A Fluidization Process for Making Sodium Sulphate From Sodium Chloride.

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A FLUIDIZATION PROCESS FOR MAKING
SODIUM SULPHATE FROM SODIUM CHLORIDE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by

Roger Foster Detman
B.S., Louisiana State University, 1939
M.S., Louisiana State University, 1948
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ABSTRACT

The problem undertaken was the application of the technique of fluidization to the Hargreaves process for making sodium sulphate from sodium chloride. The more important commercial methods of manufacturing sodium sulphate are described together with their advantages and disadvantages in order to provide a basis for evaluation of the process developed.

The problem was divided into two parts; the first part involved determination of the fluidization properties of sodium chloride and the design of equipment in which a fluidized solid could be contacted with a gas in countercurrent flow; the second part was to find the necessary conditions under which sodium chloride in a fluidized state could be converted to sodium sulphate.

In fluidization experiments with salt of various particle sizes, the smoothest operation was obtained with table salt. The pressure drop through a bed of table salt for various gas rates is presented. Several laboratory units were built and operated using table salt to show that solids and gases could be contacted countercurrently in a series of fluidized beds. Drawings or photographs of these units and their gas and solid flow rates are presented.

The experiments conducted to find out if sodium chloride could be converted to sodium sulphate in a fluidized bed were started using the conditions employed in the Hargreaves process. Considerable difficulty was encountered due to the formation of products which caused solidification...
of the fluidized bed. Lower temperature and more violent agitation of
the salt permitted longer periods of operation and greater, though in-
complete, conversion of the salt. As the temperature was lowered still
further, unsatisfactory operation was obtained as a result of condensa-
tion of a liquid thought to be sulphuric acid. Consequently the formation
of appreciable amounts of sulphuric acid was prevented by introducing the
sulphur dioxide into the air stream at the reactor instead of at the fur-
nace inlet. All subsequent runs using this arrangement were carried out
without solidification of the bed, but at very low conversion rates. The
formation of sulphuric acid vapor in the gas before entering the salt bed
was then considered of primary importance in the reaction and conditions
favorable to its formation were believed necessary to give satisfactory
reaction rates.

Further experiments were conducted in which sulphuric acid vapors
were produced by the addition of a catalyst chamber in the furnace. In
these runs the conditions for satisfactory operation were discovered. A
reduction in concentration of water vapor as well as sulphur dioxide was
found to eliminate stickiness and resulted in a uniform product of com-
mercial grade.

From the observed behavior and theoretical considerations a mechanism
illustrated by the following series of equations was postulated:

\[
2 \text{SO}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{SO}_3 (g)
\]
\[
2 \text{SO}_3 (g) + 2 \text{H}_2\text{O} (g) \rightarrow 2 \text{H}_2\text{SO}_4 (g)
\]
\[
2 \text{H}_2\text{SO}_4 (g) + 2 \text{NaCl} (s) \rightarrow 2 \text{NaHSO}_4 (l) + 2 \text{HCl} (g)
\]
\[
2 \text{NaHSO}_4 (l) \rightarrow \text{Na}_2\text{S}_2\text{O}_7 (l) + \text{H}_2\text{O} (l)
\]
\[
\begin{align*}
\text{Na}_2\text{S}_2\text{O}_7 (l) + \text{H}_2\text{O} (l) & \rightarrow 2 \text{NaCl} (s) \rightarrow 2 \text{Na}_2\text{SO}_4 (s) + 2 \text{HCl} (g) \\
2 \text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) + 2 \text{H}_2\text{O} (g) & \rightarrow 4 \text{NaCl} (s) \rightarrow 2 \text{Na}_2\text{SO}_4 (s) + 4 \text{HCl} (g)
\end{align*}
\]

Photomicrographs of the salt particles at different degrees of conversion as well as the equilibrium data for the gaseous reactions support the arguments in favor of the proposed mechanism. The limiting conditions of temperature and gas concentration are determined by the formation of liquid which causes fluidization to cease. High temperatures of about 400°C cause the formation of liquid intermediates in sufficient quantity to melt the bed and form a cake. Low temperatures of about 240°C permit condensation of sulphuric acid vapor with attendant stickiness and poor fluidization. High concentrations of water vapor and sulphur dioxide result in high reaction rates and excessive rates of formation of liquid intermediates as well as concentrations of sulphuric acid vapor which result in liquid condensation. Reaction rate data at various temperatures are presented; the higher temperatures giving the higher rates. At a temperature of 340°C, with a water vapor concentration of 34.0% and sulphur dioxide concentration of 4.7%, satisfactory operation was obtained.

A preliminary process flow diagram is presented and the economic feasibility of the process proposed is indicated as favorable by a comparison with a similar process, the manufacture of sulphuric acid.
The transportation of solids by aeration or pneumatic conveying is fairly well known at the present time. It is comparatively new, however, and new applications of the principle are continually being found. Contrasted with older methods of movement of solids, in many cases, aeration has many distinct advantages among which are lower power consumption, less expensive equipment, lower maintenance cost, greater convenience, and lower labor cost for operation. Of course all problems of movement of solids are not amenable to solution by aeration. The solid must first have a suitable particle size distribution. The reduction of solids to suitable sizes and movement by aeration may in some cases prove more economical or convenient than movement by other means.

This discussion of the advantages of aeration, which is comparatively well known, is intended to introduce and indicate similar advantages for "Fluidization" a newer companion process to be more fully discussed.

Standard fluidization nomenclature and definitions have recently been proposed (14) and are presented in part to describe the process and clarify later discussion. The following is quoted from reference (14):

"When the velocity of a gas or liquid flowing up through a mass of solid particles is sufficient to support any of the solid, the mass is called a fixed bed or moving bed depending on whether the solid is stationary or moving with respect to the containing vessel. With increasing fluid velocities in the absence of channeling, the pressure drop through the bed rises until it approaches the net effective weight of the solid per
unit area, when the packing arrangement of the particles becomes more open so that the bed expands; with slight further increases in velocity the particles are fully supported and the expanding bed becomes fluidized. Just at the point of fluidization the mass may form a quiescent fluidized bed. With liquid-solid systems, further increases in fluid velocity give a progressive separation of the particles which remain individually and uniformly dispersed in particulate fluidization. With many gas-solid systems the bed expands only to a limited extent, and a portion of the gas tends to accumulate in gaspockets or bubbles passing through the fluidized bed in aggregative fluidization. In small tubes, these bubbles may grow to a size substantially filling the cross section of the vessel, resulting in slugging. Normally, however, the bubbles remain small with respect to the vessel and the mass becomes a turbulent fluidized bed. Such a turbulent bed can even be maintained above the free-falling velocity for the solid particles in a gas-solid system if the rate at which solids are fed is kept high enough. Finally, if the fluid velocity is still further increased or if the solids feed rate is too low, the surface of the fluidized bed disappears and the whole mass becomes a dispersed suspension." The following definitions were proposed in the same reference:

"A fluidized bed is a mass of solid particles which exhibits the liquidlike characteristics of mobility, hydrostatic pressure, and an observable upper free surface of boundary zone across which a marked change in concentration of particles occurs."
"A quiescent fluidized bed is a dense fluidized bed which exhibits little or no mixing of the solid particles."

"A turbulent fluidized bed is a fluidized bed in which mixing of the mass of solid takes place."

"Channeling is the establishment of flow paths in a bed of solid particles through which a disproportionate quantity of the introduced fluid passes."

"Slugging is a condition in which pockets or bubbles of the supporting fluid grow to the diameter of the containing vessel, and the mass of particles trapped between adjacent pockets moves upward in a pistonlike fashion."

Fluidization is a step forward from movement by aeration since some additional purpose is served besides mere movement. The interaction of the solid and gas to produce a desired change in one or the other of the materials is the important development. At the present time many applications of this principle are under investigation and many more are envisioned.

The widest application of fluidization to-date is catalytic cracking of petroleum fractions in which the second purpose is presentation of new catalytic surface for chemical reaction. There are other advantages that may be enumerated for fluidized systems besides those related to movement by aeration and the presentation of surface for reaction. The ability of a fluidized solid to obtain intimate contact with the aerating gas is of importance in many processes such as vaporization, heat transfer, adsorption,
desorption and chemical reactions involving gases or vapors. The ability of a fluidized system to obtain rapid homogeneity is of great importance where heat is being evolved or absorbed by the materials. This property allows rapid heat equalization and prevents local overheating which is a common fault of other systems.

The technique of fluidization is being utilized in many new developments. One of the most important is the synthesis of hydrocarbons from carbon monoxide and hydrogen using a fluidized catalyst. Other applications of the same technique are the gasification of coal, recovery of oil from shale, burning of lime, and the Hypersorption process for separation of light hydrocarbons. There are many applications of the fluidization principle yet to come, since its inherent advantages indicate its superiority over certain methods of operation now in use. To cite an example, the drying of granular materials in rotary equipment could very well be handled to advantage by fluidization. Higher coefficients of heat transfer between solid and gas may be expected in fluidized systems since more intimate mixing is effected than in a rotary cylinder. Another advantage of fluidization is that reactions which are not economically or physically possible by methods previously attempted due to processing difficulties or high labor and handling costs may be successfully carried out using a fluidization technique. The same approach may be employed in processes in commercial operation as a means of producing a cheaper product.

At present, processes employing fluidization may variously be described as fixed bed or moving bed, upflow or downflow, single bed or single
stage units. This terminology refers to the movement of solid material. Fluidized beds in commercial operation consist mainly of single units in which the gaseous phase makes one pass through one bed of fluidized solid. The solid however may be moved continuously between two fluidized beds each using a different type gas or vapor. The reason for the second bed in this case is for regeneration of the solid. In operations where the solid is materially affected by the reaction, as happens in catalytic cracking, the retention time of the solid in the primary or reactor bed is of great importance as it loses its activity at a rate which is proportional to its time of residence in the primary reactor. The rate of mixing in a fluidized bed operating under commercial conditions is very great, so that the composition of the bed is quite uniform throughout. In view of this fact it is evident that of the solid being removed it may be said that it contains some solid material which had just recently entered the bed as well as some solid which had been in the bed for quite some time. The bed may therefore contain a substantial amount of solid which had not fulfilled its function of catalysis to the optimum degree before being removed as well as a substantial amount of solid which had long since ceased to function satisfactorily as a catalyst.

In view of these considerations it appears that an advantage would be gained if the one large bed were subdivided into a series of fluidized beds in which the solid is moved continuously from one bed to the next in such a manner as to move countercurrent to the flow of gas. This application of the principle of countercurrent flow to fluidized systems is
expected to have wide application should a unit be designed to permit satisfactory operation.

Two such designs are proposed with operating data on gas and solid flow rates given for laboratory models. It is evident that no single design of such a unit could be universally applied to all fluidized systems. For that reason this investigation was restricted to a single process on which the designs are based. The process chosen was the manufacture of sodium sulphate or salt cake from sodium chloride or salt. Several commercial processes are described for comparison with the one developed.

In this investigation the conditions necessary for the successful application of fluidization to the production of salt cake are shown and the probability of successful operation on a commercial scale is indicated.
DESCRIPTION OF COMMERCIAL PROCESSES

A brief discussion of the methods of manufacture of sodium sulphate is of value for comparison with the process proposed in this dissertation. An actual economic comparison of the proposed process with present methods must be restricted to estimates based on laboratory equipment since time did not permit construction and operation of larger units.

The most important method of manufacture of salt cake is the Mannheim process in which salt and sulphuric acid are the reactants. The Mannheim furnace is an upright cylinder eleven to eighteen feet in diameter, with a fire box in the lower portion. Above the fire forming the top of the fire box is a cast iron pan, depressed in the center, and having a series of scrapers or plows which move the reactants slowly toward the outer periphery. The pan is covered with a cast iron top forming a closed vessel or muffle. The flue gases pass over the top of the muffle aiding in the heating process. A large uptake for the gas generated ascends vertically from the center of the top of the muffle. The reactants are both introduced through this opening and fall to the center of the pan. The overall reaction is as follows:

\[ \text{H}_2\text{SO}_4 + \text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{HCl} \]

Various authors have described the reaction as occurring in two steps as follows:

\[ \text{H}_2\text{SO}_4 + \text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 + \text{HCl} \]
\[ \text{NaH}_2\text{SO}_4 + \text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 + \text{HCl} \]
The first step proceeds at ordinary temperatures, while the second step requires considerable heat to complete the reaction. The solid product overflows from the outer edge of the pan through openings provided for that purpose. The product is a cake which may contain unreacted sulphuric acid and also some bisulphate. The gases passing off are pure hydrogen chloride which may be absorbed in water or used directly in some other process. When the Mannheim process is used the desired product is usually hydrogen chloride and the salt cake is considered a by-product. The properties of the solid product are controlled by the efficiency of the operation, but usually are such as to make handling and shipment difficult and costly.

The Laury furnace of the rotary kiln type uses salt and bisulphate or nitre cake and produces a more satisfactory solid product and dilute hydrogen chloride gas.

The Hargreaves process used for many years in Europe employs salt and sulphur as the primary raw materials. There is only one commercial plant in this country due to the fact that the process entails high labor and handling costs. This one plant, The Bay Chemical Company at Weeks Island, Louisiana, utilizes waste salt dust from nearby salt mining operations and sulphur which is also obtained from a local source. The process is commercially successful due to its proximity to raw materials of very low cost.

