carried out until enough of the dried monohydrate was collected to supply sufficient feed for the required runs in the study and a necessary sample for analysis. This same procedure was carried out on all of the monohydrates investigated in this work.

Temperature measurement was made by use of an iron-constantan thermocouple in conjunction with a potentiometer. The thermocouple was located in the center of the bed along the vertical axis of the reactor. The surrounding thermowell was a piece of pyrex glass tubing. A temperature gradient of less than 2° from top to bottom of the reactor was normal under operating conditions. Feed rates were determined and kept within limits by measuring the rate of discharge from the unit.

The procedure for calcining dried monohydrate or light ash was the same. A heat-up time of about 90 minutes was required before any steady state conditions could be achieved. This heat-up period provided time to get the furnace, combustion gases, gas ducts, and the reactor at high enough temperature to insure that the fluid bed could be maintained at the desired temperature level. Following the heating period, ash was fed to the fluid bed and the air rate was adjusted by a needle valve in order to obtain a desired level of ash in the bed. Next, the feed rate was regulated to give a predetermined retention time. Finally, the gas feed to the furnace was adjusted to give the proper temperature. This adjustment was quite critical and frequently required adjustment. With these adjustments made, a period of line-out followed in which steady state conditions were maintained within as narrow limits as possible. This condition was maintained through a period of not less than the anticipated retention time prior to starting the run proper. At the end of this period the run was continued until a sample of 800 to 1000 grams of calcined ash was collected. At this time the run was completed. Operating data was recorded every three minutes through the period in which a sample was being collected. These data consisted of:

1. Elapsed time
2. Gross weight of ash collected
3. Pressure drop across the bed
4. Temperature within the fluid bed.

By way of illustration, assume that it was desired to make a run at the following conditions:

Temperature - 350°C
Retention time - 20 minutes
Bed weight - 900 grams.

Knowing the desired bed weight and retention time allowed the calculation of the proper feed rate. This was done by dividing the bed weight by the retention time, giving a value of 45 grams of ash per minute. Before such a run was started, the reactor temperature was brought to a little over 600°C. Figure 5 (see appendix) shows a typical heat-up curve where the temperature is that measured in the empty reactor. Ash was then added to the bed to bring the weight up to 900 grams. This was accomplished by using a monometer to indicate the pressure drop across the bed. This manometer was connected to the fluidizing air stream at a point just outside the furnace. In this way the total pressure differential was indicated on the manometer and this, in turn, indicated the approximate amount of ash present at any instant in the bed. Table II (see appendix) shows values of corresponding bed weights and manometer readings. From Table II it can be seen that the bed should be run with a manometer reading of about 17 to 17.5 inches of water in order to maintain a bed weight of 900 grams. To accomplish this, the proper air rate was selected and the feed rate adjusted to be 45 grams per minute. Once these adjustments were completed, the final adjustment on the furnace was made and the temperature brought to the desired level. Following this step, continuous measurements and adjustments were made throughout the run to maintain the desired operating conditions. After a sufficient period of steady state condition, which in this example was considered to be a minimum of 20 minutes, the run was continued until a

sample of 800 to 1000 grams had been collected. Operating data was recorded every three minutes. Table III (see appendix) is a copy of the operating data as taken June 24, 1957 on a run similar to that just described.

Once a sample was collected as illustrated in Table III, it was stored in a polyethylene freezer bag, placed inside a sealed, hard plastic container, and stored prior to analysis. When a group of samples, say 8 to 10 samples, had been collected, they were packaged and mailed to Green River, Wyoming for analysis.

As mentioned previously, the starting materials for the various runs consisted essentially of monohydrates and light ash. Table IV (see appendix) lists the manner in which the source of the various starting materials are referred to in the tabulated data.

In essence, each starting material was used to make a series of runs in which retention time and temperature were varied. For light ash a series was also made in which the bed density of the ash was varied. All runs made with light ash are designated simply by number. Runs made with Drum 1 (monohydrate) contain a prefix "M" before the number. Runs made to determine the effect of $NaNO_3$ additions are designated "MN-". One other brief study was made to observe the effects of steam in the fluidizing stream. These series were accomplished by adding water to the hot air (called steam series "S-"). Table V and VI (see appendix) present the operating data and analytical data collected for this work. In addition, some cross-index tables are included to show

the various runs made using similar retention times or similar temperatures, etc.

VIII Analysis of Ash

The analyses of the ash were made at Green River, Wyoming by the Intermountain Chemical Company. It was felt that because some of these tests were empirical, it would be best if the analytical work were done by those people who were best trained to perform the tests. In this way, a more consistent set of data might be obtained. In the appendix are copies of the instructions for performing some of the various analytical steps.

Three tests performed on the product of the fluid calciner are not outlined in these instructions. These tests are standard in the analysis of a soda ash sample but are empirical. Determination of bulk density is made by dropping a charge of ash from a spring-loaded split dish into a vessel of known weight and volume. The charge is placed on the split metal dish and the vessel is placed in position beneath the charge. Upon triggering the mechanism, the two halves of the split dish are pulled quickly apart, causing the charge to fall into the collecting vessel. A straight edge is used to smooth the top surface of the ash and scrape away the excess material. The vessel and ash are then weighed and the results are reported as bulk density.

Foam height, also an empirical test, is a measure of the foaming characteristics of the ash. This determination is made through use of a 100-centimeter glass column and some proper tubing near the bottom of the glass column. A charge of soda ash is placed in the vertical column

and phosphoric acid is run into the column through the tubing at the bottom of the column. In each case the same amount of acid is added at the same rate and the highest column of foam is recorded as foam height.

The third determination, that of reflectance or sodium tripolyphosphate reflectance, is made by comparing the reflectance of light from a white block (standard and accepted as 100% reflectance) and a sample of finely ground soda ash. This result is reported as percent reflectance either from the soda ash or from sodium tripolyphosphate prepared from the calcined ash.

The reflectance and foam heights are indications of the chemical quality of the ash where high reflectance and low foam heights are the most desirable in a saleable product. A high bulk density is also desirable.

IX Analysis of Results

Two distinct mechanisms of removal of the organic material from the ash seem feasible. First, the material could be oxidized in the fluid bed and removed as CO_2 and H_2O. This would be a mechanism of chemical reaction and, because of the low levels of organic matter in the ash and the amount of air needed to fluidize the bed, a simple assumption of first order reaction would seem reasonable. In differential form a first order reaction can be expressed by

$$-\frac{dC}{d\theta} = bC \qquad (1)$$

or

$$-\frac{dC}{C} = bd\theta \qquad (2)$$

$$\text{or} \quad -\int_{C_o}^{C_F} \frac{dC}{C} = b \int_{\theta}^{\theta} d\theta \qquad (3)$$

$$\text{or} \quad \ln(C_o/C_F) = b\theta \qquad (4)$$

where C is the concentration of contaminants
θ is time
b is a constant

From equation 4 it can be seen that a plot of the log of the ratio of the starting to the resulting concentration of organic material plotted against time should give a straight line of slope K. It might be remembered that the reaction rate constant, K, is a function of temperature so runs must be picked for this plot where temperature is not a variable. Table VIII (see appendix) is a summary of calculations for this kinetic plot.

Table VIII pertains to light ash from Drum 1 containing 362 ppm COD level as a starting material. By using the ratio COD_o/COD_f, no need of further conversion to concentration is necessary since the ratio would be the same in any other units as it is in terms of COD level. Figures 6, 7, and 8 (see appendix) present the data of Table VIII as a plot of $\log(COD_o/COD_f)$ against time (retention time of the ash within the bed). With this type of plot it should be remembered that the function $\log(COD_o/COD_f)$ versus time goes through the origin. It is quite clear that very poor correlation can be found under the mechanism of chemical reaction concerning the light ash from Drum 1. Picking a group of runs made from Drum 3 and a temperature near 475°C, this same poor correlation

can be shown concerning chemical reaction.

Figure 9 (see appendix) shows the data of Table IX (kinetic data for Drum 3 light ash) plotted as $\log(COD_o/COD_f)$ versus time and here, again, no correlation can be found for this data where the mechanism is one of chemical reaction. This same sort of calculation and plot could be used to show that a chemical reaction mechanism is not the proper mechanism to correlate the removal of organic material from the monohydrate ash. Table X (see appendix) presents data similar to Tables VIII and IX; however, this table pertains to monohydrate with some added nitrate.

Figure 10 (see appendix) shows a plot of the data presented in Table X where $\log(COD_o/COD_f)$ is plotted against retention time, and again no linear correlation seems indicated.

A second mechanism that could account for the removal of organic material from the soda ash is mass transfer. The simple mass transfer equation is given as

$$N = K_1 a(P_i - P_b) \qquad (5)$$

where

N is the rate of transfer
K_1 is the mass transfer coefficient
a is the area available for transfer of mass
P_i is the pressure of the organic material at the interface of the transfer area
P_b is the pressure of the organic material in the bulk air stream.

Because of the low concentration of the organic material, the pressure of the organic material in the bulk air stream (P_b) can be considered zero. Using this assumption we get

$$N = K_1 a(P_i) \qquad (5\,b)$$

To make use of this equation we must get an estimate of how P_i changes with temperature. This can be done by making some simplifications in the Clausius-Clapeyron equation

$$dP/dT = \Delta HP/RT^2. \qquad (6)$$

where P is vapor pressure
T is absolute temperature
ΔH is molar heat of vaporization
R is the gas constant

On rearranging, we get

$$dP/P = (\Delta H/R)\ dT/T^2. \qquad (7)$$

On integration, we get

$$\ln P = (-\Delta H/R)\ 1/T + C. \qquad (8)$$

At the normal boiling point (T_B) the vapor pressure of a liquid is one atmosphere. This is used to evaluate the constant of integration

$$\ln (1) = 0 = (-\Delta H/R)\ 1/T_B + C \qquad (9)$$

$$C = \Delta H/RT_B \qquad (10)$$

therefore $$\ln P_i = \Delta H/RT + \Delta H/RT_B \qquad (11)$$

The exponential form of equation 11 is

$$P_i = e^{(\Delta H/RT_B - \Delta H/RT)} = e^{\Delta H/RT_B}\ e^{-\Delta H/RT} \qquad (12)$$

Since the quantity $\Delta H/RT_B$ is a constant, equation 12 can be rewritten as

$$P_i = K_2 e^{-\Delta H/RT} \qquad (13)$$

where $$K_2 = e^{\Delta H/RT_B}$$

Using the relation of equation 13, equation 5b can be rewritten as

$$N = K_1 a K_2 e^{-\Delta H/RT} = K_3 e^{-\Delta H/RT} \qquad (5c)$$

The quantity H is the heat of vaporization of the organic material being transferred from the soda ash. While it does vary with temperature, this variation is small in the temperature range involved and so the latent heat of vaporization will be considered a constant here. If the log of equation 5c is taken, an equation in two arbitrary constants results.

$$\log N = \log K_3 + (-\Delta H/RT) \log e$$

or

$$\log N = \log K_3 + 0.434\ K'/T. \qquad (14)$$

By use of a least squares process these constants K_3 and K' can be evaluated. Since K_3 has incorporated in it as a multiplying factor the mass transfer coefficient (K_1), provision must be made for the removal of the effect of temperature and the degree of fluidity of the bed.

Mass transfer coefficients as defined by Treybal[9] are

$$K_1 = D_{AB}/RTZ_G \qquad (15)$$

where

K_1 is the mass transfer coefficient
D_{AB} is the diffusivity of component A into component B
R is the universal gas constant
T is the absolute temperature
Z_G is a fictitious or effective laminar film thickness whose resistance to molecular diffusion is the same as that offered to mass transfer by a real laminar film, buffer zone, and turbulent region, all combined.

Further, Treybal states that diffusivity varies with $T^{3/2}$. Using this statement ($D_{AB} = \alpha T^{3/2}$) we could rewrite equation 15.

$$K_1 = \alpha T^{3/2}/RTZ_G = \alpha T^{\frac{1}{2}}/RZ_G \qquad (16)$$

Writing two of these equations each at a different temperature and

taking their ratio results in

$$(K_1)_{T_1}/(K_1)_{T_2} = \alpha T_1^{1/2}/RZ_G \Big/ \alpha T_2^{1/2}/RZ_G$$

On rearranging and canceling, equation 17 results.

$$(K_1)_{T_1} = \sqrt{T_1/T_2}\ (K_1)_{T_2} \qquad (17)$$

Equation 17 gives a relation between mass transfer coefficients for different temperatures, all else being equal.

Just as temperature was used as an operating variable in the collection of data, so was bed density or bed weight. Since the same reaction vessel was used in all the runs, bed density is directly proportional to the bed weight. In the collection of data the bed weight was measured after each run and as presented earlier in Table II, the bed weight is a linear function of the pressure drop across the bed. This data is illustrated in Figure 11 (see appendix) where the pressure drop across the bed is plotted against bed weight. In order to get a relation between the mass transfer coefficient and the various bed weights used in the various runs, a short review must be made of some work done by Millikan[5] and reported by Knudsen and Katz[3]. The stagnant boundary layer about a particle depending upon its shape can be determined by the equation

$$UZ_G^2/r_o\nu = K_4 \qquad (18)$$

where
- U is the velocity of the fluid stream
- Z_G is the thickness of the stagnant layer
- r_o is a characteristic measure of the dimension of the particle
- ν is the kinematic viscosity of the moving fluid
- K_4 is a constant depending upon the shape of the particle.

For the purposes here, r_o, v, and K_4 may be considered invariant giving the relation

$$Z_G^2 = K_5/U \tag{19}$$

where K_5 encompasses K_4, r_o, and v.

On rearranging this relation, equation 20 was obtained.

$$Z_G = K_6 \sqrt{1/u} \tag{20}$$

One relation still remains to be discussed and that is the relation between bed weight and velocity of the fluid through the bed. Under normal conditions a pressure drop versus velocity plot for a fluid bed situation such as this has the general properties that the pressure drop across the bed rises with increasing velocity to the point of fluidization. At this point the trend reverses and the pressure drop declines as the velocity of the fluid medium is increased. This is an inverse relation and could be expressed in the region where the fluid velocity is at least sufficient for fluidization of the ash as

$$\Delta P = K_7/u. \tag{21}$$

From Figure 11 (see appendix) we have the relation that

$$BW = K_8 \Delta P \tag{22}$$

Substituting this (22) into equation 21, we obtain

$$BW = K_9/u \tag{23}$$

Using equation 23 in equation 20, we can obtain

$$Z_G = K_{10} \sqrt{BW} \tag{24}$$

Putting this (24) into equation 15, a relation was obtained between mass transfer coefficients and the bed weight at which this transfer

takes place.

$$K_{11} = D_{AB}/RTK_{10}\sqrt{BW} \tag{25}$$

A ratio of two of these equations (25) at different bed weights will result in the desired relation

$$(K_{11})_{BW_1} = \sqrt{BW_2/BW_1}\ (K_{11})_{BW_2} \tag{26}$$

Combining this relation with the relation outlined in equation 17, a correcting factor can be obtained for any run made in the soda ash series which will refer it to a reference condition. This relation would be

$$K_{12} = \sqrt{T_1BW_2/T_2BW_1}\ \ K_{13} \tag{27}$$

Using this correction factor for the effects of temperature as well as bed weight, the fundamental mass transfer equation can now be written as

$$N = K\ \sqrt{T_1BW_2/T_2BW_1}\ \ e^{K'/T} \tag{28}$$

This form of the equation has a correction factor in it to reduce the effects of any run to those at a reference state. For this reason the reference state will be considered as a temperature of 410°C and a bed weight of 900 grams. These values were picked primarily as reference because considerable data have been gathered at or near these conditions. In a manner similar to finding equation 14 but with the correction for bed weight and temperature, we can obtain equation 29 by taking the log of equation 28

$$\log N = \log K + \log \sqrt{T_1BW_2/T_2BW_1} + .434\ K'/T \tag{29}$$

and on redefining some terms we can write

$$n = k + \log \sqrt{T_1BW_2/T_2BW_1} + k't \tag{30}$$

where $n = \log N$
$k = \log K$
$k' = .434\ K'$
$T = 1/T°K$

Table XI presents data pertaining to mass transfer at a retention time of 19 to 21 minutes. From these data a least squares analysis can be made to find the best approximation for K and K' in equation 29. Equation 30 can be rewritten as

$$n - k - \log \sqrt{T_1 BW_2 / T_2 BW_1} - k't = 0 \qquad (31)$$

and for the method of least squares

$$\sum (n - k - \log \sqrt{T_1 BW_2 / T_2 BW_1} - k't)^2 = R \qquad (32)$$

Taking the partial differential of R with respect to k and k' and setting each to zero the normal equations are obtained for evaluating k and k'.

$$\partial R / \partial k = 0 = 2 \sum (n - k - \log \sqrt{T_1 BW_2 / T_2 BW_1} - k't) \qquad (33)$$

$$\partial R / \partial k' = 0 = 2 \sum (n - k - \log \sqrt{T_1 BW_2 / T_2 BW_1} - k't)t \qquad (34)$$

Rearranging equation 33 gives

$$\sum n - \sum k - \sum \log \sqrt{T_1 BW_2 / T_2 BW_1} - k't = 0$$
$$3.23256 - 3k - 0.05803 - .0041988k' = 0 \qquad (33)$$

Similarly, with equation 34 the following results

$$\sum nt - \sum kt - \sum t \log \sqrt{T_1 BW_2 / T_2 BW_1} - \sum k't^2 = 0 \qquad (34)$$

$$0.0045291 - 0.0041988k - 0.000079745 - 0.0000058836k' = 0$$

The solution of these two equations gives the following values

$K' = -299.3$
$K = 17.6$

To run an additional check on the calculations presented above, the value of K' was used and values of K were calculated from raw data with

the use of the equation

$$N = K \sqrt{T_1 BW_2 / T_2 BW_1} \quad e^{K'/T} \qquad (28)$$

Referring to equation 14 it can be seen that $\Delta H/R$ has been replaced by K'. However, this should not be construed to mean that ΔH can be approximated from K' since N as used in these equations is the rate of COD reduction rather than the molar rate of organic removal. K' is related to the rate of COD reduction in the same manner as $\Delta H/R$ is related to the molar transfer of organic matter. This value of K' should be a constant through any one lot of ash and will be considered constant for Drums 1, 2, and 3 of light ash. K is only constant for a particular retention time. Table XII presents Ks for runs made at retention times of 19 to 21 minutes calculated from the raw data using a value of K' as calculated above. Two additional runs not used for the least squares calculation have been introduced for a check and show reasonable agreement. Tables XIII, XIV, and XV present mass transfer data for runs made at various retention times. Again, the adjusted Ks for runs of similar retention time remain quite constant.

In Figure 12 these data are plotted where K is shown as a function of retention time. This curve indicates that a mechanism is one of mass transfer. Referring to Table XVI (Run 32), an adjusted value of K of 17.7 was obtained at a retention time of 19.5 minutes when N_2 was used as the fluidizing medium instead of air. This value is indicated by (N) on Figure 12 and falls very close to the curve. This is further support that the mechanism is one of mass transfer rather than oxidation.

Table XVII presents mass transfer data for several runs made at temperatures below 400°C. In each case the adjusted values of K are considerably lower than those indicated by the curve of Figure 12 which was plotted from the data of runs all of which were made at temperatures above 400°C. This indicates that the temperature relationship $\sqrt{T_1/T_2}$ as used in equation 28 is not valid for temperatures below 400°C.

The data presented thus far have been for runs made with a light ash having an initial COD value of 362 ppm. Table XVIII presents mass transfer data for runs made with a light ash having an initial COD value of 483 ppm. These data are plotted in Figure 13. Although a similar correlation results the mass transfer coefficients increase with increased COD level.

Table XIX presents mass transfer data on runs made with ash having a starting COD level of 317 ppm. The adjusted Ks are all lower at a given retention time than those for corresponding runs of higher COD level. Runs 38, 39, and 40 in this group were all made with low bed weight (below 500 gms) and the resulting Ks for these three runs when plotted against retention time show the expected correlation, although the curve does not fit the value for K obtained from Run 43 which was made at a bed weight of 1060 gms. If Run 43 is considered along with Runs 45, 46, and 47 from the Nitrogen series (Table XVI) which were made with the same starting ash and bed weights between 900 and 1200 grams, a correlation is indicated for this group. Adjusted Ks for this group of four runs are also plotted in Figure 13. If this curve is valid, it

acts as additional support for the mass transfer mechanism. The fact that two distinct curves were plotted for this ash would indicate that the bed weight relationship $\sqrt{BW_2/BW_1}$ as used in equation 28 is not valid for bed weights below 500 or 600 grams. Above 600 grams the relationship seems to hold. The K for Run 42 plots below either of the two curves mentioned because of the invalid temperature relationship.

Once again it should be pointed out that while reference is made throughout this paper to bed weight as one of the variables, a more universal term might be bed density or as appears in some literature, bed deficiency. Only because the reactor volume remains constant for all runs, can comparison be made on the basis of bed weight. The volume of the fluid bed used to make the runs appearing in this study was 0.077 cubic feet. A 900-gm bed would then correspond to a bed density of 25.8 pounds per cubic foot. Figure 14 shows the relationship between bed weight and bed density.

Referring again to Figure 13, if Ks are picked from this curve at retention times of 5, 7, 8, 10, and 20 minutes for each of the three light ash samples studied, final COD levels can be calculated from these values. These data are presented in Figure 15. This figure indicates that for a given temperature and bed weight, equilibrium is reached after sufficient retention time at the same COD level regardless of the starting COD level. For light ash with COD values in the range of 300 to 500 ppm, 10 minutes seems to be sufficient for reaching equilibrium.

