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THE DEHYDRATION OF GLAUBER'S SALT

A thesis submitted to the faculty of the Graduate School of the University of North Dakota

by

ROBERT F. SCHULTZ

In partial fulfillment of the requirements for the degree of Master of Science.

Acknowledgements

I wish to take this opportunity to express my appreciation to Dr. Irvin Lavine and the members of the faculty of the Department of Chemical Engineering whose helpful supervision and cooperation have been especially valuable.

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Introduction

Naturally occurring sodium sulfate is found in two forms. The deposits in the Southwestern part of the United States are thenardite, the anydrous salt, while those in the northwest are mirabilite, the decahydrate. The former have been worked to the greater extent since they produce a material comparable to salt cake. The mirabilite deposits have been exploited on a smaller scale owing to the necessity of dehydrating before shipping.

Eight beds or deposits of mirabilite were discovered in the northwestern part of North Dakota during the summer of 1934 by a group under the direction of Dr. Irvin Lavine,(1) Professor of Chemical Engineering, University of North Dakota. All deposits were found in lake bottoms having no drainage outlet where salt-laden waters had evaporated leaving a concentrated brine and a deposit of the decahydrate crystals. These lake bottoms were the low points into which large areas drained.

Seven of the sodium sulfate deposits, just described, located from 1½ to 7 miles from rail transportation and 8 to 15 miles from abundant lignite supplies, were thoroughly prospected and were estimated to contain over 25,000,000 tons of mirabilite. The salt found in these lake bottoms was unusually pure, containing on the basis of an average of a large number of samples the constituents shown in table 1.

Table 1

Constituent	Per Cent	
	High	Low
$Nacl$	1.90	0.45
Al_2O_3	0.97	0.15
Fe_2O_3		
Na_2CO_3	7.21	
$NaHCO_3$	4.00	0.44
$CaSO_4$	1.90	0.40
$MgSO_4$	2.92	0.71
Na_2SO_4	94.84	86.00

Pure sodium sulfate decahydrate, commonly known as Glauber's salt, contains approximately 56% water as water of hydration. The necessity for the dehydration of this salt may be more fully realized by a consideration of the distance from North Dakota deposits to the nearest market-a matter of about 800 miles.

The markets closest to the North Dakota deposits, Minnesota, Wisconsin and Michigan, obtain their supply of salt cake as a by-product from various sources in Illinois and Ohio. A large portion also comes from Canadian deposits, entering the United States at Portal, North Dakota.

The annual consumption of salt cake in the paper pulp industry of Minnesota, Wisconsin and Michigan is 45,000 to 50,000 tons. This would be an ideal market for salt cake from the North Dakota deposits. The immediate development of these mirabilite resources has been held in check by the entrance of duty-free salt cake from Saskatchewan. High freight rates have also been a hindrance. The latter may vary from $7.00 to $9.00 per ton from Grenora, North Dakota to points in Minnesota. However, these rates might be reduced when shipment of the material commences.

A high quality natural salt cake can easily compete in the glass industry with the acidic by-product of chemical plants. Glass plants in Indiana and Illinois which are not too far from the North Dakota deposits to be served by them, constitute a potential salt cake market.

Survey of Literature

Up to the present a number of methods have been developed for the production of anhydrous sodium sulfate which are discussed briefly in the following survey of patent literature prepared by Kobe and Hauge.(2)

John Davis in U. S. Patent 990,116 (April 18, 1911) mixes the decahydrate crystals with a porous vehicle incapable of dissolving in the melted crystals at a temperature sufficient to evaporate the moisture. The purpose of the porous vehicle is to prevent the formation of a fluid mass when the sodium sulfate dissolves in its water of crystallization on the application of heat. Sufficient vehicle is kept in a semi-dry condition. The resulting product of dry vehicle and dehydrated sodium sulfate can be treated mechanically or chemically to separate the salt from the vehicle. However, the inventer prefers to use a vehicle consisting of ingredients which, when combined with the sodium sulfate and fused, will produce glass or one of the sodium salts ordinarily made from sodium sulfate. For glass, the vehicle is sand and lime; for sodium carbonate, the vehicle is limestone and coal.

C. W. Hancock and C. Ide, in Canadian Patent 216,621 (Mar. 14, 1922) made use of the fact that sodium sulfate is practically insoluble in sodium chloride solutions. Sodium chloride is introduced into a saturated solution of sodium sulfate, formed either by melting the decahydrate at 33°C. or by dissolving it in excess water. The sodium sulfate is precipitated out as the anhydrous salt and is removed and dried. The solution is evaporated to recover the sodium chloride.

J. W. Hill, in Canadian Patent 261,891 (June 22, 1926), heats a solution of sodium sulfate saturated at 32.4°C. to a temperature of approximately 100°C. The inverted solubility curve of the salt causes a portion of the salt to precipitate as the anhydrous salt.

Arthur Lambert, in U. S. Patent 1,660,561 (Feb. 28, 1928), treats a natural brine containing sodium sulfate, chloride and carbonate with ammonia and carbon dioxide, precipitating sodium bicarbonate as in the Solvay process.

H. L. Robinson, in Canadian Patent 268,056 (Feb. 1, 1927), treats the Glauber's salt in a closed vessel with ammonia vapor and separates the anhydrous sodium sulfate from the ammoniacal liquor. The ammonia is recovered and reused.

W. H. Dickerson, in U. S. Patent 1,734,289 (Nov. 5, 1929) discloses an apparatus suitable for the spray drying of sodium sulfate solutions.

G. F. Anderson, in Canadian Patent 295,436 (December 10, 1929) and U. S. Patent 1,651,901 (Mar. 25, 1930), has patented what appears to be the natural process of crystallization of the hydrated salt from its brine. In U. S. Patent 1,913,470 (June 13, 1933) he has a dehydrating process and apparatus in which the pulverized salt is subjected to air of increasing temperature until all the moisture is removed without having the decahydrate melt.

A. T. W. Warnken, in U. S. Patent 1,798,993 (Mar.31, 1931), obtains anhydrous sodium sulfate by treating the deposit of Glauber's salt with fresh water, subjecting the water to the natural temperature conditions of day and night so that the solution process during the day produces a dense solution which naturally gravitates toward a central vat where crystallization occurs during the cool night. The heat of the day apparently melts the deposited crystals to give the anhydrous salt, as it is claimed that this is removed.

L. E. Drummond, in Canadian Patent 314,908 (Sept. 1, 1931), has a cydic process in which the Glauber's salt is first melted at 32.4°C., the saturated solution removed to a cooling zone and Glauber's salt recrystallized from the solution. The salt is put through the process again and the mother liquor cooled to deposit more crystals.

W. F. Seyer, in Canadian Patent 319,415 (Feb. 2, 1932), Crushes the wet decahydrate crystals to 0.5 to 2.0 mm. diameter, slowly mixes 3 parts by weight of the ground decahydrate with 5 parts by weight of dry sodium sulfate at a room temperature of 30°C. and then dries the mixture in a rotary drum drier. Thus, when the decahydrate crystals melt there is sufficient dry salt present to give the mixture sufficient consistency to prevent the formation of a crust of sodium sulfate on the inside of the drier.

J. B. Pierce, Jr., in U. S. Patent 1,886,580 (Nov. 8, 1932), has a process similar to that of Seyer. He mixes with the saturated solution of Sodium sulfate a sufficient quantity of dehydrated sodium sulfate to convert the mass into a substantially solid phase corresponding to the condition of damp sand in order to prevent the liquification or caking of the mass when heated at an elevated temperature in a rotary drier until the salt is anhydrous.

An evaporation system operating on sodium sulfate solutions was studied by Badger and Caldwell.(3) Under normal operating conditions excessive crystallization made it necessary to clean out the evaporation within one hour. However, by withdrawing the solution from the evaporator continuously, superheating, and flashing it under the tubes, seed crystals formed. The vigorous circulation obtained permitted a 10.5 hour operating period followed by a 1.5 hour boil-out.

Submerged combustion evaporation, studied by Kobe, Conrad, and Jackson,(4) is described as "a method of heating a liquid by the direct contact of the flame from a burner which projects the hot gases of the flame directly into and at any depth below the surface of the liquid." This process possesses numerous advantages. Direct contact of hot gases with the liquid brings about higher rated of heat transfer and results in thermal equilibrium between them. For gaseous fuels, efficiencies of 105.2% of the net or 94.5% of the gross heating valvue were reported. The water of combustion is condensed in this process therefore the efficiency on a basis of net heating value could easily be as high as reported.

Since no large metal heating surfaces are used, corrosion is reduced considerably. The containing vessel does not transfer heat, and is subjected to only law thermal stresses. Therefore ceramic materials may be used in its construction.

Chemical solutions are usually heated by steam coils immersed in the vessel or by injecting live steam. In the latter case the solution is diluted. Submerged combustion would be a suitable remedy.

Some difficulties were encountered in the application of submerged combustion evaporation to sodium sulfate solutions. Scaling occurred on the burner tip to such an extent that as the cake increased in size, the flow of gases was impeded. Eventually the flame was extinguished. The shape and permancy of these scale formations seemed to depend on operating conditions. Changes in the gas-air ratio, changes in the gas velocity or movement of the burner caused the shape of the scale formation to change or fall away. This scale never appeared to be solidly attached to the burner. However, they were so firmly attached as to impede gas flow. It was found that a sharp nozzle orifice, high gas velocity and high flame temperature successfully prevented scale formation.

Several of the methods of producing anhydrous sodium sulfate from the decahydrate such as controlled humidity drying and spray drying seem satisfactory, but, as in air drying, large installations are required and a fine, powdery product is formed which may not find a ready market. High dust losses for a number of these processes have also been reported.

It was found that in evaporation processes, the size of the sodium sulfate crystals varies with operating conditions. In submerged combustion evaporation 29.4% of the product passed a 200 mesh screen when the burner projected far enough below the liquid surface to agitate the entire solution. When the burner projected only a short distance beneath the surface, permitting the presence of a quiet zone in the lower portion of the evaporator, the crystal size was much the same as that found in commercial salt cake in that a large percentage was retained on a 100 mesh screen.

Theoretical Considerations

The difficulties arising in the dehydration of the decahydrate are ascribed to the several properties of the salt. This material melts at 32.4°C at which point solid anhydrous sodium sulfate and a saturated solution exist simultaneously. As shown in Figure 1, plotted from the data (5) in Table 2, the solubility curve is inverted beyond the transition point. In view of its inverted solubility, the matter of scaling on heating elements of evaporators is more fully understood.