The overall reaction is as follows:

\[ 2 \text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl} \]
The sulphur is burned in an excess of air to form sulphur dioxide which is mixed with steam to form the reaction gas. Iron chloride is used as a catalyst to the extent of one half of one percent of the weight of salt. The salt and catalyst are formed into oval shaped briquettes about one by three inches in size. The briquettes are dumped into one of eight reaction chambers having a 98 ton capacity. These chambers are lined with fire brick and are cubic in shape measuring about twenty feet on a side. One of the eight chambers is normally out of service for removal of product and recharging. The other seven are operated in series, the fresh gas rate being controlled to maintain the reactor temperature below 593°C. A rise in temperature above 593°C causes fusion of the mixture with consequent reduction in percent conversion. Any fused material must be broken up manually and ground for re-processing. When the gas analysis indicates completion of the reaction a reactor is removed from the system and cooled by circulating air. The product is removed from the chamber by a pneumatic system and ground. The impurities amounting to about three percent consist mainly of salt, iron oxide, calcium salts, and silica. The exhaust gases are sent to an absorbing system which produces commercial muriatic acid. The time for completion of the reaction of one chamber is three days. One advantage of this process over those previously mentioned is that the exothermic nature of the reaction reduces the fuel cost, however the necessity for large amounts of hand labor in charging and removal of products from the chambers reduces
to some extent the advantages of a higher grade product and lower fuel requirements.

There are other sources of commercial salt cake besides those mentioned. The chemical industries produce small quantities as a by-product due to the use of caustic as a neutralizing agent for sulphuric acid or sulphates. A synthetic salt cake is made by sintering a mixture of sulphur and soda ash. This mixture is then reduced to the sulphide for use in kraft paper manufacture. It has been a major competitor for salt cake in the South, but has recently gone out of production due to competition with manufactured and natural salt cake.

Natural salt cake recovery is increasing and provides a cheap source of the material in areas adjacent to its location. These areas are generally in the arid regions of the West and Northwest. A very large amount of salt cake is now being recovered in Canada for shipment to the United States.

The South is an excellent location for a commercial salt cake plant since the kraft industry there must import the chemical from Canada or buy the relatively high prices product made in the South. The present price of commercial salt cake in the South ranges from $18.50 to $22.00 per ton. The price varies somewhat with the purity and the source and is subject to shipping charges.

The principle advantage of a fluidization process over the Hargreaves process is lower operating cost. Lower costs are obtainable by eliminating the formation of briquettes, heavy machinery for solids movement, the
manual operation of removal of fused cake, and the grinding of briquettes
to form a uniform product.
FLUIDIZATION EXPERIMENTS

Particle Size Considerations

The literature contains some data from which the fluidization properties of solids may be predicted (1). Any particular solid may have properties which make general correlations unreliable and in such cases the fluidization characteristics must be determined experimentally. Sodium chloride was chosen as the solid for the experimental studies of fluidization as it would be used later as the reacting solid in the reaction experiments. It behaves ideally in sizes larger than 65 mesh which is the size of fine table salt. Smaller sizes especially if they are sharp rather than cubic crystals have a tendency to slug in small diameter vessels or to channel in larger vessels. The reason for this behavior appears to lie in the fact that small jagged salt particles do not possess a symmetrical electrostatic field and thus stick together readily. In mixtures of ground salt where there is a large proportion of larger sizes of approximately 48-65 mesh, fines do not prevent satisfactory fluidization. They appear to adhere to the larger particles which do not themselves stick together due to their larger size. Rock salt ground to pass 35 mesh was found to have satisfactory fluidization characteristics. Photomicrographs of the salt used are shown in Illustration I.

In preparing a solid for a reaction it is expected that the greatest advantage would be gained in reaction time by grinding as fine as possible so as to expose the greatest possible surface for reaction. In the case of salt however, the limit as to the smallness of the average particle
ILLUSTRATION I

Photomicrographs of Salt Used

II Table salt reflected light

IB Table salt transmitted light

IC Rock salt reflected light

ID Rock salt transmitted light
will be determined primarily by the ability to design equipment to handle it in the fluidized state. Of course the cost of grinding may enter the economics of the operation and limit the size reduction. One alternative solution may be the use of a carrier solid which is inert and serves as an aid to fluidization, thus allowing handling of finer particles. The carrier may be a suitably sized fraction of the product of reaction and thus minimizes the difficulties of separation of the carrier from the product.

The optimum particle size distribution will have to be determined economically based upon considerations of reactor design, reaction time, and grinding cost. It is expected that the normal procedure would be to design a unit to handle a solid which has a particle size distribution obtainable on a standard commercial grinder. The reaction time and fluidization characteristics for a solid of such size would be the basis for reactor design. A reactor constructed on the basis of these considerations should be tested for the actual limits of operability as the grinding operation is adjusted for finer and finer particle size. The finest particle size consistent with good operation and reasonable grinding cost should give the most economical operation. A similar procedure should be followed if the source of salt is brine which must be crystallized and dried before use.

It is expected that, for equivalent particle size, a bed of salt crystals having uniform shape will exhibit less tendency to channel than a bed of ground salt which has particles of jagged and non-uniform shape.
The exothermic character of the reaction indicates some economic advantage may be gained by obtaining the salt in the form of brine and evaporating the brine using the heat evolved in the reaction. The size of the salt crystals may thus be controlled for most efficient processing to the sulphate. The present cost of rock salt in car load lots at the mine is about $3.00 per ton while salt in a 25% solution is $1.15 per ton of dry salt which is slightly less than half that of the rock salt.

The experimental work was carried out for the most part with ordinary table salt for two reasons. It is a convenient uniform material and it has excellent fluidization properties. Comparable results were obtained in experiments with table salt and rock salt of equivalent particle size.

Experimental Work

Considerable work has been done recently on fluidization of various solids and correlations have been made to show the relationships between the characteristics of the material and pressure drops through it as a function of gas velocity (2). A theoretical equation has been developed from which the pressure drop through a fluidized bed may be calculated (3). The equation involves several properties which must be obtained by measurement such as \( V_T \), the dumped volume of the solid (cubic feet), \( A_T \) cross sectional area of the fluidization vessel (square feet), \( \delta \) fractional voids in the bed (no dimension), \( \rho_s \) particle density (pounds per cubic foot), and \( \rho \) fluid density (pounds per cubic foot). The pressure drop \( \Delta P \) is then:

\[
\Delta P = \frac{V_T}{A_T} (1 - \delta) (\rho_s - \rho)
\]
The measurements of the various terms in the equation is subject to error and since the salt was available the pressure drop was determined experimentally. The data is presented in the appendix and graphically in Figure 1. The screen analysis of this material is also presented in the appendix.

From Figure 1 it is seen that pressure drop is virtually independent of mass velocity of the gas for the fluidized bed. Any increase of pressure drop with increase in mass velocity is due to friction between the gas stream and the retaining walls of the vessel and connecting pipes. This pressure loss is predictable by conventional methods.

A three stage countercurrent flow reactor was designed and built of laboratory equipment to test the operability of the design. A sketch of the apparatus is shown in Figure 2. Flow rates obtainable on this model are presented in the appendix. This model is the basis for a suggested design of a commercial size countercurrent unit which is presented in Figure 3.

A second laboratory size countercurrent flow reactor (reactor number 8) was built and the flow rates for it are presented in Figure 4 and a photograph of it is presented in Illustration II. A third reactor which is a combination of parallel and countercurrent flow (reactor number 9) was built and tested for operability. Data for it are presented in the appendix and a photograph of it is presented in Illustration III.

Parallel flow lends itself more readily to design than countercurrent flow since the solid in a countercurrent system must be introduced into a
FIG. 2
LABORATORY FLUIDIZATION UNIT

FRESH SOLID INLET

STOPCOCK

TWO INCH DIAMETER
FOUR INCHES HIGH

ONE INCH DIAMETER
TWO INCHES HIGH

STOPCOCK

ONE FOURTH INCH TUBING

STOPCOCK

GAS INLET

SOLIDS OUTLET

GAS OUTLET
FIG. 3

COMMERCIAL FLUIDIZATION UNIT
CONTINUOUS REACTOR FLOW RATES

reactor number 8

AIR RATE

ft³/min.

SOLID RATE and HOLDUP

grams/min. grams

SOLID RATE

HOLDUP

0
0.1
0.2
0.3
0.4
0.5
0.6
0
20
40
60
80
100
ILLUSTRATION II

Reactor Number 8

Illustration IIA

Note constriction above four way joint.

Illustration IIB

Jacketed with glass tube and wound with heater wire.
ILLUSTRATION III

Reactor Number 9
bed at higher pressure than the one it is leaving. In countercurrent units this head is overcome by a vertical feed pipe of solid higher than the bed height. The control of solid flow must be maintained by the pressure differential of this vertical column of solid. This has been accomplished in commercial units by the use of differential pressure control of feed valves. This method is impractical or very difficult on laboratory scale equipment necessitating manual control of feed by glass stopcocks (reactor number 9). An alternate method used for control of downward flow of solid was by introduction of a suitable constriction at the bottom of the fluidized bed and adjusting the downward flow rate of solid through the constriction by control of the gas velocity (reactor number 8). The amount of solid held in the reactor as well as the solid flow rate is a function of the gas velocity. This relationship is shown in Figure 4. This reactor forms the basis for the design of a commercial reactor suggested in Figure 5.
FIG. 5
DESIGN FOR COMMERCIAL REACTOR

CROSS SECTION OF PLATES

TOWER PLATES

BOTTOM PLATE
DESCRIPTION OF REACTION EXPERIEMENTS

The starting point for experimental work was the design of a single stage fluidization unit in which the reaction could be studied to determine, if possible, the effect of the operating variables upon the reaction rate. The conditions were chosen to approximate, as closely as possible, those employed in the Hargreaves process. The desired temperature was 538°C and the gas composition desired was stoichiometric proportions according to the following overall reaction:

\[
\text{NaCl} + 2 \text{SO}_2 + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 2 \text{Na}_2\text{SO}_4 + \text{H}_2\text{Cl}
\]

Illustration IV is a photograph of the apparatus. Provisions were made to regulate and measure sulphur dioxide flow from a cylinder of the gas.

Compressed air was handled by regulator and rotameter before passing through an eight foot humidifying tower packed with half inch reschig rings. The temperature of the water used in the humidifying tower was controlled by a water blender to give the air the desired moisture content. The moist air and sulphur dioxide were mixed and passed into a four foot bank of half inch pipes (Illustration V) heated by two longitudinal gas burners.

The reactor was located at the exit of the bank of furnace tubes. The waste gases coming from the reactor were passed through a scrubber tower made of three lengths of six inch terra cotta pipe packed with ceramic berl saddle packing.
ILLUSTRATION IV

Apparatus

1. Sulphur dioxide regulator
2. Sulphur dioxide rotameter
3. Air rotameter
4. Humidifying column
5. Steam jacketed line
6. Furnace
7. Insulated reactor
8. Scrubber
ILLUSTRATION V

Furnace Tubes
The first reactor (reactor number 1) consisted of a one foot section of pyrex glass tube four inches in diameter. The salt was supported on a screen at the bottom of the tube. The entire reactor was supported on an iron base which contained a gas distribution plate to provide equal distribution of gas through the bed of solid.

The description of the experiments together with analysis of products and corrective changes made to the apparatus are presented in chronological order in order to show the path of the development clearly. The difficulties that arose are discussed and the manner in which they are resolved is described.

Run #1

When the air temperature above the screen reached 510°C with about a one inch salt bed present the sulphur dioxide was introduced at a low rate. The pressure drop was fluctuating widely from about ten to twenty-five inches of water. The manometer blew out after about thirty minutes of operation when the temperature was 538°C. The bottom of the salt bed had several lumps of crystalline solid adhering to the screen which had become brittle and broke very easily when handled. The analysis of the bed showed an equivalent of ten grams of salt cake based on a sulphate determination or about five percent conversion.

The cause for the pressure fluctuations and plugging was discovered to be due to water condensation in the lines preceding the furnace. The condensate absorbed sulphur dioxide to form sulphurous acid which dissolved.
iron in the cooler pipes and deposited the salts at the entrance to the furnace forming a heavy scale.

Changes Prior to Run #2

A steam jacket was installed on the moist air line to prevent water condensation and a new bed support was constructed. The new support consisted of two stainless steel plates one eighth inch apart having small holes for passage of the gas, the holes in each plate being offset to prevent downflow of solid. This variation of the first reactor was called Reactor number 2 and is shown in Illustration VI.

Run #2

The run was started similarly to the first run. After five minutes operation the bed suddenly solidified. Numerous small channels formed in the salt, each above a hole in the steel plate. The odor of sulphur dioxide became strong and smoke issued from the discharge side of the reactor.

The channels were later examined and found to have a powdery white core much whiter than the surrounding salt and more firmly fused. The bottom plate contained a round area about the center which appeared to have been wet during the run. It contained hardened piles of salt. The cores were found to contain much more sulphate than the surrounding bed. Neither was found to contain any moisture.

Changes Prior to Run #3

A trap was installed in the moist air line at the furnace entrance to catch any condensate formed in the unheated portion of the line.
NOTE: Gas distribution plate on the left fits inside the iron support.
Run #3

The run was started similarly to the first two and after six minutes the center portion of the bed stopped fluidizing. The unit was opened and the bed was stirred, but the holes seemed to be plugged up. The unit was operated for two more minutes when the entire bed stopped fluidizing.

The same cores were found again and also the holes in the center portion of the top plate were closed with a rusty scale.

Changes Prior to Run #4

A Corrundum plate was made to cover the upper steel plate and glass wool was placed in the space between the plates (reactor number 3).

Run #4

Results were the same as Run #3 with the exception that the holes did not plug up and the operation lasted ten minutes.

Changes Prior to Run #5

A new reactor was designed (reactor number 4) to provide greater agitation of the bed in order to prevent solidification. It consisted of a two and one half inch glass tube tapered toward the bottom in a length of about twelve inches. The lower diameter was three eighths inch. A half inch perforated ceramic disk was placed in the lower portion to support the bed of solid.

Run #5

Improved operation was noted over previous runs. Temperature was maintained between 400 and 420°C. About twenty minutes of satisfactory
operation was followed by about thirty minutes of poor operation when
the bed became increasingly more sticky in appearance until it would no
longer fluidize even when stirred. A cake had formed on the ceramic
disk with the usual channels leading upward. The major portion of the
bed was loose after cooling and analyzed about 60% sodium sulphate based
on the sulphate analysis. The cake on the disk analyzed 98.5% on the same
basis.