Until now the ash considered in this report has been grade 100 light soda ash with various starting levels of organic material. As mentioned earlier, another type of ash was treated in this study. This was monohydrate with controlled amounts of sodium nitrate added. Although the investigation on monohydrate was more limited in scope and was concerned primarily with retaining high reflectance, an attempt was made with the limited data available to show that mass transfer was again the controlling mechanism. All of these monohydrates have a much higher COD starting level than the light ash used in this investigation and also had a different crystalline form. Because of these differences, equations 33 and 34 were again used to calculate new values of K and K' by the least squares process. Again, standard conditions for temperature and bed weight were set at 410°C and 900 grams, respectively. Table XX presents the data used for these calculations.

$$4.91242 - 3k - .06521 - .0041172k' = 0 \qquad (33)$$

$$.0067337 - .0041172k - .000086328 - .0000056973k' = 0 \qquad (34)$$

The solution of the above equations gives results of

$$K' = -243$$
$$K = 57.6$$

Again, using the above value for K', Ks were calculated for several runs made with monohydrates which had no added nitrate. These values appear in Table XXI and are plotted as a function of retention time in Figure 16. Although the data are limited and cover a very narrow range of retention times, the same tendencies and types of curves result. Ks decrease with increased retention time and increase with increased con-

centration of organic material. The indication is that equilibrium is reached at a higher COD level than with light ash for the same processing conditions.

From the shape of the curves and the fact that mass transfer coefficients are a function of the starting level of organic material, some speculation can be made as to the distribution of this organic material within the soda ash crystal. If the contaminant were on the outer surface only, mass transfer coefficients would remain relatively constant to a point of depletion. This does not appear to be the case since no evidence of a constant region was found in these coefficients. For light ash the COD level decreased at progressively slower rates from 0 to 10 minutes, at which time equilibrium was reached. If the contaminant were distributed through the particle, the rate of diffusion through the pores of the crystal would control the rate of depletion. Concentration would also affect this rate and results similar to those obtained in this study would be expected. An equilibrium level would also be expected. Further evidence is obtained by observing Runs MN-34 and MN-35 which were made using a starting material that had, in one case, all the material above 20 mesh removed and in the second case, all of the material above 28 mesh removed. The screening alone did not affect the COD level which might be expected if the contamination were primarily on the surface. By comparing these runs with Runs MN-4, -13, -14, and -15, it did affect the rate of removal and the final (equilibrium) COD level which is what would be expected if the contaminant had to

diffuse to the surface from within the particle.

In the study involving light ash no marked effect on the reflectance of the ash was indicated. With the monohydrate, however, the ash reflectance was seriously lowered by the calcining treatment. In an attempt to retain high ash reflectance, a study was made to determine the effect of adding small quantities of sodium nitrate to the hydrating liquor from which the monohydrate was made. Four batches of monohydrate were prepared containing controlled amounts of sodium nitrate varying from 0.0 to 9.95 pounds per ton of ash. The data from runs made with this ash appear in Table V. These runs are labeled with the prefix 'MN' in this table. Figure 17 presents a plot of ash reflectance versus temperature with parameters of pounds of $NaNO_3$ per ton of ash. From this figure two major facts stand out. First, without addition of nitrate the reflectance falls off with increasing calcining temperature. Second, the addition of nitrate does have a beneficial effect toward retaining high reflectance levels when the calcining temperature is above 400°C. Additions of nitrate above the 2.3 pounds per ton level does not have an appreciable effect. Table V also includes data on the reflectance of sodium tripolyphosphate (STPP) made from the ash. In order for the chemical quality of the soda ash to be acceptable, the reflectance of STPP made from the ash should be 93 per cent or higher. Although high temperature treatment of the ash before making phosphate improves the STPP reflectance, it requires higher temperatures without $NaNO_3$ to attain the desired value. High temperature calcination of soda ash in com-

bination with small amounts of sodium nitrate produces an ash which, under all conditions studied, will produce an ash which can be used "as is" for making acceptable sodium tripolyphosphate.

Sodium nitrate also seems to have had some effect on lowering the final COD level. Table XXII presents data from several similar runs with and without added nitrate. During the calcining of the ash with added nitrate, nitrites are formed which should increase the COD value obtained upon analyzing the product. However, even though absolute COD values are therefore misleading, it appears as though there is a slight lowering of the final COD level attributed to organic contaminants.

In Table V, bulk density was reported only on the light ash and not on the monohydrate ash. As mentioned before and presented in Table VII, there was no significant change in particle size distribution between the treated and untreated ash; however, there was an effect upon the bulk density of the ash when treated in the fluid state. In Figure 18 the results of some runs are plotted with temperature as the parameter, showing that at any temperature the bulk density increases with residence time and at constant residence time, higher density results from higher temperature.

No correlation between the operating variables and foam height could be found; however, it should be noted that a significant decrease in the foam height resulted from the fluid calcination. In the case of the ash from Drum 2, a reduction in foam height as much as 75 per cent of the original was noted.

Discussion and Summary

As the program was set up, the object was to decrease the organic content, increase the bulk density, lower the foam height, and maintain or improve the reflectance of the ash and sodium tripolyphosphate made from the ash. Fluid calcination of soda ash will do each of these things and operation of the process is continuous.

Analysis of the results indicate that removal of organics is a matter primarily of mass transfer and the variables that affect mass transfer (temperature, bed weight, and retention time) must be considered. For a given type of ash calcined at set temperature and bed density, an equilibrium level is reached, after sufficient time, which is independent of the starting level. Figure 15 illustrates this point.

Extending these data a little farther for light ash, coefficients taken from Figure 12 permit per cent COD reduction to be calculated for a variety of operating conditions with the aid of equation 28. This information is presented in the following figures:

Figure 19 Percent COD Reduction vs Retention Time (T = 410°C)

Figure 20 Percent COD Reduction vs Retention Time (BW = 900 gms)

Figure 21 Percent COD Reduction vs Temperature (Retention Time = 20 minutes)

Figure 22 Percent COD Reduction vs Temperature (BW = 900 gms)

Figure 23 Percent COD Reduction vs Bed Weight (T = 410°C)

Figure 24 Percent COD Reduction vs Bed Weight (Retention Time = 20 minutes)

Figures 19 and 20 again bring out the point that for a given temperature and bed weight there is a practical limit to the removal of any further organic material. The effect of bed weight and temperature can also be observed. Figures 21 and 22 give a somewhat clearer picture of the effect of temperature on the organic removal and likewise Figures 23 and 24 are aimed at showing more clearly the effect of bed weight.

From these figures, then, three general facts can be summarized.

1. Little is gained by increasing retention time above 10 minutes.
2. A decrease in bed weight (fluid bed density) brings about a marked reduction in COD level.
3. Only about 6 to 8 per cent additional reduction in COD level is realized by increasing the temperature from 400 to 500°C.

Although these data were presented for the light ash with a starting COD level of 362 ppm, similar curves would result for the other light ash stock and final COD levels could be estimated from this data for light ash of varying initial COD level.

A further word might be said about bed weight. Since the lower bed densities involve higher rates of fluidizing air through the unit, the more efficient removal that results might be attributed to the air film effect around the particle. Less resistance will permit greater removal. This increased removal with decreased fluid bed densities brings up one further consideration. Depending upon the economics of providing the additional air and additional heat and depending upon

what is considered as a satisfactory maximum COD level, consideration might be given to decreasing the bed weights while at the same time decreasing retention time in order to keep up the throughput. The following data, although sparse, illustrate what might be done.

Run	RT min	Temp °C	BW	Throughput gms/min	COD_o	COD_f
36	4.77	413	650	138	362	158
40	2.4	409	264	110	317	183
18	11.5	411	802	82.5	362	158

If the additional throughput of similar quality product can offset the added operating cost, this type of approach must also be considered.

Concerning the reflectance of the treated monohydrate, the addition of $NaNO_3$ in amounts above 2.3 pounds per ton of ash holds the reflectance at high level (90% reflectance, or better) in the temperature range above 400°C. The same is true of the STPP reflectance. Again, consideration might be given to using low fluid bed densities in conjunction with low retention times. Referring to Run M-7 in Table V, it will be noted that a low bed density in conjunction with a low retention time resulted in removal of organic material comparable to some of the better runs without lowering the ash reflectance. This was accomplished without the use of sodium nitrate as an addition. The STPP reflectance, however, was not improved. High STPP reflectance is apparently more dependent on high temperature.

In the course of this work a group of runs was made in which water vapor was introduced with the air fluidizing stream. Runs of comparable nature were picked from Table V and presented in Table XXIII. From this

collection of data it can be seen that for light ash not a great deal is gained inasfar as the resulting COD level is concerned by the addition of steam to the fluidizing stream. In the case of the predried monohydrate runs, however, a significant reduction in resulting COD level can be noted. Concerning any of the other physical measurements made on the ash samples, the addition of steam made no difference.

Fluid calcining affects the bulk density favorably. As shown in Figure 18, resulting bulk density is a function of both temperature and retention time.

It is beyond the scope of this study to go into the economics of a commercial operation. However, along with the necessary cost data, product specifications, heat transfer data, etc., the correlations developed in this report should help in setting up the most favorable conditions for a fluid calcination unit to treat and improve the quality of a similar ash.

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TABLE I PRODUCT QUALITY AND SPECIFICATIONS

Typical Analysis		Typical Screen Analysis	
Na_2O, %	58.44	Through 14 mesh, %	---
Na_2CO_3, %	99.88	Through 16 mesh, %	100
		Through 20 mesh, %	---
		Through 30 mesh, %	---
NaCl, %	0.02	Through 40 mesh, %	93
		Through 100 mesh, %	16
Na_2SO_4, %	0.02	Through 200 mesh, %	2
Fe_2O_3, ppm	8		

Specifications

Na_2O, % (as total alkali)	58.0 min.
Na_2CO_3, %	99.2 min.
NaCl, %	0.2 max.
Fe_2O_3, ppm	30 max.
Water insoluble, %	0.05 max.

TABLE II CORRESPONDING BED WEIGHTS AND MANOMETER READINGS

Pressure (inches of water)	Bed Weight (grams)
4	107
7	264
11	472
13.5	570
17.5	905
18	980

TABLE III OPERATING DATA TAKEN June 24, 1957

Time Elapsed (min)	Temperature °C	Amount Collected (grams)	Pressure Drop Across Bed (inches H_2O)
0	342	0	18
3	340	130	17
6	340	270	17
9	343	415	17
12	341	550	18
15	337	725	17
18	342	845	17.5

Source - Drum 1 Light Ash
Bed Weight - 940 grams
Feed Rate - 45.9 grams/min.
Retention Time - 20.5 min.
Average Temperature - 341°C.

TABLE IV STARTING MATERIALS

Light Ash	Drum 1 Drum 2 Drum 3
Monohydrate	Drum 1 (mono) 9.95# $NaNO_3$/ton of Ash 5.5 # $NaNO_3$/ton of Ash 2.3 # $NaNO_3$/ton of Ash 0.0 # $NaNO_3$/ton of Ash Chamber Product

TABLE V ANALYTICAL AND OPERATING DATA

Run No.	Reten. Time (min)	Ave. Temp. (°C)	Bed Wt. (grams)	Fluid Medium	△ P Bed	Remarks	Source	Bulk Den. #/ft³	Fe ppm	Foam Height (cm)	D-40 ppm	COD ppm	Ash Refl.	STPP Refl.	NaCl (%)
Drum 1	--	--	--	--	--	--	Drum 1	50.0	4	48+	69	362	97		
13	37	439	903	A	10		"	54.3	10	22	12	117	88		
14	16.2	439	893	A	16.5		"	53.7	9	22	16	130	91		
15	19.9	443	910	A	16		"	53.9	8	34	26	120	88		
16	10.8	450	935	A	16.5	Broken See 34	"	--	--	--	--	---	--		
17	29.1	411	740	A	16		"	52.1	8	13	19	142	90		
18	14.6	411	802	A	16		"	51.4	9	21	15	150	92		
19	19.7	412	865	A	16		"	52.5	9	18	16	139	92		
20	11.5	411	950	A	17		"	51.6	9	21	17	158	95		
21	31.2	478	765	A	16.5		"	53.7	10	23	21	118	89		
22	15.2	475	850	A	17	Broken	"	53.5	--	--	--	127	--		
23	20.5	472	830	A	15.5		"	53.9	17	28	14	108	91		
24	11.1	478	865	A	16		"	53.7	8	25	25	127	92		
25	28.5	513	720	A	15		"	56.9	9	30	15	100	90		
26	16.0	513	825	A	17		"	54.8	8	24	14	105	92		
27	19.6	514	855	A	17		"	55.3	9	24	3	122	89		
28	22.1	332	900	A	16	Broken; See 33	"	--	--	--	--	--	--		
29	12.1	503	690	A	13		"	54.6	12	31	4	116	80		
30	19.1	556	690	A	15		"	58.0	12	--	4	100	80		
31	22.3	333	1080	N	21		"	51.0	11	48+	41	305	92		
32	19.5	510	1084	N	19		"	55.2	10	24	26	132	80		
33	20.5	341	940	A	17.5		"	50.7	12	28	3	237	90		
34	11.6	443	945	A	16.5		"	52.9	8	32	9	134	92		
35	4.78	349	875	A	15		"	50.3	10	23	30	267	90		
36	4.72	413	650	A	12		"	49.9	12	24	9	158	89		
37	8.39	413	965	A	17		"	50.0	6	30	8	159	89		

TABLE V ANALYTICAL AND OPERATING DATA (continued)

Run No.	Reten. Time (min)	Ave. Temp. (°C)	Bed Wt. (grams)	Fluid Medium	Δ P Bed	Remarks	Source	Bulk Den. #/ft³	Fe ppm	Foam Height (cm)	D-40 ppm	COD ppm	Ash Refl.	STPP Refl.	NaCl (%)
Drum 2	--	--	--	-	--		Drum 2	49.7	5	88	71	317	95	65	
38	10.7	412	472	A	11		"	52.2	6	20	17	149	95		
39	11.7	414	247	A	7.7		"	52.2	5	22	16	148	95		
40	2.4	409	264	A	7		"	50.4	5	26	20	183	97		
41	0.94	415	107	A	4		"	51.2	11.2	30	29	350	95		
42	5.7	346	1025	A	14		"	--	9.8	40	12	274	96		
43	8.6	415	1060	A	14		"	52.5	8.5	25	16	161	94		
44	16.7	344	1005	N	15.5		"	51.7	9.6	42	26	286	96	76	
45	22.3	403	1190	N	15.5		"	52.0	10.4	30	25	207	93.5	86	
46	15.2	451	970	N	16.0		"	51.8	8	19	0	153	88	85	
47	16.3	512	1020	N	16.5		"	52.1	8	39	0	128	83	79	
Drum 3	--	--	--	-	--		Drum 3	49.4	19	--	82	483	98		
48	8.5	478	905	A	17.5		"	54.8	21	17	1	111	87		
49	11	477	980	A	18		"	54.5	23	16	2	145	90		
50	17.1	476	990	A	17.5		"	55.5	20	21	1	95	90		
52	24.5	477	890	A	18.0		"	55.5	22	19	1	93	88		
53	10.6	406	990	A	17.5		"	51.9	24	18	9	176	95		
54	15.9	420	970	A	18		"	52.9	24	15	10	270	92		
55	18.9	411	960	A	18		"	52.6	29	13	7	149	94		
56	24.7	414	945	A	18		"	52.7	22	15	7	233	94		
57	19.9	476	940	A	18		"	55.7	23	20	2	174	85		
Mono Drum 1	--	--	--	-	--		Mono Drum 1	--	--	100	64	571	94	69	
Predried Feed	--	100 150	--	A	--		"	57.4	8.5	80	58	459	91	64	

TABLE V ANALYTICAL AND OPERATING DATA (continued)

Run No.	Reten. Time (min)	Ave. Temp. (°C)	Bed Wt. (grams)	Fluid Medium	Δ P Bed	Remarks	Source	Bulk Den. #/ft³	Fe ppm	Foam Height (cm)	D-40 ppm	COD ppm	Ash Refl.	STPP Refl.	NaCl (%)
							Mono								
M-1	15.8	410	668	A	14		Drum 1	59.8	9.8	50	50	318	83	74	
M-2	10.5	450	455	A	12		"	59.0	9.2	20	52	256	75	77	
M-3	14.2	478	(500)	A	12.5		"	59.6	20.4	30	31	256	72	82	
Predried		100													
Feed	--	150	--	A	--		"	59.5	20.4	84	68	640	92	63	
M-4	12.0	509	510	A	11.2		"	57.0	26.1	25	28	238	65	92.5	
M-5	13.1	478	510	A	12.0		"	58.5	11.2	31	22	254	72	84	
M-6	14.0	354	555	A	13.5		"	56.9	13.2	24	45	352	97	--	
M-7	.96	416	110	A	5.0		"	52.5	9.8	45	11	181	95	67	
M-8	18.3	433	1080	A	19.0		"	58.8	13	42	8	174	81	77	
Predried		100													
Feed	--	150	--	A	--				22	100+	161	1260		89	0.29
M-9	16.2	465	960	A	14				33	43	59	45		90	0.31
Predried		100													
Feed	--	150	--	A	--				9	100+	118	539		77	0.07
M-10	13.7	468	780	A	13				14	27	17	48		82	0.07
Predried		100													
Feed	--	150	--	A	--				64	59	331	1655		87	0.52
M-11	18.0	463	890	A	14				66	30	108	125		70	0.51
Dried		100				Mono-	9.95 -		8	100+	98	1004	95	93	.19
Sample		150	--	A		hydrate	$NaNO_3$								
MN-1	17.2	479	1100	A	14.5		"								
MN-5	14.8	390	975	A	14.5		"		10	24	10	505	84	97.5	.22

TABLE V ANALYTICAL AND OPERATING DATA (continued)

Run No.	Reten. Time (min)	Ave. Temp. (°C)	Bed Wt. (grams)	Fluid Medium	Δ P Bed	Remarks	Source	Bulk Den. #/ft³	Fe ppm	Foam Height (cm)	D-40 ppm	COD ppm	Ash Refl.	STPP Refl.	NaCl (%)
							9.95 -								
MN-6	11.0	433	935	A	14.5		$NaNO_3$		7	30	12	480	89	101	.21
MN-7	15.8	546	830	A	14.5		"		7	20	10	318	90	96.5	.23
Dried		100													
Sample	--	150	---	A	--		5.5 $NaNO_3$		12	100+	58	831	94	86	.19
MN-2	15.3	478	980	A	14.0		"		11	23	12	335	93	92.5	.18
MN-8	18.0	390	1000	A	14		"		8	23	11	421	91	98	.12
MN-9	13.9	436	985	A	14		"		10	17	10	415	92	87	.21
MN-10	10.3	550	775	A	14.7		"		12	19	10	222	95	97	.17
Dried		100													
Sample	--	150	--	A	--		2.3 $NaNO_3$		13	85	63	949	94	77.5	.21
MN-3	11.3	474	880	A	14		"		11	30	46	389	90	93	.19
MN-11	13.6	394	895	A	14.5		"		11	18	11	406	89	94.5	.17
MN-12	13.5	439	1050	A	15		"		26	20	13	354	92	93.5	.18
MN-16	12.5	560	1050	A	15		"		13	19	11	314	91	91.5	.18
Dried		100													
Sample	--	150	--	A	--		0.0 $NaNO_3$		20	40	58	910	94	65	.16
MN-4	15.4	478	1212	A	14		"		18	17	24	389	69	88	.17
MN-13	11.1	393	855	A	15		"		20	32	20	461	86	87	.15
MN-14	10.8	435	815	A	14.5		"		21	34	11	436	74	85	.17
MN-15	11.9	558	950	A	16		"		21	53	7	362	66	95	.17
Dried		100													
Sample	--	150	--	A	--		5.5 $NaNO_3$		9	100+	31	928	95	98	.17
MN-17	26.0	435	1140	A	13.5		"		12	22	6	359	92	93	.18
MN-18	7.0	442	810	A	10.5		"		14	28	22	461	89.5	97	.16
MN-19	9.0	433	690	A	8		"		13	19	18	419	85	97	.16
MN-20	2.74	430	290	A	7.5		"		12	12	18	461	83.5	95	.15

TABLE V ANALYTICAL AND OPERATING DATA (continued)

Run No.	Reten. Time (min)	Ave. Temp. (°C)	Bed Wt. (grams)	Fluid Medium	Δ P Bed	Remarks	Source	Bulk Den. #/ft³	Fe ppm	Foam Height (cm)	D-40 ppm	COD ppm	Ash Refl.	STPP Refl.	NaCl (%)
Dried		100													
Sample --		150		A			9.95 $NaNO_3$		38	100+	24	933	94.5	98.5	.16
MN-21	12.9	481	975	N	13.0		"		10	38	7	513	86	97.5	.16
MN-22	12.6	391	860	N	12.0		"		17	22	9	534	71	94	.17
MN-23	11.7	441	1010	N	13.5		"		10	20	7	525	83	93	.17
Dried		100													
Sample --		150		A			0.0 $NaNO_3$		7.0	70	61	793	92	66	
MN-24	13.9	391	920	N	15		"		18	75	48	383	67	67	
MN-25	13.6	448	950	N	15.5		"		16	58	24	233	61	72	
MN-26	13.3	412	890	A	12.5		"		16	35	16	217	79	77	
Dried		100													
Sample --		150					2.3 $NaNO_3$		9	86	62	638	93	85	
MN-27	15.8	386	805	A	9.3		"		10	20	8	117	86	93	
MN-28	15.3	442	870	A	13		"		11	14	0	84	88	94	
Dried		100													
Sample --		150					5.5 $NaNO_3$		20	100+	74	812	94	85	
MN-29	16.5	394	910	A	13		"		24	29	48	213	84	92	
MN-30	16.8	485	1050	A	14		"		13	13	41	58	89	97	
Dried		100													
Sample --		150					9.95 $NaNO_3$		15	100+	81	847	95	89	
MN-31	12.5	396	860	A	13		"		10	32	40	174	83.5	94	
MN-32	12.5	427	840	A	13		"		11	19	52	161	89	99	
MN-33	18.0	477	990	A	13.5		"		8	16	5	20	84	96	.24