Table 2

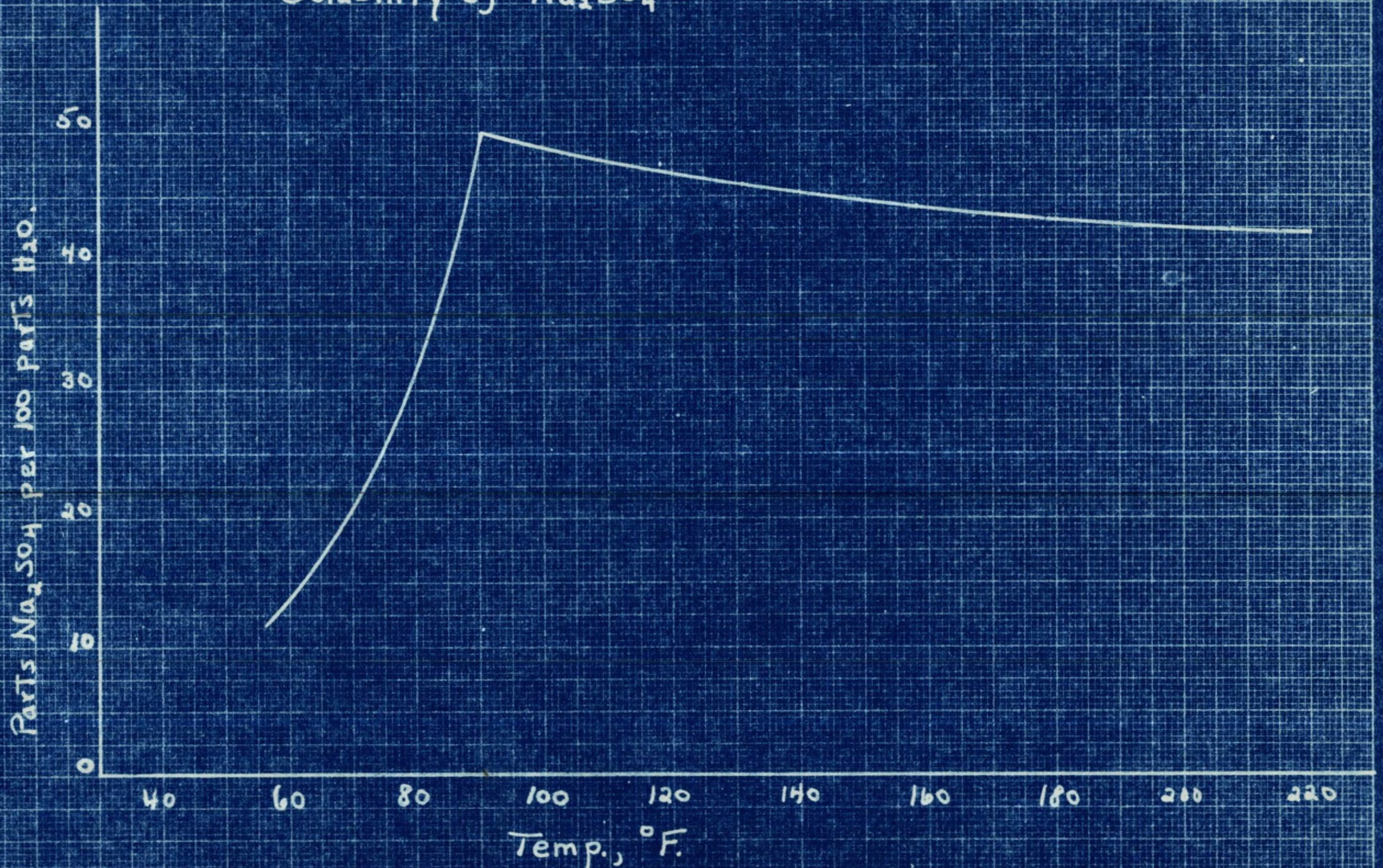
Vapor pressures and concentrations in parts per 100 of water solutions of sodium sulfate.

Temp. of	P, mm.	Parts Na_2So_4	Temp. °F	P, mm.	Parts Na_2So_4
59		13.2	149	165.7	44.7
68		19.2	158	207.2	44.2
77		27.4	167	257.5	43.4
86		40.8	176	317.4	43.2
90.4	30.8	49.8	185	386.9	42.9
95	35.9	49.3	194	472.5	42.6
104	47.4	48.25	203	571.7	42.35
113	62.0	47.4	212	686.4	42.2
122	80.4	46.6	216.5	760	42.1
131	103.2	46.0	230	974.7	41.9
140	131.2	45.25			

In a paper by Pitzer and Coulter (6) the average dissociation pressure of the

Figure 1

Solubility of Na_2SO_4



decahydrate was reported as 19.19 mm or 0.02525 atm. at 25°C. In the reaction,

(1) Na_2So_4 (solid) + $1oH_2o$ (gas) = $Na_2So_4'1oH_2o$ (solid) the free energy change is delta F = $RT\ln P^{10}$ where P is the dissociation pressure of the decahydrate. Solving this expression it is found that delta F = -21,795 cal. The change in heat content in equation (1) may be found by the use of the reactions.

(2) Na_2SO_4 (solid) = $2Na^+$ (aq.) + $SO_4^=$ (aq)

(3) $Na_2SO_4'10H_2O$ (solid) = $2Na^+$ (aq.) + $SO_4^=$ (aq.) + $10H_2O$ (liq.)

(4) H_2O (liq.) = H_2O (gas)

By performing the operation, (2) - (3) - 10(4), the following equation results:

Na_2SO_4 (solid) + 10 H_2O (gas) = $Na_2SO_4'10H_2O$ (solid). This is seen to be identical to (1).

The heats of reaction for equations (2) and (3) are the heats of solution of the anhydrous and the decahydrate salts respectively. From table 3 the value delta H_2-delta H_3 is found to be approximately -19,400 cal. per mol. The heat of vaporization of water (delta H_4) was taken from Keenan and Keyes as 10,518 cal. per mol at 25°C.

Table 3

Heats of Solution of Na_2SO_4 and $Na_2SO_4'10H_2O$ at 25°C. in Water.

Substance	Heat absorbed Cal. per mol.	Delta H of dilution	Delta H° Cal. per mol.
Na_2SO_4	-323	-241	-564
	-316	-240	-556
av.			
$Na_2SO_4'10H_2O$	19,075	-234	
	19,085	-242	
	19,076	-238	
av.			18,840

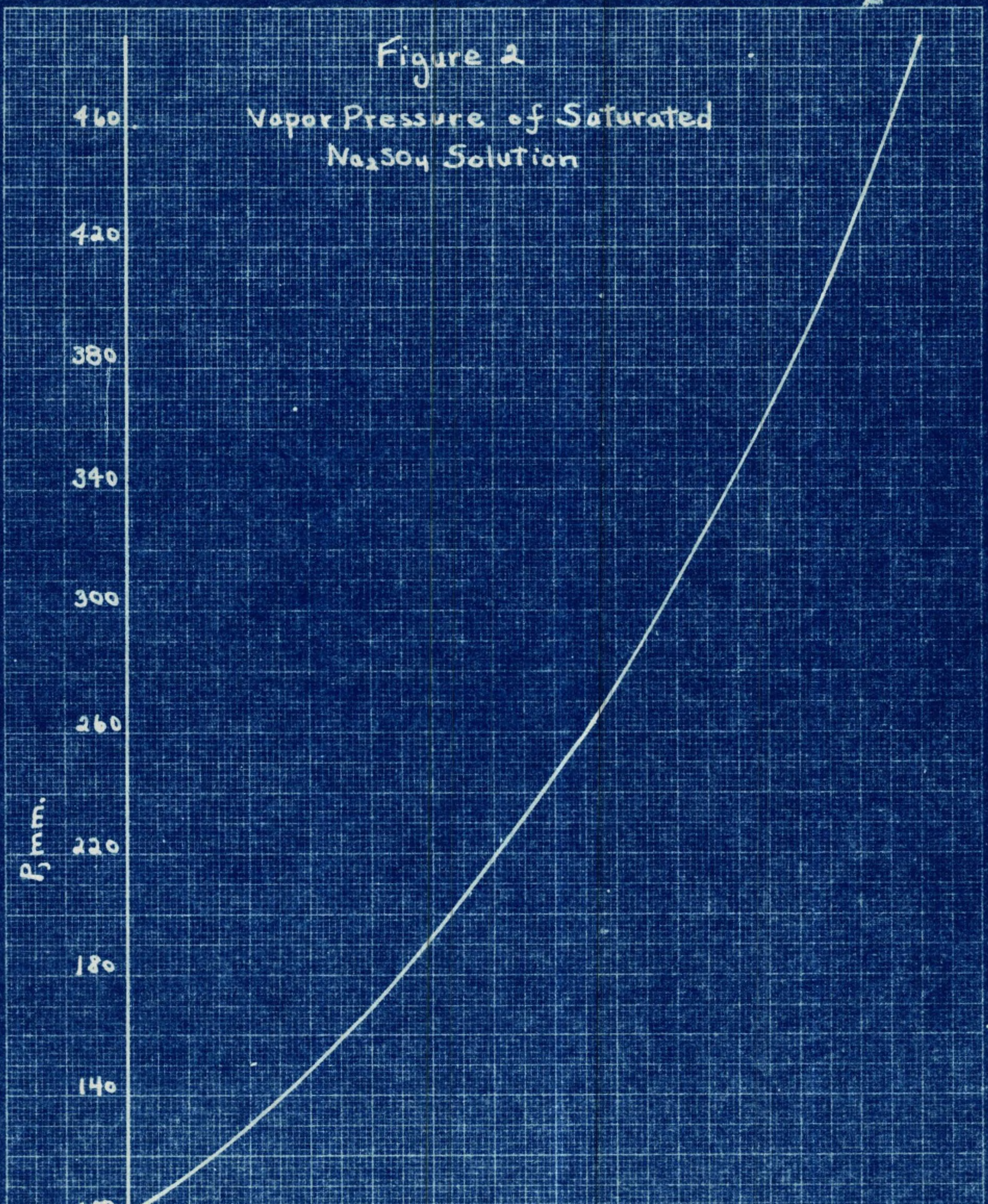


Figure 2

Vapor Pressure of Saturated Na_2SO_4 Solution

Then, for equation (1), delta H = -124,580 ± 100 cal.

and delta S, = -344.8 cal. per degree

the entropy of $Na_2SO_4 \cdot 10H_2O$ may be calculated from the entropy of the anhydrous salt, water vapor entropy and the entropy change of equation (1).

$$S^{\circ} = 10S_{H_2O} + S^{\circ}_{Na_2SO_4} + \text{delta S},$$

$$= 451.3 + 35.7 - 344.8$$

$$= 142.2 \text{ cal. per degree.}$$

This value differs somewhat with that shown in Table 4. Pitzer and Coulter attribute this discrepancy to "some randomness in the position of the protons which are forming hydrogen bonds in the crystal."

Table 4.

Entropies of Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$

Range	Na_2SO_4	$Na_2SO_4 \cdot 10H_2O$
0-14°K (T^3 extrapolation)	0.06	0.50
14-298.1°K (graphical)	35.67	140.0
$S^{\circ}_{298.1} - S^{\circ}_{0}$	35.73	140.5

The molal heat capacities reported by Pitzer and Coulter are shown in Table 5. From this material the heat capacity curve, figure 3, was plotted.