Run #6

Conditions were identical with Run #5 except for a lower temperature
which was expected to reduce the melted cake found previously. It had
little effect on cake formation or stickiness.

Changes Prior to Run #7

The ceramic disk was removed completely and a ninety degree bend
made at the bottom of the reactor to eliminate the dead zone existing
at the periphery of the ceramic disk (reactor number 5).

Run #7

Results were similar to the previous runs; the product was 39% so-
dium sulphate and the run lasted fifteen minutes before the salt stopped
fluidizing.

Changes Prior to Run #8

A fluidization promoter was installed in the bottom of the reactor
since it was noticed that the gas was channeling up the side opposite the
inlet (reactor number 6). The promoter was a small spiral made of glass
rod.
Run #8

Stickiness was observed after five minutes and the run was terminated. The promoter had become stuck in the bottom of the reactor and cake had formed around it.

Run #9

The run duplicates run #8 except that the promoter was not stuck. Cake formed in both runs.

Run #10

The temperature was reduced to about 220°C to find a lower temperature at which reaction proceeds without formation of cake. The operation was fairly successful since only 23.4 grams of cake formed of a 20 gram charge in an hour of operation. The product analyzed 49% sodium sulphate based on sulphate.

Run #11

A higher temperature of about 260°C was attempted to increase the reaction rate, but fluidization ceased after twenty-seven minutes. The product was 54% salt cake.

Run #12

A reduction in sulphur dioxide concentration was next attempted as a means to reduce the surface temperature of the reacting particle and thus remove a possible cause of stickiness. The reaction did not proceed and it was assumed that no sulphur dioxide reached the salt. Although the sulphur dioxide rotameter fluctuated widely it was found to do so even
with the supply shut off. The fluctuations were caused by the pressure variation across the fluidised bed.

Run #13

A glass wool plug in the line reduced the fluctuations to permit satisfactory operation. Concentration of sulphur dioxide was reduced when the solid became sticky permitting continued reaction. The run was ended after fifty minutes and yielded a product of 89% sodium sulphate. The temperature reached 360°C at the end of the run when the solid was beginning to appear sticky.

Run #11

The turbulence promoter was broken in removal from the reactor on run #13 so its use was discarded for this run, but excessive carryover prevented a satisfactory operation.

Changes in Operation Prior to Run #15

At the conclusion of run #11, liquid was noticed condensed on the walls of the reactor even though its temperature was 150°C. For this reason the water concentration of the reactor gas was reduced by decreasing the humidifier tower temperature from 65.6°C to 32.2°C. A turbulence promoter was also used again.

Run #15

The temperature varied from 330-370°C during a seventy minute run. Samples were taken at intervals until the bed was nearly depleted. The operation was satisfactory for over an hour when a slight stickiness was
noticeable, but a uniform product was obtained which analyzed 98% sodium sulphate based on a chloride analysis. The last sample removed analyzed 92.5% sodium sulphate based on sulphates and contained negligible acidity since it appeared basic to methyl orange indicator.

Run #16

A lower temperature was used to obtain rate data. This data is presented in the discussion of results. The temperature was held at 240°C for over four hours yielding 15% conversion.

Run #17

At about 295°C the same conversion was obtained in two hours, however the bed became sticky at the end of the run reducing the reaction rate considerably.

Run #18

At about 315°C the same conversion was obtained in seventy-five minutes. The run was interrupted by an increase in sulphur dioxide rate due to a faulty valve. The same stickiness was noted near the end of the run, the sticky portion beginning at the fluidization promoter forming a hollow cone and then disintegrating.

Changes Prior to Run #19

An extension of one foot was added to the top of the reactor to eliminate the fluidization promoter and also to prevent carryover (reactor number 7, shown in Illustration VII).
Run #19

The temperature rose gradually from 260° to 330°C, the run lasting two hours and twenty minutes to give a product of 80% sodium sulphate. Some stickiness was still noted.

Run #20

A continuous type reactor was set up to test its operability (reactor number 8). The gas rates were set before introduction of salt. The first salt to flow immediately stuck to the glass vessel at widely scattered points, mainly at the constrictions reducing their diameter and preventing downward flow.

Run #21

The same conditions were used as in the previous run except the salt was started before the sulphur dioxide. Operation was satisfactory for about five minutes when solid formed about the lower constriction. Liquid was noticed condensed to a single drop at the bottom of the reactor.

Changes Prior to Run #22

The sulphur dioxide line was connected to the furnace outlet instead of the furnace inlet to prevent formation of liquid.

Run #22

Reactor #8 was operated at a very low throughput for fifty minutes at a temperature of 385°C at the same gas concentration previously used. The product contained no sulphate.
VIIIB and VIIIC are fast action photographs showing the position of the salt particles while the bed is fluidizing.
Run #23

The temperature was raised as much as possible by increasing the fuel rate to the furnace. After fifteen minutes at 421°C the product contained a trace of sulphate estimated at one or two percent.

Run #24

A catalyst added to the salt (.2% Ferric chloride) had no noticeable affect. A trace of sulphate was again produced.

Run #25

The sulphur dioxide rate was increased ten fold causing a slight improvement in yield. About three percent conversion was obtained in thirteen minutes.

Run #26

The reactor was reinsulated and wound with heater wire to give more even heating. Results were no better; only a trace of sulphate was produced in eighty-six minutes at about 471°C.

Run #27

Reactor number 2 was installed to permit higher gas rates. A one half inch bed of salt was used and operated for thirty-eight minutes at maximum rotameter readings of air and sulphur dioxide. A trace of sulphate was found in the product.

Run #28

Reactor number 9 a two stage combination parallel counter flow reactor was operated for about ten minutes at 543°C. The product showed a trace of sulphate.
Run #29

Reactor number 7 uninsulated was operated with red iron oxide added as a catalyst. The maximum temperature obtainable in the salt bed was 240°C. No conversion was noted.

Run #30

Reactor number 7 wound with heater wire and insulated was operated with red iron oxide added to the salt as a catalyst. The reactor temperature at the top of the bed reached 400°C by means of the heating wire alone. With salt present the temperature reached 380°C at the maximum gas rate. The temperature was much higher at the reactor inlet since the reactor bent downward due to its own weight during the run. The product showed a heavy trace of sulphate.

Changes Prior to Run #31

The furnace was redesigned to produce hotter gas at a lower rate by installing smaller heater tubes of one eighth inch pipe. Insulation was placed between the heater wire and reactor to reduce local overheating.

Run #31

The run was started at a reactor temperature of 520°C. A charged of thirty grams of salt was used to which about five grams of iron oxide reduced from the sulphate was added. After seven minutes the temperature had reached 600°C and fluidization ceased. At a temperature of 540°C some smoke was noted escaping from the reactor exit. The entire bed had solidified with a small hole through one side of it. A large fused
cake had formed which contained appreciable sulphate. The top portion of the bed had become dark grey in color indicating a change in form of the iron oxide.

Run #32

A blank was run without catalyst for comparison. The same trace of sulphate was found as previously.

Run #33

A forty gram charge of salt with five grams of activated iron oxide catalyst were fluidized at progressively higher temperatures until reaction was noted by a sample tested with barium chloride solution. Reaction began at about 490°C and increased slowly with rise in temperature until the maximum obtainable was reached. After progressive increases the temperature was maintained at 585°C for twenty-two minutes. The product of this run contained 5% salt cake.

Run #34

An unsuccessful attempt was made to switch from sulphur dioxide to trioxide by heating oleum and passing it into the system. The sulphuric acid was also partially vaporized and in condensing in the rotameter prevented satisfactory operation.

Changes Prior to Run #35

The very low reaction rates noted in the runs where sulphur dioxide was introduced at the furnace outlet led to the conclusion that faster reaction would occur if the sulphur dioxide were first oxidized to the
trioxide and then combined with the water vapor to produce gaseous sulphuric acid. Consequently a catalyst chamber was installed in the furnace. The catalyst consisted of iron oxide supported on asbestos fibre contained in a four foot section of half inch pipe. The catalyst was made and activated by reducing iron sulphate in a muffle furnace at 650°C.

Run #35

Prior to introduction of salt and fuel to the furnace the reaction gas was analyzed for sulphur dioxide by absorption in iodine solution and also by absorption in dilute caustic solution. The gas was found to contain 4.5% sulphur dioxide. The furnace was heated and a second analysis showed sulphur dioxide to be 1.6% based on absorption in iodine solution. The caustic gave the percent of both sulphur dioxide and trioxide as 2.7%. The decrease was assumed to be caused by absorption of gas by the catalyst since equilibrium was probably not set up when the analysis was made, or by condensation of sulphuric acid gas in the cool sampling tubes. The analysis of the gas leaving the reactor after ten minutes of operation with salt in the reactor showed 5.0% sulphur dioxide based on absorption in iodine solution and 5.3% of both gases based on caustic solution. It is believed that the percent of sulphur trioxide present in the last analysis is negligible since the usual smoke which indicates the presence of sulphur trioxide disappears completely when salt is placed on the reactor. The difference in the last two values is within the experimental error of the analysis. The run was continued
for an hour until the faulty operation of the sulphur dioxide rotameter caused its termination. The product analyzed 37% sodium chloride. The average temperature was 340°C. A slight amount of cake was found at the bottom of the reactor.

Run #36

A lower temperature of 230°C was used to improve conversion of sulphur dioxide, but the salt became sticky after only ten minutes operation. A cake had formed in the bottom of the reactor.

Changes Prior to Run #37

The humidity of the air was reduced to lower the partial pressure of sulphuric acid gas and thus prevent its condensation. An external heater was added to the upper portion of the reactor and the voltage was reduced on the inner heater since exceedingly high temperatures were found to exist in the inlet tube at the base thus explaining the bending of the glass in run #31 and #32.

Run #37

The average temperature was 340°C. The dew point of the air at the start of the run was 21.1°C and at the end was 30°C. The run progressed smoothly for three hours without any signs of stickiness. A sample taken from the bed analyzed 96.5% salt cake based on a chloride analysis of 3.5% sodium chloride. The reactor showed no signs of cake and the product was uniform in appearance except for a few balls that had formed from drops of acid which had condensed on the exit tube and
dropped back into the bed.

**Run #38**

The operation without caking or stickiness may have been due to reduced local overheating or reduced humidity. This run was made at an air dew point of 32.2°C with a mixture of ground rock salt finer than sixty-five mesh. Stickiness and caking was noted after thirty minutes operation. The product analyzed 71% sodium chloride.

**Run #39**

Run #38 was repeated using table salt, but plugging ended the run after seventy-three minutes. It was concluded that the dew point was too high.

**Run #40**

The air stream was split, part being sent through the humidifying tower the remainder was sent directly to the furnace. This arrangement permitted control of the air dew point. Reactor number 6 was jacketed with a glass tube upon which heater wire was wound. The temperature of the reactor reached 210°C utilizing the heating wire only. The unit was operated for about two hours at zero rate of solid removal since the bottom outlet caked from liquid condensation. No cake formed during the operation in the upper part of the reactor, but a few particles of salt stuck to the glass in the uppermost sections. This probably occurred due to the failure of the jacket heater to provide sufficient heat in that section. The product analyzed 14.5% sodium chloride.
DISCUSSION OF RESULTS

Observation of the behavior of the bed of solid in the first runs at a temperature of about 520°C indicated that a liquid was being formed on the surface of the salt as a result of the reaction, and this liquid caused the particles to stick together to form a solid cake. The assumption was made at first that sodium sulphate was produced on the salt surface and the heat of reaction may have been high enough to raise the surface temperature to the melting point of the eutectic which is 623°C.

In an attempt to overcome this caking a conical shaped reactor was used which permitted greater agitation of the salt. Longer runs were then obtained at a lower temperature of about 410°C but the same caking conditions were found to exist. Several changes were made to eliminate completely the existence of any salt which was not in motion in the gas stream. When this was accomplished, reaction was evident at a still lower temperature of 220°C and the weight of cake formed was reduced to about one percent of the charge. A higher temperature of 260°C with the improved apparatus, employed to obtain a higher reaction rate, was unsatisfactory due to an increase in the amount of cake.

A reduction in concentration of sulphur dioxide was then considered as a means of lowering the rate of conversion in order to decrease surface temperature. The run was started at the usual concentration and when the tendency of the salt particles to stick together was noted, a reduction in the sulphur dioxide flow rate was found to eliminate this tendency.
momentarily. Continued reduction of the sulphur dioxide rate at intervals permitted the reaction to proceed to eighty-nine percent conversion. The appearance of condensed liquid on the walls of the reactor prompted the reduction of the water vapor concentration in the following run which achieved practically complete conversion, although stickiness was noticeable.

At this stage in the development several assumptions were made based on the observation of liquid condensate which appeared during the reaction at low temperatures. Some other explanation of stickiness and cake formation was sought than the original assumption of high surface temperature. The formation of cake at lower temperatures as well as the appearance of condensed liquid indicated that there might be a different explanation for the unsatisfactory operation. The appearance of mist at the scrubber outlet which had the odor of sulphur trioxide led to the supposition that sulphur dioxide was being partially oxidized in the furnace tubes to form sulphur trioxide which reacted with the water vapor present to form sulphuric acid gas. The condensation of this sulphuric acid gas on the cooler surfaces of the reactor would explain the appearance of the liquid.

To prevent these reactions which formed sulphuric acid gas in the furnace tubes the sulphur dioxide was introduced into the air stream at the furnace exit rather that the furnace entrance. This change, besides eliminating the undesirable effects also reduced considerably the rate of conversion to the sulphate. The rate was practically zero until the temperature was raised to about 450°C. At 500°C only five percent
conversion was obtained in about twenty-five minutes. Still higher temperatures were employed but the bed solidified to form a hard cake which was assumed to be caused by the formation of the liquid eutectic. Activated iron oxide mixed with the salt was used as a catalyst in these high temperature runs, and sulphuric acid mist was noted issuing from the reactor after formation of the cake mentioned in the previous sentence. The conclusion was then reached that sulphur trioxide was formed in the furnace tubes in all of the earlier runs and also to some extent in the reactor in the later runs in which the sulphur dioxide by-passed the furnace and entered the salt bed containing iron oxide as a catalyst.