TABLE V ANALYTICAL AND OPERATING DATA (continued)

Run No.	Reten. Time (min)	Ave. Temp. (°C)	Bed Wt. (grams)	Fluid Medium	ΔP Bed	Remarks	Source	Bulk Den. #/ft³	Fe ppm	Foam Height (cm)	D-40 ppm	COD ppm	Ash Refl.	STPP Refl.	NaCl (%)
Dried Sample						-20 mesh	0.0 $NaNO_3$		7	100+	72	907	88	65	.19
MN-34	20.8	457	1000	A	15.5	"	"		12	64	7	125	74	79	.19
Dried Sample						-28 mesh	"		10	100+	66	898	91	85	.20
MN-35	16	454	755	A	13	"	"		10	38	9	106	77	82	.19
S-1	24.5	435	785	A	11	Steam	Drum 2 Light	52.5	12.6	28	26	129	96	96	
S-2	12.4	387	570	A	11	"	"	52.2	12.6	23	10	82	89	92.5	
Dried Sample		100 150		A			9.95 $NaNO_3$		7	100+	63	846	94	92	.22
S-3	15.8	460	870	A	11.5	"	"		10	25	8	69	92	92	.24
S-4	13.3	427	830	A	12.5	"	"		9	24	6	106	89	96	.23
S-5	13.1	402	830	A	13.5	"	"		9	32	5	173	88	96	.23
Dried Sample		100 150		A			5.5 $NaNO_3$		11	94	56	829	92	87	.19
S-6	15.7	437	880	A	11	"	"		14	38	6	101	89	92	.20
S-7	11.5	412	770	A	11.5	"	"		14	56	6	128	89	93	.20
S-8	12.1	475	750	A	14	"	Drum 2 Light	52.9	7	68	4	65	91	84	.03
S-9	13.7	412	860	A	15	"		51.7	11	47	5	113	92	83	.03
S-10	13.3	510	785	A	15	"	"	53.0	10	75	3	56	87	84	.03
S-11	10.1	450	758	A	13.5	"	"	52.8	13	70	7	40	90	88	.05

TABLE V ANALYTICAL AND OPERATING DATA (continued)

Run No.	Reten. Time (min)	Ave. Temp. (°C)	Bed Wt. (grams)	Fluid Medium	△P Bed	Remarks	Source	Bulk Den. #/ft³	Fe ppm	Foam Height (cm)	D-40 ppm	COD ppm	Ash Refl.	STPP Refl.	NaCl (%)
Dried Sample		100 150					0.0 $NaNO_3$		14	100+	58	851	86	55	.18
S-12	11.9	401	740	A	14.5		"		16	53	27	263	81	79	.19
S-13	11.4	459	660	A	12.5		"		17	67	13	147	77	76	--

TABLE VI CROSS INDEX OF OPERATING DATA

Grade 100 Ash Retention Time Index ± 2 min.

Index	Run No.	Retention	Temperature
2	40	2.4	409
	41	0.94	415
6	35	4.78	349
	36	4.72	413
	42	5.7	346
10	16	10.8	450
	20	11.5	411
	24	11.1	478
	34	11.6	443
	37	8.39	413
	38	10.7	412
	39	11.7	414
	43	8.6	415
	48	8.5	478
	49	11.0	477
	53	10.6	406
14	18	14.6	411
	22	15.2	475
	26	16.0	513
	29	12.1	503
	46	15.2	451 (N)
	54	15.9	420
18	14	16.2	439
	15	19.9	443
	19	19.7	412
	27	19.6	514
	30	19.1	556
	32	19.5	512 (N)
	44	16.7	344 (N)
	47	16.3	512 (N)
	50	17.1	476
	55	18.9	411
	57	19.9	476

TABLE VI CROSS INDEX OF OPERATING DATA (continued)

Index	Run No.	Retention	Temperature
22	23	20.5	472
	28	22.1	332
	31	22.3	333 (N)
	33	20.5	341
	45	22.3	403 (N)
	52	24.5	477
	56	24.7	414
28+	13	37	439
	17	29.1	411
	21	31.2	478
	25	28.5	513

Grade 100 Ash Temperature Index ± 10°C

Index	Run No.	Retention	Temperature
390-	28	22.1	332
	31	22.3	333 (N)
	33	20.5	341
	35	4.78	349
	42	5.7	346
	44	16.7	344 (N)
410	17	29.1	411
	18	14.6	411
	19	19.7	412
	20	11.5	411
	36	4.72	413
	37	8.39	412
	38	10.7	412
	39	11.7	414
	40	2.4	409
	41	0.94	415
	43	8.6	415
	45	22.3	403 (N)
	53	10.6	406
	54	15.9	420
	55	18.9	411
	56	24.7	414

TABLE VI CROSS INDEX OF OPERATING DATA (continued)

Index	Run No.	Retention	Temperature
450	13	37.0	439
	14	16.2	439
	15	19.9	443
	16	10.8	450
	34	11.6	443
	46	15.2	451 (N)
470	21	31.2	478
	22	15.2	475
	23	20.5	472
	24	11.1	478
	48	8.5	478
	49	11.0	477
	50	17.1	476
	52	24.5	477
	57	19.9	476
510	25	28.5	513
	26	16.0	513
	27	19.6	514
	29	12.1	503
	32	19.5	510 (N)
	47	16.3	512 (N)
	30	19.1	556

Monohydrate and Added $NaNO_3$

#$NaNO_3$/ton	Run No.	Retention	Temperature
0	M-1	15.8	410
	M-2	10.5	450
	M-3	14.2	478
	M-4	12.0	509
	M-5	13.1	478
	M-6	14.0	354
	M-7	0.96	416
	M-8	18.3	433
	M-9	16.2	465
	M-10	13.7	468
	M-11	18.0	463
	MN-4	15.4	478
	MN-13	11.1	393
	MN-14	10.8	435

TABLE VI CROSS INDEX OF OPERATING DATA (continued)

Monohydrate and Added $NaNO_3$

#$NaNO_3$/ton	Run No.	Retention	Temperature
0	MN-15	11.9	558
	MN-24	13.9	391 (N)
	MN-25	13.6	448 (N)
	MN-26	13.3	412
	MN-34	20.8	457
	MN-35	16.0	454
2.3	MN-3	11.3	474
	MN-11	13.6	394
	MN-12	13.5	439
	MN-16	12.5	560
	MN-27	15.8	386
	MN-28	15.3	442
5.5	MN-2	15.3	478
	MN-8	18.0	390
	MN-9	13.9	436
	MN-10	10.3	550
	MN-17	26.0	435
	MN-18	7.0	442
	MN-19	9.0	433
	MN-20	2.74	430
	MN-29	16.5	394
	MN-30	16.8	485
9.95	MN-1	17.2	479
	MN-5	14.8	390
	MN-6	11.0	433
	MN-7	15.8	546
	MN-21	12.9	481 (N)
	MN-22	12.6	391 (N)
	MN-23	11.7	441 (N)
	MN-31	12.5	396
	MN-32	18.0	477
	MN-33	12.5	427

TABLE VI CROSS INDEX OF OPERATING DATA (continued)

Nitrogen used as Fluidizing Medium
LA = Light Ash
MN-X = Monohydrate + X Pounds $NaNO_3$ added/ton

Run No.	Retention	Temperature	Material
31	22.3	333	L A
32	19.5	510	L A
44	16.7	344	L A
45	22.3	403	L A
46	15.2	451	L A
47	16.3	512	L A
MN-21	12.9	481	MN-9.95
MN-22	12.6	391	MN-9.95
MN-23	11.7	441	MN-9.95
MN-24	13.9	391	MN-0
MN-25	13.6	448	MN-0

Runs Made Using a Mixture of Ligh Ash and Monohydrate
Light Ash from Drum 2
Monohydrate from Drum 1

Run No.	Retention	Temperature	Gms Monohydrate / Gms Light Ash
RM-L-1	13.4	438	1 / 2
RM-L-2	19.4	451	1 / 1
RM-L-3	12.7	432	2 / 1

Runs Made Using Light Ash or Monohydrate and Steam in the Fluidizing Air

Run No.	Retention	Temperature	Kind of Ash
S-1	24.5	435	L A
S-2	12.4	387	L A
S-3	15.8	460	MN-9.95
S-4	13.3	427	MN-9.95
S-5	13.1	402	MN-9.95
S-6	15.7	437	MN-5.5
S-7	11.5	412	MN-5.5
S-8	12.1	475	L A
S-9	13.7	412	L A

TABLE VI CROSS INDEX OF OPERATING DATA (continued)

Runs Made Using Light Ash or Monohydrate in the Fluidizing Air

Run No.	Retention	Temperature	Kind of Ash
S-10	13.3	510	L A
S-11	10.1	450	L A
S-12	11.9	401	MN-0
S-13	11.4	459	MN-0

Chamber Product

Run No.	Retention	Temperature
C-1	14.4	501
C-2	17.6	522
C-3	19.3	553

TABLE VII TYPICAL SCREEN ANALYSIS

Cumulative Percent Retained on U. S. Screen

Screen	Drum 3	Run 48	Run 49	Run 50	Run 52	Run 53	Run 54	Run 55	Run 56	Run 57
+30	3.7	1.5	1.9	1.7	2.7	1.4	3.0	1.5	2.1	3.9
+40	17.2	8.8	11.1	10.9	13.9	9.4	16.3	12.1	12.1	16.8
+100	79.8	72.1	73.6	74.2	78.8	71.7	78.8	76.1	76.1	79.1
+140	92.7	89.5	89.8	90.2	92.3	88.7	91.4	90.6	90.6	91.5
+200	98.1	97.3	97.0	97.3	98.1	96.5	97.2	97.0	97.0	97.2
+325	99.6	99.8	99.7	99.6	99.9	99.4	99.5	99.7	99.7	99.4
-325	0.4	0.2	0.3	0.4	0.1	0.6	0.5	0.3	0.3	0.6

TABLE VIII FIRST ORDER REACTION DATA (Drum 1)

Run No.	COD_o	COD_f	log COD_o/COD_f	Retention	Temp. °C
13	362	117	.490	37	439
14	"	130	.444	16.2	439
15	"	120	.480	19.9	443
34	"	134	.432	11.6	443
17	"	142	.407	29.1	411
18	"	150	.382	14.6	411
19	"	139	.416	19.7	412
20	"	158	.360	11.5	411
36	"	158	.360	4.72	413
37	"	159	.357	8.39	413
21	"	118	.487	31.2	478
22	"	127	.455	15.2	475
23	"	108	.525	20.5	472
24	"	127	.455	11.1	478

TABLE IX CHEMICAL REACTION DATA (Drum 3)

Run No.	COD_o	COD_f	log COD_o/COD_f	Retention	Temp. °C.
48	483	111	.638	8.5	478
49	"	145	.523	11.0	477
50	"	95	.707	17.1	476
52	"	93	.715	24.5	477
57	"	174	.444	19.9	476

TABLE X CHEMICAL REATION DATA (Monohydrate Ash)

Run No.	$NaNO_3$/ton	COD_o	COD_f	log COD_o/COD_f	Reten.	Temp. °C.
MN-17	5.5	928	359	.412	26	435
MN-18	5.5	928	461	.304	7	442
MN-19	5.5	928	419	.346	9	433
MN-20	5.5	928	461	.304	2.74	430

TABLE XI MASS TRANSFER DATA FOR LIGHT ASH

Run No.	Reten.	Temp. °K	B.W.	COD_o	COD_f	N	log N	t	$\sqrt{\frac{900\ T}{683\ BW}}$	$\log\sqrt{\frac{900\ T}{683\ BW}}$
19	19.7	685	865	362	139	11.32	1.05385	.0014599	1.027	.01157
15	19.9	726	910	362	120	12.17	1.08529	.0013966	1.021	.00903
23	20.5	745	830	362	108	12.40	1.09342	.0013423	1.090	.03743

TABLE XII MASS TRANSFER DATA FOR LIGHT ASH (19-21 min.)

Run No.	Reten.	Temp. °K	B.W.	COD_o	COD_f	N	$\sqrt{\frac{900\ T}{683\ BW}}$	$e^{K't}/T$	K
19	19.7	685	865	362	139	11.32	1.027	.646	17.1
15	19.9	716	910	362	120	12.17	1.021	.658	18.1
23	20.5	745	830	362	108	12.40	1.090	.669	17.0
27	19.6	787	855	362	122	12.2	1.11	.684	16.1
30	19.1	829	690	362	100	13.7	1.26	.697	15.7

TABLE XIII MASS TRANSFER DATA (14-16 min.)

Run No.	Reten.	B.W.	COD_o	COD_f	N	Temp. °K	$e^{K'}/T$	$\sqrt{\frac{900\ T}{683\ BW}}$	K
14	16.2	893	362	130	14.3	712	.657	1.03	21.1
18	14.6	802	362	150	14.5	684	.645	1.06	21.2
26	16.0	825	362	105	16.0	786	.684	1.12	20.9

TABLE XIV MASS TRANSFER DATA (10-12 min.)

Run No.	Reten.	B.W.	COD_o	COD_f	N	Temp. °K	$e^{K'}/T$	$\sqrt{\frac{900\ T}{683\ BW}}$	K
20	11.5	950	362	158	17.74	684	.645	.974	28.3
24	11.1	865	362	127	21.17	751	.671	1.07	29.4
29	12.1	690	362	116	20.33	776	.680	1.218	24.8
34	11.6	945	362	134	19.66	716	.658	.999	29.8

TABLE XV MASS TRANSFER DATA ABOVE 21 MINUTES AND BELOW 10 MINUTES.

Run No.	Reten.	B.W.	COD_o	COD_f	N	Temp. °K	$\sqrt{\frac{900\ T}{683\ BW}}$	e^{K}/T	K
13	37.0	903	362	117	6.62	712	1.02	.656	9.9
17	29.1	740	362	142	7.56	684	1.11	.645	10.6
21	31.2	765	362	118	7.85	751	1.14	.671	10.2
25	28.5	720	362	100	9.19	786	1.20	.684	11.2
36	4.72	650	362	158	43.22	686	1.19	.647	56.0
37	8.39	965	362	159	24.20	686	0.97	.647	37.4

TABLE XVI MASS TRANSFER DATA FOR NITROGEN RUNS

Run No.	Reten.	B.W.	COD_o	COD_f	N	Temp. °K	$\sqrt{\frac{900\ T}{683\ BW}}$	e^{K}/T	K
32	19.5	1084	362	132	11.8	783	.980	.682	17.7
45	22.3	1190	317	207	4.93	676	.870	.642	8.8
46	15.2	970	317	153	10.8	724	.995	.661	16.5
47	16.3	1020	317	128	11.6	785	1.01	.682	16.9

TABLE XVII MASS TRANSFER DATA FOR LIGHT ASH
(Temperatures Below 400°C)

Run No.	Reten.	Temp. °K	B.W.	COD_o	COD_f	N	$\sqrt{\frac{900\ T}{683\ BW}}$	$e^{K'/T}$	K
33	20.5	614	940	362	237	6.1	0.933	.613	10.6
35	4.78	622	875	362	267	19.87	0.97	.618	33.1

TABLE XVIII MASS TRANSFER DATA FOR LIGHT ASH (Drum 3)

Run No.	Reten.	Temp. °K	B.W.	COD_o	COD_f	N	$\sqrt{\frac{900\ T}{683\ BW}}$	$e^{K'/T}$	K
48	8.5	751	905	483	111	43.76	1.05	.671	56.7
49	11.0	750	980	483	145	30.7	1.01	.671	45.3
50	17.1	749	990	483	95	22.6	1.00	.670	33.8
52	24.5	750	890	483	93	15.92	1.01	.671	23.5
53	10.6	679	990	483	176	28.9	.955	.643	47.1
54	15.9	749	970	483	270	13.4	.971	.650	21.2
55	18.9	684	960	483	149	17.7	.973	.645	28.3
56	24.7	687	945	483	233	10.12	.98	.647	16.1
57	19.9	749	940	483	174	15.5	1.03	.670	22.5

TABLE XIX MASS TRANSFER DATA FOR LIGHT ASH (Drum 2)

Run No.	Reten.	B.W.	COD_o	COD_f	Temp. °K	N	$e^{K'/T}$	$\sqrt{\frac{900\ T}{683\ BW}}$	K
38	10.7	472	317	149	685	15.7	.646	1.39	17.6
39	11.7	247	317	148	687	14.4	.648	1.92	11.6
40	2.4	264	317	183	682	55.83	.644	1.85	46.8
42	5.7	1025	317	274	619	7.54	.616	.89	13.8
43	8.6	1060	317	161	688	18.14	.647	.92	30.2

TABLE XX MASS TRANSFER DATA FOR MONOHYDRATES

Run No.	Reten.	Temp. °K	B.W.	COD_o	COD_f	n'	t	$\log\sqrt{\frac{900\ T}{683\ BW}}$
MN-13	11.1	666	855	910	461	1.60692	.0015015	.00604
MN-14	10.8	708	815	910	436	1.64227	.0014124	.02898
MN-15	11.9	831	950	910	362	1.66323	.0012033	.03019

TABLE XXI MASS TRANSFER COEFFICIENTS FOR MONOHYDRATES

Run No.	Temp. °K	B.W.	COD_o	COD_f	N	Reten.	$\sqrt{\frac{900\ T}{683\ BW}}$	$e^{K'}/T$	K
M-1	683	688	459	318	8.93	15.8	1.15	.701	11.1
M-2	723	455	459	256	19.3	10.5	1.45	.715	18.6
M-3	751	500	459	256	14.3	14.2	1.41	.724	14.0
M-4	782	510	640	238	33.5	12.0	1.43	.733	32.2
M-5	751	510	640	254	29.4	13.1	1.41	.724	28.9
M-6	627	555	640	352	20.6	14.0	1.22	.679	24.9
M-7	689	110	640	181	47.9	0.96	2.88	.703	237.0
MN-4	751	1212	910	389	33.8	15.4	0.905	.724	51.7
MN-13	666	855	910	461	40.45	11.1	1.014	.694	57.6
MN-14	708	815	910	436	43.88	10.8	1.069	.709	58.0
MN-15	831	950	910	362	46.05	11.9	1.072	.747	57.6
MN-34	730	1000	907	125	37.7	20.8	0.98	.716	53.8
MN-35	726	755	898	106	49.5	16.0	1.13	.715	61.4

TABLE XXII FINAL COD VALUES FOR MONOHYDRATES AT VARIOUS TEMPERATURES AND AMOUNTS OF ADDED NITRATE CORRECTED TO 900g BW.

Run No.	$NaNO_3$ #/ton of Ash	Temp. °C	COD_f Corrected
MN-13	0	393	473
MN-11	2.3	394	405
MN-8	5.5	390	438
MN-14	0	435	462
MN-12	2.3	439	308
MN-9	5.5	436	396
MN-15	0	558	348
MN-16	2.3	560	264
MN-10	5.5	550	268

TABLE XXIII COMPARISON OF STEAM RUNS TO NORMAL CALCINATION.