Figure 3

Molal Heat Capacity of $Na_2SO_4 \cdot 10H_2O$

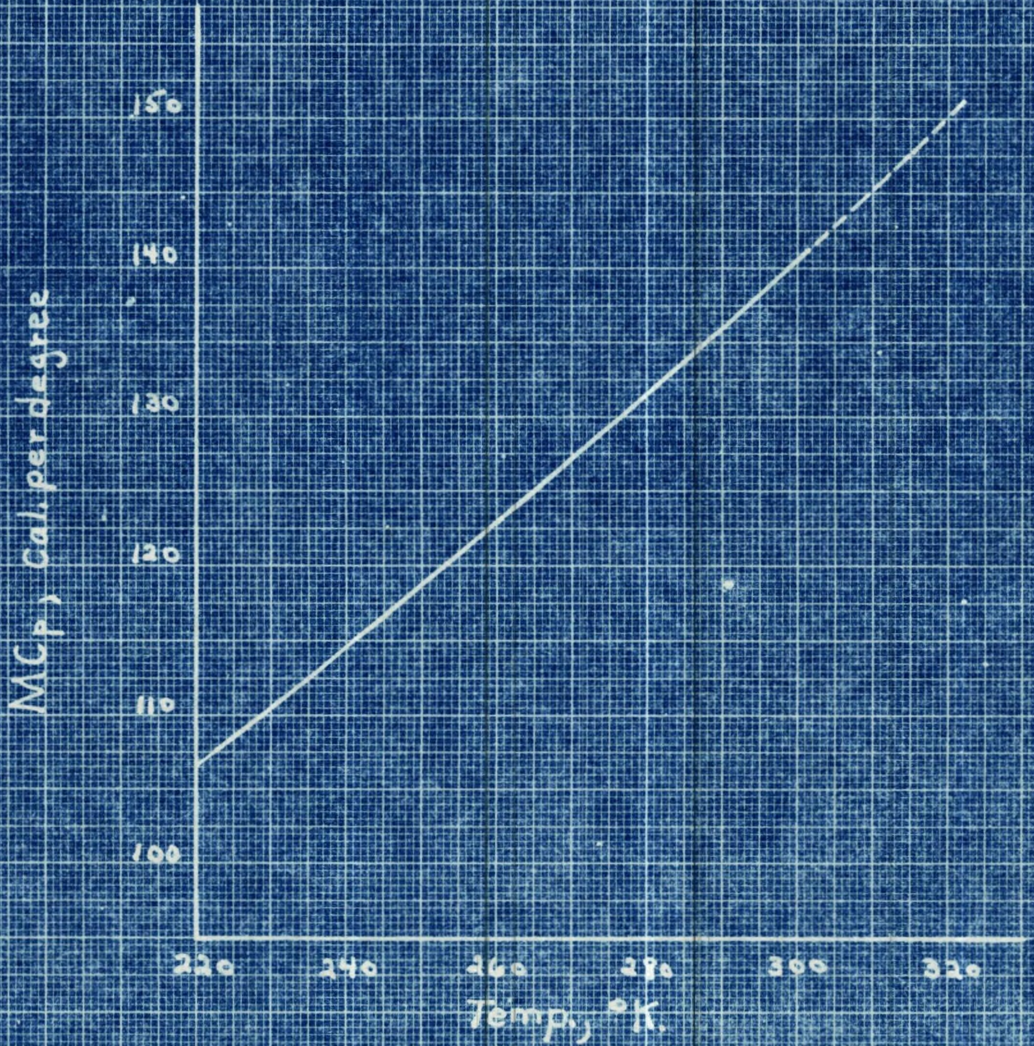


Table 5
Molal heat capacity of Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$

T, °K	Cp, Cal. Per Degree		T, °K	Cp, Cal. Per Degree	
	Na_2SO_4	$Na_2SO_4 \cdot 10H_2O$		Na_2SO_4	$Na_2SO_4 \cdot 10H_2O$
15	0.22	1.94	100	15.43	56.19
20	0.581	4.20	120	18.45	65.93
25	1.213	7.30	140	20.50	75.10
30	1.99	10.63	160	22.35	83.68
35	2.980	13.96	180	23.82	91.54
40	4.077	17.51	200	25.23	99.18
45	5.222	21.18	220	26.51	106.8
50	6.423	24.95	240	27.67	114.7
60	8.743	32.38	260	28.73	122.9
70	10.85	39.25	280	29.67	131.4
80	12.76	45.43	300	30.51	140.5
90	14.44	50.97			

Vapor pressure data for saturated solutions of sodium sulfate is shown also in Table 2.(5) The vapor pressure curve, figure 2, was plotted from this data.

The heat capacity curve, figure 4, for saturated solutions of sodium sulfate was plotted from data in Table 6.(7)

Figure 4.

Heat Capacity of Saturated Solutions of Na_2SO_4

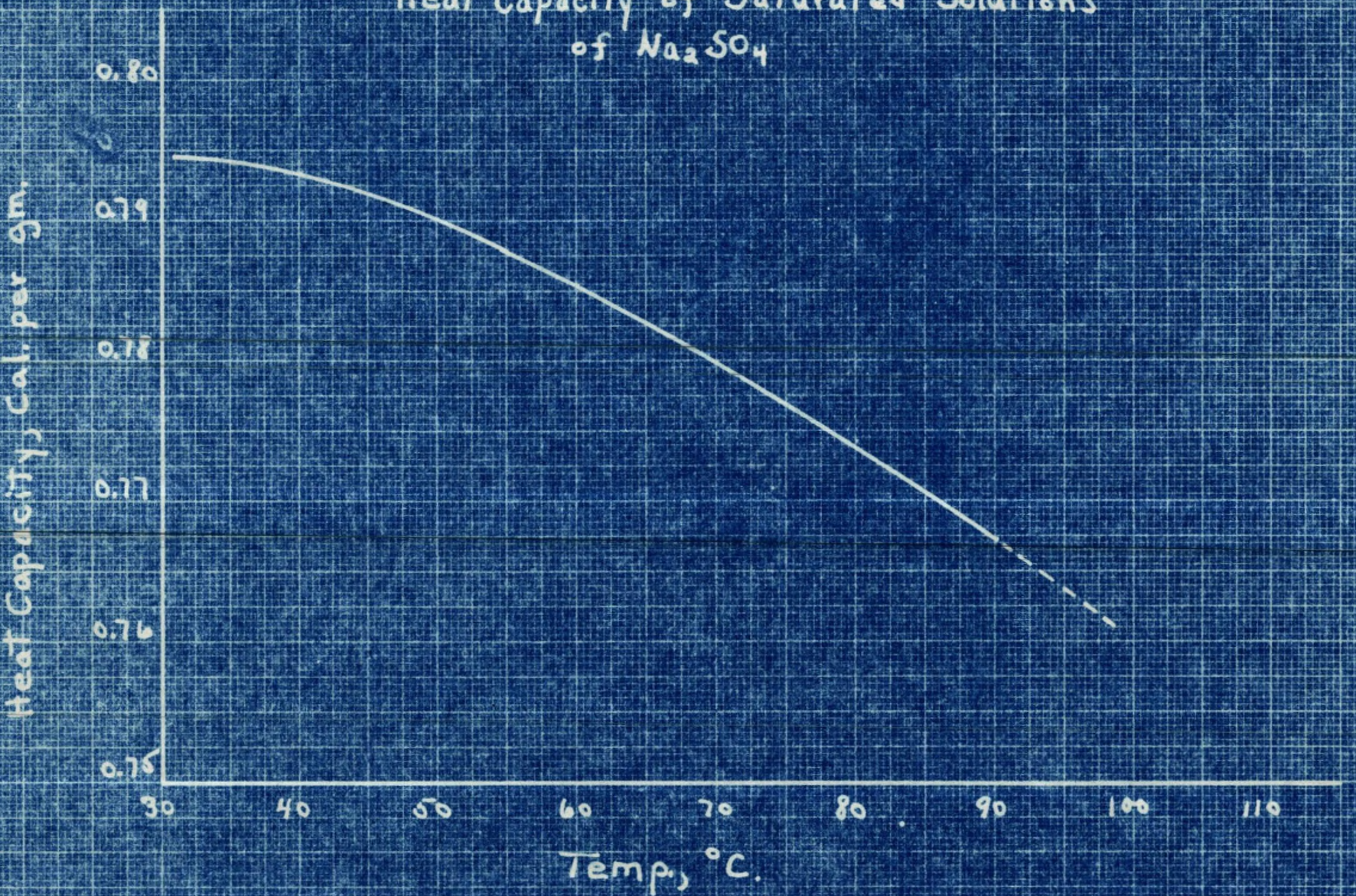


Table 6
Heat capacity of Saturated
Sodium sulfate solution

Temp., °C	Cp, Cal per degree
32.5	0.7946
40	0.7934
50	0.7902
60	0.7854
70	0.7799
80	0.7742
90	0.7672

The feed for a submerged combustion evaporator may be a saturated solution or solid decahydrate. In the latter case the salt is merely dropped into the vessel where it melts with the subsequent evaporation of the saturated solution formed upon melting. When a solution, saturated at 32.4°C, is heated, sodium sulfate precipitates as the temperature rises. Thus, when the temperature of the solution reaches 100°C, 15.2% of the salt introduced initially will have dropped out of solution.

If solid decahydrate is heated, a greater recovery may be realized than with a saturated solution. If the temperature is brought to 100°C., 46.7% of the salt can be recovered as a solid. Submerged combustion evaporators operate at a liquid temperature of about 90°C, at which point the recovery is approximately 46%. The remaining 54% is contained in the saturated solution.

An interesting comparison of the thermal requirements or performances of evaporating systems operating on liquid feed and solid feed is shown here.

Datum temp.: $20^\circ C$.

Basis: 1gm. mol $Na_2SO_4 \cdot 10H_2O$

1. Heat required to raise the decahydrate to the transition temperature.

   Heat capacity of decahydrate = 140.0 cal per mol.

   (integration of heat cap. curve, figure 3.)

   140 (32.4 - 20) = 1736 cal.

2. Heat of transition = 18,700 cal.

3. Heat needed to raise saturated solution from $32.4^\circ C$ to $90^\circ C$.

   Av. weight of solution = 261.7 gms

   Mean heat capacity = 0.784 cal per gm per degree

   (90 - 32.4) (261.7) (0.784) = 11,820 cal

   Average weight of solution obtained by integration of solubility curve, figure 1. Mean heat capacity found by integration of heat capacity curve, figure 4.

4. Heat required to raise precipitated salt from $32.4^\circ C$ to $90^\circ C$

   Av. weight of salt = 60.2 (integration of solubility curve.)

   8

   Specific heat of Na_2SO_4 = 0.21

   (90 - 32.4) (60.2) (0.21) = 728 cal

5. Evaporation of water in saturated solution

   Latent heat at $90^\circ C$ = 531 cal per gm. (see following discussion)

   180 x 531 = 95,500 cal

Datum temp = $20^\circ C$

6. Basis: Saturated solution containing 1 gm mol Na_2SO_4

   (142 gms Na_2SO_4 + 740 gms H_2O)

   Heat required to raise solution from $20^\circ C$ to $102.8^\circ C$

   (9a)

   Specific heat = 0.84

(102.8 - 20) (882) (0.84) = 61,400 cal

7. Heat required to evaporate water

heat of vaporization at 102.8 = 526 cal per gm

740 x 526 = 389,000 cal

The heat of vaporization was estimated from the following expression (10) derived from the clausius equation:

$$Q = Q_w \frac{T^2}{T_w^2} \frac{dT_w}{dT}$$

where T and Q are the absolute temperature and molal heat of vaporation of the solution, respectively; T_w and Q_w are the absolute temperature and molal heat of vaporization, respectively, of water at a pressure corresponding to that of the vapor over the solution.

From figure 2 the vapor pressure over the solution at 90°C. (194°F.) is seen to be 472 mm. The corresponding temperature and latent heat for water (11) were taken as 87.2°C and 547 cal per gm; respectively. The slope of the Diehring line, $\frac{dT_w}{dT}$, was taken (12) as 0.956.

$$\text{Therefore } Q = 547\frac{(363)^2}{(360.2)^2}(0.956) = 531 \text{ cal per gm.}$$

From the above data, summarized in Table 7, it is seen that the requirements for a liquid feed system are roughly three times greater than for solid feed.

Table 7

Process	Cal Required	gms Na_2SO_4 pptd.	Cal per gm.
Heating $Na_2SO_4 \cdot 10H_2O$ to b. p. (9000) and evaporating	128,484	142	905
Heating saturated solution to b. p. (102.8°C) and evaporating	450,400	142	3,170

Statement of Problem

It is evident from the above that the problem of processing Glauber's salt consists of the following:

1. The removal of the water of hydration under such conditions that the anhydrous material is obtained without any mechanical difficulties.
2. The removal of the water of hydration under the most favorable economic conditions.

The process employed consisted of bubbling or drawing hot furnace gases through sodium sulfate solutions in which the transfer of heat from the gases to the solution brought about evaporation of the liquid.