On the basis of this conclusion, the early experiments indicated that the presence of appreciable amounts of sulphur trioxide at high temperature caused rapid formation of solid cake. Later higher temperature experiments showed that the introduction of sulphur dioxide directly into the reactor with consequent low sulphur trioxide concentration permitted satisfactory operation but low reaction velocity. Comparison of these two types of operation at high temperature shows that the reaction rate depends on the sulphur trioxide concentration. With appreciable amounts of sulphur trioxide present, lower temperatures reduced the rate of reaction as well as the tendency toward stickiness. The immediate cause for caking or stickiness was assumed to be the formation of liquid on the surface of the salt particle which resulted either from the appearance of a melted solid on the surface or from liquid condensation.
High temperatures of about 500°C were found to form cake which was assumed to result from the formation of a liquid product on the solid surface. Lower temperatures of about 240°C were found to cause stickiness which was assumed to result from condensation of sulphuric acid gas. At intermediate temperatures of 300 to 350°C both effects were noticeable until the water vapor content of the air was reduced below that employed in any of the previous runs. This was accomplished in run #37. The percentage composition of the gas used in run #37 is shown below:

<table>
<thead>
<tr>
<th></th>
<th>Mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>92.3</td>
</tr>
<tr>
<td>Water Vapor</td>
<td>3.0</td>
</tr>
<tr>
<td>Sulphur Dioxide</td>
<td>4.7</td>
</tr>
</tbody>
</table>

100.0

Under these conditions at a temperature of 340°C neither caking nor stickiness was noted throughout the operation.

Beginning with run #15 a technique was developed for withdrawing samples from the reactor during the run. Chemical analysis of these samples form the basis for reaction rate data. The variation of the fraction reacted with time for several runs is shown in Figure 6. The slope of the line is indicative of the speed of reaction, greater slope indicating higher reaction rate. In order to include the data from the various runs on a single plot for comparison purposes, corrections for initial time, weight of salt charged, and weight of samples withdrawn
FIG. 6  REACTION RATES

F
fraction reacted

RUN 19  310°C
RUN 18  310°C
RUN 17  290°C
RUN 16  240°C
RUN 15  340°C
RUN 37  340°C

NOTE:
THE REACTION RATE IS INDICATED BY THE SLOPE

Time (min.)
have been applied. Equivalent gas concentrations were used with the exception of run #37 which has less water vapor than the other runs.

Photomicrographs of the products of reaction at various degrees of conversion (see Illustrations VIII and IX) show that the original shape of the particle is maintained throughout the reaction with the exception of the corners which become rounded. Particles which were partially converted were broken under the microscope and were found to consist of cubic shaped shells of small crystals enclosing a smooth core of transparent salt. (see Illustration X). The thickness of the shell surrounding the salt varied in proportion to the conversion, indicating progressively deeper penetration of the reaction surface. The linear relation between the fraction reacted and the time indicates that the exposure of salt surface to the gas does not control the reaction rate until the conversion is near completion.

The utilization of sulphur dioxide was noted to vary with the temperature, the higher temperatures causing higher reaction rate and consumption of more sulphur dioxide. In the single stage reactor at 340°C the sulphur appearing in the product amounted to about ten percent of the sulphur charged as sulphur dioxide. In reactor number 8 used in run #40 about twenty percent of the sulphur charged as gas appeared in the solid product. Since reactor number 8 has a deeper bed for the same weight of salt, the data indicates an advantage may be gained by countercurrent operation. A more efficient conversion of the sulphur dioxide to the trioxide and operation of a countercurrent type
ILLUSTRATION IX

IXA 55% Conversion

IXB 82.5% Conversion

IXC 92.1% Conversion

IXD 96.7% Conversion
Particles of salt 80% converted fractured under the microscope. Note the transparent core of sodium chloride in the center of Illustration XA, and the two layers of the shell below the center in Illustration XB.
unit appear to be the indicated improvements necessary for pilot plant development of the process.
THEORETICAL ASPECTS OF THE REACTION

The overall reaction is shown below:

$$2 \text{NaCl (s)} + \text{H}_2\text{O (g)} + \text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4 (s) + 2 \text{HCl (g)} \quad (1)$$

The reaction is exothermic at 25°C as indicated by a value for $\Delta H$ of $-49,300$ calories. The probability that it will proceed in the direction shown is indicated as favorable by a value of $-37,200$ calories for $\Delta F$ at 25°C.

It is reasonable to assume that the reaction must occur in steps since the simultaneous collision of the four reactants is highly improbable as is also the simultaneous adsorption of the three gases on the surface of the salt. There are many possible ways the reaction may be broken down into shorter steps. The most logical path for a given set of conditions of temperature, pressure, and concentrations may be deduced from the previously observed behavior of the reactants.

Two reactions considered to be involved in the process are the following:

$$\text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) = \text{SO}_3 (g) \quad (2)$$

$$\text{SO}_3 (g) + \text{H}_2\text{O (g)} = \text{H}_2\text{SO}_4 (g) \quad (3)$$

The equilibrium constants for both are shown in Figure 7 as a function of temperature. It is noted that a low temperature favors the formation of both sulphur trioxide and sulphuric acid gas and high temperature increases the rate of approach to equilibrium with higher concentrations of the reactants. Mellor (5) states that the steps taking place in the Hargreaves
FIG. 7  EQUILIBRIUM CONSTANTS

\[ \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) \]

\[ \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{H}_2\text{SO}_4(\text{g}) \]
reaction at 500°C are first the reaction of salt, sulphur dioxide, and water to form sodium sulphite and hydrochloric acid and second the reaction of sodium sulphite and oxygen to form sodium sulphate. These reactions are shown below:

$$2 \text{NaCl (s)} + \text{H}_2\text{O (g)} + \text{SO}_2 (g) \rightarrow \text{Na}_2\text{SO}_3 (s) + 2 \text{HCl (g)} \quad (1)$$

$$\text{Na}_2\text{SO}_3 (s) + \frac{3}{2}\text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4 (s) \quad (5)$$

This does not explain the function of the iron catalyst.

The experimental results as well as the equilibrium data previously mentioned indicate a different mechanism from that suggested by Mellor at a lower temperature of about 300°C. There is also some doubt of the mechanism mentioned by Mellor at the higher temperature. The lower temperature favors the formation of sulphuric acid gas, and sulphuric acid reacts readily with salt to form the bisulphate and hydrogen chloride according to the reaction:

$$\text{H}_2\text{SO}_4 + \text{NaCl} \rightarrow \text{NaHSO}_4 + \text{HCl} \quad (6)$$

The existence of this reaction is indicated by the disappearance of the familiar sulphuric acid mist from the reactor outlet when salt is placed in the reactor.

The final step of formation of sodium sulphate may occur in several ways. It is probable that the sodium bisulphate formed from salt and sulphuric acid gas is rapidly transformed into sodium pyrosulphate since the bisulphate decomposes readily at the reaction temperature to form the
pyrosulphate and water according to the following equation:

\[ 2 \text{NaHSO}_4 \rightarrow \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \]  

(7)

The final step in the reaction may then be as follows:

\[ \text{Na}_2\text{S}_2\text{O}_7 + 2 \text{NaCl} + \text{H}_2\text{O} \rightarrow 2 \text{Na}_2\text{SO}_4 + 2 \text{HCl} \]  

(8)

(The combination of equations (7) and (8) is the second step in the Mannheim reaction.)

There are a few observations in favor of this hypothesis. One is the observation that pure sodium bisulphate when heated, begins to decompose at about 150°C forming a solution of the pyrosulphate and the bisulphate. Continued heating causes evolution of bubbles of water vapor from a viscous solution which does not form a dry solid as the temperature is raised. The melting point of the pyrosulphate is 400.5°C. This decomposition occurring on the surface of the salt would provide suitable conditions for the reaction proposed.

Microscopic examination of the surface shell of particles has revealed the existence of two distinct layers besides the core of salt. (see Illustration XI) The intermediate layer may be the intermediate product. There is little doubt that one or the other of the intermediate products exists in sizable proportions during the operation since the high acidity values on some samples cannot be accounted for by condensed sulphuric acid alone, especially since the samples appear bone dry.

Another reaction which must be considered along with the others proposed is the following:

\[ \text{Na}_2\text{S}_2\text{O}_7 \rightarrow \text{Na}_2\text{SO}_4 + \text{SO}_3 \]  

(9)
A particle of salt 85% converted fractured under the microscope. Illustration XIA shows the particle after the initial fracture. Illustration XIB shows the same particle more completely broken. Note the concentric layers or shells.
According to Johnstone (6) this occurs above 300°C. The contribution of this reaction to the amount of final product is considered slight due to the slow decomposition rate at the reaction temperature. The reaction:

\[ 2 \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{HCl} \]  

may account for a portion of the product also.

The mechanism of the reaction was considered in order to explain and help overcome the difficulties encountered in accomplishing the primary aim of the investigation, the application of the fluidized solids technique to the manufacture of sodium sulphate. The difficulties of cake formation encountered at high sulphur dioxide and water concentrations are explained by the mechanism proposed since at these concentrations a high rate of formation of the liquid intermediates (bisulphate and pyrosulphate) would occur. The rate of removal of these liquid products by reaction to form sodium sulphate and hydrogen chloride is independent of the concentration of the gases since the reaction occurs in the liquid phase. As in the Mannheim reaction, high temperature favors the rapid completion of the final step. The difficulty encountered at low temperature, the condensation of the sulphuric acid on the salt and on the reactor itself, is directly connected to the caking difficulty. Too large a concentration of water vapor and sulphur dioxide permit the partial pressure of sulphuric acid gas to reach the dew point, with resultant stickiness and caking. The partial pressure of 99.23% and 98.06% sulphuric acid are shown in Figure 8. This sticky condition is noticeable
FIG. 8
PARTIAL PRESSURE of
SULPHURIC ACID

99.23%

98.06%

PARTIAL PRESSURE
mm. Hg.

TEMPERATURE °C
in those runs where satisfactory reaction rates and operation were obtained until high conversions were reached. At this point stickiness was seen to become more severe as conversion increased, until the bed of solid stopped fluidizing completely. At low conversions in the early part of the run the sulphuric acid gas was removed rapidly enough by reaction with the salt to prevent its reaching the dew point. As the run progressed, the rate of removal of sulphuric acid gas decreased permitting its partial pressure to rise until condensation took place. This difficulty was overcome by the reduction of the concentrations of sulphur dioxide and water vapor to such an extent that the partial pressure of sulphuric acid gas remained below the dew point of sulphuric acid throughout the run.
SUMMARY

The problem under investigation was the application of the technique of fluidization to the reaction taking place in the Hargreaves process for the manufacture of sodium sulphate. Experiments were conducted to determine the behavior of salt of various average particle sizes when suspended in a stream of air. The size found to be most suitable was that of common table salt; consequently the resistance to the flow of air of this material in a fluidized condition was determined. In considering the design of equipment in which the reaction under study was to be carried out it was though that the most efficient type of operation would involve the countercurrent flow of solid and gas. With this principle in view several laboratory units were designed, constructed, and operated to show that the countercurrent principle could be successfully applied to the contacting of solid with gases in a fluidized system. Designs for two larger units are presented based on the knowledge obtained from the operation of the laboratory units.

Experiments were conducted to determine whether the reaction could be successfully carried out in a fluidized bed. Numerous difficulties were encountered. The solidification of the salt bed in the course of the reaction at high temperature led to the supposition that intermediate products were formed in a liquid state. From the formation of liquid condensate at low temperatures and the appearance of sulphuric acid mist, the existence of sulphuric acid vapor in the gas stream was concluded. A mechanism for the reaction was then proposed which might explain the phenomena observed at the various
operating conditions. Satisfactory operation was obtained when reductions in gas concentrations were made in accordance with conclusions reached from consideration of the proposed reaction mechanism.

The necessary steps in the process as well as the conditions of operation such as temperature and gas concentration were discovered. The first step in the application of the fluidization technique to a commercial process, successful operation on a laboratory scale, was accomplished.

Other information of value to further development on a pilot plant scale such as reaction velocity, pressure losses, gas flow rates, and material losses were also obtained. In the development of the process the difficulties which were encountered and overcome indicate the probable temperature and concentration limits for larger scale operation. On the basis of these considerations a process flow diagram was developed which is presented.

In the absence of sufficient data from which the power and other costs may be estimated, the commercial feasibility of the proposed process may be indicated from a comparison with the manufacture of sulphuric acid by the contact process. These two processes have many similar features for which the operating and fixed costs should be about the same. The conversion of sulphur to the trioxide is accomplished in both. Heat economies effected in the contact process may also be obtained in the process suggested. Iron oxide, a much cheaper catalyst
FIG. 9  PROCESS FLOW DIAGRAM
than Vanadium or Platinum may be employed in the manufacture of salt cake since lower sulphur dioxide concentrations and the presence of water vapor are more favorable to conversion of sulphur dioxide than the conditions employed in the contact process.

The cost of raw materials and the market value of the products resulting from the consumption of one ton of sulphur will be the basis for comparison of the two processes. The cost of a ton of sulphur as quoted by the management of the local sulphuric acid plant is $20.00. Complete conversion of one ton of sulphur to sulphuric acid would result in an increase in value to $49.00 based on a selling price of $16.00 per ton for pure sulphuric acid. The increase in value is obtained by consideration of the following weight balance:

\[ S + \frac{3}{8}O_2 + H_2O \rightarrow H_2SO_4 \]

1 Ton \( \neq \) 1.5 Tons \( \neq \) .56 Tons = 3.06 Tons

The cost of the oxygen and water are assumed small in comparison with the cost of the sulphur and are therefore neglected. This shows an advantage of $33.00 which represents the combined cost of processing and profit from the conversion of one ton of sulphur.