Run No.	Temp. °C	Reten. (min)	Bed Wt. (gms.)	COD_i ppm	COD_f ppm	% Red. COD	% Red. COD corrected to BW 900 gms.	COD_f corrected to BW 900 grams
S-9	412	13.7	860	317	113	64.4	62.9	117
S-1	435	24.5	785	317	129	59.3	55.5	141
S-11	450	10.1	758	317	40	87.5	80.4	62
S-8	475	12.1	750	317	65	79.5	72.5	87
S-10	510	13.3	785	317	56	82.3	76.8	74
19	412	19.7	865	362	139	61.7	60.5	143
14	439	16.2	893	362	130	64.1	64.1	130
34	443	11.6	945	362	134	63.0	64.5	129
24	478	11.1	865	362	127	65.0	63.7	131
26	513	16.0	825	362	105	71.2	68.0	116
S-12	401	11.9	740	851	263	69.1	62.7	318
S-13	459	11.4	660	851	147	82.6	70.8	248
MN-13	393	11.1	855	910	461	49.4	48.0	473
MN-14	435	10.8	815	910	436	52.1	49.6	459
S-7	412	11.5	770	829	128	84.6	78.3	180
S-6	437	15.7	880	829	101	87.8	87.0	108
MN-8	390	18.0	1000	831	421	49.4	52.0	400
MN-9	436	13.9	985	831	415	50.1	52.5	395
S-5	402	13.1	830	846	173	79.5	76.3	201
S-4	427	13.3	830	846	106	87.5	84.0	135
MN-5	390	14.8	975	1004	505	49.6	51.7	487
MN-6	433	11.0	935	1004	480	52.1	53.1	471

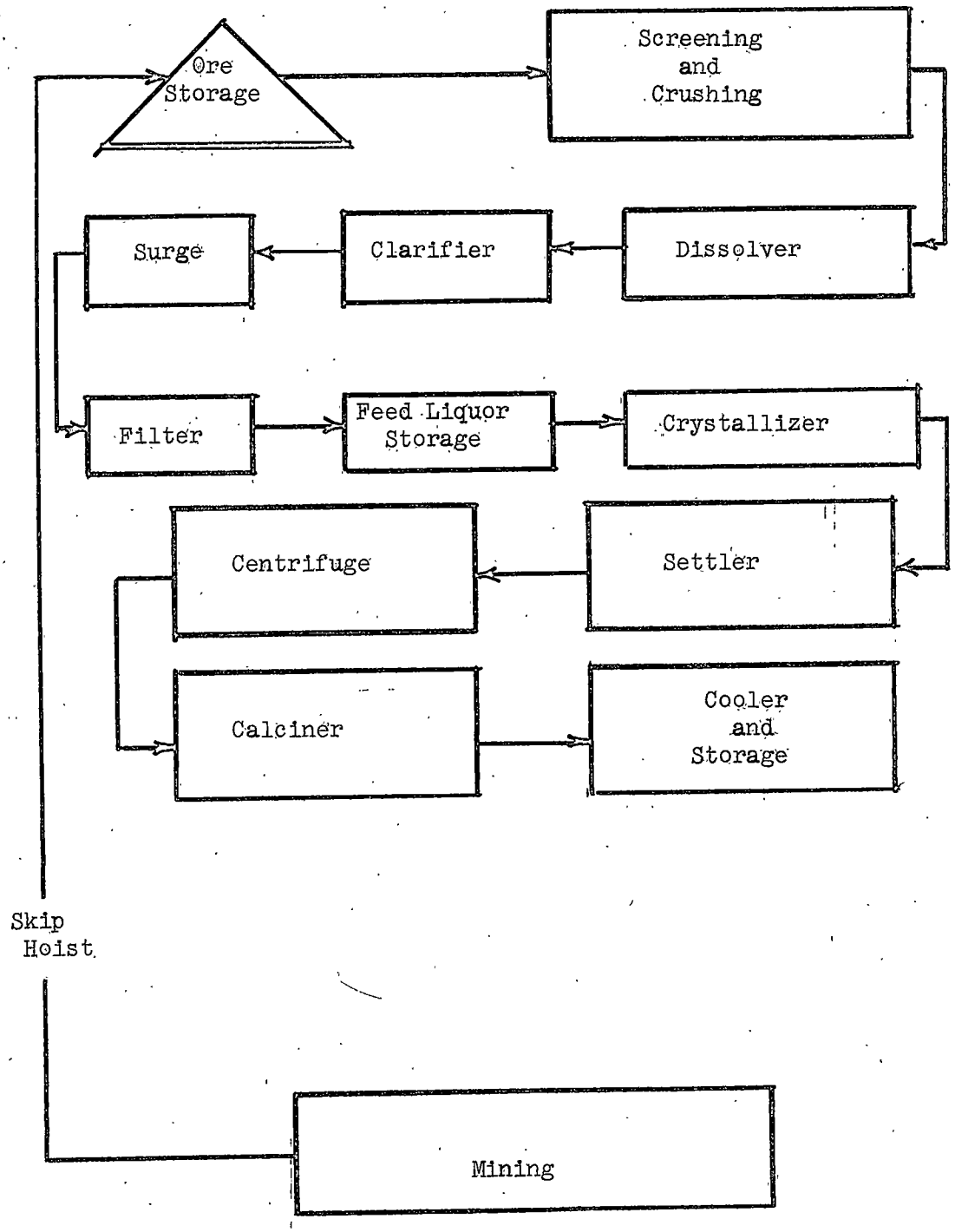
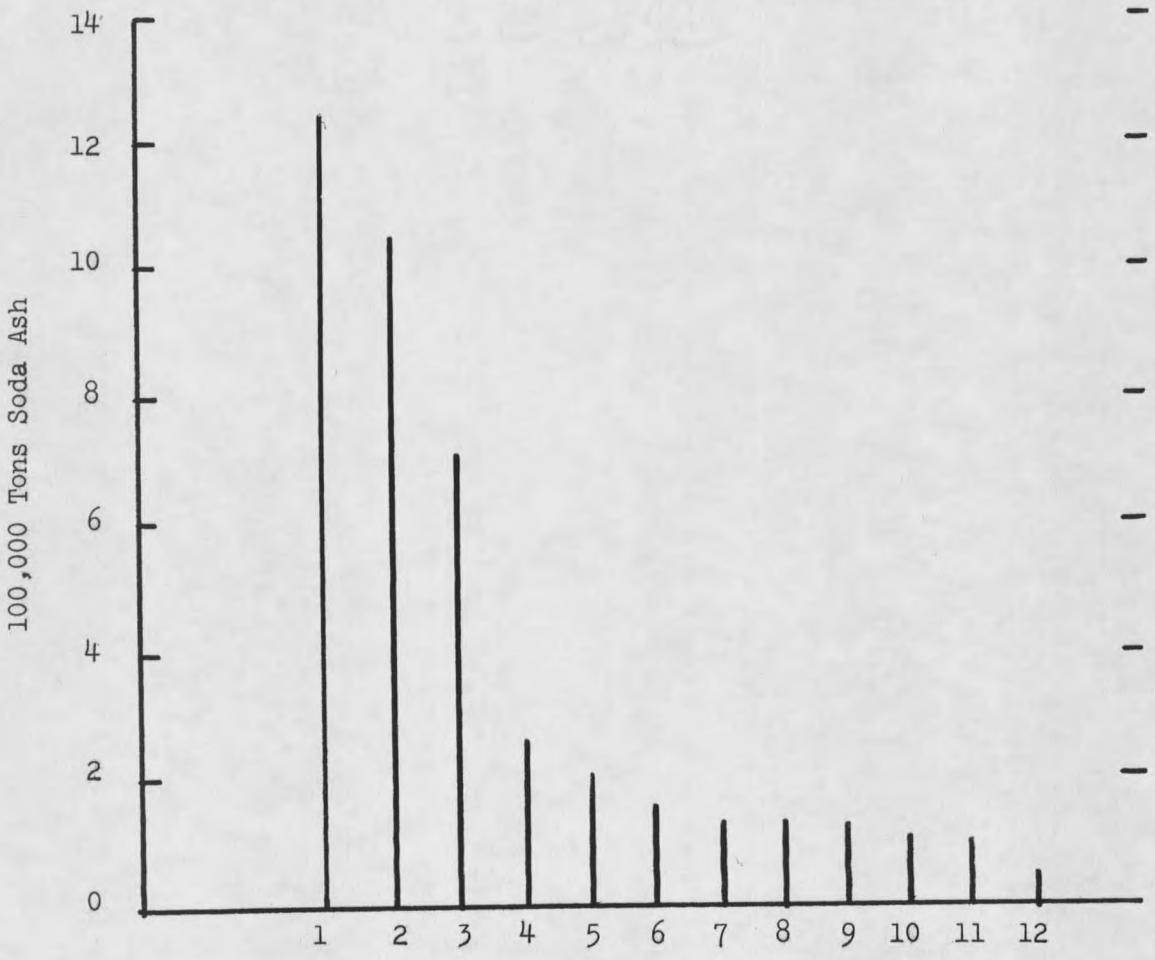


Figure 1. Manufacture of Westvaco Soda Ash.



Uses of Soda Ash

1 Glass
2 Other Chemicals
3 Caustic & Bicarbonate
4 Non-ferrous Metals
5 Pulp & Paper
6 Miscellaneous
7 Cleansers & Modified Sodas
8 Soap
9 Water Softeners
10 Textiles
11 Exports
12 Petroleum Refining

Figure 2. Soda Ash Distribution.

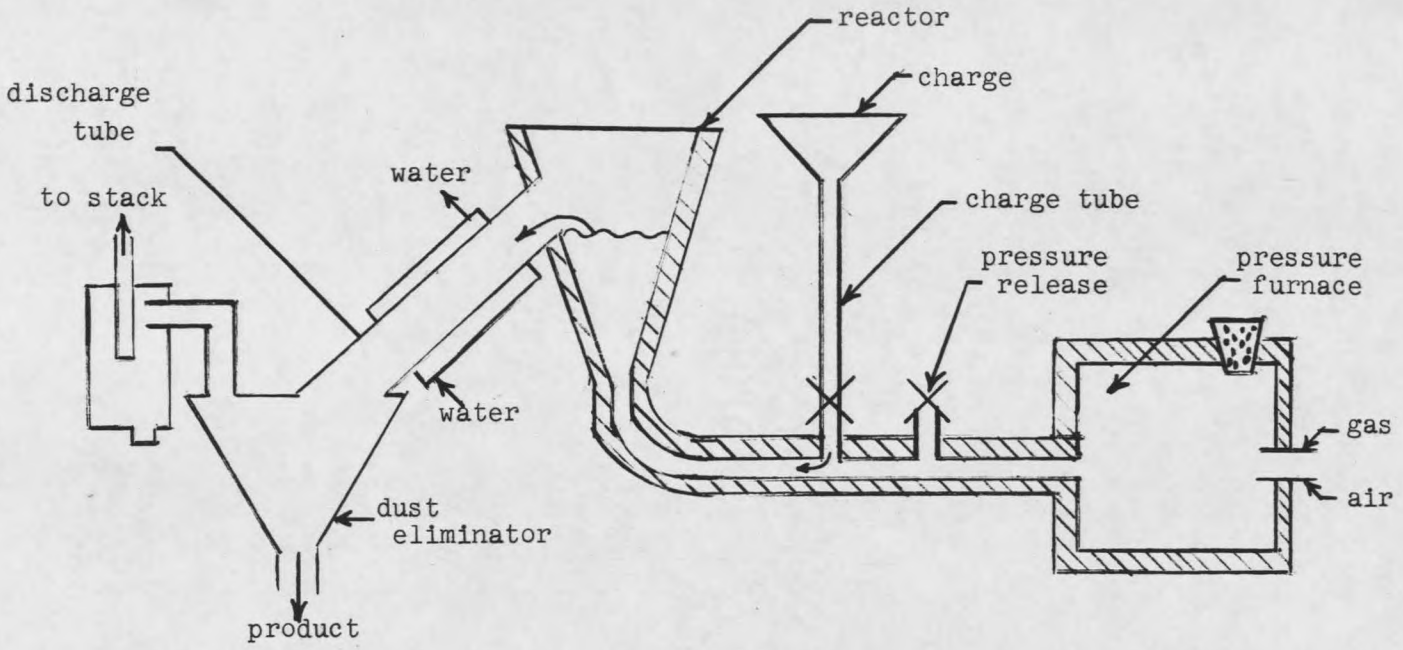


Figure 3. First Fluid Calciner.

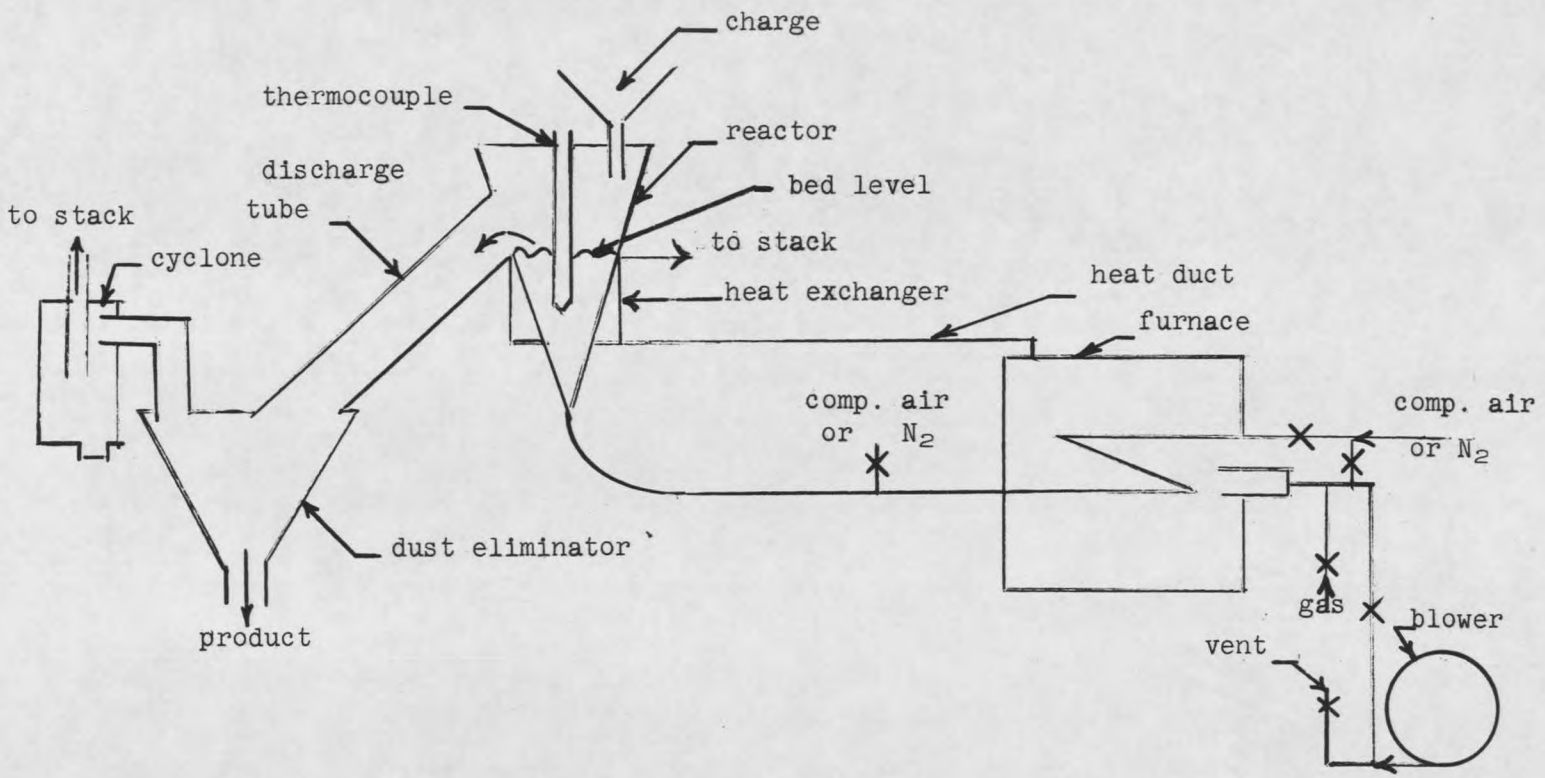


Figure 4. Schematic Flow Diagram of Final Fluid Calciner.

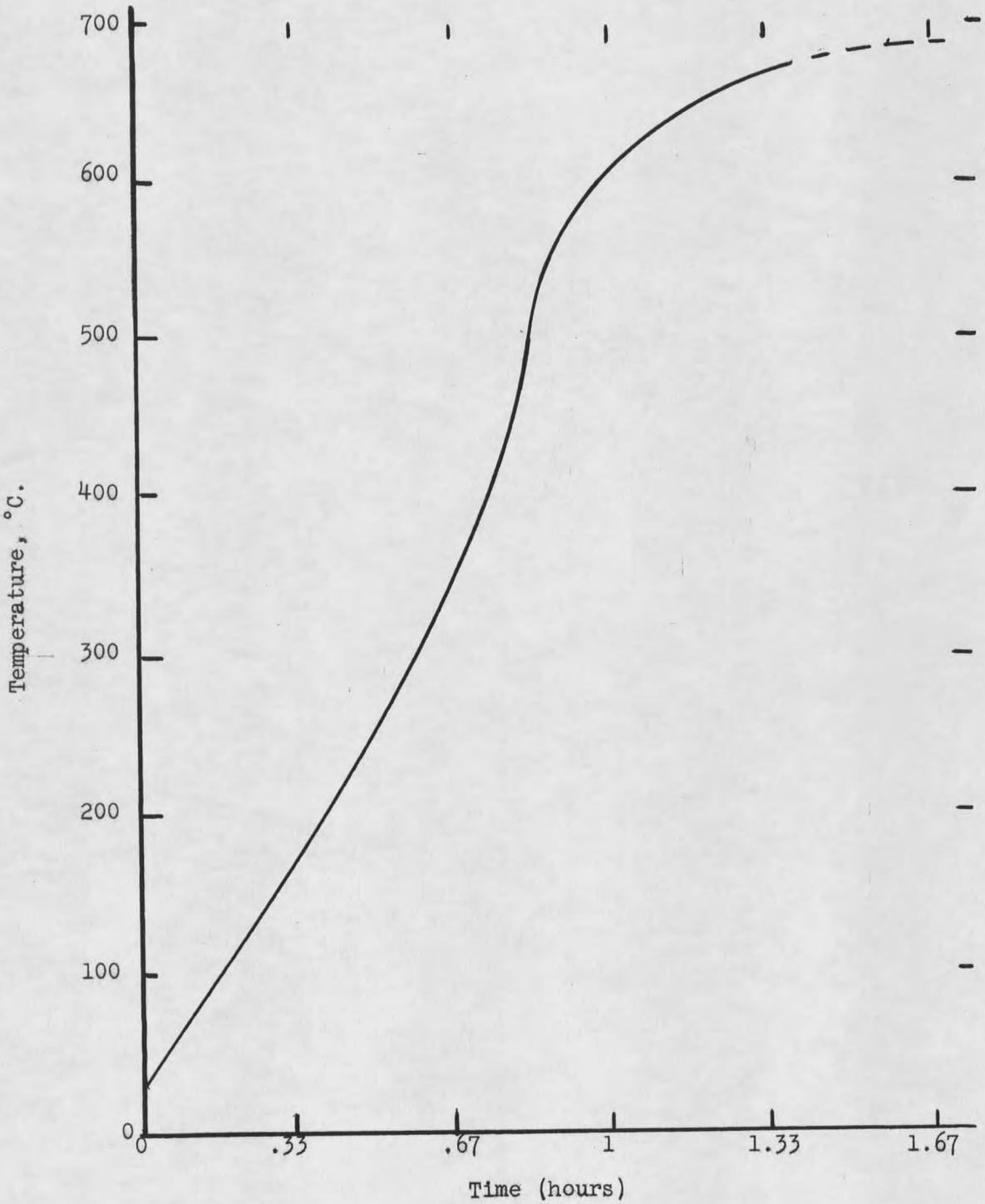


Figure 5. Heat-up Curve for Unit.

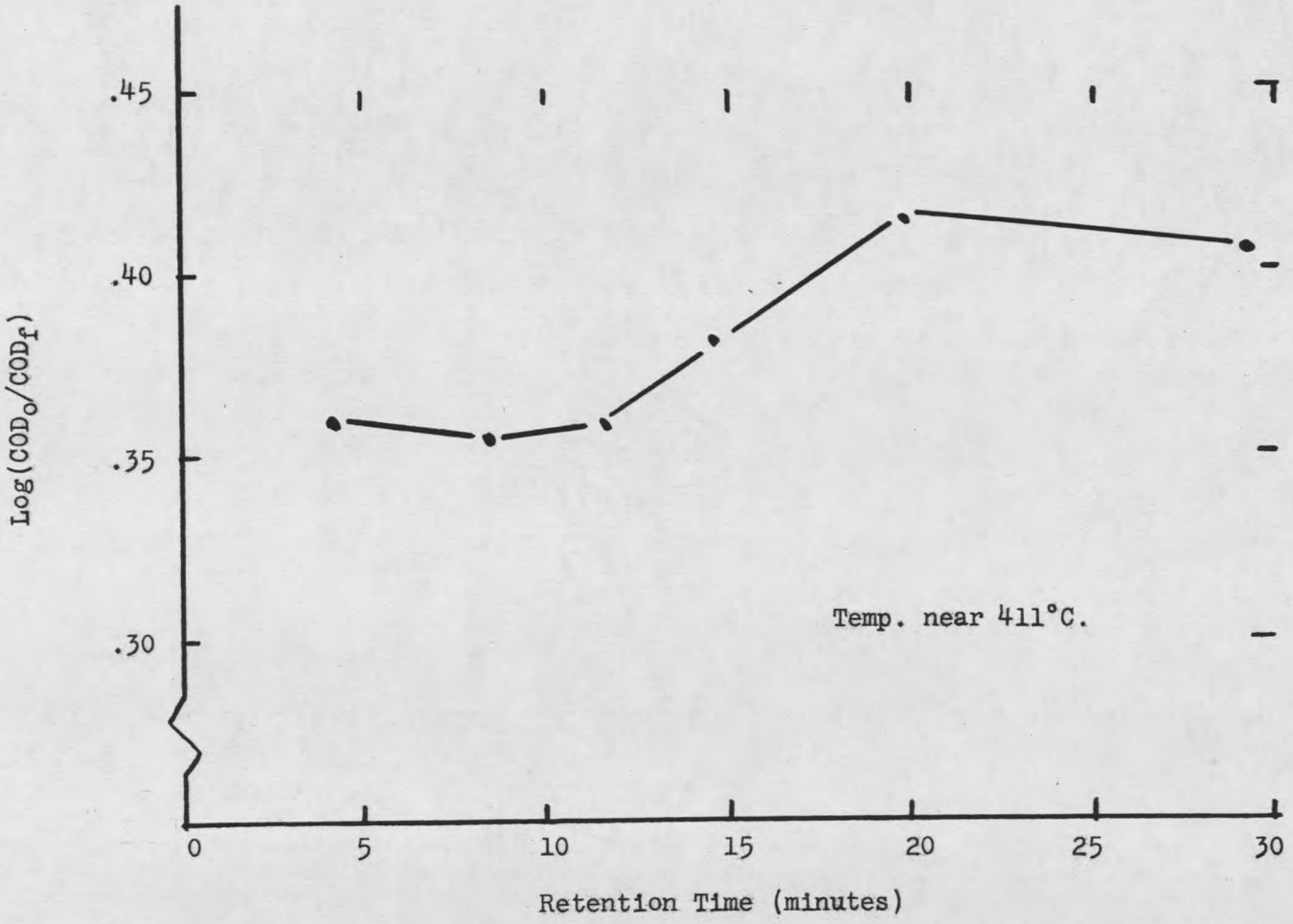


Figure 6. Log(COD$_o$/COD$_f$) vs. Retention Time.