Since the North Dakota Glauber's salt deposits are in the lignite area of western North Dakota, it was deemed advisable to investigate the possibilities of lignite as a fuel for the process.

Description of Equipment.

The two principle pieces of equipment, as shown in figure 5. were the (1) evaporator and the (2) furnace. The former consisted of two 52 gal. oil-drums welded end to end with a cone (3) bottom to which was attached a 2-inch quick closing valve. The evaporator head was a circular sheet of ¼ inch boiler plate to which three, vertical 2-inch pipes (not shown) were welded. These 2-inch pipes, spaced equally throughout the evaporator cross-section, extended down into the body of the evaporator. Pipes (not shown), attached to the head by means of tees, extended from the chimney to the evaporator. The three horizontal pipes were welded to an 8 x 20 inch drum set into the brickwork of the (4) chimney. The opposite end of the 8 inch drum was fitted with a (5) flange to which an emergency (6) stack was bolted. During operation a blank could be inserted in this flange connection to prevent the escape of gases to the stack. The stack was in use only at the beginning and end of a run.

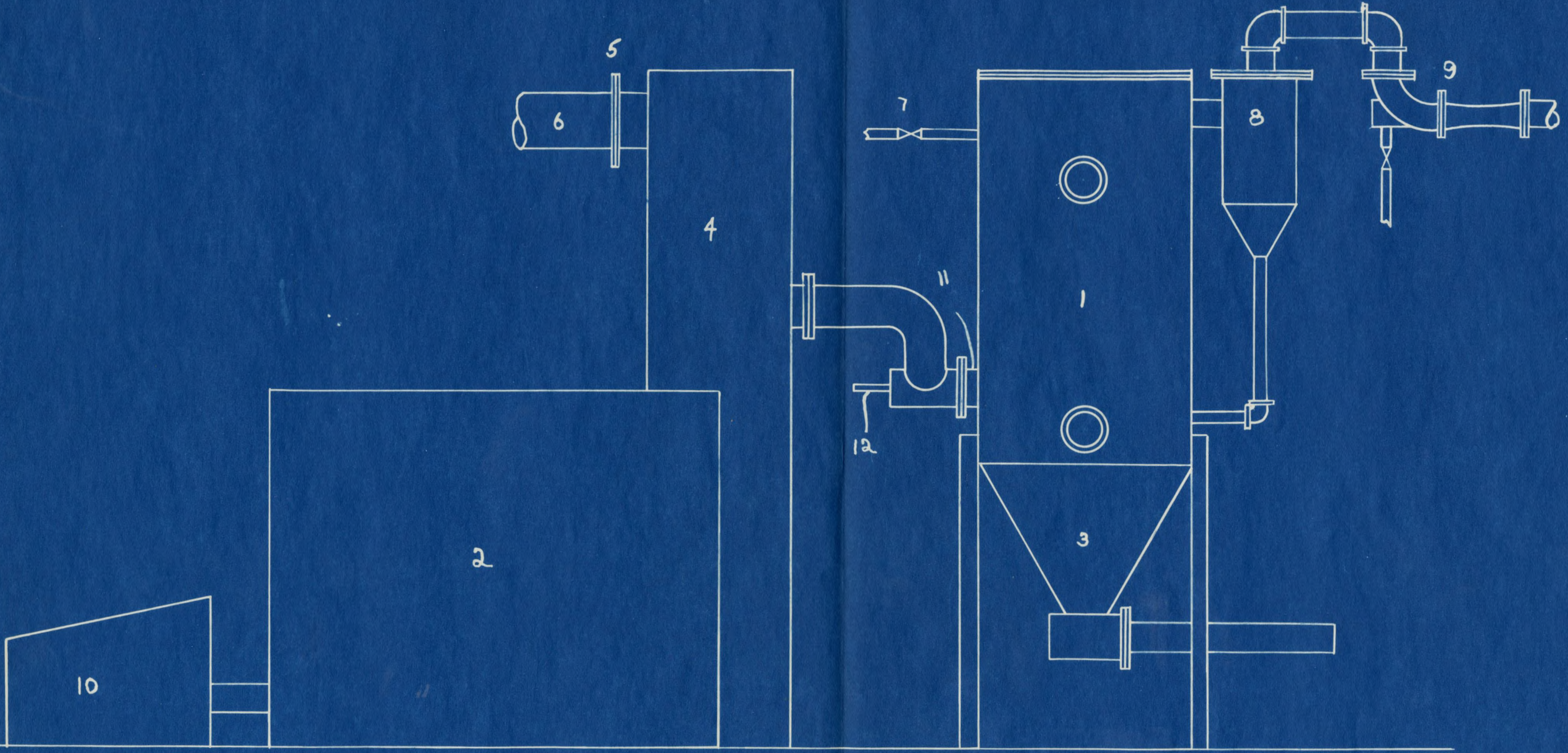


Figure 5

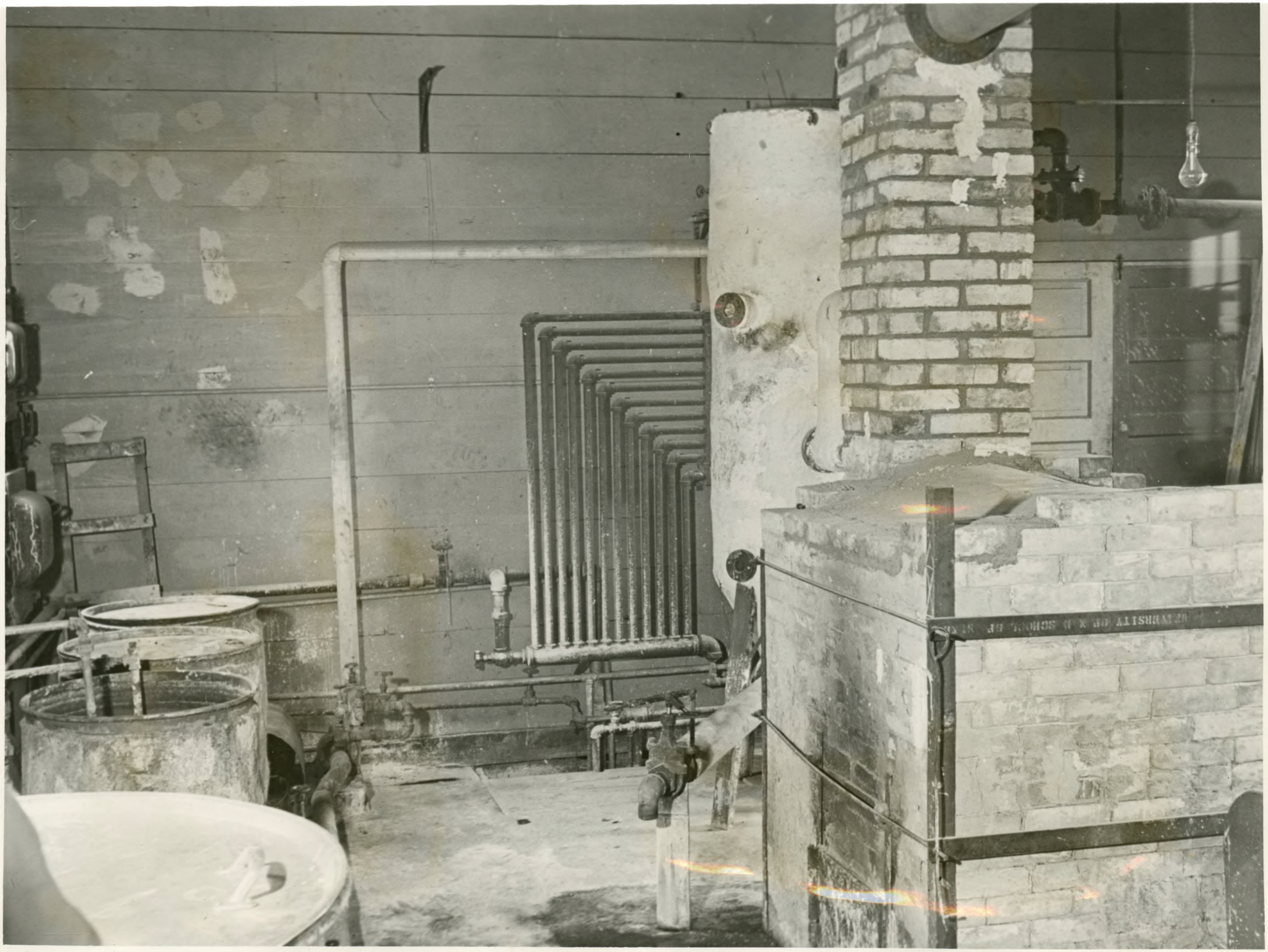


Figure 5b

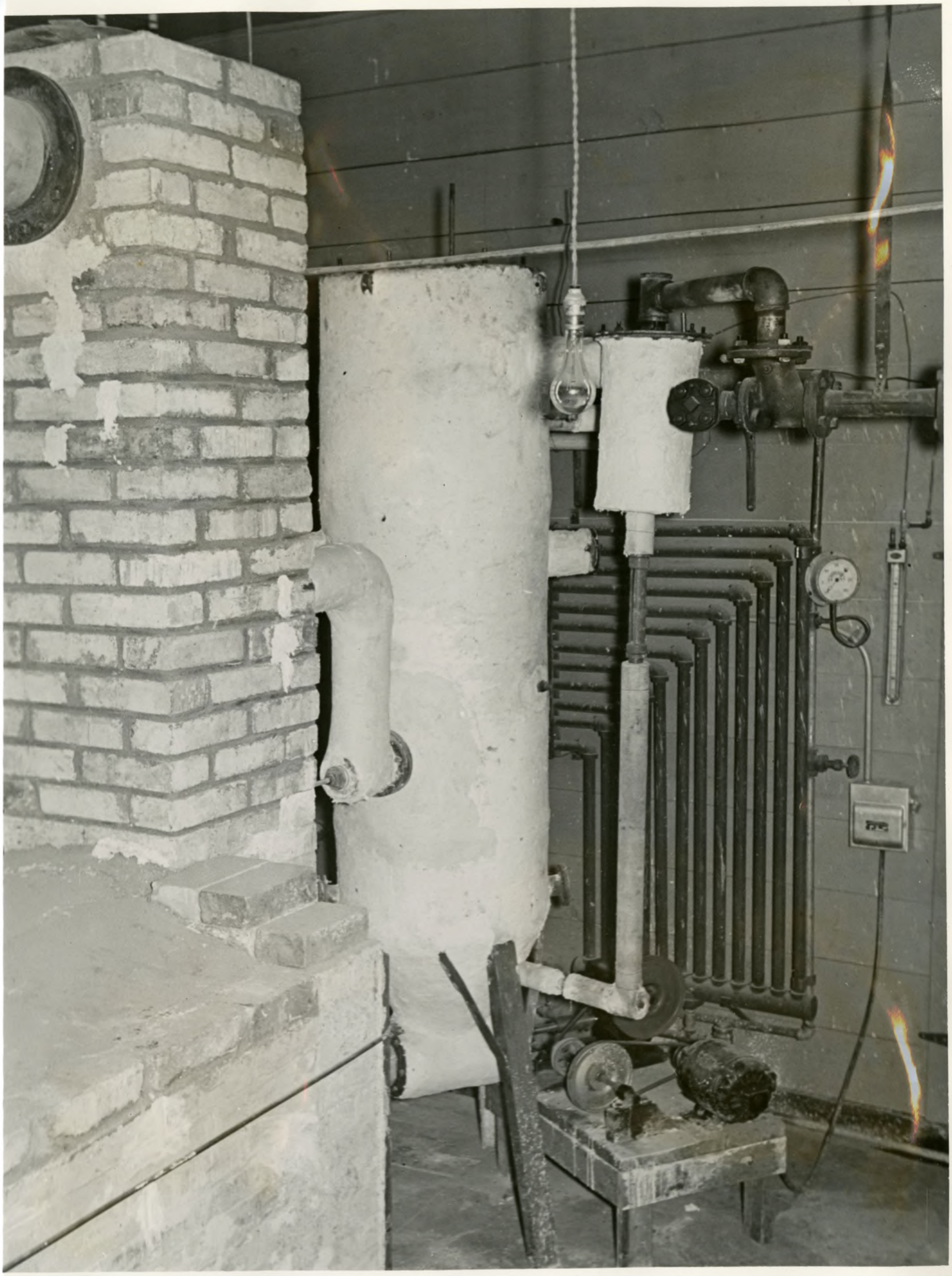


Figure 5c

A three-fourths inch feed line (7) entered the evaporator about a foot below the head of the vessel.