A cost of $1.45 per ton of dry salt obtained as a twenty-five percent solution, and values of $18.00 per ton for salt cake and $45.00 per ton of pure hydrochloric acid are taken as representative for these materials. These values were obtained from a local industry which manufactures salt cake and hydrochloric acid. The value for salt cake is
taken as at the factory and does not include shipping charges. The value for the pure acid refers to any quantity of weak acid which contains the equivalent of one ton of pure hydrogen chloride. It is also taken as the price at the factory and does not include shipping charges. A weight balance for the proposed process similar to the one made for the contact process is shown below:

$$3 \rightarrow \text{H}_2\text{O} \rightarrow 2 \text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 \rightarrow 2 \text{HCl}$$

1 Ton ≠ 1.5 Tons ≠ 56 Tons ≠ 3.66 Tons = 4.44 Tons ≠ 2.28 Tons

A comparison of prices of raw materials and products for the proposed process similar to the one made for the manufacture of sulphuric acid shows an advantage of $157.90 of product value over raw material cost per ton of sulphur utilized. This figure is more than four times as large as the corresponding one for the manufacture of sulphuric acid.

The same monetary advantage may be claimed for the Hargreaves Process as well as for a process consisting of a combination sulphuric acid plant and Mannheim salt cake plant. The undesirable features of high labor and power cost have previously been suggested as the reason for the limited use of the Hargreaves Process. The commercial success of the only plant in operation in this country is due in part to its location at a source of sulphur and cheap salt. A combination sulphuric acid and Mannheim salt cake plant would entail costs which are eliminated by the fluidization process. It eliminates the formation of liquid sulphuric acid and the costs attendant to its handling and storage,
It eliminates the high initial and maintenance costs of a Mannheim furnace. It is also expected to produce a more uniform solid product which will entail lower handling and shipping cost.

The equipment shown in the process flow diagram which is not present in a contact sulphuric acid plant are the salt evaporator, centrifugal, dryer, storage vessel, reactor and salt cake cooler. Since heat recovered from the burning of sulphur is to be utilised for evaporation and power generation, the operating cost of making crystaline salt should be low. The major item of expense for which the process is chargeable, in addition to those involved in a sulphuric acid plant, is the initial cost of the equipment in which salt or salt cake is handled. With the exception of the reactor, such equipment is of standard design and its cost should not be excessive. At the present stage of development the cost of a reactor cannot be predicted with any degree of certainty, but the designs previously suggested are of a type construction for which the cost should be in line with the other equipment.

The comparison of the proposed salt cake process with the contact process for the manufacture of sulphuric acid was considered to be a reasonable one and it provided a basis upon which an economic appraisal might be made.

A consideration of the similarity of the two processes and a comparison of the increase in value of products resulting from equivalent amounts of sulphur processed indicate that the economic feasibility of the fluidization process is highly favorable.
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(2) Leva, Max "Pressure Drop Through Packed Tubes"; Chem. Engr., Vol. 43, No. 10, 549-554; No. 11, 633-638; No. 12, 713-718.

(3) Leva, Max et al "Introduction to Fluidization"; Chem. Engr., Vol. 44, No. 7, 511-520; No. 8, 619-626.


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APPENDIX

Pressure Drop Through Table Salt

Depth of Bed — — — — — 6 inches
Diameter of Vessel — — — — 4 inches
Weight of Salt Charged — — 4 pounds

<table>
<thead>
<tr>
<th>Reading No.</th>
<th>ΔP Inches Carbon Tetrachloride</th>
<th>Lb/ft²</th>
<th>Time Min.</th>
<th>Volume of Air ft³</th>
<th>G lb/ft²-hr</th>
<th>Dp G μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.4166</td>
<td>1.33</td>
<td>.1</td>
<td>3.73</td>
<td>.0796</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.0833</td>
<td>66</td>
<td>.1</td>
<td>7.51</td>
<td>.161</td>
</tr>
<tr>
<td>3</td>
<td>1.625</td>
<td>0.1355</td>
<td>833</td>
<td>.2</td>
<td>11.90</td>
<td>.255</td>
</tr>
<tr>
<td>4</td>
<td>2.375</td>
<td>0.1980</td>
<td>2.835</td>
<td>.1</td>
<td>17.50</td>
<td>.375</td>
</tr>
<tr>
<td>5</td>
<td>3.375</td>
<td>0.2810</td>
<td>393</td>
<td>.2</td>
<td>25.20</td>
<td>.540</td>
</tr>
<tr>
<td>6</td>
<td>4.125</td>
<td>0.3340</td>
<td>1.193</td>
<td>1.0</td>
<td>41.6</td>
<td>.890</td>
</tr>
<tr>
<td>7</td>
<td>4.140</td>
<td>0.3450</td>
<td>952</td>
<td>1.0</td>
<td>52.1</td>
<td>1.115</td>
</tr>
<tr>
<td>8</td>
<td>4.140</td>
<td>0.3450</td>
<td>81</td>
<td>1.0</td>
<td>91.2</td>
<td>1.310</td>
</tr>
</tbody>
</table>

Sample Calculation

Density of carbon tetrachloride 1.584 x 62.4 = 98.8 lb/ft²

Density of air (90°F, 1 atmosphere) \(\frac{29}{359} \times \frac{192}{550} = 0.0722 \text{ lb/ft}³\)

Cross sectional area of vessel .0873 ft²

\(G = \frac{1.33 \times 0.0722 \times 60}{0.0873} = 3.73 \text{ lb/ft}² \text{-hr.}\)

\(Dp = 0.00093 \text{ ft.} \mu (100°F) = 0.0435 \text{ lb/hr-ft.}\)
Pressure Drop Through Table Salt

Check determination

Depth of Bed — — — 6 inches

Diameter of Vessel — — 4 inches

Weight of Salt Charged — 4 pounds

<table>
<thead>
<tr>
<th>Reading No.</th>
<th>∆P</th>
<th>Lb/ft²</th>
<th>Time Min.</th>
<th>Volume of Air ft³</th>
<th>G lb/ft²-hr</th>
<th>Dp G μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.2125</td>
<td>12.35</td>
<td>.804</td>
<td>1.2</td>
<td>11.22</td>
<td>.24</td>
</tr>
<tr>
<td>2</td>
<td>.335</td>
<td>20.90</td>
<td>3.53</td>
<td>1.2</td>
<td>16.73</td>
<td>.358</td>
</tr>
<tr>
<td>3</td>
<td>.3735</td>
<td>23.27</td>
<td>.89</td>
<td>1.4</td>
<td>22.30</td>
<td>.477</td>
</tr>
<tr>
<td>4</td>
<td>.4750</td>
<td>29.62</td>
<td>1.01</td>
<td>.6</td>
<td>28.60</td>
<td>.612</td>
</tr>
<tr>
<td>5</td>
<td>.5250</td>
<td>32.75</td>
<td>.634</td>
<td>.4</td>
<td>37.70</td>
<td>.806</td>
</tr>
<tr>
<td>6</td>
<td>.5315</td>
<td>33.18</td>
<td>1.36</td>
<td>1.0</td>
<td>37.50</td>
<td>.803</td>
</tr>
<tr>
<td>7</td>
<td>.5480</td>
<td>34.19</td>
<td>1.115</td>
<td>1.0</td>
<td>43.40</td>
<td>.928</td>
</tr>
<tr>
<td>8</td>
<td>.5525</td>
<td>34.75</td>
<td>.943</td>
<td>1.0</td>
<td>52.60</td>
<td>1.128</td>
</tr>
<tr>
<td>9</td>
<td>.5570</td>
<td>34.75</td>
<td>.853</td>
<td>1.0</td>
<td>58.10</td>
<td>1.215</td>
</tr>
</tbody>
</table>

Air Temperature 85°F

Air Density \( \frac{29}{359} \times \frac{1422}{515} = .073 \) lb/ft³
# Table Salt Screen Analysis

Weight of sample 1005 grams.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Hole Size Inches</th>
<th>Weight Retained</th>
<th>% Retained</th>
<th>Size of Retained Particles</th>
<th>Weighted Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>.0328</td>
<td>none</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>.0232</td>
<td>.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>.0164</td>
<td>30.0</td>
<td>3.0</td>
<td>.0198</td>
<td>.0594</td>
</tr>
<tr>
<td>48</td>
<td>.0116</td>
<td>41.4</td>
<td>41.2</td>
<td>.0140</td>
<td>.5760</td>
</tr>
<tr>
<td>65</td>
<td>.0082</td>
<td>386.5</td>
<td>38.5</td>
<td>.0099</td>
<td>.3810</td>
</tr>
<tr>
<td>100</td>
<td>.0058</td>
<td>99.1</td>
<td>9.9</td>
<td>.0070</td>
<td>.0693</td>
</tr>
<tr>
<td>over 100</td>
<td>74.7</td>
<td>7.4</td>
<td>.0040</td>
<td>.0296</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1005.0</strong></td>
<td></td>
<td></td>
<td><strong>1.1153</strong></td>
<td></td>
</tr>
</tbody>
</table>

Average diameter .0112 inches

Fines over 100 mesh .17% below 70 microns

Specific Gravity using Varsol (80°F)

weight of sample 53.296 grams

increase in volume of varsol 25.00 ml

Specific Gravity \( \frac{53.296}{25} = 2.131 \)
Flow Rates for Three Stage Countercurrent
Laboratory Fluidization Unit
(shown in Figure 2)

Air and solid rates are independent.
Gas rates were varied from zero to two cubic feet per minute. Solid rates were varied from zero to 280 grams per minute.

Flow rates for Reactor number 9
Air and solid rates are independent.
Gas rates were varied from zero to one cubic foot per minute. Solid rates were varied from zero to 100 grams per minute.
Operating Data Run #1
(Reactor number 1)

Charge 200 grams table salt.

When the thermocouple indicated 950°F one quarter inch above the screen, sulphur dioxide was introduced even though the pressure drop was fluctuating widely from about ten to twenty-five inches of water.

Air Rate 1.8 cubic feet per minute

The sulphur dioxide rate below .5 cubic feet per minute

Pressure drop continued to fluctuate widely even when the air rotameter reading was reduced to five. After about thirty minutes the pressure manometer blew out (above thirty inches of water). Operation was ended after forty minutes. Temperature one quarter inch above the screen 1000°F.

Salt Bed Analysis

The bottom of the bed had several lumps of crystalline solid adhering to the screen which had become very brittle and cracked in several places. Analysis of the bed material indicated an equivalent of 10 grams of sodium sulphate.

The inlet of the heater coil was plugged with a tan colored scale at a point where the first chromel spring turbulence promoter began. The spring itself was apparently unaffected. Analysis showed the scale to be iron sulphite.
Changes Made Prior to Run #2

A double pipe heat exchanger was installed between the top of the humidifying tower and the junction of the sulphur dioxide entrance. The purpose of the exchanger was to jacket the wet air line with steam to superheat the water vapor and thus prevent condensation of moisture in the line which occurred in Run #1.

Rotameters were exchanged to permit the lower capacity meter to be used on the sulphur dioxide feed line.

Construction of a double plate stainless steel distribution plate for the bottom of the reactor (Reactor number 2). Holes were five sixty fourths on three eighth inch centers, square pitch, plates separated by one sixteenth inch asbestos gasket, holes offset in plates to prevent downflow of solid.

Operating Data Run #2

(Reactor number 2)

Charge: 250 grams table salt

Air rate: .7 cubic feet per minute

Sulphur dioxide admitted at 980°F. Sulphur dioxide rate .3 cubic feet per minute. Unit fluidizing satisfactorily. After five minutes reactor bed suddenly solidified forming numerous small channels, each channel located above a hole in the steel plate. The size of channel holes about the same as the holes in the plate. The odor of sulphur dioxide became very strong and smoke appeared coming out of the cracks around the discharge side of the reactor. The unit was immediately shut down.
Changes Prior to Run #3

A trap was installed in the wet air line at the furnace entrance to catch any condensate formed in the unheated portion of the line.

Operating Data Run #3

(Reactor number 2)

Charge: 200 grams table salt

Air rate: 1.5 cubic feet per minute

Air flow was started then steam to the jacket then heater was lit. The salt was added slowly to the reactor at about 600°F. Bed fluidizing satisfactorily. Hot water admitted to humidifying tower. Sulphur dioxide started at a rate of 0.2 cubic feet per minute when reactor temperature reached 980°F. Unit fluidizing satisfactorily. Smoke appeared coming out of exit of the scrubber tower; appears to be sulphur trioxide. After six minutes center portion of bed not fluidizing. Flow of sulphur dioxide was stopped, the reactor cover was removed, the bed was stirred with a wire. Holes in center and on one side of plate appear plugged. Bed temperature was 1080°F. Air to burners was reduced, cover replaced, sulphur dioxide started again. Fluidizing area of bed narrowed to a crescent section on one edge, continued to decrease in size until only a few holes were fluidizing. The scraping was repeated but a heavy cake appears to be formed on the plate and cannot be scraped off. Run terminated after two more minutes.
Operating Data Run #3 (Continued)

Appearance of Bed After Cooling

Bottom portion consists of a loose cake containing white cores similar to those of Run #2. The outer periphery was not caked and consisted of darker colored salt crystals having a spherical appearance. The center portion of the upper plate was plugged. Each hole contained some rusty looking crystalline deposit indicating corrosion of the plate at the hole. The bottom plate was clear.

Changes Prior to Run #4

A corundum plate was made to fit on top of the upper stainless steel plate and holes were drilled in it to correspond with the holes in the plate. Glass wool was placed between the two steel plates. (Reactor number 3)

Operating Data Run #4

(Reactor number 3)

Results were the same as Run #3 with the exception that holes did not plug up. The bed solidified after ten minutes operation at high temperature.