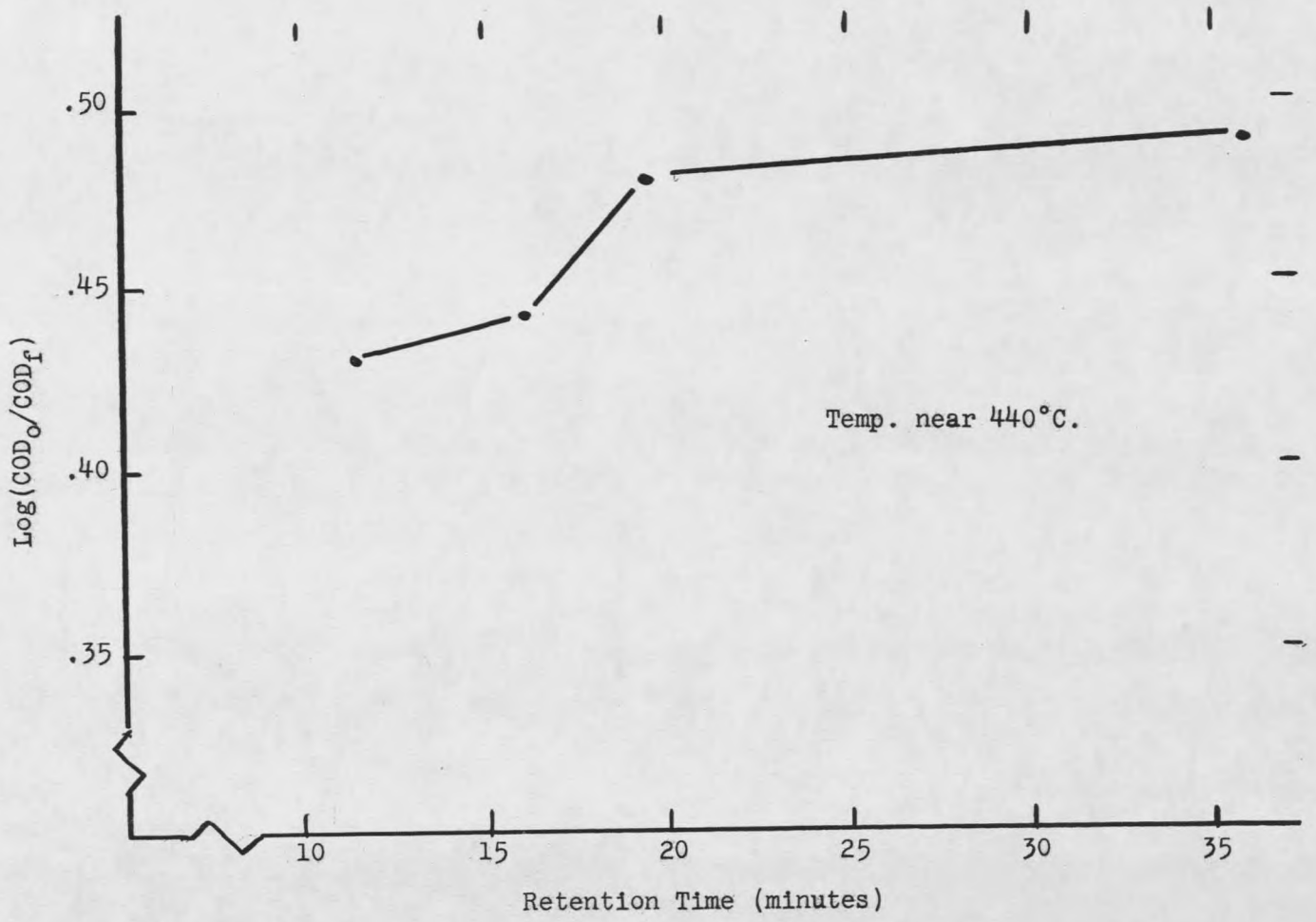


Figure 7. Log(COD$_o$/COD$_f$) vs. Time.

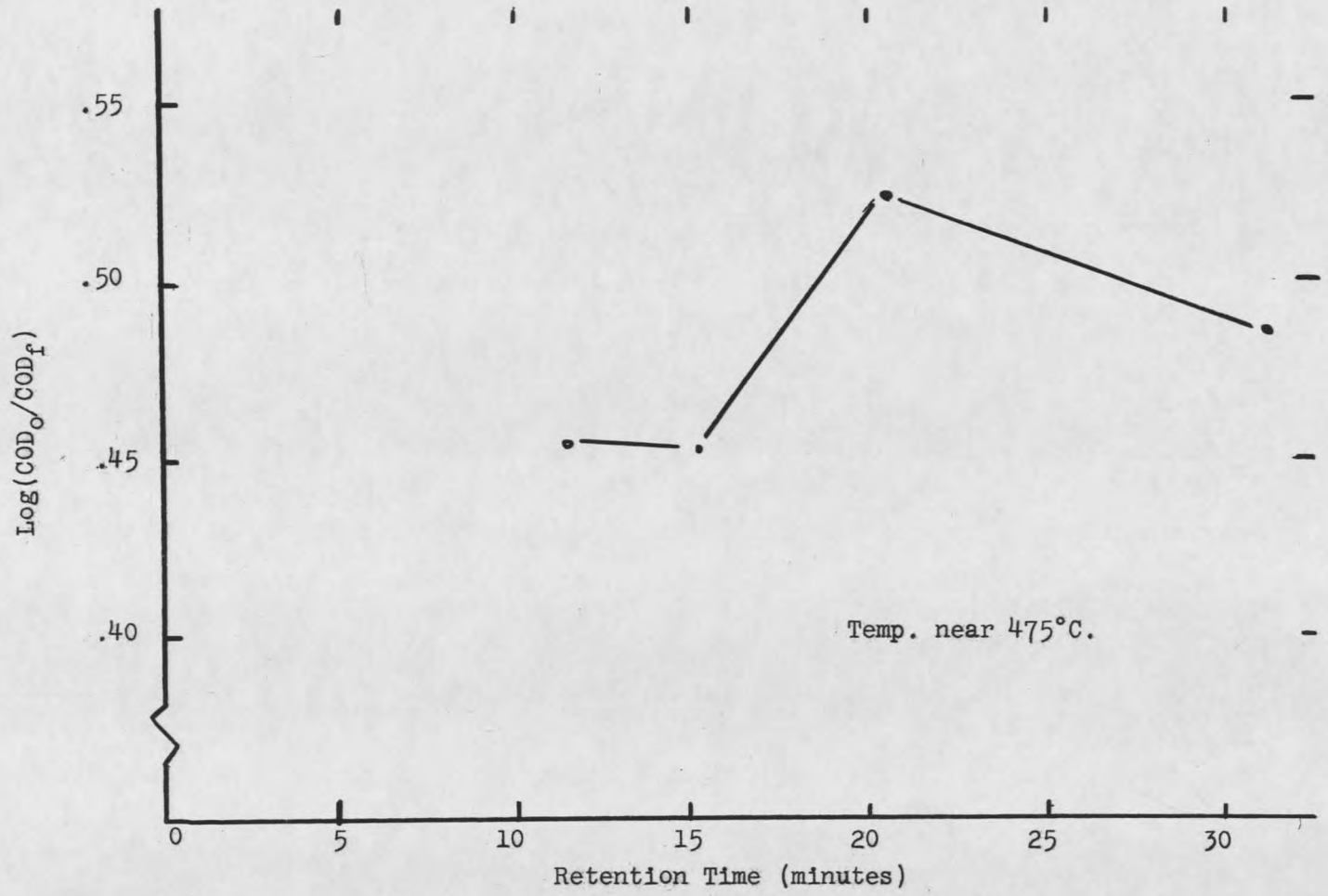


Figure 8. Log(COD$_o$/COD$_f$) vs. Time.

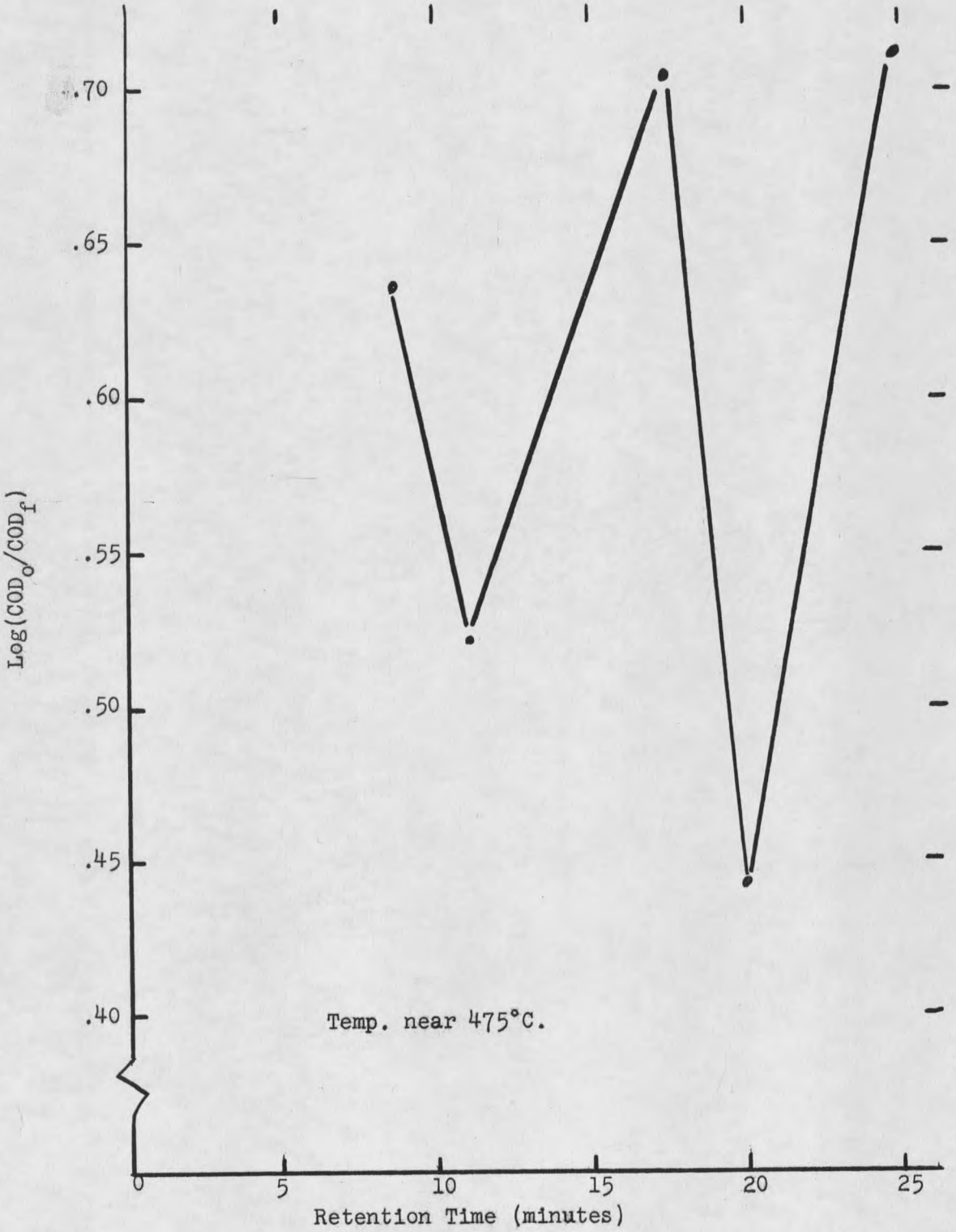


Figure 9. Log(COD$_o$/COD$_f$) vs. Time. (Drum 3)

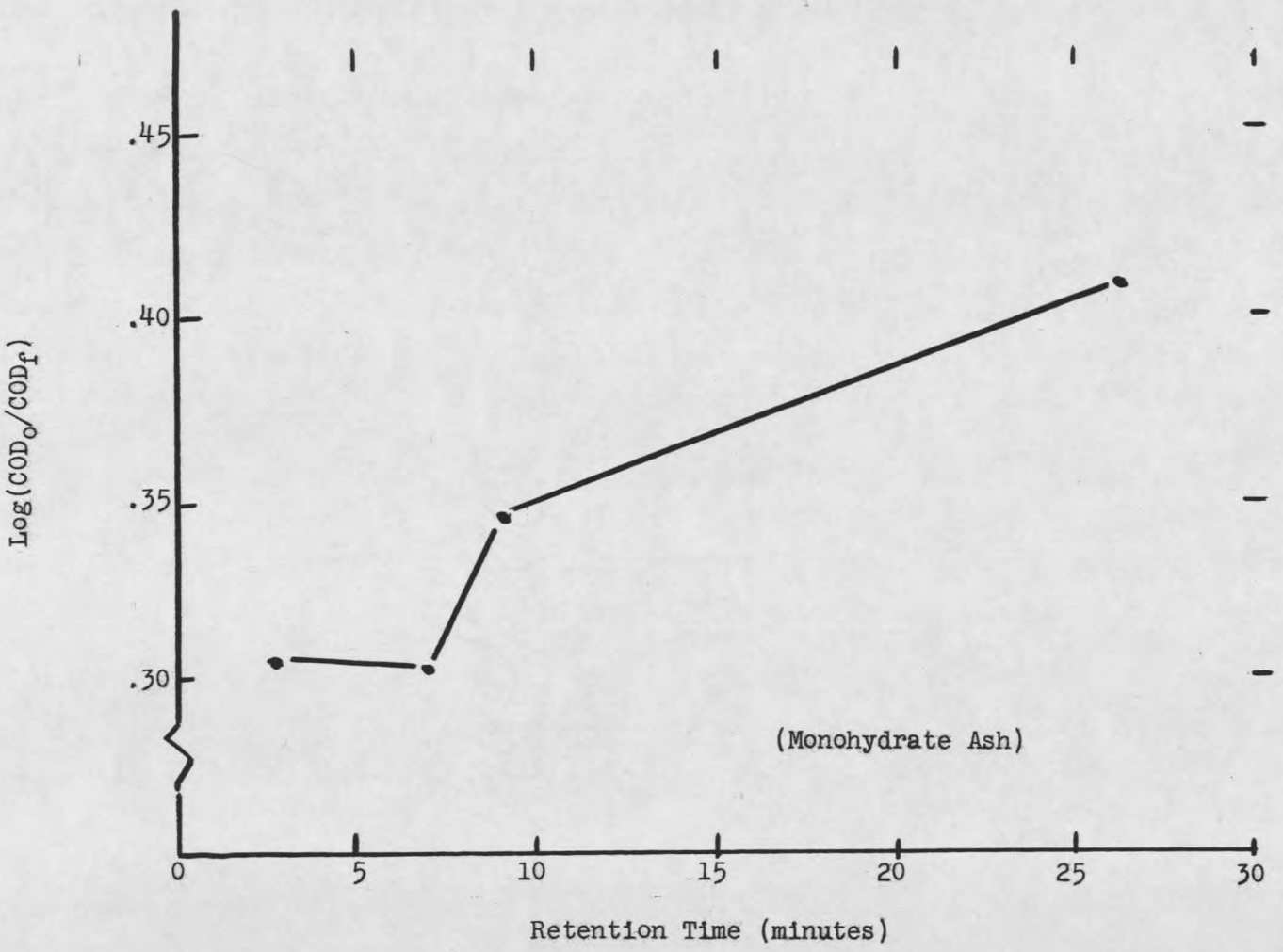


Figure 10. Log(COD$_o$/COD$_f$) vs. Time.

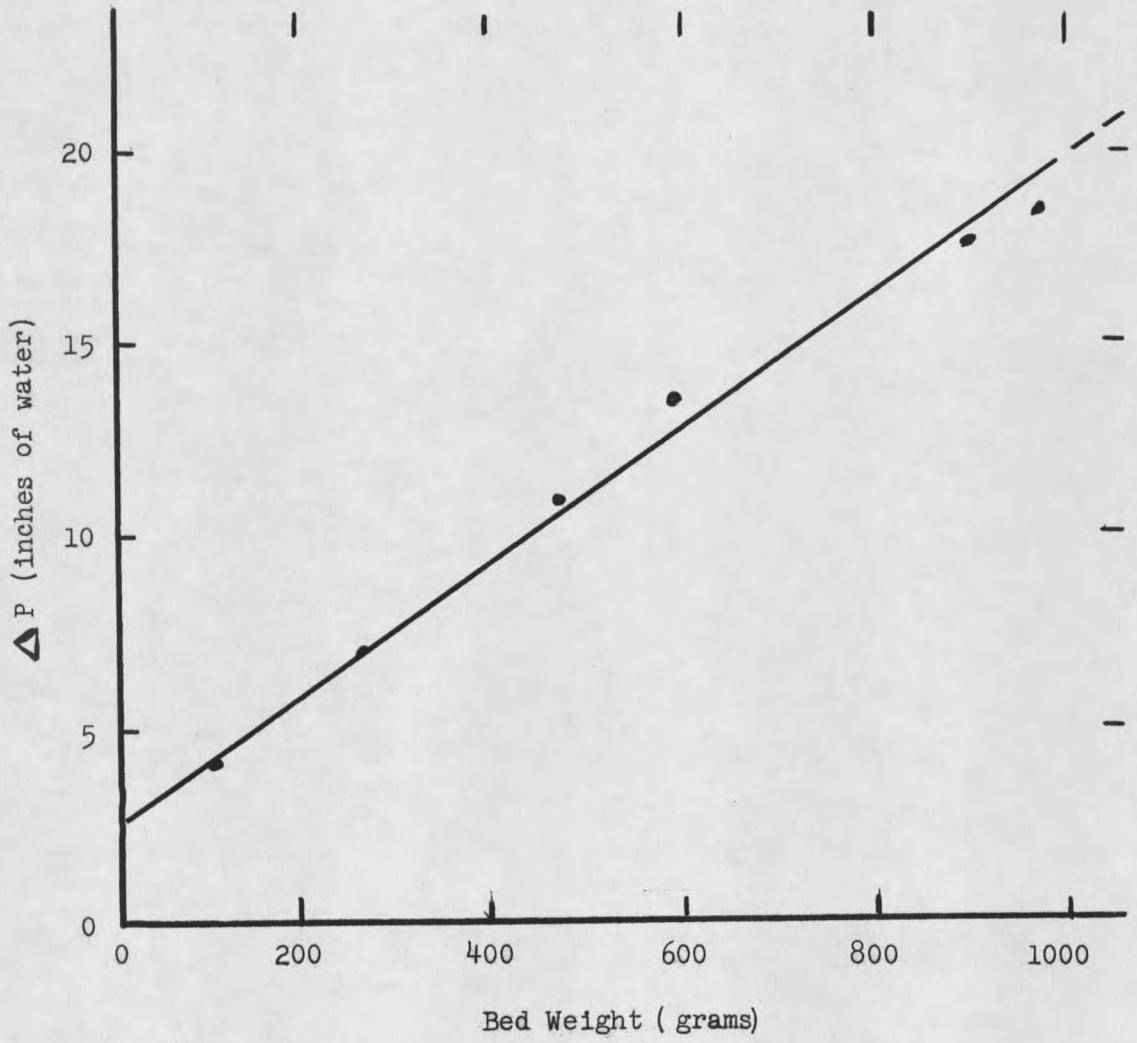


Figure 11. Pressure Drop vs. Bed Weight.