Four windows and a 4 foot liquid-level glass served as means of observation.

Three, insulated, 60 gal. steel drums, connected to a centrifugal pump by means of a common, 1 inch suction line, served as feed tanks. The motor-driven pump discharged into the three-fourths inch feed line. Hose connections were also installed on both the suction and discharge lines of the pump. A small steam-coil was placed in one of the 60 gal. drums for the purpose of making up hot saturated solutions, the other two drums serving merely as storage vessels.

A simple separator (8) was attached to the 2 inch gas discharge port near the head of the evaporator as a means of preventing undue foaming and entrainment losses. A more effective separator replaced this after the first series of runs.

The furnace gases were drawn through the entire system by means of a 2½ N. P. A. Worthington steam ejector, (9) designed to operate on 10 lb. pressure.

The furnace was built entirely of fire brick with a 24 x 38 inch combustion chamber, separated from the rear portion of the furnace by one course of brick which served as a baffle, installed in an effort to combat the fly-ash problem. The furnace was fired with an automatic stoker, (10) domestic type, the capacity of which varied from 10 to 50 lbs. of lignite per hour.

The 20 x 20 inch chimney, extending about 8 feet above the floor was also built of firebrick and was lined with 6 inch tile pipe to prevent leakage.

The temperature of the gases entering the evaporator was determined by means of a chromel-alumel thermocouple which was inserted through one of the tees on the head of the vessel. The temperature of the gases leaving the furnace was found by means of a similar thermocouple inserted in the chimney about 3 feet above the floor. A gas sampling tube was also inserted at the same point.

In the second series of runs the hot gases were introduced to the evaporator through a single 2-inch horizontal pipe. In effecting this change, a 4-inch nipple(11), was welded to the side of the evaporator about 18 inches above the top of the cone. A close 2-inch nipple was attached to the 4-inch coupling by means of suitable reducing fittings and extended inward toward the center of the evaporator. Connection was made to the chimney by means of a tee and suitable lengths of 4-inch pipe, offset vertically so that a scraper(12) could be operated through the tee. This assembly was heavily insulated.

Discussion of Results.

In the first six runs the hot furnace gases were introduced into the evaporator by means of three vertical 2-inch pipes as indicated in the description of the apparatus. The lower extremeties of these pipes were threaded so that suitable nozzles might be attached thereto.

During the first run no nozzles of any sort were attached to the hot gas inlet tubes. Relatively dilute solutions were fed into the vessel during the early part of the run. In this interval the amount of water evaporated was not sufficient to bring about crystallization. A feed solution, essentially saturated, was prepared and fed to the evaporator after which crystallization occurred. No serious caking occurred on the tubes prior to 8:00 p.m. (see table 8), the time at which precipitation of anhydrous sodium sulfate commenced. From this point on, considerable caking occurred on the tips of the tubes. As caking continued, a ring of scale, forming on the inside surfaces of the pipes, gradually closed the ends of the pipes. This caused an appreciable decrease in the rate of gas flow as indicated by a considerable drop of furnace gas temperature and an increase in vacuum.

When the vacuum rose to 4 or 5 inches Hg, the scale formation on the tips

Table 8, Run 1

Time	Vacuum, in Hg	Level, in	Ejector Steam, Psi	Furnace Gas temp., °F	Wet Bulb, °F	Dry Bulb, °F	Co$_2$, %
p.m. 12:45	1.2	12	10	820	146	168	9.2
1:45	1.3	12	10	880	160	171	
2:45	1.3	12	13	1000			15.8
3:45	1.3	12	13	1130	168	176	12.0
6:15	1.5	10	13	1230	162	174	15.8
6:45	2.0	10	13	1270	169	176	9.2
7:45	2.5	10	13	560			6.0
8:15	4.5	10	13	390			
9:15	1.5	10	16				
9:45	3.3	10	16				10.5
10:15	5.3	10	16		151	158	
11:15	1.8	10	16				
a.m. 12:30	3.1	10	16				6.0
1:15	1.2	8	16				4.2
2:15	2.7	8	10				
2:45	1.0	8	10		154	163	
4:15	3.3		10				
4:45	1.3	8	10		155	162	8.0

of the pipes was broken away by means of a ½" rod introduced through the tees in the hot gas lines at the head of the evaporator.

The stoker was operated at an average rate of 22 lb. of fuel per hour, and the rate of feed was approximately 52 lbs. per hour, equivalent to about 37 lbx. of H_2O per hour. From these figures about 1.77 lbs. of water were evaporated per lb. of fuel fired.

The ejector steam pressure was varied successively from 10 to 16 lb. gage in an effort to determine what effect gas velocity might have on the rate of scale formation. The hot gas tubes were cleaned at two hour intervals but the vacuum rose to nearly the same value at the end of each period regardless of the gas velocity. The fluctuations in gas flow rates, however, were such that it was impossible to maintain an even fire as shown by the CO_2 analysis in Table 8.

Run 2 was made with a minor change in equipment. 2 to 1 inch reducing couplings, to which were threaded 1-inch, short, sharp-edged nipples, were attached to the 2-inch gas inlet pipes. The liquid level was regulated so that the tips of the 1-inch nipples were submerged for a depth of 7 inches.

The vacuum rose from about 2 inches to 4-5 inches of Hg. in 1.5 hours, at the end of which time the tubes were cleared of scale in a manner similar to that of run 1.

(Table 9)

The stack gas temperatures, were lower than those in run 1, owing to lowered capacity and lowered combustion rate. However, a more even fire was maintained in this run as shown by the CO_2 analysis.

Thermal equilibrium was not readily attained at higher rates of gas flow. This may be born out by the fact that the wet bulb-dry bulb temperature difference increased as the steam pressure to the ejector was increased.

A short run was made to determine the relative merits of various

In three 2 inch caps

nozzle or orifice designs. 1-inch holes were countersunk, externally in one

Table 9, Run 2

Time	Vacuum, in. Hg	Level, in.	Ejector Steam, Psi	Furnace gas temp., °F	Wet bulb °F	Dry bulb °F	Co$_2$,%
p.m. 9:30	0.9	7	10	420	148	156	
10:30	1.2	7	10	530	147	157	14.4
11:30	2.4	7	10	540	146	154	15.6
a.m. 12:30	2.9	7	10		142	150	15.0
1:00	3.5	7	10				
1:30	1.8	7	17	600	137	145	7.1
2:30	1.6	7	17	660	137	151	9.4
3:30	3.4	7	22	740	142	158	8.7
4:00	4.4	7	25	720	141	159	5.0
4:30	3.5	7	25	790	143	164	10.6
4:45	4.2	7	25	780			13.6
5:00	5.0	7	25	770			
5:30	6.3	7	25	730			13.9

Table 10, Run 3

Time	Vacuum in. Hg.	Level, in.	Ejector Steam	Furnace Gas temp., °F	Wet bulb °F	Dry bulb °F	CO_2, %
p.m. 3:30	1.3	8	23	530	142	152	13.2
4:25	2.5	8	23	970	-	-	10.7
5:00	4.1	8	23	850	140	154	13.8
5:30	1.6	8	23	720	-	-	-
6:15	4.1	8	23	830	-	-	-
7:00	1.9	8	23	720	141	153	11.7
8:30	2.2	8	23	1150	141	152	13.8
9:30	5.7	8	23	860	-	-	-

case and internally in the other. The remaining cap was untouched. The fittings thus prepared were threaded to the tips of the hot gas inlet pipes in the evaporator.

It was found that the internally countersunk orifice brought about a lower rate of scale deposition, while, in the case of the externally countersunk fitting, scale removal was facilitated. Neither possessed any advantage over the other in any other respect.

In the fourth run cones made of light gauge sheet metal with thirty-five ¼ inch perforations were welded within 2 inch couplings. These fittings were threaded to the ends of the hot gas tubes. Scale formed about these perforations with such rapidity that often after thirty-five minutes of operation, all openings in the cones were practically closed.

For the fifth run screwed flanges were fitted to the ends of the hot gas inlet tubes. ¼ inch plates, into which 1½ inch sharp-edged orifices had been machined, were bolted to the flanges. Scrapers, shaped to fit the openings in the ¼ inch orifice plates, were operated by means of ½ inch rods introduced through packing glands in the tees at the head of the evaporator.

At times the scrapers were rather difficult to operate owing to the heavy deposit which accumulated on the flanges and discs. At some points on the orifice plate the scale was well over 2 inches thick. Some conception of the severity of scaling may be gained from figure 6-A.

Thermal equilibrium was not attained in this run as indicated by the liquid-gas temperature difference which varied from 14° to 18°F. during the run.

The cake of anhydrous sodium sulfate, adhering to the flanges as described above, built up to such an extent that the tip of the scraper, protruding below the orifice plate, was completely covered with scale, leaving only a very small opening.

In run 6, the orifice plates were removed from two of the hot gas

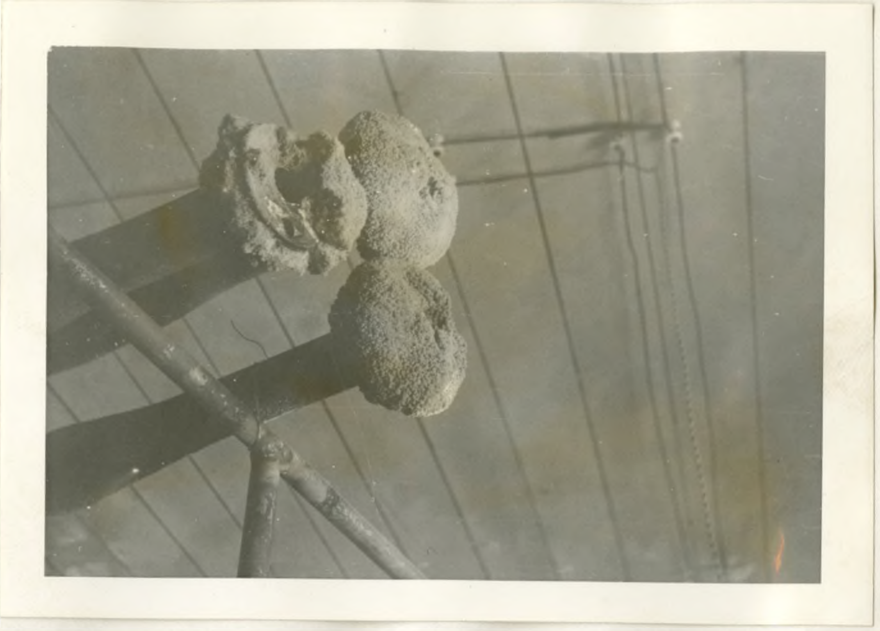


Figure 6a

Figure 6b

Table 11, Run 5

Time	Vacuum in Hg. Before Cleaning	After Cleaning	Level, in.	Ejector Steam, Psi	Furnace Gas Temp °F.	Liquid Temp. °F.	Exhaust Temp. °F.
p.m. 1:40	.8		6	25	620	144	156
2:30	1.0		7		900	151	165
2:40	1.3	0.9	8				
2:45	1.1				870	149	163
3:10	1.6	1.1			910	150	164
3:40	1.6	1.0			990	154	171
4:05	1.7	1.0			1020	157	173
4:30	2.2	1.0			1120	159	182
5:00	2.4	1.1			1190	160	187
5:15	2.1				1210	162	184
5:30	2.7	1.1			1250	163	185
6:00	2.4	1.1			1250	163	184
6:30	2.7	1.1			1310	165	177
7:00	2.5	1.1			1260	164	182
7:30	2.4	1.1			1270	166	183
8:05	2.8	1.1			1260	167	186
8:30	2.7	1.1			1260	167	184
9:00	2.4	1.1			1260	168	186
9:30	2.7	1.0			1190	166	184
10:00	2.7	1.1			1200	164	180
10:30	2.6	1.4			1200	164	176
11:00	2.2	1.3			1180	161	168
11:30	2.7	1.8	8	25	1190	160	164

inlet pipes. A 1½ inch sharp-edged orifice in the form of a 2-inch ring was welded to the tip of the third pipe. Scrapers were operated in all three tubes.