Changes Prior to Run #5

A tapered glass reactor having a two and one half inch diameter and overall height of eighteen inches with a tapered section of twelve inches at the bottom and a bottom opening of three eighths inch was made. A half inch perforated ceramic disk was placed in the lower portion to support the salt bed. (Reactor number 4)
Operating Data Run #5

(Reactor number 4)

Air rate: .5 cubic feet per minute
Sulphur Dioxide rate: .1 cubic feet per minute
Temperature: 420°C average

Bed fluidised satisfactorily; pressure drop six inches of water; bed depth four inches. When the temperature reached 400°C the salt became sticky; particles stuck to the walls of the reactor. At 420°C the bed would solidify until the reactor was tapped and then it fluidized again. The solidification and necessary tapping began to increase in frequency (the air was cut off from the fuel gas to the furnace but the temperature remained at 420°C) until it was necessary once a second. At this point the run was discontinued. About ten to twenty percent of the salt was adhering to the walls. Total time at 400°C about twenty minutes, told time above 400°C about thirty minutes.

The reactor when cooled contained loose product as well as cake on the ceramic disk which contained the familiar channels. It appeared to be fused cake rather than sintered. Analysis of loose material, 60% sodium sulphate based on sulphate analysis, the cake was 98.5% sodium sulphate.

Operating Data Run #6

The unit was operated at a lower temperature than Run #5 but at the same gas rates.
<table>
<thead>
<tr>
<th>Time Min.</th>
<th>Temperature °C</th>
<th>Pressure Drop inches of water</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>315</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>343</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>371</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>377</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>377</td>
<td>7</td>
<td>salt is sticky</td>
</tr>
<tr>
<td>23</td>
<td>382</td>
<td>7</td>
<td>reduced fuel to furnace</td>
</tr>
<tr>
<td>25</td>
<td>371</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>371</td>
<td>7</td>
<td>cake forming</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>very sticky</td>
</tr>
<tr>
<td>33</td>
<td>366</td>
<td>7</td>
<td>less sticky</td>
</tr>
<tr>
<td>36</td>
<td>343</td>
<td>7</td>
<td>sticky—more cake present (molten)</td>
</tr>
<tr>
<td>39</td>
<td>338</td>
<td>7</td>
<td>more cake present</td>
</tr>
<tr>
<td>40</td>
<td>349</td>
<td>7</td>
<td>sulphur dioxide cut off air rate increased</td>
</tr>
<tr>
<td>42</td>
<td>354</td>
<td>7</td>
<td>reduced fuel to furnace</td>
</tr>
<tr>
<td>43</td>
<td>349</td>
<td>7</td>
<td>fluidizing well again</td>
</tr>
<tr>
<td>45</td>
<td>332</td>
<td>7</td>
<td>fluidizing well again</td>
</tr>
<tr>
<td>48</td>
<td>315</td>
<td>7</td>
<td>fluidizing well again</td>
</tr>
<tr>
<td>49</td>
<td></td>
<td></td>
<td>terminated the run</td>
</tr>
</tbody>
</table>

Analysis of the bed 60% sodium sulphate
# Screen Analysis of Product and Feed Run #6

<table>
<thead>
<tr>
<th>Weight Percent</th>
<th>Product</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caught on 20 Mesh</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Caught on 28 Mesh</td>
<td>3.0</td>
<td>trace</td>
</tr>
<tr>
<td>Caught on 35 Mesh</td>
<td>10.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Caught on 48 Mesh</td>
<td>37.7</td>
<td>41.2</td>
</tr>
<tr>
<td>Caught on 65 Mesh</td>
<td>37.1</td>
<td>38.5</td>
</tr>
<tr>
<td>Caught on 100 Mesh</td>
<td>9.6</td>
<td>9.9</td>
</tr>
<tr>
<td>Passed 100 Mesh</td>
<td>2.1</td>
<td>7.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>
Changes Prior to Run #7

The ceramic disk was removed and a ninety degree bend was made in the tube at the bottom of the reactor.

Operating Data Run #7

Charge 48-65 mesh rock salt about 20 grams

Air rate: .18 cubic feet per minute

Sulphur dioxide rate: .1 cubic feet per minute

<table>
<thead>
<tr>
<th>Time (Min.)</th>
<th>Temperature (°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>316</td>
<td>salt is sticky</td>
</tr>
<tr>
<td>14</td>
<td>343</td>
<td>sticky - cut fuel out entirely</td>
</tr>
<tr>
<td>15</td>
<td>343</td>
<td>bed solidified</td>
</tr>
</tbody>
</table>

Product analysis 39% sodium sulphate

Changes Prior to Run #8

A turbulence promoter was made of glass rod in the form of a spiral to fit into the bottom of the reactor. This was used to prevent carry-over at high gas rates.

Operating Data Run #8

Charge same as Run #7

Air rate: .21 cubic feet per minute

Sulphur dioxide rate: .09 cubic feet per minute

After six minutes the temperature reached 282°C, the salt was sticky,
and liquid had formed around the turbulence promoter which had become stuck in the reactor.

Product analysis 15\% sodium sulphate.

Operating Data Run #9

Charge same as Run #7

Air rate: .16 cubic feet per minute

Sulphur dioxide rate: .06 cubic feet per minute

After four minutes the temperature reached 277°C and the bed had formed cake in the bottom. The fluidization promoter became stuck in liquid at the bottom. A hallow core of cake formed upward into the loose salt.

Product analysis 12\% sodium sulphate.

Operating Data Run #10

Charge same as Run #7 about 20 grams

Air rate: .29 cubic feet per minute

Sulphur dioxide rate: .09 cubic feet per minute

The sulphur dioxide was started when the temperature reached 170°C. After 18 minutes the temperature was 220°C and after 66 minutes 240°C. Satisfactory fluidization was obtained, however a slight amount of cake formed (.23\% grams) around the fluidization promoter. The cake contained 80\% sodium sulphate.

Product analysis 14\% sodium sulphate.
Operating Data Run #11

Charge same as Run #7 about 20 grams

Air rate: \(0.27\) cubic feet per minute

Sulphur dioxide rate: \(0.09\) cubic feet per minute

<table>
<thead>
<tr>
<th>Time (Min.)</th>
<th>Temperature (°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>190</td>
<td>Fluidizing</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>Fluidizing</td>
</tr>
<tr>
<td>10</td>
<td>230</td>
<td>Fluidizing</td>
</tr>
<tr>
<td>15</td>
<td>240</td>
<td>Fluidizing</td>
</tr>
<tr>
<td>18</td>
<td>250</td>
<td>Fluidizing</td>
</tr>
<tr>
<td>19</td>
<td>260</td>
<td>Fluidizing</td>
</tr>
<tr>
<td>22</td>
<td>260</td>
<td>Sticking to walls of reactor</td>
</tr>
<tr>
<td>24</td>
<td>240</td>
<td>Cut sulphur dioxide</td>
</tr>
<tr>
<td>27</td>
<td>230</td>
<td>Bed stuck completely</td>
</tr>
</tbody>
</table>

Product analysis: 51% sodium sulphate

Operating Data Run #12

Charge same as Run #7

Air rate: \(0.6\) cubic feet per minute

Sulphur dioxide rate unknown due to wide oscillation of the rotameter float (a smaller rotameter was installed on the sulphuric dioxide).

The unit was operated for 47 minutes without any visible signs of reaction, the odor of sulphur dioxide was absent and the assumption was made that sulphur dioxide was not flowing into the system.

Product analysis - no sulphate
Operating Data Run #13

Pressure fluctuations at the new rotameter were reduced by insertion of a plug of glass wool in the line.

Charge same as Run #7 20 grams

<table>
<thead>
<tr>
<th>Time Min.</th>
<th>Temperature °C</th>
<th>Air Rate Cfm.</th>
<th>Sulphur Dioxide Rate Cfm.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>280</td>
<td>.6</td>
<td>.05</td>
<td>Fluidizing</td>
</tr>
<tr>
<td>2</td>
<td>290</td>
<td>.6</td>
<td>.05</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>.6</td>
<td>.05</td>
<td>some salt carryover</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>.47</td>
<td>.05</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>.47</td>
<td>.05</td>
<td>salt is getting sticky</td>
</tr>
<tr>
<td>8</td>
<td>305</td>
<td>.47</td>
<td>.05</td>
<td>Fluidizing again</td>
</tr>
<tr>
<td>9</td>
<td>305</td>
<td>.47</td>
<td>.05</td>
<td>sticky again</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>Reduced sulphur dioxide rate because salt is sticking together and to the reactor wall. Sulphur trioxide smoke coming out of scrubber.</td>
</tr>
<tr>
<td>11</td>
<td>305</td>
<td>.47</td>
<td>.02</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td>Raised air rate to .6</td>
</tr>
<tr>
<td>18</td>
<td>340</td>
<td>.6</td>
<td>.02</td>
<td>fluidizing but sticky smoke coming out of scrubber</td>
</tr>
<tr>
<td>21</td>
<td>340</td>
<td>.6</td>
<td>.02</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>350</td>
<td>.6</td>
<td>.02</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>360</td>
<td>.6</td>
<td>.02</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>terminated the run</td>
</tr>
</tbody>
</table>

Product analyzed 89% sodium sulphate
### Operating Data Run #14

Turbulence promoter omitted

Charge same as Run #7, 20 grams

<table>
<thead>
<tr>
<th>Time (Min)</th>
<th>Temperature (°C)</th>
<th>Air Rate (Cfm)</th>
<th>Sulphur Dioxide Rate (Cfm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>230</td>
<td>.6</td>
<td>.023</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>.6</td>
<td>.023</td>
<td>getting salt carry-over cut rates</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>.5</td>
<td>.020</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>230</td>
<td>.5</td>
<td>.020</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>235</td>
<td>.5</td>
<td>.020</td>
<td>took sample 1 from bed</td>
</tr>
<tr>
<td>13</td>
<td>240</td>
<td>.5</td>
<td>.020</td>
<td>bed depleted by carry-over. Terminated the run</td>
</tr>
</tbody>
</table>

### Operating Data Run #15

The humidifying tower which was operated at an inlet water temperature of 67.8°C in all previous runs will now be operated at an inlet water temperature of 32.2°C. A turbulence promoter will be used.

Charge same as Run #7, 20 grams.
### Operating Data Run #15 (Continued)

<table>
<thead>
<tr>
<th>Time Min.</th>
<th>Temperature °C</th>
<th>Air Rate Cfm.</th>
<th>Sulphur Dioxide Rate Cfm.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>280</td>
<td>.6</td>
<td>.015</td>
<td>fluidizing</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>.6</td>
<td>.015</td>
<td>smoke coming out of scrubber</td>
</tr>
<tr>
<td>4</td>
<td>320</td>
<td>.6</td>
<td>.015</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>340</td>
<td>.6</td>
<td>.015</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>sample 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>350</td>
<td>.6</td>
<td>.013</td>
<td>fluidizing</td>
</tr>
<tr>
<td>15</td>
<td>showing signs of stickiness - hanging on walls not sticking</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>360</td>
<td>.6</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>sample 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>360</td>
<td>.6</td>
<td>.013</td>
<td>periodically hanging on walls</td>
</tr>
<tr>
<td>23</td>
<td>removed electric heat from reactor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>sample 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>380</td>
<td>.6</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>375</td>
<td>.6</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>370</td>
<td>sample 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>365</td>
<td>.6</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>replaced electric heat to reactor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>360</td>
<td>.6</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>sample 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>360</td>
<td>.6</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>365</td>
<td>removed electric heat from reactor</td>
<td>Inlet water temperature to humidifier 33.9°C</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>370</td>
<td>.6</td>
<td>.013</td>
<td>sticky - hanging on walls</td>
</tr>
<tr>
<td>45</td>
<td>370</td>
<td>.6</td>
<td>.013</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>375</td>
<td>.6</td>
<td>.013</td>
<td>sample 6</td>
</tr>
<tr>
<td>51</td>
<td>375</td>
<td>.6</td>
<td>.013</td>
<td>smoke still coming out of scrubber</td>
</tr>
<tr>
<td></td>
<td>sampling tube smokes when withdrawn from reactor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>365</td>
<td>.6</td>
<td>.012</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>340</td>
<td>.6</td>
<td>.012</td>
<td>sample 7</td>
</tr>
<tr>
<td>61</td>
<td>335</td>
<td>.6</td>
<td>.012</td>
<td>tapping reactor to get good fluidization.</td>
</tr>
<tr>
<td></td>
<td>A few seconds after tapping smoke comes out of scrubber.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>325</td>
<td>.6</td>
<td>.012</td>
<td>sample 8</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
<td></td>
<td>bed is empty or not fluidizing</td>
</tr>
<tr>
<td>71</td>
<td></td>
<td></td>
<td></td>
<td>reduced sulphur dioxide rate to zero</td>
</tr>
<tr>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td>smoke still coming out of scrubber</td>
</tr>
<tr>
<td>77</td>
<td></td>
<td></td>
<td></td>
<td>smoke still coming out of scrubber</td>
</tr>
<tr>
<td>81</td>
<td></td>
<td></td>
<td></td>
<td>smoke still coming out of scrubber</td>
</tr>
<tr>
<td>84</td>
<td></td>
<td></td>
<td></td>
<td>smoke still coming out of scrubber</td>
</tr>
<tr>
<td>85</td>
<td></td>
<td></td>
<td></td>
<td>terminated the run - average weight of sample .3 grams</td>
</tr>
</tbody>
</table>
Appearance of Reactor and Product from Run #15

Microscopic examination of sample 1 indicates reaction has progressed far enough on the surface to make the crystals completely opaque. Surface crystals of sample 8 are very large and well defined indicating nearly complete reaction. The inside of the reactor was coated with sticky particles that appeared to have been wet or melted. The bottom contained a large lump of particles very easily broken up by picking it up with thumb and forefinger. This lump had the appearance of very nearly complete conversion to sodium sulphate (later analyzed as 99.7% based on sulphates). It is believed that the electric heat may have caused the reactor walls to get hot enough to form the melted cake which was found on them.