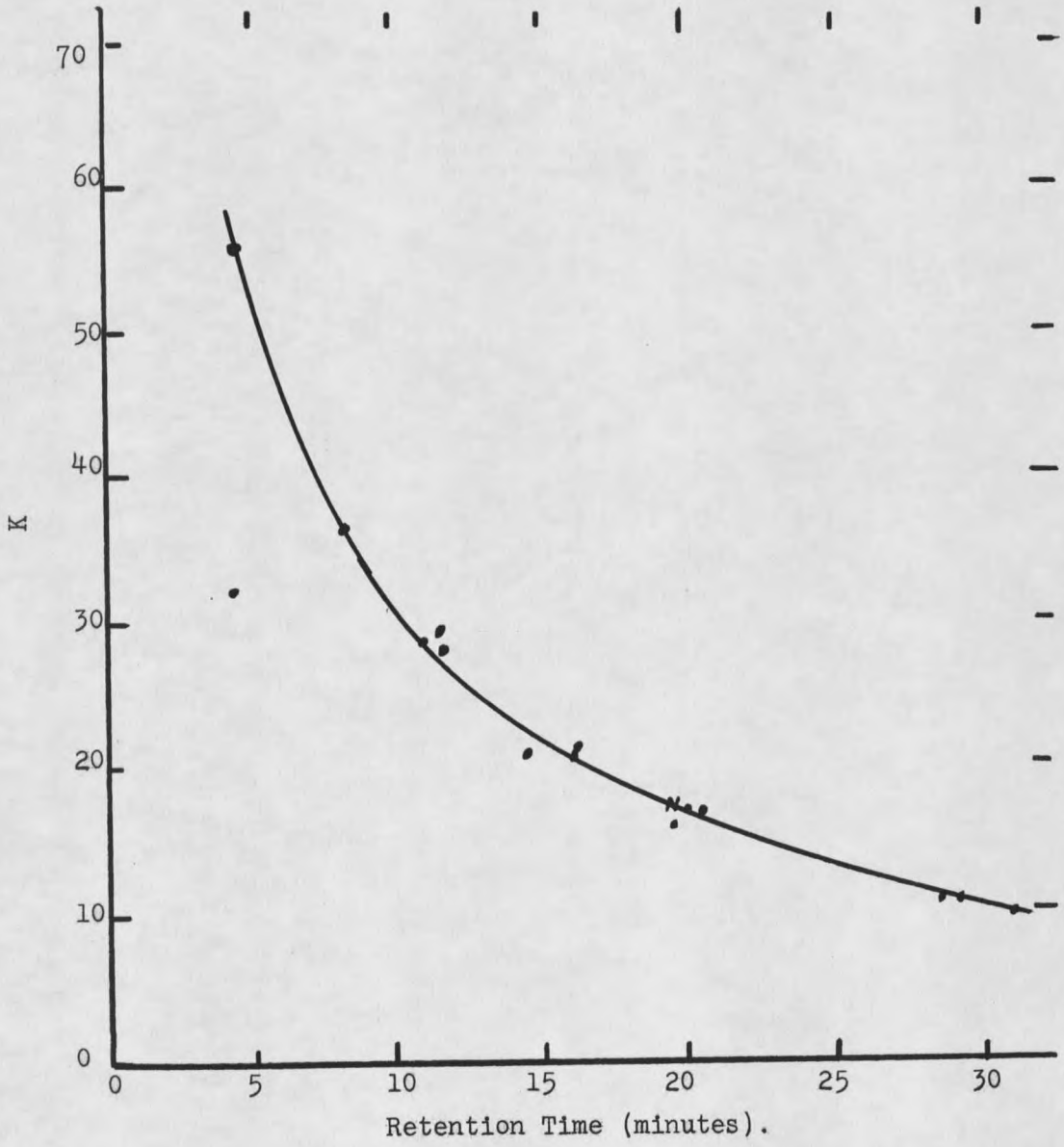


Figure 12. Mass Transfer Coefficients vs. Retention Time for Drum 1 Light Ash.

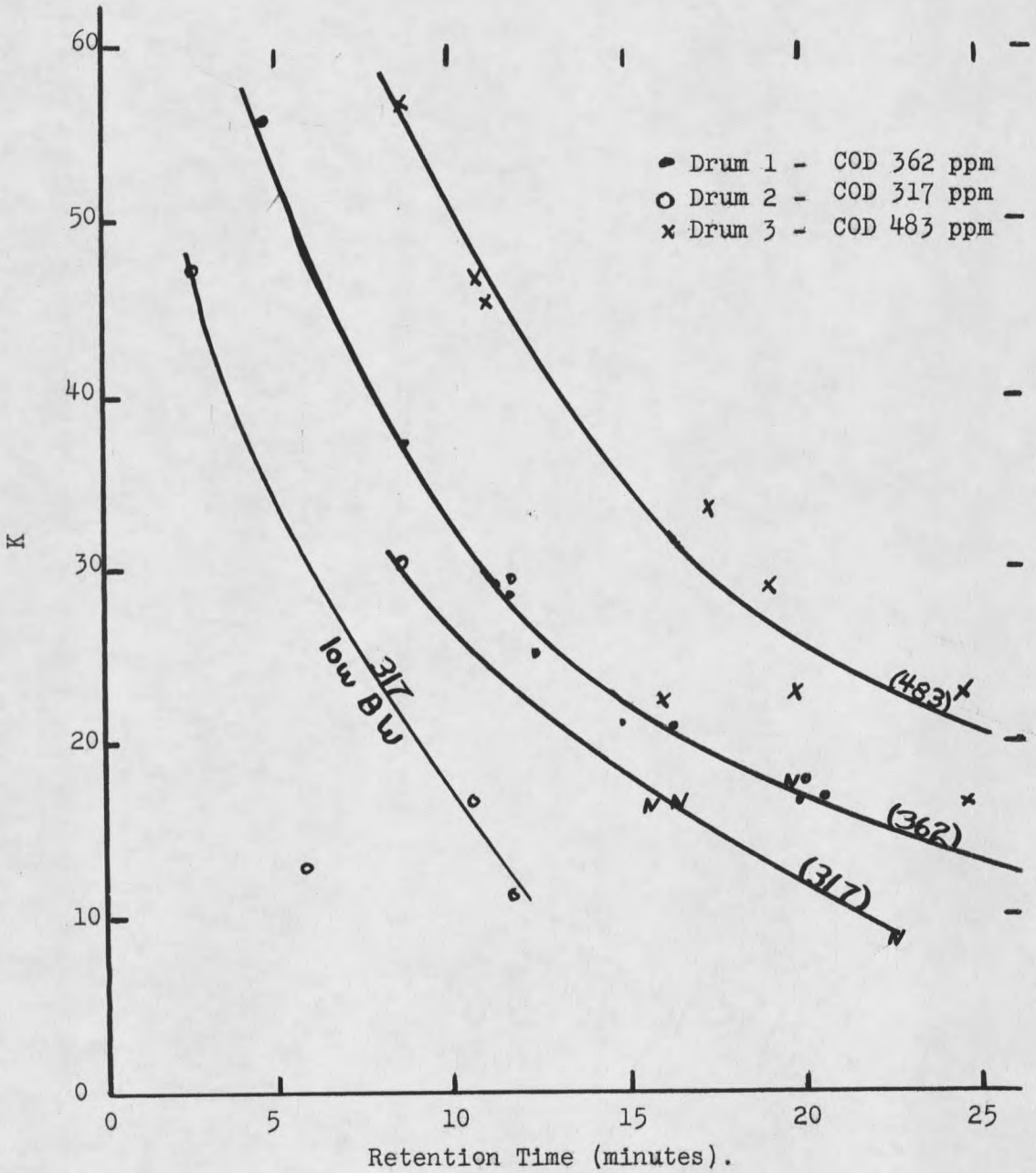


Figure 13. Mass Transfer Coefficients vs. Retention Time.

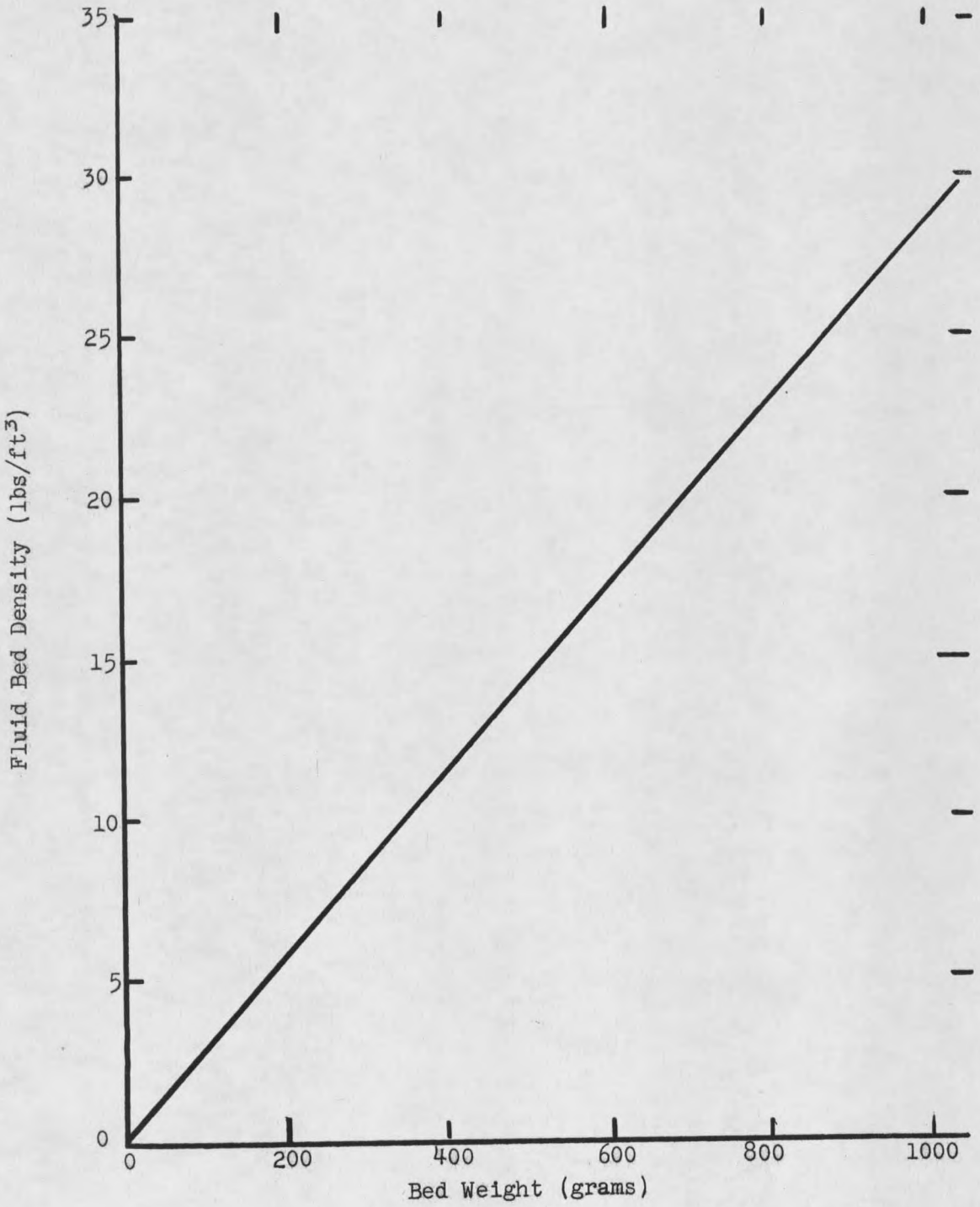


Figure 14. Fluid Bed Density vs. Bed Weight.

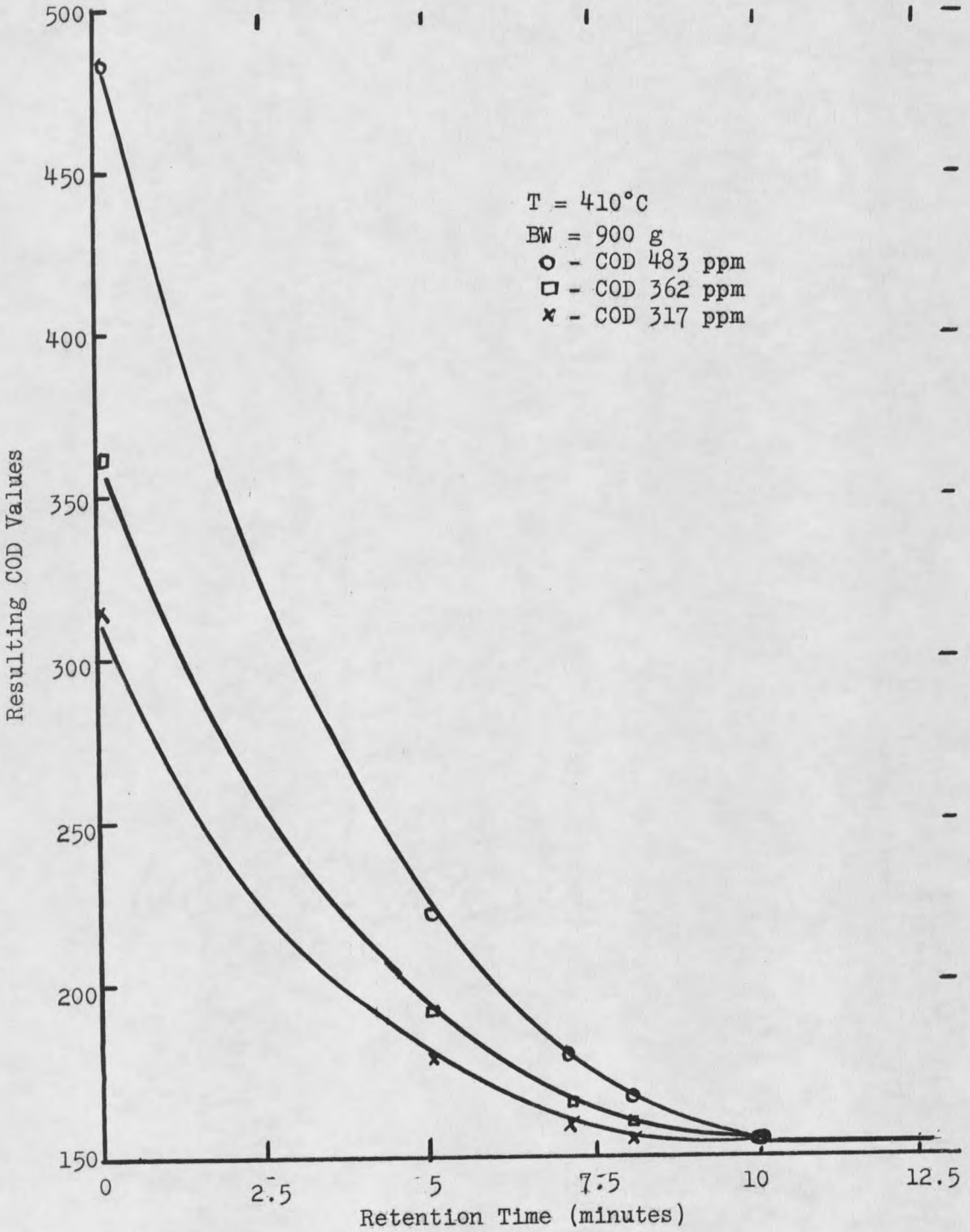


Figure 15. Resulting COD Values vs. Retention Time For Light Ash.

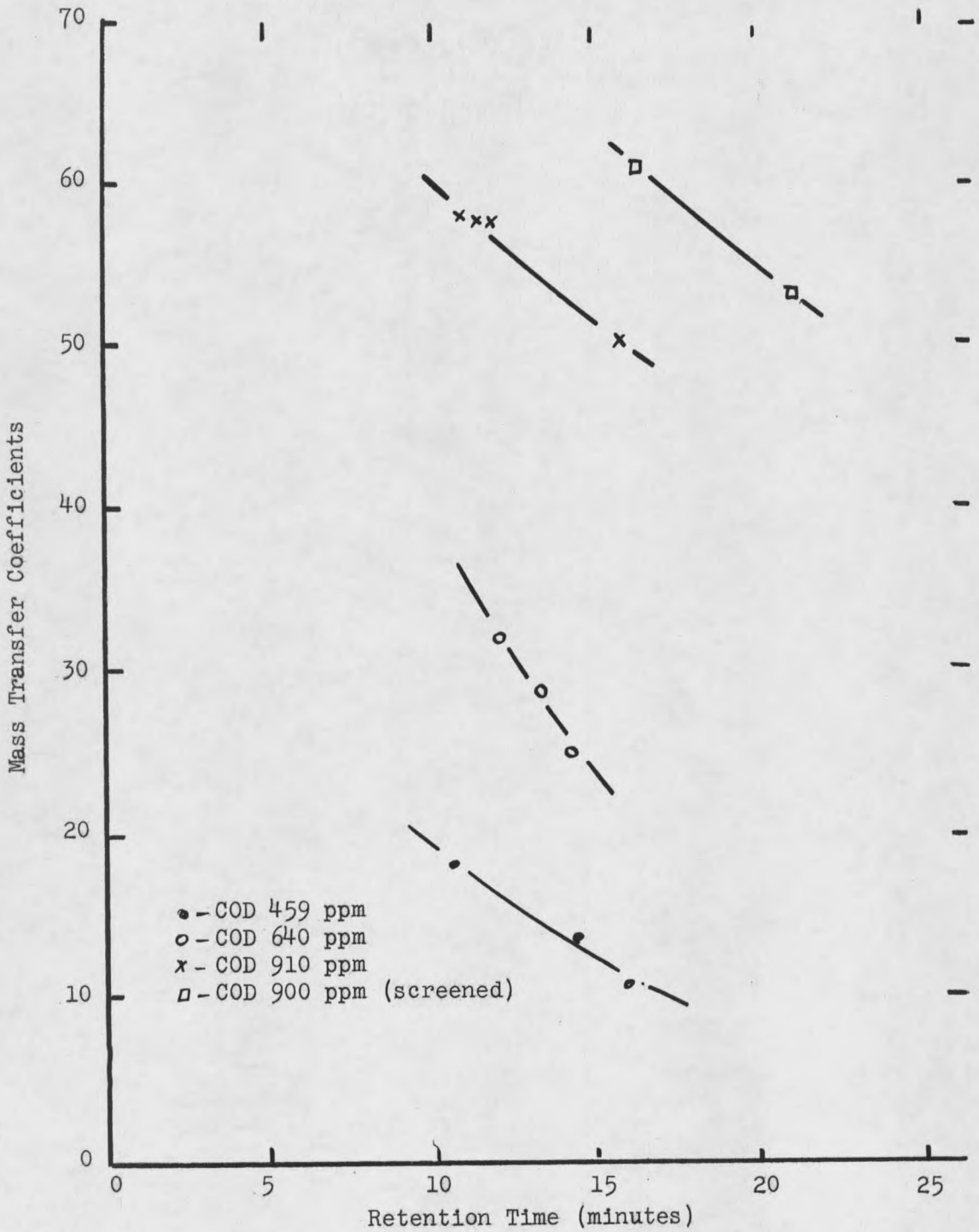


Figure 16. Mass Transfer Coefficients vs. Retention Time For Monohydrates.

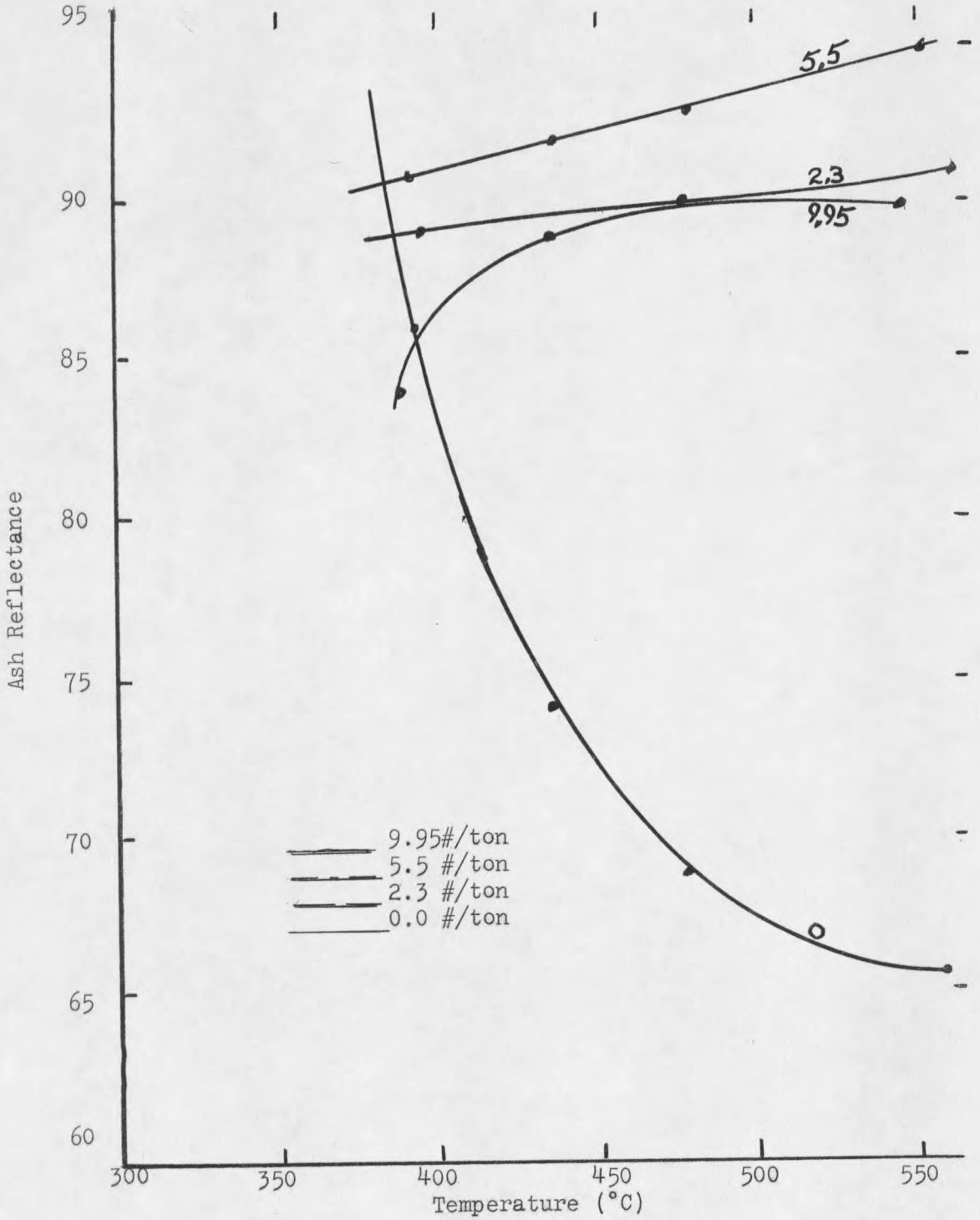


Figure 17. Reflectance vs. Temperature.