It was found that the scrapers in the open tubes were more difficult to operate than that in the tube fitted with an orifice. Caking or scaling was more severe in the two open tubes, as shown in figure 6-B, bringing about greater difficulty in scale-removal. The inner surfaces of the two open pipes were wetted to a greater extent than was the tube containing an orifice.

Toward the end of the run the vacuum fell off somewhat. The stoker feed was reduced, of necessity, from 37 lb. per hour to about 15 lb. per hour. The marked decrease in capacity was caused by severe caking around the evaporator gas-discharge part, the separator, and the ejector intake. Examination also revealed that the liquid return line of the separator was closed completely. Chips and lumps of anhydrous sodium sulfate, dislodged from the tips of the hot gas inlet pipes by the scrapers, collected in the cone and made salt removal difficult during the early part of the run. Larger fragments of scale later blocked the salt discharge valve completely.

Entrained liquid caused the excessive scaling in the gas discharge system. Up until this time no baffles of any sort had been placed in the evaporator body to prevent the discharge of slugs of liquid during operation.

Conditions of equilibrium were not fully attained at all times between the gases and the solution, but a considerable improvement was noted over conditions in previous runs. The liquid-gas temperature difference did not exceed 2°F. at any time.

Run 7 was of short duration, its purpose having been to investigate the relative merits of horizontal and vertical (direct upward) nozzles.

Fittings were attached to two of the 2-inch gas inlets in the evaporator such that the gases were directed into the evaporator horizontally in one case and vertically upward in the other. The piping arrangement was such that the

Table 12, Run 6

Time	Vacuum, in. Before Cleaning	Vacuum, in. After Cleaning	Level, in.	Ejector Steam Psi	Furnace Temp. Gas °F.	Liquid Temp. °F.	Exhaust Temp., °F.
p.m. 12:45	0.9		8	25	680	157	157
1:15	0.9				820	155	155
1:45	0.9				900	151	152
2:15	1.0				970	153	155
2:45	1.3				990	153	156
3:15	2.3	1.0			1030	154	156
3:45	1.7				1050	155	157
4:00	2.5	1.0			1030		
4:15	1.2				1050	155	157
4:45	2.2	1.0			1050	156	158
5:15	2.3	1.0			1160	160	162
5:45	2.2	1.1			1220	162	164
6:15	1.9	1.3			1180	162	162
6:45	2.0	1.1			1150	161	163
7:15	1.8	1.3			1150	161	161
7:45	1.5				1160	160	160
8:15	2.2	1.3			1190	160	160
8:45	1.9	1.3			1190	160	160
9:15	1.7	1.2			1200	160	160
9:45	1.8	1.0			1220	161	158
10:15	1.9	1.1			1200	161	162
10:45	1.9	1.1	8	25	1190	162	163

Table 13, Run 7

Time	Vacuum in Hg.	Level in.	Liquid Temp. °F.	Discharge Temp., °F.	Stack Temp., °F.	Ejector Steam, Psi
p. m. 3:15	1.10	8			520	25
3:30	1.15				940	
3:35	1.25		1.52	157	960	
3:40	1.30				970	
3:45	1.40		154	158	990	
3:50	1.45		155	158	1000	
3:55	1.50		155	158	1020	
4:00	1.80		155	158	1040	
4:05	1.95		155	158	1050	
4:15	2.40		156	158	1040	
4:20	2.60		156	158	1040	
4:30	3.20		156	157	1030	
4:35	4.00		156	158	1030	
4:40	4.30		155	156	1030	
4:45	5.0		154	154	1020	
4:48	5.30	8				25

tips of both tubes were in the same horizontal plane.

At the end of the run a ½ inch opening remained in the horizontal nozzle while the vertical nozzle was closed completely.

In Run 8 suitable changes were made, as described in the discussion of the apparatus, so that the hot furnace gases could be admitted to the evaporator through a horizontal nozzle.

During this run a short piece of 2-inch pipe was used as a nozzle which was cleared of scale at 20 minute intervals by means of a scraper. In a 20 to 30 minute period the vacuum rose from 1.6 to 2.2-7 inches of Hg. This caused no apparent fluctuation in furnace conditions, but after longer periods the scale formation on the nozzle became increasingly difficult to remove.

The stoker was set at a rate of 35 lb. of fuel per hour. The average rate of feed to the evaporator was 95.2 lb. of solution per hour, equivalent to 68.5 lb. of water per hour. From these approximate values, 1.96 lb. of water were evaporated per lb. of fuel.

During the last hour of the run the vacuum dropped to 1.2 - 1.4 inches of Hg. which was below that attained initially when the hot gas inlet tube was entirely free of scale. This was accompanied by a decrease in capacity noticeable in both the evaporator and furnace conditions.

Examination at the end of the run revealed that the gas discharge lines of both the evaporator and the separator were choked by heavy accumulations of anhydrous sodium sulfate, but the body and liquid return line of the separator were relatively clean.

The efficiency attained in this run was the highest reported thus far. Higher stack temperatures than in any previous run, owing to better furnace conditions, were reported.

An effort was made in Run 9 to prevent the large cakes of salt ~~discharge~~ dislodged from the nozzle from clogging the cone and salt discharge valve. A

-21a.

Table 14, Run 8

Level = 8 in. Ejector Steam = 25 Psi

Time	Vacuum, in. Hg.	Furnace Gas Temp., °F	Exhaust Temp. °F.	Time	Vacuum in. Hg.	Furnace Gas Temp., °F.	Exhaust Temp., °F.
p. m. 2:45	1.55	1000	160	p. m. 10:00	1.9	1250	164
3:10	1.50	1040	165	10:30	1.6	1340	167
3:30	1.80	1130	165	11:00	2.0	1350	168
3:55	1.95	1200	168	11:30	1.7	1380	171
4:15	1.50	1170	166	12:00	1.5	1440	173
4:40	2.30	1210	165	a. m. 12:30	1.8	1460	169
5:00	2.0	1230	166	1:00	2.3	1500	172
5:30	1.8	1290	168	1:30	2.1	1540	173
6:00	1.65	1270	166	2:00	1.55	1520	173
6:30	1.95	1280	166	2:30	1.6	1510	169
7:00	1.55	1300	166	3:00	1.55	1520	170
7:30	2.7	1280	162	3:30	1.95	1510	171
7:45	1.7	1290	162	4:00	1.6	1540	170
8:30	2.0	1160	154	4:30	2.0	1540	170
9:00	2.0	1240	162	5:00	1.9	1530	170
9:30	1.8	1260	163	5:30	1.4	1500	171

screen, shaped to fit the evaporator cross section, was placed about 6 inches below the nozzle to retain the larger fragments of scale. This greatly facilitated salt removal, but after 18 hours of operation the material accumulated on the screen to such an extent that the precipitated salt could not pass down to the cone. The run was discontinued for this reason.

The nozzle was cleaned every 15 minutes by means of a scraper similar to those used previously. Since some difficulty had been encountered in runs prior to this with the gas discharge system, vacuum readings were taken at both the evaporator head and the ejector intake as a means of detecting scaling in the discharge system.

Little fluctuation occurred during the run as seen by the fairly constant stack gas temperatures in Table 15. The furnace gas composition, checked at hourly intervals is shown in Table 16. In a number of instances negative values for ~~co~~ CO were recorded but not shown in the table. The apparatus was necessarily placed in the proximity of the furnace. Volatilization of the Hcl in the test solution probably gave rise to these discrepancies.

At the end of this run a 1 inch scale had accumulated on the walls of the evaporator. The walls had been purposely untouched so that some conception of the rate of scaling might be obtained. This 1 inch scale built up on the evaporator walls in the course of 60 hours of operation. This scale was smooth, quite hard and not readily dissolved even by hot water. It was quite similar in appearance to that which formed on the nozzle although it appeared, in some cases, that the latter was fused. From the figures in Table 15 approximately 2.2 lb. of water were evaporated per lb. of fuel.

In Run 10 a venturi shaped nozzle with a 1 inch throat was attached to the 2 inch gas inlet connection.

The mouth of the nozzle was fouled with salt except for the opening cleared by the cleaner. The rear part of the nozzle remained free of caking up to the

Table 15, Run 9

Time	Vacuum, in. Hg.		Furnace Gas Temp., °F.	Exhaust Temp., °F.	Liquid Temp., °F.
	Evap.	Ejector			
p.m. 12:15	1.7	2.4	880	-	-
12:30	1.9	2.6	960	155	158
1:00	2.6	3.2	1200	162	166
1:30	1.9	2.5	1250	166	169
2:00	2.0	2.7	1320	164	168
2:30	2.0	2.8	1390	166	169
3:00	2.7	3.3	1390	165	168
3:30	3.1	3.7	1310	162	167
4:00	2.4	3.0	1600	172	172
4:30	3.1	3.7	1520	175	175
5:00	2.7	3.3	1540	172	172
5:30	3.0	3.6	1520	172	172
6:00	2.9	3.4	1490	172	172
6:30	2.1	2.7	1490	172	172
7:00	2.0	2.7	1480	168	169
7:15	3.2	3.8	1460	168	170
7:30	2.8	3.4	1490	168	168
8:00	2.7	3.3	1370	164	164
8:30	2.5	3.1	1410	166	166
9:00	2.5	3.1	1410	166	166
9:30	2.8	3.4	-	-	-
10:00	2.1	2.8	1410	166	166
10:30	2.2	2.9	1420	166	167
11:00	2.4	3.2	1410	166	166

Table 15, Run 9 (Continued)

Time	Vacuum in. Hg.		Furnace Gas Temp., °F.	Exhaust Temp., °F.	Liquid Temp., °F.
p.m. 11:30	2.5	3.1	1430	168	167
12:00	1.7	2.3	1420	165	168
a.m. 12:30	2.3	2.9	1470	168	168
1:00	2.8	3.3	1570	169	168
1:30	2.4	3.0	1500	168	167
2:00	2.2	2.9	1490	168	167
2:30	2.1	2.8	1470	166	165
3:00	2.0	2.7	1440	165	164
3:30	2.0	2.7	1560	169	163
4:00	2.0	2.7	1460	167	162
4:30	2.4	3.2	1450	164	161
5:00	3.1	3.8	1420	163	159
6:00	1.9	2.7	1430	165	157
,6:30	2.7	3.5	1430	165	167
7:00	2.7	3.5	.450	164	156
7:30	1.8	2.7	1430	165	155
8:00	2.5	3.3	1410	162	153
8:30	2.2	3.0	1410	163	153

throat.