Conversion Calculations Based on Sulphate Analysis

\[ X = \text{pounds of reaction mixture per pound of feed} \]
\[ Y = \text{weight fraction of sodium sulphate in the reaction mixture} \]
\[ F = \text{fraction of sodium chloride reacted} \]

"Y" is obtained for each sample by chemical analysis then: \( 1 - F = x(1 - y) \)

Conversion Data for Run #15

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time Min.</th>
<th>Y</th>
<th>(1 - y)</th>
<th>X</th>
<th>1 - F</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>.16</td>
<td>.84</td>
<td>1.03</td>
<td>.865</td>
<td>.135</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>.28</td>
<td>.72</td>
<td>1.05</td>
<td>.759</td>
<td>.241</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>.38</td>
<td>.62</td>
<td>1.07</td>
<td>.666</td>
<td>.334</td>
</tr>
<tr>
<td>4</td>
<td>32</td>
<td>.51</td>
<td>.49</td>
<td>1.10</td>
<td>.539</td>
<td>.461</td>
</tr>
<tr>
<td>5</td>
<td>39</td>
<td>.60</td>
<td>.40</td>
<td>1.12</td>
<td>.448</td>
<td>.552</td>
</tr>
<tr>
<td>6</td>
<td>49</td>
<td>.79</td>
<td>.21</td>
<td>1.16</td>
<td>.244</td>
<td>.756</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>.925</td>
<td>.075</td>
<td>1.69</td>
<td>.209</td>
<td>.791</td>
</tr>
<tr>
<td>8</td>
<td>69</td>
<td>.95</td>
<td>.05</td>
<td>1.20</td>
<td>.0601</td>
<td>.939</td>
</tr>
<tr>
<td>product</td>
<td>80</td>
<td>.995</td>
<td>0</td>
<td>1.215</td>
<td>0</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Operating Data Run #16

Charge same as Run #7 40 grams

Air rate: .6 cubic feet per minute

Sulphur dioxide rate: .015 cubic feet per minute

Temperature maintained throughout the run: 240°C

Smooth fluidization was obtained throughout the run without stickiness or cake formation. No smoke was seen coming from the scrubber outlet at any time during the run. Samples were taken and analysed for sodium sulphate based on a sulphate analysis, the results were converted to fraction reacted.

Average sample weight .8 grams.

Conversion Data Run #16

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time Min.</th>
<th>Y</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>.010</td>
<td>.008</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
<td>.019</td>
<td>.015</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>.030</td>
<td>.024</td>
</tr>
<tr>
<td>4</td>
<td>47</td>
<td>.055</td>
<td>.036</td>
</tr>
<tr>
<td>5</td>
<td>55</td>
<td>.051</td>
<td>.011</td>
</tr>
<tr>
<td>6</td>
<td>70</td>
<td>.069</td>
<td>.056</td>
</tr>
<tr>
<td>7</td>
<td>83</td>
<td>.078</td>
<td>.063</td>
</tr>
<tr>
<td>8</td>
<td>97</td>
<td>.091</td>
<td>.073</td>
</tr>
<tr>
<td>9</td>
<td>110</td>
<td>.110</td>
<td>.090</td>
</tr>
<tr>
<td>10</td>
<td>123</td>
<td>.125</td>
<td>.103</td>
</tr>
<tr>
<td>11</td>
<td>142</td>
<td>.154</td>
<td>.138</td>
</tr>
<tr>
<td>12</td>
<td>156</td>
<td>.175</td>
<td>.146</td>
</tr>
<tr>
<td>13</td>
<td>171</td>
<td>.205</td>
<td>.174</td>
</tr>
<tr>
<td>14</td>
<td>183</td>
<td>.240</td>
<td>.205</td>
</tr>
<tr>
<td>15</td>
<td>200</td>
<td>.270</td>
<td>.232</td>
</tr>
<tr>
<td>16</td>
<td>215</td>
<td>.300</td>
<td>.261</td>
</tr>
<tr>
<td>17</td>
<td>230</td>
<td>.380</td>
<td>.334</td>
</tr>
<tr>
<td>18</td>
<td>240</td>
<td>.410</td>
<td>.364</td>
</tr>
<tr>
<td>Product</td>
<td>250</td>
<td>.500</td>
<td>.451</td>
</tr>
</tbody>
</table>
Operating Data Run #17

Charge same as Run #7 40 grams

Air rate: 6 cubic feet per minute

Sulphur dioxide rate: .015 cubic feet per minute

Turbulence promoter still in use. Humidifier 31.1°C

The temperature averaged about 290°C for a 116 minute run; samples were taken at intervals. The only noteworthy observation was a one half inch variation in pressure drop through the entire apparatus as the bed formed hollow cones of salt which gradually fell apart from the bottom to resume fluidization. One gram samples were taken.

Conversion Data Run #17

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time Min.</th>
<th>Y</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>.034</td>
<td>.027</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>.075</td>
<td>.062</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>.127</td>
<td>.105</td>
</tr>
<tr>
<td>4</td>
<td>58</td>
<td>.194</td>
<td>.165</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>.260</td>
<td>.223</td>
</tr>
<tr>
<td>6</td>
<td>83</td>
<td>.305</td>
<td>.265</td>
</tr>
<tr>
<td>7</td>
<td>92</td>
<td>.390</td>
<td>.311</td>
</tr>
<tr>
<td>8</td>
<td>102</td>
<td>.457</td>
<td>.442</td>
</tr>
<tr>
<td>9</td>
<td>111</td>
<td>.49</td>
<td>.464</td>
</tr>
<tr>
<td>10</td>
<td>116</td>
<td>.55</td>
<td>.469</td>
</tr>
<tr>
<td>Product</td>
<td></td>
<td>.55</td>
<td>.469</td>
</tr>
</tbody>
</table>
Operating Data Run #18

Charge same as Run #7 30 grams

Air rate: .6 cubic feet per minute

Sulphur Dioxide rate: .015 cubic feet per minute

Turbulence promoter used but broken. Humidifier 30.6°C

An average temperature of 310°C was maintained after introduction of sulphur dioxide, the temperature before its introduction 290°C. Stickiness began to be noticeable after thirty five minutes when the bed formed into a cone and then fell apart again. At about forty minutes the sulphur dioxide rotameter went off scale due to a faulty valve and the temperature rose rapidly to 355°C. The run was ended after fifty six minutes. Average weight of samples one gram.

Conversion Data Run #18

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time Min.</th>
<th>Y</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.5</td>
<td>.06</td>
<td>.050</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>.15</td>
<td>.126</td>
</tr>
<tr>
<td>3</td>
<td>36</td>
<td>.20</td>
<td>.170</td>
</tr>
<tr>
<td>4</td>
<td>47</td>
<td>.29</td>
<td>.252</td>
</tr>
<tr>
<td>5</td>
<td>56</td>
<td>.36</td>
<td>.316</td>
</tr>
<tr>
<td>Product</td>
<td></td>
<td>.46</td>
<td>.412</td>
</tr>
</tbody>
</table>
Operating Data Run #19

Charge table salt 40 grams

Air rate: .6 cubic feet per minute

Sulphur dioxide rate: .015 cubic feet per minute

Fluidization promoter eliminated by extending the reactor height one foot. Humidifier 32.2°C.

An average temperature 310°C was used and stickiness became noticeable after sixty-two minutes. Hollow cones formed occasionally from eighty-five minutes until one hundred-forty minutes when the run was terminated.

Conversion Data Run #19

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time Min.</th>
<th>Y</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>.094</td>
<td>.079</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>.177</td>
<td>.148</td>
</tr>
<tr>
<td>3</td>
<td>43</td>
<td>.268</td>
<td>.231</td>
</tr>
<tr>
<td>4</td>
<td>53</td>
<td>.300</td>
<td>.261</td>
</tr>
<tr>
<td>5</td>
<td>71</td>
<td>.453</td>
<td>.405</td>
</tr>
<tr>
<td>6</td>
<td>92</td>
<td>.520</td>
<td>.470</td>
</tr>
<tr>
<td>7</td>
<td>108</td>
<td>.610</td>
<td>.563</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>.670</td>
<td>.626</td>
</tr>
<tr>
<td>9</td>
<td>136</td>
<td>.770</td>
<td>.734</td>
</tr>
<tr>
<td>product</td>
<td></td>
<td>.800</td>
<td>.767</td>
</tr>
<tr>
<td>Dust carryover</td>
<td></td>
<td>.860</td>
<td></td>
</tr>
</tbody>
</table>
Operating Data Run #20

 Reactor number 8 was insulated and provided with a heated feed container which was filled with one pound of table salt.

 Feed temperature: 316°C

 Air rate: .25 cubic feet per minute

 Sulphur dioxide rate: .015 cubic feet per minute

 The sulphur dioxide was started before the salt. The salt feed vessel was plugged at the bottom, but flow was started by clearing the feed port with a wire, however several lumps of salt entered at the beginning. This salt which was at the bottom of the feed vessel was not close enough to the heater wire to have reached the reactor temperature. The first salt to flow immediately stuck to the glass vessel at widely scattered points, mainly at the constrictions reducing their diameter and preventing downward flow. The run was terminated due to the poor flow conditions.

 Operating Data Run #21

 Reactor number 8. Average inlet gas temperature: 260°C

 Air rate: .22 cubic feet per minute

 Sulphur dioxide rate: .007 cubic feet per minute

 Total pressure drop through entire apparatus before introduction of salt one and one half inches of water; after introduction of salt five and one half inches of water.

 Five minutes of satisfactory operation was obtained by starting the flow of sulphur dioxide gas after starting the flow of salt. Liquid was noticed condensed to form a single drop at the bottom of the reactor.
Liquid condensation was assumed to be the cause of the salt sticking to the glass at the lower constriction.

Changes Prior to Run #22

The sulphur dioxide entrance was changed from the furnace inlet to the outlet.

Operating Data Run #22

Reactor number 8. Average inlet gas temperature 385°C.

Air rate: .24 cubic feet per minute

Sulphur dioxide rate: .006 cubic feet per minute

The air rate was gradually decreased over a period of forty-nine minutes from the initial rate of .24 cfm. to .19 cfm. The sulphur dioxide rate was held constant. The product contained no sulphates.

Operating Data Run #23

Reactor number 8. Average inlet gas temperature 424°C.

Air rate: .29 cubic feet per minute

The reactor was operated for fourteen minutes and gave a product showing a trace of sulphates estimated to be about one or two percent.

Operating Data Run #24

Reactor number 8. Average inlet gas temperature 402°C.

Air rate: .3 cubic feet per minute

Sulphur dioxide rate: .003 cubic feet per minute

A solution of ferrous chloride was sprayed on the feed which was then dried. The amount of iron on the salt was estimated to be about .2%.

Twelve minutes operation resulted in a product showing a trace of sulphates.
Operating Data Run #25

Reactor number 8. Average inlet gas temperature 400°C.

Air rate: .26 cubic feet per minute

Sulphur dioxide rate: .045 cubic feet per minute

The same feed was used as in Run #24. After twelve minutes operation the product showed a trace of sulphates. The conversion had taken place only on the largest salt particles which were thought to have been located at the lower portion of the reactor where the temperature was the highest.

Changes Prior To Run #26

The reactor was reinsulated and wrapped with heater wire to produce more even heating and higher temperatures.

Operating Data Run #26

Reactor number 8. Average inlet gas temperature 477°C

Air rate: .2 cubic feet per minute

Sulphur dioxide rate: .026 cubic feet per minute

The same feed was used as in Run #24.

After eighty-six minutes operation the product showed a trace of sulphates.

Operating Data Run #27

Reactor number 2. Average reactor temperature 390°C

Air rate: 1.5 cubic feet per minute

Sulphur dioxide rate: .045 cubic feet per minute

A half inch bed of table salt was placed in the reactor.
After twenty minutes smoke was noted at the scrubber exit. The run was terminated after thirty-eight minutes. The product contained a trace of sulphate.

Operating Data Run #28

Reactor number 9. (electrically heated and insulated)

Average temperature of inlet gas 546°C

Air rate: .11 cubic feet per minute

Sulphur dioxide rate: .01 cubic feet per minute

The unit was operated for ten minutes. The product contained a trace of sulphate. The temperature of the salt was assumed to be much lower than the inlet gas temperature because of uninsulated downcomer tubes.

Operating Data Run #29

Reactor number 7, uninsulated

Charge 100 grams table salt plus 5 grams iron oxide. The highest temperature obtainable was 240°C at an air rate of .1 cubic feet per minute. Because of the low temperature sulphur dioxide was not started and the run was discontinued.

Operating Data Run #30

Reactor number 7, wound with heater wire and insulated

Charge same as Run #29

The temperature in the reactor reached 400°C without salt present and no gas flowing. After the flow of reaction gas was started and the salt was placed in the reactor the temperature reached 380°C. The lower
section of the reactor bent due to its own weight after about twenty minutes. The product contained a trace of sulphate. Microscopic examination showed a pitted surface on the salt but not sufficient reaction to render the crystal opaque.

Changes Prior to Run #31

Several changes in the design of the furnace were made in an attempt to obtain higher gas temperatures at lower rates. Satisfactory results were obtained with twenty-five feet of one eighth inch pipe. Reactor number 7 used in the following runs.

Operating Data Run #31

Charge 30 grams table salt plus 5 grams of iron oxide reduced from iron sulphate.