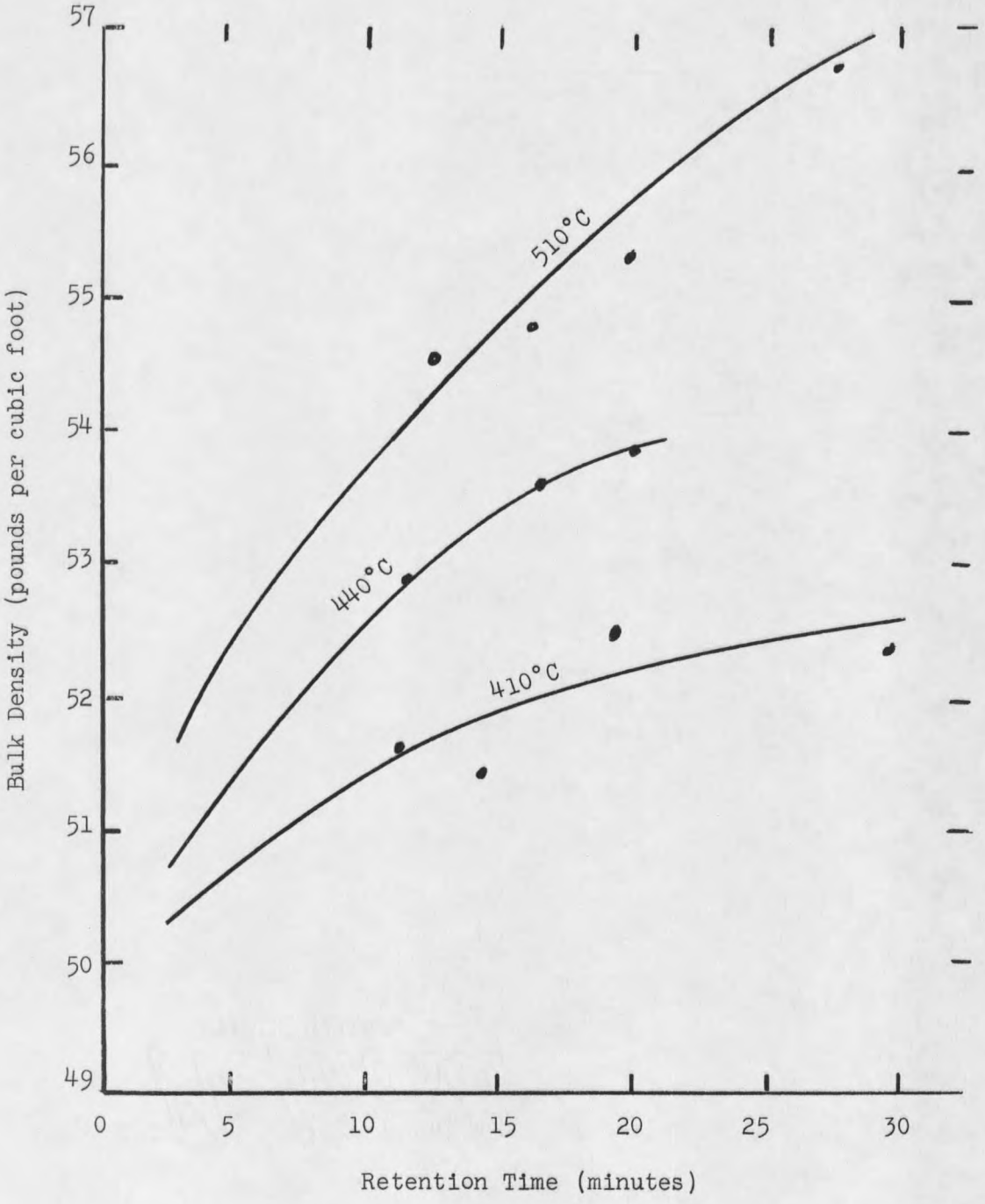


Figure 18. Bulk Density vs. Retention Time.

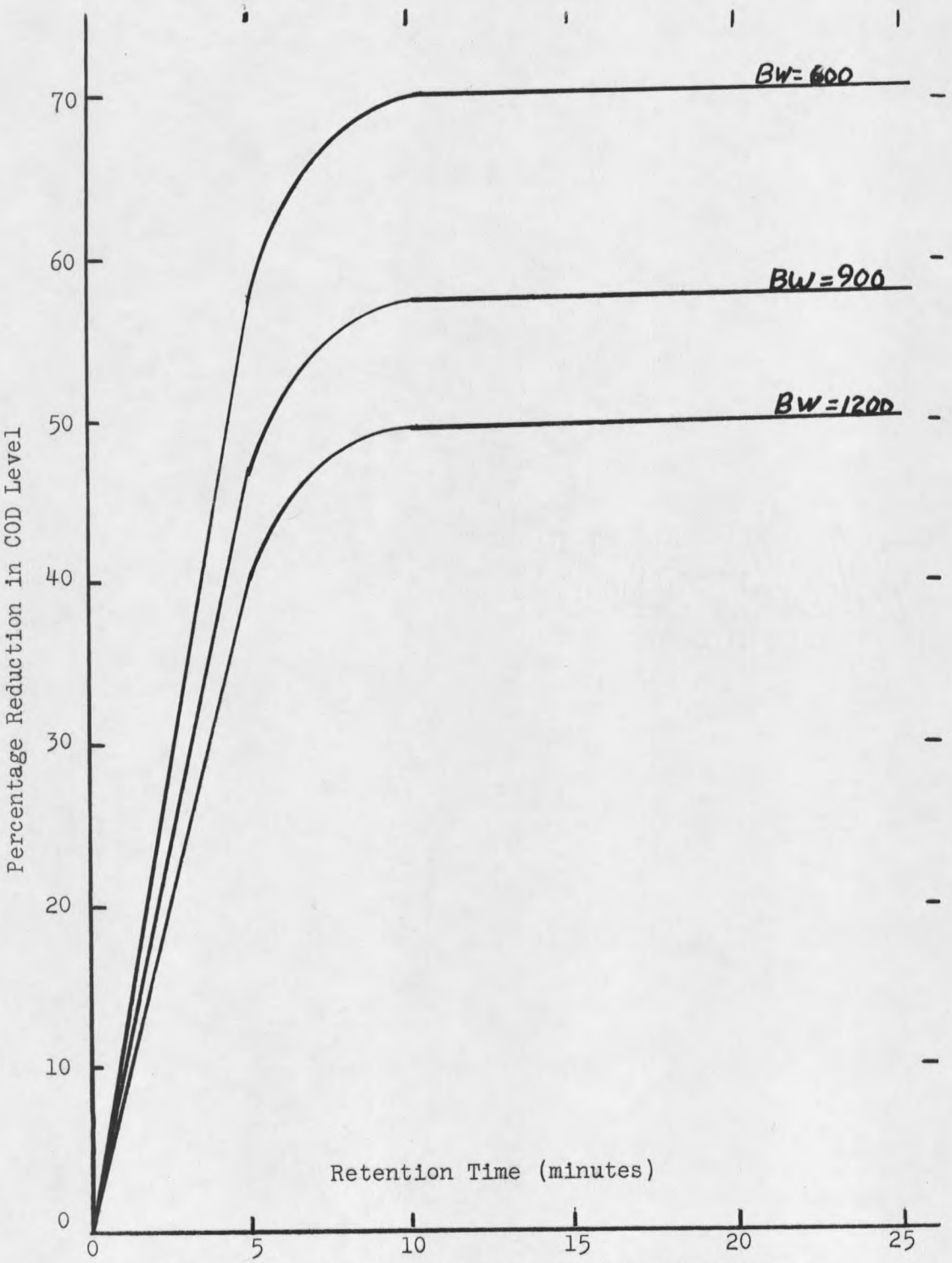


Figure 19. Percentage Reduction in COD Level vs. Retention Time (T = 410).

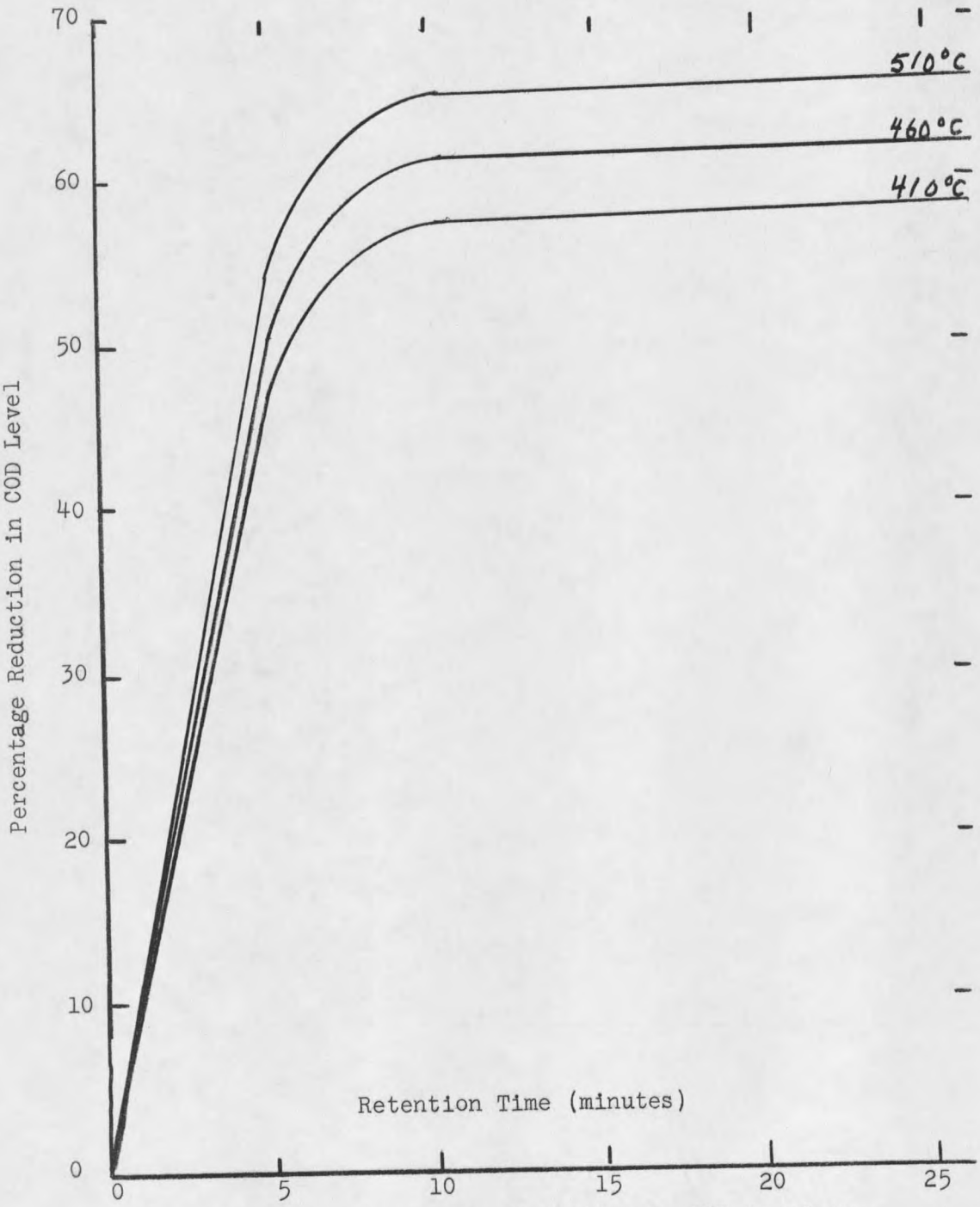


Figure 20. Percentage Reduction in COD Level vs. Retention Time (BW = 900).

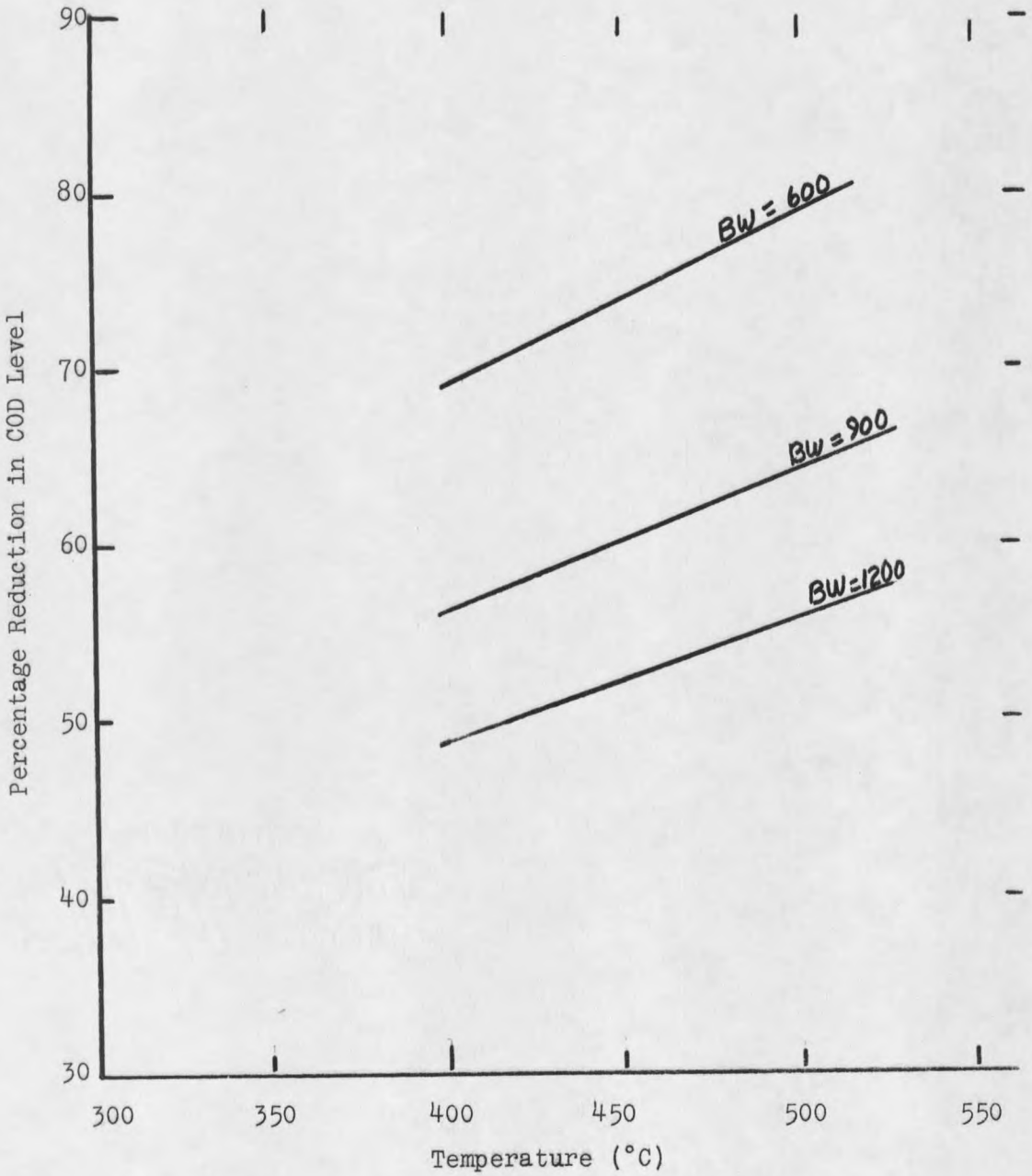


Figure 21. Percentage Reduction in COD Level vs. Temperature (Retention Time = 20 min.).

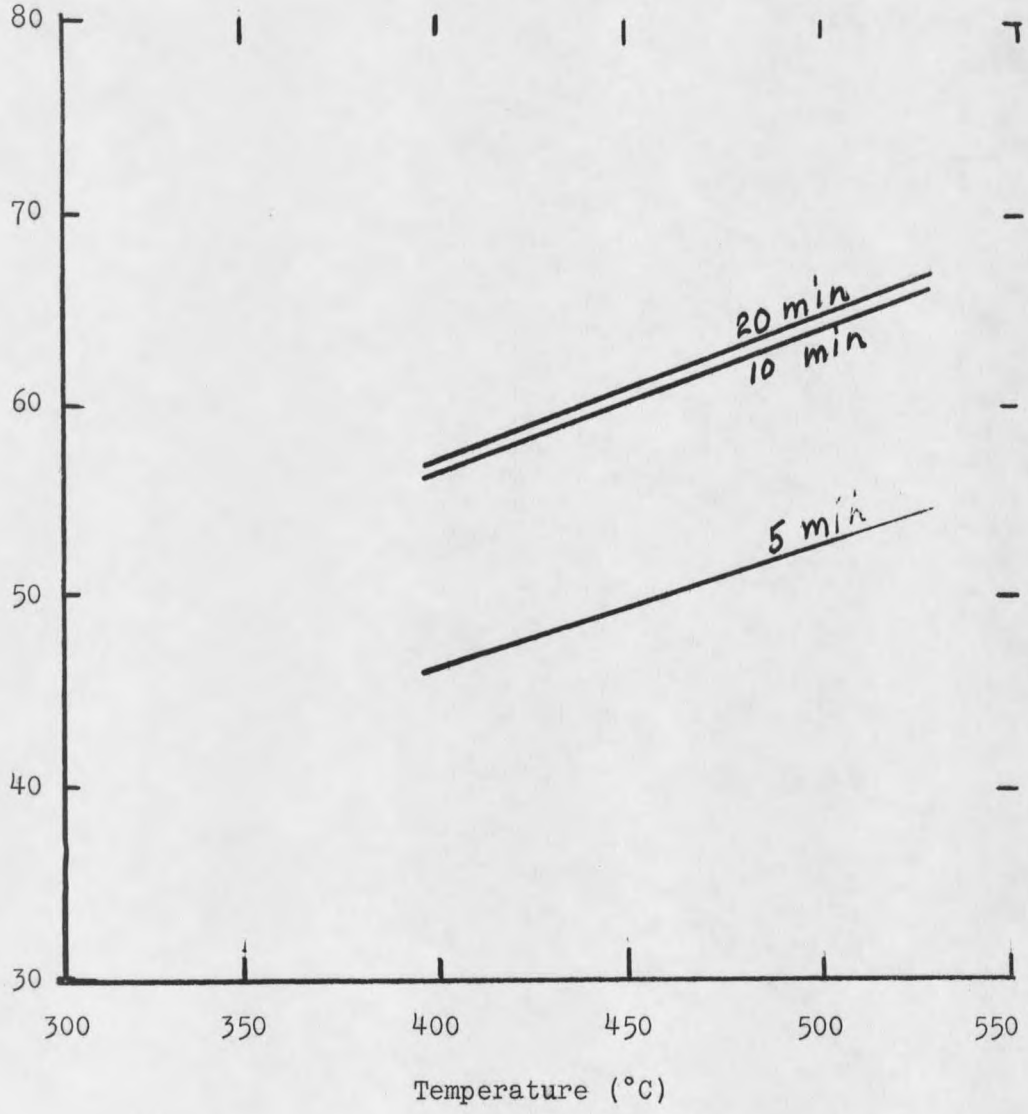


Figure 22. Percentage Reduction in COD Level vs. Temperature (BW = 900).