A $\frac{1}{2}$ inch cake built up on the inner surface of the nozzle just beyond the throat. The deposit was not particularly difficult to remove but it was found necessary to operate the scraper at 15 minutes intervals.

As seen by the furnace gas temperatures in Table 17, it was impossible to maintain a hot fire. The 1 inch construction in the nozzle was apparently too small for good operation since the rate of flow of furnace gases was reduced considerably. The relatively small opening at the throat of the nozzle also made for a higher vacuum in the evaporator which made salt removal difficult.

The nozzle used in run 11 was machined from a 6 inch length of steel shafting. The internal diameter of the nozzle was 2 inches at the mouth. The discharge end was turned down so that a sharp edge was produced. The opposite end was threaded to fit a 2 inch coupling.

The screw conveyor shown in Figure 5 attached to the cone to facilitate salt discharge was too highly geared for continuous operation. Salt was drawn from the vessel at intervals varying from 1 to 2 hours. Its performance otherwise was satisfactory.

Apparently the cone was too shallow to allow the precipitated salt to drop into the conveyor. The fine precipitate adhered to the sides of the cone and caused a considerable deposit of salt to accumulate in the evaporator. At the end of the run about 453 lb. of salt were removed from the vessel. The moisture content of this residue was 23.9%.

Small amounts of Na_2SO_4 were deposited in the separator and in the ejector intake but not in large enough quantities to impede operation during the first 38 hours of the run. During the last 6 hours the rate decreased noticeably as a result of the fouling in the separator, the ejector intake and the evaporator gas outlet.

No caking or crystallization occurred in the evaporator. Small lumps of

Table 17, Run 10

Time	Vacuum in. Hg.		Furnace Gas Temp., °F.	Exhaust Temp., °F.	Liquid Temp., °F.
	Evap.	Ejector			
p.m. 2:00	3.3	3.9	1090	146	152
2:30	4.7	5.4	1130	150	156
3:00	5.0	5.6	1080	142	162
3:30	4.2	4.7	1070	144	150
4:00	5.4	5.9	1060	142	150
4:30	5.4	5.9	1060	142	149
5:00	5.7	6.1	1070	144	150
5:30	5.8	6.3	1080	144	150
6:00	5.9	6.4	1090	144	150
6:30	5.7	6.2	1070	143	148
7:00	5.6	6.1	1070	145	149
7:30	6.0	6.4	1060	141	149
8:00	6.5	6.8	1060	142	147
8:30	6.1	6.6	1050	139	147
9:00	6.6	7.0	1160	143	149
9:30	6.4	6.8	1130	145	151
10:00	6.0	6.5	1120	146	150
11:00	6.2	6.6	1120	144	149

salt, found in the discharged material, were dislodged from the nozzle but these fragments unlike those in previous runs were quite soft and could easily be mashed. The walls of the vessel remained quite clean with the exception of a few spots where surface irregularities caused the adherence of small quantities of salt.

The efficiency of this run was higher than in previous runs. The evaporation rate was calculated as 2.905 lb of water per lb. of fuel. The rate of fuel consumption was found to be 30.4 lb. per hour.

The high total losses as indicated in the heat balance were attributed to furnace conditions and limitations of the stoker. The blower could not furnish sufficient air at a pressure high enough to maintain a positive pressure within the furnace. As a consequence, quantities of cold air were drawn into the system. This was substantiated by the fact that the average CO_2 analysis and the average furnace gas temperature for the run were rather low. With proper furnace regulation temperatures from 400 to 500°F above those reported should have been attained. The quality of the fuel may have played an important part. In some instances the fuel contained a relatively large percentage of fines which would necessitate a stronger draft.

Heat and Material Balance

Total weight of feed = 5493 lbs. Wt. of fuel = 1351 lbs.

Water in feed = 3815 lbs. (feed = 30.55% Na_2SO_4)

Water in coal = 1351 x 0.337 = 455 lbs.

Water of combustion = $\frac{2.9}{2} \times 18 \times \frac{1351}{100}$ = 352 lbs.

Total water,, in = 3815 + 455 + 352 = <u>4622</u> lb.

Water out, in salt = 1815.5 x 0.313 = 567.4 lb.

Water out, in residue = 453 x 0.239 = 108

A portion of residue (not weighed) was dissolved to form 12" of solution whose specific gravity was 1.29.

$$68 \times \frac{.239}{.761} = 21.4$$

Water out, in salt = 567.4 + 108 + 21.4 = 698 lb.

Water evaporated = 4622 - 698 = 3924 lb.

Salt in = 5493 x .3055 = 1678 lb.

Salt out = 1815.5 x 0.687 = 1248 lb.

Salt in residue = 453 x 0.761 = 344

Salt in 12 in. of 1.29 gravity solution: $12 \times 1.29 \times 2.3 \times 62.4 \times \frac{44}{144}$ = 68 lb.

Total salt out: 1248 + 344 + 68 = 1660 lb.

Salt unaccounted for: 1678 - 1660 = 18 lb.

Datum Temp. = 90°F.

Heat in = heat in feed + heat in furnace gases.

Av. feed temp. = 133°F. Sp. heat = 0.783

Heat in feed = (133 - 90) (.783) (5493) = 185,100 BTU

Heat in furnace gases:

$(\frac{2.9}{2} \times 18) - 33.7 = 59.8$ lb H_2O per 100 lb. lignite.

$= 3.32$ mols H_2O

$3.32 \times \frac{12}{44} \times 9 = 8.55$ mols H_2O per 100 mols dry furnace gas.

(13)

Sensible heat in furnace gases:

CO_2 : $(1300 - 32)(9)(11.25) - (90 - 32)(9)(8.9) = 123,660$ BTU

O_2 : $(1300 - 32)(10.3)(7.7) - (90 - 32)(10.3)(6.95) = 96,350$

N_2 : $(1300 - 32)(80.7)(7.3) - (90 - 32)(80.7)(6.95) = 714,400$

H_2O : $(1300 - 32)(8.55)(8.75) - (90 - 32)(8.55)(8.05) = 91,000$

Latent heat of water : $8.55 \times 18 \times 1042$ $= \underline{160,500}$

Total heat per 100 mols dry furnace gas (per 257 lb. fuel) 1,185,910 BTU

Total heat for run: $\frac{1361}{257} \times 1,185,910 = 6,230,000$ BTU.

Heat required to raise feed from 133 to 162°F.:

$5493 (162 - 133)(.783) = 124,400$ BTU.

Heat required to vaporize water:

Latent heat $= Q_w \frac{T^2}{T_w^2} \frac{dT_w}{dT} = 1003 \times \frac{(622)^2}{(617)^2} \times 0.956 = 970$ BTU per lb.

$3924 \times 970 = 3,810,000$ BTU. for vaporization.

Total heat absorbed = heat absorbed by feed + heat of vaporization.

$= 3,810,000 + 124,400 = 3,934,400$ BTU.

Heat out = heat in slurry + heat in exhaust gases + losses.

Heat in slurry (1248 lb. dry Na_2SO_4 + 567.4 lb. H_2O)

$567.4 \times \frac{144}{100} = 816$ lb. of sat. solution.

$1815 - 816 = 999$ lb. salt. Sp. ht. of $Na_2SO_4 = 0.21$

$999(162 - 90)(0.21) + 816(162 - 90)(.783) = 61,220$ BTU

Heat in exhaust gases:

CO_2 : (162 - 32) (9) (9.06) - (90 - 32) (9) (8.9) = 5960

O_2 : (162 - 32) (10.3) (7) - (90 - 32) (10.3) (6.95) = 5220

N_2 : (162 - 32) (80.7) (6.95) - (90 - 32) (80.7) (6.95) = 40,400

H_2O : (162 - 32) (206) (8.08) - (90 - 32) (206) (8.05) = 121,000

$\frac{1351}{257}$ x 51,580 = 271,500 BTU in dry gas

121,000 BTU in H_2O vapor
392,500 BTU, total sensible heat

Total heat in fuel, BTU	9,980,000	100.0%
Heat absorbed in evaporator, BTU	3,934,400	39.4%
Heat in slurry, BTU.	61,220	0.6%
Sensible heat in exhaust gases, BTU.	392,500	3.9%
Losses unaccounted for, BTU.	5,591,880	56.1%

Total heat entering evaporator, BTU.	6,230,000	100.0%
Heat absorbed in evaporator, BTU.	3,934,400	63.1%
Heat in slurry, BTU.	61,220	1.0%
Sensible heat in exhaust gases, BTU.	392,500	6.3%
Losses unaccounted for	1,841,880	29.6%

Lb. H_2O evaporated per lb. of coal = $\frac{3924}{1351}$ = 2.905 lb.

Table 18, Run 11 (Steam Pressure = 30,) (Level = 8 in.)

Time	Vacuum Evap.	Vacuum Ejector	Furnace Gas Temp., °F.	Liquid Temp., °F.	Exhaust Temp., °F.	%CO_2	%O_2
p.m. 10:45	1.7	2.5	1000	144	150	5.8	12.8
11:00	1.8	2.6	960	146	152		
11:30	2.0	2.8	1040	160	156	6.5	12.9
12:00	1.9	2.7	1090	158	156		
a.m. 12:30	2.9	3.6	1130	160	158	8.0	11.0
12:55	2.0	2.8	1110	163	158		
1:30	2.05	2.90	1190	158	162	10.4	8.7
2:00	3.2	3.95	1240	164	162		
2:30	2.1	3.0	1285	168	160	11.6	8.4
3:00	1.9	2.8	1270	162	162		
3:30	1.7	2.5	1210	160	158	5.0	13.8
4:00	1.9	2.7	1200	160	152		
4:30	3.0	3.7	1190	162	157	6.9	12.2
5:00	2.7	3.5	1200	160	158		
5:30	1.8	2.6	1170	158	160	6.0	13.6
6:00	2.4	3.2	1170	156	160		
6:30	2.6	3.4	1180	156	160	7.4	12.4
7:00	2.5	3.2	1160	156	155		
7:30	2.0	2.8	1290	156	159	5.8	14.2
8:00	2.5	3.2	1190	157	158		
8:30	1.6	2.4	1290	152	162	4.2	14.0
9:00	2.4	3.2	1300	149	162		
9:30	2.6	3.3	1310	144	162	11.1	8.8

Table 18, Run 11 (Continued)

Time	Vacuum		Furnace Gas Temp., °F.	Liquid Temp., °F.	Exhaust Temp., °F.	% CO_2	% O_2
	Evap.	Ejector					
p.m. 10:30	2.1	2.9	1290	144	161	8.8	10.8
11:00	2.9	3.6	1330	143	164		
11:30	1.7	2.6	1370	144	161	10.4	7.1
12:00	2.7	3.5	1370	152	165		
p.m. 12:30	3.4	3.9	1360	150	162	9.8	10.0
1:00	2.2	2.9	1360	150	166		
1:30	1.8	2.8	1360	148	165	10.4	8.4
2:00	3.1	3.7	1360	148	162		
2:30	3.3	3.9	1390	147	166	4.0	16.0
3:00	3.1	3.6	1450	148	167	16.2	3.2
3:30	1.6	2.5	1460	145	166	15.0	4.3
4:00	1.8	2.5	1490	145	167		
4:30	3.3	3.9	1480	144	166	13.4	6.1
5:00	3.6	4.2	1400	140	155		
5:30	2.7	3.3	1380	147	156	6.4	13.6
6:00	2.0	2.8	1460	145	165		
6:30	1.7	2.5	1470	143	163	12.6	7.3
7:00	1.7	2.5	1480	144	165		
7:30	3.1	3.6	1480	147	165	12.2	7.5
8:00	3.0	3.6	1480	151	166		
8:30	2.2	2.7	1470	148	163	11.8	8.2
9:00	3.2	3.8	1470	149	166		
9:30	1.8	2.5	1440	145	164	10.6	9.4
10.00	2.7	3.3	1520	146	172		
10:30	1.6	2.3	1490	145	168	13.8	6.9