Air rate: .4 cubic feet per minute

Sulphur dioxide rate: about .05 cubic feet per minute

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>520</td>
<td>sulphur dioxide rotameter fluctuating over entire scale</td>
</tr>
<tr>
<td>4</td>
<td>540</td>
<td>smoke forms in upper part of reactor and escapes from leaks at reactor cover</td>
</tr>
<tr>
<td>7</td>
<td>600</td>
<td>removed air from fuel mixture</td>
</tr>
<tr>
<td>13</td>
<td>560</td>
<td>no signs of fluidization sulphur dioxide rotameter stopper fluctuating. Run terminated.</td>
</tr>
</tbody>
</table>

The bed was solid with a hole on one side. A large cake had formed which contained appreciable sulphate. Iron catalyst on the surface has partially turned black.
### Operating Data Run #32

Charge: 40 grams table salt, no catalyst

<table>
<thead>
<tr>
<th>Time (Min.)</th>
<th>Temperature (°C)</th>
<th>Air Rate (Cfm.)</th>
<th>Sulphur dioxide Rate (Cfm.)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>500</td>
<td>.35</td>
<td>.01</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>510</td>
<td>.35</td>
<td>.01</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>495</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>480</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>480</td>
<td></td>
<td></td>
<td>sample 1 slight trace of sulphate</td>
</tr>
<tr>
<td>22</td>
<td>485</td>
<td>.35</td>
<td>.045</td>
<td>Increased sulphur dioxide rate .045</td>
</tr>
<tr>
<td>23</td>
<td>490</td>
<td>.35</td>
<td>.045</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>495</td>
<td>.35</td>
<td>.045</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>495</td>
<td></td>
<td></td>
<td>sample 2 heavy trace of sulphate</td>
</tr>
<tr>
<td>38</td>
<td>500</td>
<td>.30</td>
<td>.045</td>
<td>Increased fuel rate to the furnace reduced air rate</td>
</tr>
<tr>
<td>40</td>
<td>520</td>
<td>.30</td>
<td>.045</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>560</td>
<td>.30</td>
<td>.045</td>
<td>stopped fluidizing</td>
</tr>
<tr>
<td>45</td>
<td>550</td>
<td>.30</td>
<td>.026</td>
<td>Cut sulphur dioxide rate to zero</td>
</tr>
<tr>
<td>47</td>
<td>600</td>
<td></td>
<td></td>
<td>tapped reactor - fluidizing in center - cake on walls</td>
</tr>
<tr>
<td>48</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>600</td>
<td></td>
<td></td>
<td>sample 3 same trace of sulphate as sample 2</td>
</tr>
<tr>
<td>61</td>
<td>650</td>
<td>.30</td>
<td>.026</td>
<td>added 10 grams of salt containing catalyst, started gas</td>
</tr>
<tr>
<td>62</td>
<td>660</td>
<td>.30</td>
<td>.026</td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>670</td>
<td>.30</td>
<td>.026</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>680</td>
<td>.30</td>
<td>.026</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>690</td>
<td>.32</td>
<td>.024</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>500</td>
<td>.32</td>
<td>.024</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>510</td>
<td>.32</td>
<td>.024</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>510</td>
<td>.32</td>
<td>.024</td>
<td></td>
</tr>
</tbody>
</table>

Sample 4 heavy trace sulphate
Sample 5 heavy trace sulphate

Terminated the run
Operating Data Run #33

Charge: 40 grams table salt plus 5 grams activated iron oxide

Air rate: .35 cubic feet per minute

Sulphur dioxide rate: .012 cubic feet per minute

<table>
<thead>
<tr>
<th>Time (Min.)</th>
<th>Temperature (°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>350</td>
<td>Heat was increased after each sample was taken. Sample 1 no sulphates.</td>
</tr>
<tr>
<td>10</td>
<td>380</td>
<td>Sample 2 no sulphates</td>
</tr>
<tr>
<td>36</td>
<td>430</td>
<td>Sample 3 trace of sulphate</td>
</tr>
<tr>
<td>69</td>
<td>495</td>
<td>Sample 4 heavy trace of sulphate</td>
</tr>
<tr>
<td>95</td>
<td>540</td>
<td>Sample 5 heavy trace of sulphate</td>
</tr>
<tr>
<td>117</td>
<td>590</td>
<td>Sulphur dioxide rate raised to .045 cfm.</td>
</tr>
<tr>
<td>124</td>
<td>590</td>
<td>Sample 6, reactor still fluidizing.</td>
</tr>
<tr>
<td>142</td>
<td>590</td>
<td>Terminated the run.</td>
</tr>
</tbody>
</table>

Sample 6 contained 5% sodium sulphate.
Operating Data Run #34

Charge 40 grams table salt

Air rate: 0.14 cubic feet per minute

Sulphur trioxide rate: 0.006 cubic feet per minute. Sulphur trioxide was generated by heating 30% oleum.

<table>
<thead>
<tr>
<th>Time (Min.)</th>
<th>Temperature (°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>310</td>
<td>fluidizing well</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>sample 1</td>
<td>trace of sulphate</td>
</tr>
<tr>
<td>13</td>
<td>290</td>
<td>no smoke visible at any point</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulphur trioxide float sticking with liquid and turning black. Liquid may be sulphuric acid</td>
</tr>
<tr>
<td>18</td>
<td>295</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>sample 2</td>
<td>trace of sulphate</td>
</tr>
<tr>
<td>24</td>
<td>Sulphur trioxide rotameter full of liquid, Run stopped.</td>
<td></td>
</tr>
</tbody>
</table>

Changes Prior to Run #35

A new rotameter float was made of polyethylene for measuring sulphur dioxide flow. A catalyst chamber was placed in the furnace. It consisted of a forty inch section of half inch pipe containing activated iron oxide supported on asbestos fibre.

Operating Data Run #35

The unit was operated without heat or salt to determine initial sulphur dioxide concentration. Sulphur dioxide was determined by absorption of the gas in a volume of Iodine solution of known strength, and also by absorption in a caustic solution of known strength.
The initial concentration determined was 4.55% by volume. With the unit heated to give a gas temperature of 310°C the sulphur dioxide concentration dropped to 1.8% based on absorption in Iodine solution. Absorption in caustic indicated a total of 2.7% of both sulphur dioxide and trioxide. The gas sampling tube when withdrawn from the reactor fumed strongly indicating the presence of liquid oleum. The condensation is thought to account for the low concentration of gas obtained by absorption in caustic solution.

After introduction of salt in the reactor the evolution of smoke stopped completely and analyses showed only .58% sulphur dioxide and .53% of both gases. The difference of the last two figures is assumed to result from experimental error. The unit was operated for an hour and gave a product which contained 37% sodium chloride based on chloride analysis. A small amount of cake had formed in the bottom of the reactor.

Operating Data Run #36

Charge 140 grams table salt
Air rate: .54 cubic feet per minute
Sulphur dioxide rate: .02 cubic feet per minute
Temperature: 230°C

After seven minutes the salt began to stick together and to the reactor forming a funnel shaped section in the center of the bed from which salt was blown as high as the top cover of the reactor. The run was stopped after ten minutes due to stickiness and liquid condensation on the reactor walls. The product contained 91% sodium chloride based on a chloride analysis.
Changes Prior to Run #37

An external jacket heater was placed around the upper section of the reactor. The temperature of the internal heater was reduced to eliminate the existence of a local hot spot found at the reactor inlet. The humidifier was partially dried out to permit the use of air of a lower humidity.

Operating Data Run #37

Charge: 100 grams table salt

Air rate: .4 cubic feet per minute

Sulphur dioxide rate: .02 cubic feet per minute

Dew point of air at start of run: 21.1°C; at end: 30.0°C

Temperature at bottom of reactor: 340°C and 300°C at bed level using external heaters only.

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>300</td>
<td>No smoke visible</td>
</tr>
<tr>
<td>17</td>
<td>330</td>
<td>sample 1</td>
</tr>
<tr>
<td>23</td>
<td>340</td>
<td>No condensation evident</td>
</tr>
<tr>
<td>35</td>
<td>345</td>
<td>sample 2</td>
</tr>
<tr>
<td>37</td>
<td>345</td>
<td>sample 3</td>
</tr>
<tr>
<td>50</td>
<td>345</td>
<td>sample 4 white fines in discharge</td>
</tr>
<tr>
<td>63</td>
<td>340</td>
<td>sample 5</td>
</tr>
<tr>
<td>75</td>
<td>340</td>
<td>sample 6</td>
</tr>
<tr>
<td>90</td>
<td>340</td>
<td>sample 7</td>
</tr>
<tr>
<td>104</td>
<td>340</td>
<td>sample 8</td>
</tr>
</tbody>
</table>
| 121  | 340         | smoke beginning to appear from leaks in scrubber and from reactor when cover is raised.
| 122  | 335         | sample 9 |
| 130  | 325         | sample 10 smoke visible in upper reactor, fines have disappeared. |
| 145  | 320         | sample 11 |
| 154  | 320         | sample 12 |
| 167  | 320         | sample 13 |
| 180  | 320         | noted condensate dripping into bed from exit tube. Stopped the run. |
| 187  | 320         |         |

Average weight of samples - one gram
Appearance of Reactor Following Run #37

After the reactor had cooled partially it was removed and the product was poured from the bottom gas inlet - no evidence of cake formation, however there were small hard balls of product due to the acid which had condensed on the exit tube and dropped into the reactor. Evidently high temperature in the inlet elbow had caused pyrosulphate to melt in earlier runs causing cake. Low temperature insulation on the upper part had probably allowed acid condensation causing salt to stick to the walls.

Sample Analysis Run #37 Based on Chloride

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time Min.</th>
<th>% NaCl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>95</td>
<td>.050</td>
</tr>
<tr>
<td>2</td>
<td>37</td>
<td>91.8</td>
<td>.082</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>81</td>
<td>.160</td>
</tr>
<tr>
<td>4</td>
<td>63</td>
<td>77.2</td>
<td>.228</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>61</td>
<td>.360</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>55.5</td>
<td>.445</td>
</tr>
<tr>
<td>7</td>
<td>104</td>
<td>45</td>
<td>.55</td>
</tr>
<tr>
<td>8</td>
<td>121</td>
<td>19.2</td>
<td>.808</td>
</tr>
<tr>
<td>9</td>
<td>130</td>
<td>11.5</td>
<td>.885</td>
</tr>
<tr>
<td>10</td>
<td>142</td>
<td>10.3</td>
<td>.897</td>
</tr>
<tr>
<td>11</td>
<td>154</td>
<td>7.9</td>
<td>.921</td>
</tr>
<tr>
<td>12</td>
<td>167</td>
<td>6.7</td>
<td>.933</td>
</tr>
<tr>
<td>13</td>
<td>180</td>
<td>3.3</td>
<td>.967</td>
</tr>
</tbody>
</table>
Operating Data Run #38
Charge 40 grams rock salt passed 65 mesh
Dew point of air: 32.2°C
Air rate: .16 cubic feet per minute
Sulphur dioxide rate: .015 cubic feet per minute
Temperature increased from 280°C to 310°C over a thirty-four minute run. The salt began to appear sticky and formed lumps. The run was discontinued. The product contained 71% sodium chloride. The reaction rate is comparable to Run #36 but gas rates are too low for salt of this particle size. Higher gas rates cause excessive carryover. High air dew point and low temperature may have caused the formation of lumps.

Operating Data Run #39
Charge 40 grams table salt
Air rate: .35 cubic feet per minute
Sulphur dioxide rate: .02 cubic feet per minute
Dew point of air 32.2°C
Some stickiness was noticed after an hour of operation. The pressure built up during the run until the mercury manometer blew out at a pressure of fifteen inches. The furnace was found to be plugged.

Operating Data Run #40
Reactor number 8 insulated and wound with heater wire reached a temperature of 260°C without solid or gas flowing. The average inlet temperature of the gas was 285°C. The air dew point was about 25°C
Charge 60 grams of table salt.
Initial air rate: .22 cubic feet per minute

Final air rate: .10 cubic feet per minute

Sulphur dioxide rate: average .015 cubic feet per minute

After several minutes the solid rate decreased to zero due to condensation of liquid at the bottom outlet of the reactor. The unit was operated batchwise for two hours when the evolution of smoke indicated nearly complete reaction. The product contained 14.5% sodium chloride based on a chloride analysis, and sixty-five percent sodium bisulphate based on titration of the acidity.

Acidity Determinations

Calculation of the weight percent of sodium bisulphate in several samples was made based on titration with sodium hydroxide using methyl orange for an indicator. The results are shown below:

<table>
<thead>
<tr>
<th>Product Run #16</th>
<th>% Conversion</th>
<th>% Sodium bisulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Run #15</td>
<td>99</td>
<td>24.0</td>
</tr>
<tr>
<td>Sample 7, Run #15</td>
<td>92.5</td>
<td>0</td>
</tr>
</tbody>
</table>
Chemical Analysis

Sulphates were determined using a calibrated Parr turbidimeter. A sample of material was weighed and dissolved in 200 ml of solution containing 4.8 grams of sodium chloride and 0.0 ml of hydrochloric acid. One gram of barium chloride was then added, the solution shaken for one minute and the turbidimeter reading taken. The calibration was made using samples of pure sodium sulphate according to the same procedure.

Chlorides were determined by titration using a standardized silver nitrate solution and potassium chromate as an indicator. Acidity was neutralized by titration with sodium hydroxide before the chloride determination was made.
Roger Foster Detman was born in Long Island, New York in 1917. He attended elementary and grammar schools in New York, Florida and Pennsylvania. He attended high schools in Pennsylvania and Mississippi, graduating from high school at Columbia, Mississippi. His undergraduate work leading to the bachelors degree in chemical engineering was done at Louisiana State University from 1934 to 1939. He was employed by the Humble Oil and Refining Company after graduation until called to active duty in the Army in 1942, where he served as a radar officer. He was released from the armed service in the grade of captain and re-entered Louisiana State University in 1946 to pursue graduate studies in chemical engineering. He obtained the Master of Science degree in 1948, and is at present a candidate for the degree of Doctor of Philosophy.
EXAMINATION AND THESIS REPORT

Candidate: Roger F. Detman

Major Field: Chemical Engineering

Title of Thesis: A Fluidization Process for Production of Sodium Sulphate from Sodium Chloride

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

August 3, 1949