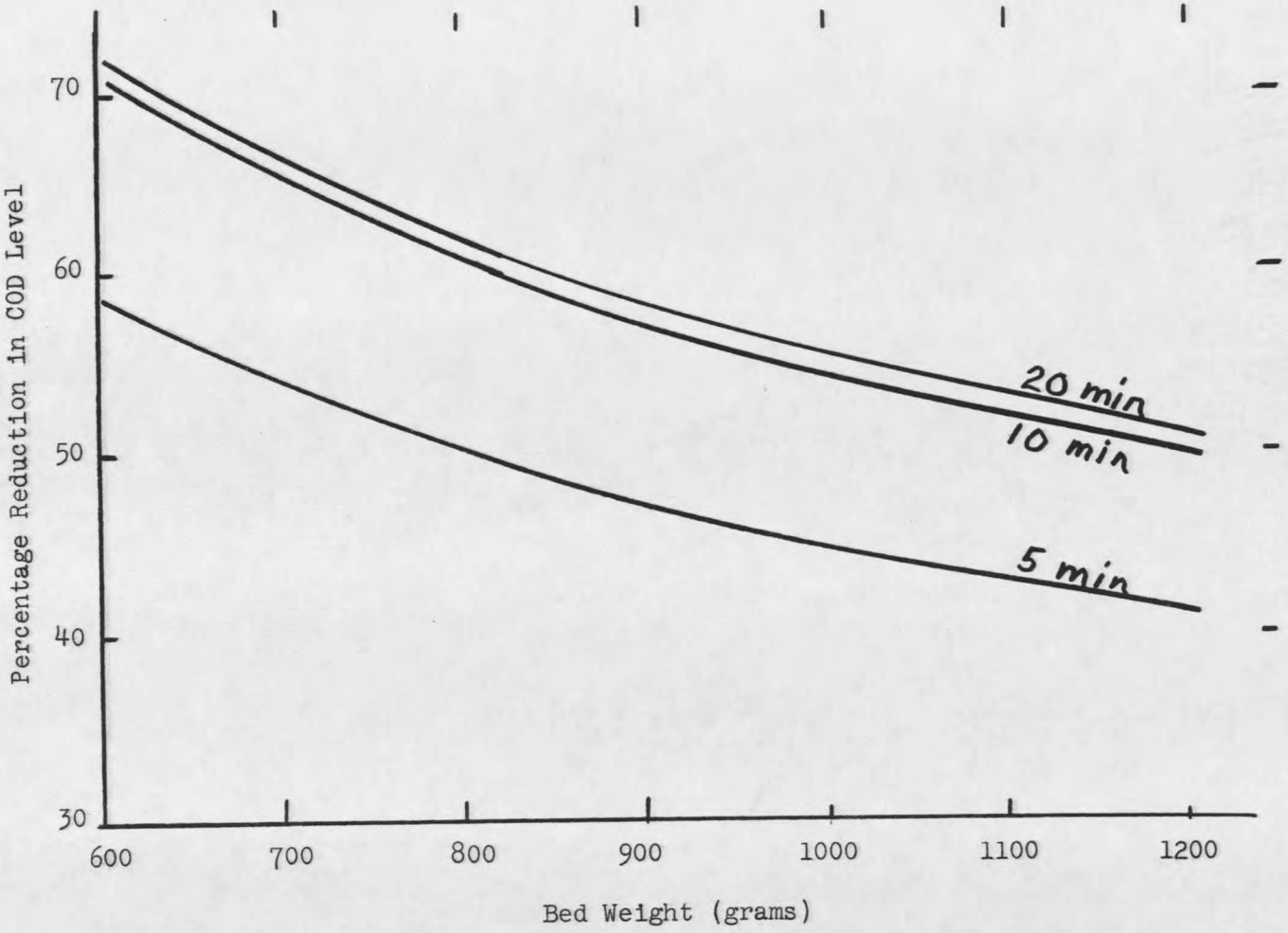


Figure 23. Percentage Reduction in COD Level vs. Bed Weight (Temperature = 410)

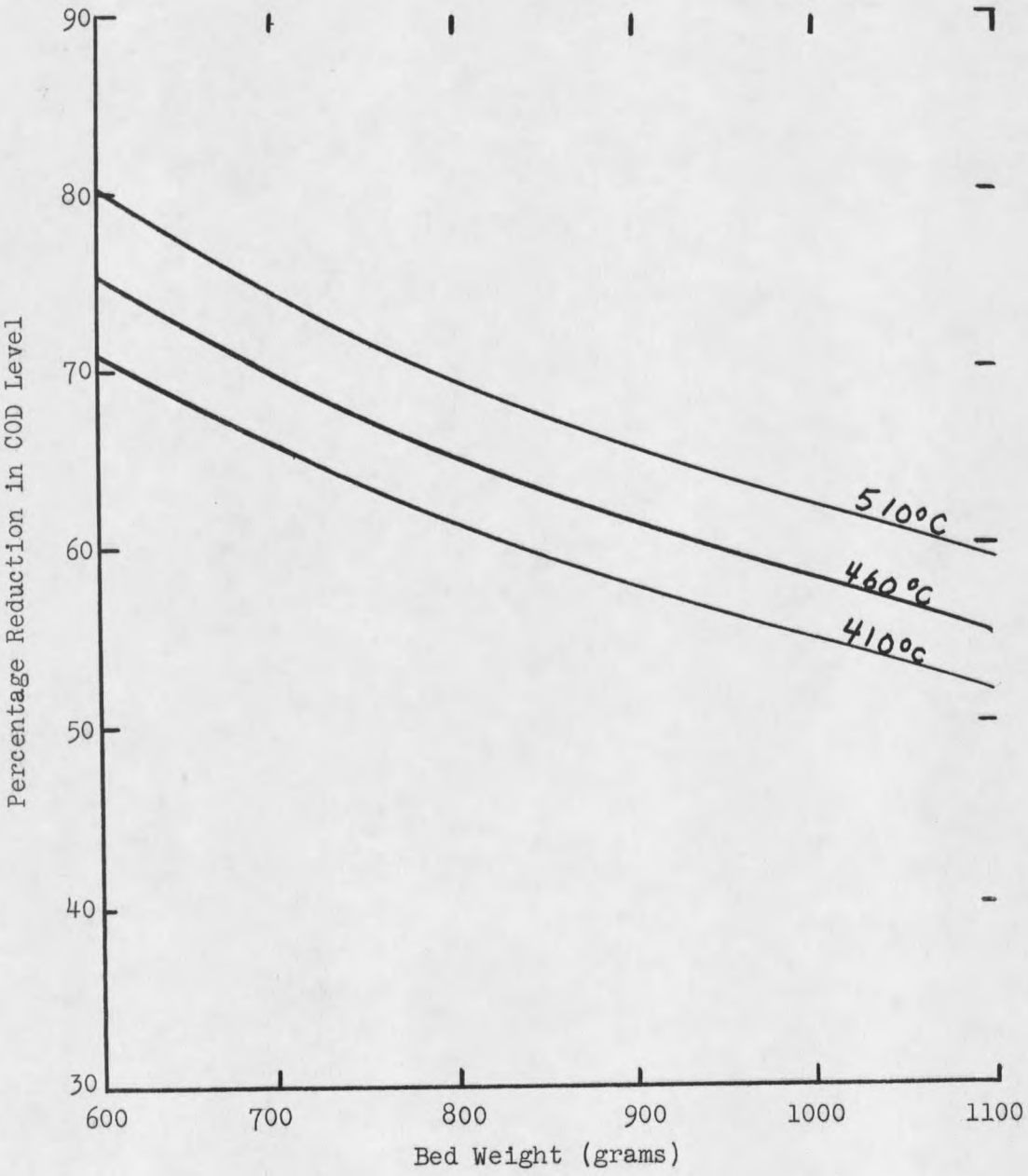


Figure 24. Percentage Reduction in COD Level vs. Bed Weight (Retention Time = 20 min.).

DETERMINATION OF SODIUM CHLORIDE IN REFINED SODA ASH

Principle

A weighed sample of soda ash is acidified and the chloride is determined by adding a known amount of silver nitrate and back titrating with ammonium thiocyanate to the ferric alum end-point. The sample is boiled after acidification to remove the hydrogen sulfide.

Procedure

1. Weigh 20 ± 0.01 gram sample and transfer to a 500 ml Erlenmeyer flask. Add about 50 ml of distilled water.
2. Add 50 ml of 1:1 nitric acid with swirling to avoid foaming out of the flask. Boil for 15 minutes, and cool.
3. Add by pipette 5.00 ml of 0.1 N silver nitrate and 2 ml of ferric alum solution.
4. Using a 5 or 10 ml buret, back titrate with 0.1 N ammonium thiocyanate to a faint permanent pink (stable for 30 seconds).
5. Titrate a blank containing 100 ml water, 5 ml of 1:1 nitric acid and 5.00 ml of 0.1 N silver nitrate solution.

Calculation

(ml blank - ml sample) x 0.293 x N = NaCl%

DETERMINATION OF TOTAL IRON IN SODA ASH OR TRONA

Principle

The soda ash or trona is fused to solubilize the iron compounds and acidified. After appropriate dilution, an aliquot is acidified, reduced with hydroxylamine hydrochloride to convert the iron to the ferrous state. Ortho-phenanthroline is added and the solution buffered with ammonium acetate. The volume of the solution is brought to 100 ml and optical density determined photometrically. The iron content is read from a calibration curve or chart.

Procedure

1. Weigh 5.00 g. of soda ash or trona and transfer to a clean platinum crucible.
2. Ignite in a muffle furnace at 875 ± 25 C for 5 minutes.
3. Cool, place crucible in a 250-ml beaker, add 40 ml of 1:1 HCl and swirl to completely dissolve.
4. Rinse and remove the platinum crucible, make the volume to 250 ml in a 250-ml graduated cylinder, and mix by inverting.
5. Filter 25 to 50 ml of the dilution through a Whatman No. 5 filter paper, capturing the filtrate in a clean-dry beaker.
6. Pipette 10.00 ml into a 250-ml Erlenmeyer flask, add 4 ml of 1:1 HCl, 2 ml of hydroxylamine hydrochloride solution and 1 ml of ortho-phenanthroline solution. Add 10 ml of 6N ammonium acetate and make to 100 ml in a 100-ml graduated cylinder, mixing by pouring back and forth between the flask and cylinder.

Let stand 15 minutes but no longer than two hours.

7. Read the optical density using the Fisher electrophotometer and the green (525) filter comparing to distilled water at zero optical density.

8. Read the micrograms of Fe_2O_3 from the calibration curve or chart.

Calculations:

$$\frac{\text{micrograms } Fe_2O_3 \times \text{dilution} \times 100}{\text{sample wt.} \times \text{aliquot} \times 1{,}000{,}000} = \% \, Fe_2O_3$$

For Routine Procedure:

$$\frac{\text{micrograms } Fe_2O_3}{2000} = \% \, Fe_2O_3$$

DETERMINATION OF D-40 IN REFINED SODA ASH

Principle:

The sample is weighed and the D-40 is titrated with standardized roccal solution until the indicator moves to the chloroform layer. A blank is run at the start of a series of D-40 determinations.

Procedure:

1. Weigh 20 ± 0.1 g. of soda ash and add approximately 60 ml of water to the sample in an 8 oz. glass stoppered bottle. Add 1 scoop, about 0.3 g. of anhydrous Na_2SO_4, approximately 2 ml of bromophenol blue indicator and 50 ml of chloroform.
2. Titrate with roccal until a light blue color forms in the chloroform layer. One or two drops should make a definite change in color.
3. A blank is run by weighing 0.5 g. of C.P. Na_2CO_3 following the above procedure.

Calculations:

$$\text{ppm D-40} = \frac{(\text{Titre} - \text{Blank}) \times \text{Factor}}{\text{Sample Weight}}$$

PROCEDURE FOR DETERMINING NITRATE IN SODA ASH

Principle:

The sample is weighed and acidified with con. sulfuric acid. Ferrous sulfate solution is added to be oxidized by the nitrate present in the sample. The excess ferrous sulfate is titrated with 0.1 N potassium dichromate using o-phenanthroline ferrous sulfate indicator. The blank minus sample titre is the amount of ferrous sulfate consumed by the nitrate.

Procedure:

1. Weigh a 20.0 ± 0.1 gram sample and place in a 500-ml Erlenmeyer flask. Add about 50 ml distilled water.
2. Add con. sulfuric acid to a ph of 1 using ph paper.
3. Pipette 25 ml of 0.2 N ferrous sulfate solution and 20 ml con. sulfuric acid shaking frequently.
4. Heat to boiling on the hot plate and boil for 3 minutes.
5. Cool by swirling under tap until lukewarm, add 50 ml distilled water and 1 ml indicator.
5. Titrate with 0.1 N potassium dichromate, until the color changes from orange over brown to blue green. The end-point is very sharp and may be recognized within a few hundredths of a milliliter.
7. Run a blank in the above procedure, omitting the sample.

Calculations:

$$\frac{\text{Blank} - \text{sample} \times 0.1 \times .02833 \times 100}{\text{Sample weight}} = \% \text{ as } NaNO_3$$

Reagents:

1. Standard $NaNO_3$ - 5.000 gm C.P. $NaNO_3$ dissolved in one liter distilled water. One ml = 5.000 mg $NaNO_3$.
2. Ferrous sulfate soln. - 0.2 N place 77.6 gm ferrous ammonium sulfate and 20 gm NaCl in a liter volumetric flask. Add 100 ml distilled water and a few drops dilute sulfuric acid. Shake until dissolved. Fill up to volume with 50% v/v sulfuric acid. Soln. must be made fresh daily.
3. Con. sulfuric acid.
4. 50% v/v sulfuric acid - add 500 ml con. sulfuric acid to 500 ml distilled water. (caution)
5. Potassium dichromate soln. - 0.1 N 4.9035 gm C.P. potassium dichromate dissolved in 1 liter distilled water.
6. O-phenanthroline ferrous sulfate indicator. Dissolve 1.485 gm. o-phenanthroline and .695 gm ferrous sulfate in 100 ml distilled water.

DETERMINATION OF SODIUM SULFATE IN SODA ASH

Principle:

A weighed sample of soda ash is acidified and the sulfate determined from the turbidity formed with Barium chloride. The sample must be filtered after acidifying and boiling to remove sulfur turbidity. The times and temperatures must be vigorously adhered to. If other than 5-g of soda ash is used, standard Na_2CO_3 or $NaHCO_3$ must be added to give the total equivalent of 5 g. of soda ash.

Procedure:

1. Weigh a 5 ± 0.01 gram sample and transfer to a 250-ml Erlenmeyer flask. Add 50 ml distilled water, 3 drops of p-nitrophenol indicator, neutralize with 1:1 HCl, and add 2 ml excess acid.
2. Boil the solution for one minute, cool and dilute with water to 100 ml in a graduated cylinder. Filter through a dry Whatman No. 5 filter paper.
3. Return most of the sample filtrate to its flask, heat to 50-60 C using a thermometer.
4. Add one scoop (0.5 - 0.7 g) of 20-30 mesh $BaCl_2$ crystals. Allow to stand 10 minutes, swirl for 5 seconds and let stand 5 minutes.
5. Swirl and read the optical density on the Fisher Electrophotometer, using "A" setting and the red (650) filter against distilled water at zero optical density. Read the mg. of Na_2SO_4 from the calibration curve.

Calculation:

$$\frac{\text{mg } Na_2SO_4}{50} = \% \ Na_2SO_4$$

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DETERMINATION OF TOTAL ALKALINITY OF SODA ASH

Principle:

An accurately weighed sample of soda ash is dissolved in water and titrated to a pH of 3.9. The method determines all substances which react down to this pH, therefore, when titrating natural soda ash samples, water-insoluble carbonates will react slowly with the acid. The titration must be stopped when a pH of 3.9 is reached, even though the end-point may tend to drift. No such drift should occur with refined soda ash.

Procedure:

1. Accurately weigh on the analytical balance, a 1.0 to 1.2 gram sample of soda ash and transfer to a clean, 250-ml beaker.
2. Standardize the pH meter at pH 4.0 with 4.0 buffer.
3. Position beaker and sample in titration assembly, add approximately 100 ml of distilled water and stir to dissolve.
4. Add 3 to 4 drops of modified methyl-orange indicator and titrate carefully to pH 3.9, checking color of indicator as verification of proper operation of pH meter. If end-point drifts when analyzing natural ash, stop titration when pH of 3.9 is first reached.
5. Read volume of titration and apply Burette and temperature corrections.

Calculation:

General

$$\frac{\text{Corrected ml} \times \text{normality} \times .053 \times 100}{\text{g. sample}} = \% \text{ total alkalinity as } Na_2CO_3$$

For above routine procedure:

$$\frac{\text{ml} \times \text{factor*}}{\text{g sample}} = \% \text{ total alkalinity as } Na_2CO_3$$

*factor = normality x .053 x 100

COD ANALYSIS

Liquor Samples

The sample is taken in a tared 4-oz. bottle. The weight of the sample is determined and is then diluted with an equal weight of water. This 1:1 solution does not set up and is easily handled. The usual practice here is to filter the diluted sample through 41-H Whatman paper to remove any foreign matter. Since all of our liquor samples contain sodium sulfide and thiosulfate these materials must be analyzed for, since both contribute to the gross COD. This is also true for chloride. Into a 500-ml wide mouth Erlenmeyer is placed 20 ml of cadmium chloride solution (12.5 g/liter of $CdCl_2 \cdot 2\text{-}1/2\ H_2O$). Obtain tare weight and then pipette 50.0 ml of the 1:1 diluted sample into the flask. Reweigh to determine sample weight. Now run the usual sulfide and thio analysis. Calculation of the blank due to sulfide and thio to be subtracted from the gross COD is as follows:

$$\frac{\text{Net ml thio} \times n \times .039 \times 32}{78} = \text{grams } O_2 \text{ to oxidize } Na_2S$$

$$\frac{\text{Net ml thio} \times n \times 32}{1000} = \text{grams } O_2 \text{ to oxidize thio}$$

The sum of the above results gives the total grams of O_2 needed to oxidize all the sulfide and thio present in 25 ml of the 1:1 diluted sample. This is as desired since 25 ml of sample is used for the COD determination. To relate all results back to the original solution, one quarter of the weight of the 50 ml of 1:1 dilution is taken as the sample weight. Therefore:

$$\frac{\text{total } gO_2 \text{ (from above)} \times 10^6}{\text{sample weight}} = \text{ppm COD blank}$$

A chloride analyses is next run on 25 g. of the 1:1 diluted material and the percent chloride is calculated on the original solution (12.5 g. sample weight). From these data, the COD blank due to chloride is then calculated as follows:

% NaCl x 1360 = ppm COD due to NaCl

This figure is added to the COD blank for Na_2S and thio and the sum is the total blank to be subtracted from the gross COD.

Into a 500-ml Erlenmeyer flask with ST 24/40 joint place by means of a pipette or burette exactly 25 ml of 0.500 N $K_2Cr_2O_7$. This solution is made up by diluting 24.5175 g. $K_2CR_2O_7$ to one liter with 20°C water. Now pipette 25.0 ml of the 1:1 diluted sample into the flask. Allow the mixture to stand for a few minutes and then by means of a burette add exactly 68 ml of concentrated sulfuric acid. Insert a boiling tube (to be described later) and reflux one hour. Now add one pellet of Ag_2SO_4 weighing 0.7 to 1.0 gram by dropping down the condenser. Continue the reflux for an additional two hours. Raise the flask from the hot plate and after a few minutes wash down the condenser with a small amount of water (use care here). Remove the flask, remove and rinse off the boiling tube with a minimum of water. Then add 180 ml of water. Cool the flask contents to room temperature. Now add 6-8 drops of ferroin indicator and back titrate the excess chromate with standard ferrous ammonium sulfate. The end-point is very sharp and goes from green to blue to bright red. Record the titration. At the same time

that the sample is being run, a blank should also be run. It is prepared as follows:

25 ml 0.500 N $K_2Cr_2O_7$
30 ml concentrated H_2SO_4
1.0 g. Ag_2SO_4

Reflux for three hours the same as the sample. After washing off the boiling tube add 86 ml water and titrate as above. The blank should be run at least once each day. The ferrous ammonium sulfate is about 0.1 N and is made up as follows:

42.8 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
20.0 ml concentrated H_2SO_4
Dilute to 1 liter with 20°C water.

The ferroin indicator is made up as follows:

1.485 g O-phenanthroline
0.695 g $FeSO_4 \cdot 7H_2O$
Dilute to 100 ml with water

Calculation of COD

$$\frac{25 \times .50}{\text{Blank Titration}} = \text{Normality of ferrous ammonium sulfate}$$

$$\frac{N_X \ 8000}{\text{Sample Weight}} = K$$

$Kx\ (B-S) = $ Gross COD

Gross COD -- (Na_2S, thio and NaCl COD blank) = net COD

The boiling tubes referred to earlier are made by sealing about 2 inches of 8-mm glass tubing to a piece of smaller glass rod of such a length (about 6 inches) that when the entire assembly is placed vertically into a 500-ml flask, the tube will protrude slightly above the neck of

the flask. The open end of the tube is placed down into the flask and controls the boiling characteristics very well.

The volumes of sulfuric acid and water which have been cited are based on the following: During the reflux period, 55 volume percent excess sulfuric acid should be present. During the titration, a total of 21.5 volume percent acid should be present. If for any reason it becomes necessary to change sample sizes the new volumes can be easily calculated by the use of two simple simultaneous equations:

1. $V + x = y$

2. $x = .55\ y$

Subracting 2 from 1

$$V = .45\ y$$

Solve for y and substituting back, solve for x

V = volume of chromate + volume of sample + volume of acid necessary to neutralize the sample

x = volume of excess acid to be added

y = total volume during reflux

When x is obtained, add to it the volume of acid necessary to neutralize sample. This gives total volume of acid to be added. To determine the volume of water to add before the titration, $\frac{y \times 55}{21.5}$ = volume V_2 to which the sample should be diluted. Therefore, $V_2 - y$ = volume of water to be added.

As far as the analyses of solid samples is concerned, no sulfide or thio analyses are run, since these two materials are very low. In the case of a refined ash sample, a 20 g sample is used. The chromate is

0.05 N (2.4518 g $K_2Cr_2O_7$ diluted to one liter with 20°C water). Fifty ml of this reagent is used with low COD ashed. The ferrous ammonium sulfate is about 0.025 N (9.800 g Fe $(NH_4)_2$ will neutralize 20 g ash.

In the case of high COD ashes such as evaporated filtrate or well brine, it is advisable to use 5 g samples with 25 ml of the stronger (0.5 N) chromate. In these samples the chloride becomes an important factor and must be corrected for. The blank for the weak chromate is run as follows:

50 ml chromate

61 ml H_2SO_4

1.0 g Ag_2SO_4

Reflux for three hours and add 173 ml water before titration.

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VITA

Jerry Dean Mason was born June 11, 1929 at Sidney, Montana, the son of Mr. & Mrs. Carl Mason. He attended elementary and high schools in Sidney, graduating from high school in June, 1947. He entered Montana State College in September 1947 and began his studies in the Chemistry Department.

A veteran of the Korean War, he entered the army in 1948 and was honorably discharged in 1952.

Re-entering Montana State College in the Department of Chemical Engineering in September 1952, he was the recipient of advanced scholarships in 1953-1956. He became a member of engineering honoraries Tau Beta Pi and Phi Kappa Phi and was graduated with honors in June 1956 with the degree of Bachelor of Science in Chemical Engineering.

Immediately following his graduation, he began work on the doctor of philosophy degree in the Department of Chemical Engineering at Montana State College. Mr. Mason was elected to Sigma Xi (associate member) in 1957 and advanced to full membership in 1959. He completed requirements for the degree of Doctor of Philosophy in Chemical Engineering in September 1959 and took employment with Standard of California at Richmond, California.

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