Table 18, Run 11 (Continued)

Time	Vacuum Evap.	Vacuum Ejector	Furnace Gas Temp., °F.	Liquid Temp., °F.	Exhaust Temp., °F.	% CO_2	% O_2
p.m. 11:00	1.6	2.2	1460	144	168		
11:30	2.7	3.2	1460	145	166	8.8	10.8
12:00	2.7	3.2	1460	144	168		
a.m. 12:30	2.3	2.9	1590	143	172	16.1	2.9
1:00	1.6	2.3	1510		170		
1:30	2.5	3.3	1470		197	9.4	10.7
2:00	2.9	3.5	1430		164		
2:30	2.7	3.5	1380		162	6.0	14.0
3:00	1.6	2.3	1400		166		
3:30	2.2	2.9	1380		160	8.0	11.8
4:00	3.0	3.7	1360		160		
4:30	1.8	2.6	1430		168	11.1	9.9
5:00	1.7	2.4	1400		172		
5:30	1.6	2.4	1380		168		
6:00	2.1	2.8	1390		168		
6:30	1.8	2.6	1350		168	8.1	10.3
7:00	1.9	2.7	1300		161		
7:30	2.4	3.1	1270		160	12.0	8.8
8:00	2.3	3.0	1350		165		
8:30	2.5	3.4	1290		168	8.1	11.1
9:00	2.0	3.0	1240		158		
9:30	1.5	2.4	1220		160	6.2	12.8
10:00	2.7	3.6	1200		160		
10:30	2.8	3.8	1270		164	11.1	6.4

Table 18, Run 11 (Continued)

Time	Vacuum		Furnace Gas Temp., °F.	Liquid Temp., °F.	Exhaust Temp., °F.	% CO_2	% O_2
	Evap.	Ejector					
11:00	4.3	5.2	1260		154		
11:30	3.4	4.3	1240		159	8.2	10.2
12:00	2.7	3.5	1220		161		
p.m. 12:30	2.5	3.2	1210		157	8.0	10.0
1:00	2.1	2.9	1200		162		
1:30	2.9	3.7	1200		152	8.0,	11.0
2:00	2.2	3.2	1240		167		
2:30	3.1	3.5	1260		169	8.8	9.2
3:00	3.8	4.0	1220		158		
3:30	2.3	2.9	1170		156	7.2	11.6
4:00	3.4	3.6	1190		158		
4:30	1.7	2.7	1170		156	4.5	13.8
5:00	3.3	3.7	1150		163		
5:30	4.1	4.2	1140		169	5.7	12.3
6:00	1.7	3.5	1100		163		
6:30	3.1	4.3	1080		155	6.2	13.5
7:00	1.8	4.9	1050		153		

Table 19, Run 11

Rate of increase in Vacuum after cleaning nozzle.

Time, min.	Vacuum, in Hg.	Time, min.	Vacuum, in. Hg.
0	1.9	7.0	2.55
0.5	2.0	7.5	2.60
1.0	2.05	8.0	2.65
1.5	2.075	8.5	2.675
2.0	2.1	9.0	2.75
2.5	2.125	9.5	2.8
3.0	2.15	10.0	2.825
3.5	2.2	10.5	2.85
4.0	2.25	11.0	2.875
4.5	2.3	11.5	2.875
5.0	2.37	12.0	2.90
5.5	2.425	12.5	2.925
6.0	2.475	12.0	2.975
6.5	2.50	13.5	3.000

In an effort to prevent the accumulation of salt in the cone of the evaporator, a scraper was fashioned to fit within the cone. This piece of equipment consisted of a length of ½ inch rod to which the scraper was attached. The arrangement was such that by rotating the rod which projected through a packing gland located in the head of the evaporator, the salt deposited on the sides of the cone could be dislodged and carried out of the evaporator by means of the screw conveyor. This scraper was operated manually at half-hour intervals during the run.

In run 12 the salt was discharged by the screw conveyor as a slurry containing approximately 30% liquid by volume. After having been permitted to settle for 20 minutes the supernatant liquor was decanted and returned to the evaporator. It was found that after an additional settling period of 2 hours 18.2% of the sample separated as liquid. It was found that after settling approximately 2 hours, the original sample would have been about 43% liquid by volume. The salt was weighed and sampled after decantation. A composite salt sample was prepared, the moisture content of which was found to be 27.7%

An examination of the interior of the evaporator at the end of the run showed that a ¼ inch scale had been deposited on the walls. Scale formation on the nozzle was more severe than in the preceding run but not so acute as to impede normal operation. A rather heavy deposit of scale accumulated in the evaporator gas discharge line and in the separator. This was made apparent during operation by the increasing pressure difference measured across the evaporator and separator. During the last 2 hours of operation the rate was also seen to drop off slowly as demonstrated by the gradual decrease of vacuum in the evaporator.

As seen in Table 18 the average furnace gas temperature for the run was 350° higher than in the previous run. Better furnace conditions were attained since a number of leaks that had developed in the furnace walls and chimney were repaired. When operating at capacity, the blower attached to the stoker could not maintain a positive pressure within the furnace. As a consequence, quantities of cold air were drawn into the system giving rise to unduly low temperatures and efficiencies. In this run all fuel was passed over a ½ inch screen in order to remove the fines, the elimination of which made higher furnace pressures possible and also made for more efficient combustion.

Operating Conditions.

Lb. fuel, Total =	273	Moisture in salt =	27.7%
Lb. feed, Total =	1093	Conc. of Na_2SO_4 in feed =	29.9%
Lb. salt, Total =	418	Av. feed temp. =	104°F

Average Values for Run 12

Vacuum, in Hg.

Evaporator:	1.8
Ejector:	3.4

Temperatures, °F.

Furnace gas:	1650
Liquid:	178
Exhaust	177

Ultimate Analysis of fuel As Received.

H_2O	37.6%
C	40.3
H	6.6
O	9.9
N	0.6
S	0.3
Ash	4.7
	100.0%

Average Furnace gas Analysis

CO_2	15.0%
CO	0.0
O_2	4.9
N_2	80.1
	100.0%

Heating value of fuel = 6711 BTU

The efficiencies attained were higher than those in run 11. The total water evaporated per lb. of fuel was 3.35. Correcting for moisture in the fuel and for water of combustion, 2.38 lb. of water were evaporated per lb. of fuel fired. According to the calculations for run 11, the total water evaporated per lb. of fuel was 2.905. Making the necessary corrections, the net water evaporated per lb. of fuel fired was 2.4 lb.

From the temperature and analysis of the furnace gases the heat input to the evaporator was computed. On this basis the heat absorbed was 92% of the heat input. The overall efficiency, based on the heating value of the fuel, was approximately 51%. From a comparison of the efficiencies of runs 11 and 12 a higher rate of evaporation might be expected for run 12. However, a consideration of the heating values of the fuels which were 7379 BTU and 6711 BTU for runs 11 and 12, respectively, should explain the discrepancy satisfactorily.

The heat losses in the slurry and in the exhaust gases were neglible as shown in the heat balance for run 11. A certain percentage of the unaccounted for losses could undoubtedly be attributed to unburned carbon in the refuse. If it be assumed that the refuse contained 50% combustible matter, then, on the basis of 100 lb. of fuel, the undeveloped heat in the refuse was,

$$\frac{4.7}{0.5} \times 0.5 \times 14{,}544 = 68{,}400 \text{ BTU.}$$

The quantity of heat lost in the refuse would therefore amount to slightly over 10% of the heating value of the fuel. If the combined losses in the slurry and in the exhaust gases may be taken as 5%, it would appear, then, that the radiation losses were approximately 34%.

Table 20, Run 12

Time	Vacuum, in Hg. Evaporator	Ejector	Temperatures, °F. Furnace Gas	Liquid	Exhaust Gas
p.m. 2:30	1.9	2.8	1550	175	175
3:00	1.8	3.0	1580	179	173
3:30	1.5	2.7	1590	176	175
4:00	2.4	3.4	1610	177	175
4:30	2.7	3.1	1620	178	176
5:00	1.6	3.2	1650	175	174
5:30	1.8	3.2	1650	179	177
6:00	1.8	3.2	1670	180	179
6:30	2.2	3.6	1650	177	177
7:00	1.4	3.3	1680	177	177
7:30	1.6	3.4	1700	179	179
8:00	1.4	3.5	1700	178	178
8:30	2.1	4.2	1730	177	180
9:00	1.6	4.6	1730	180	175
9:30	1.7	4.6	1760	180	178

Conclusions

During the first eleven runs numerous changes were affected in order to determine the most suitable type of equipment. From the results of this series of experiments the following observations were made:

1. Horizontal hot gas inlets are preferable to the vertical.

2. A sharp-edged nozzle is superior to other arrangements mentioned previously.

3. The evaporator should be of circular or of otherwise "rounded" construction.

4. No filter is necessary for the furnace gases.

The use of vertical gas inlet pipes was found undesirable because of excessive scaling. This condition was brought about by the fact that the gas, after having left the nozzle, apparently passed up through the solution in contact with the external surface of the pipe. The alternate heating and wetting of the pipe surface led to the heavy scale deposition. This difficulty was practically eliminated by the use of a horizontal gas inlet tube and nozzle.

A sharp-edged, properly shaped nozzle possessed a two-fold advantage over several of the other arrangements. Firstly, a sharp-edged nozzle presented a relatively small surface upon which a cake might adhere and build up, and secondly, with proper design the gases attain a maximum velocity at the mouth of the nozzle. High gas velocities prevented, or more correctly, reduced the wetting of the inner surfaces of the nozzle near the mouth.

Scale deposition was more apt to occur on or around surface irregularities than on the smooth portions of the surface. Scaling was found to be more severe around seams, joints, corners, etc. A circular evaporator or possibly an elongated vessel with rounded ends with a surface free of irregularities should be superior to one built along less stringent specifications.

The presence of fly-ash and occasional quantities of soot in the lignite gases presented no particular difficulty. During the first several runs a small filter-box was in use for cleaning the gases entering the evaporator, but this devicewas later found inaffective and unnecessary. On several occasions the salt discharged from the evaporator was analyzed for insoluble matter, the quantities of which never exceded 0.2%. To attribute the entire amount of water-insoluble material to fly-ash and soot would be inadvisable. A certain percentage of this material may have been introduced as scale or sediment from the piping and feed tanks. However, with suitable furnace design the quantity of fly-ash brought into the system could readily be reduced to an allowable figure.

In a number of the early runs scale deposition on the walls of the evaporator was quite severe. This occurrence was especially noticeable when fresh solutions were charged to the evaporator. The scale formed in these instances was quite hard and could be broken only with difficulty. Although these deposits consisted of anhydrous sodium sulfate, they did not appear to be ~~really~~ readily soluble in warm water. The latter fact made scale removal a time-consuming operation. During several runs when scaling was severe, it was observed that relatively coarse crystals were formed. A photomicrograph of a typical sample is shown in figure 7. From this some conception of grain size variation may be gained.

In several runs no scale was deposited on the evaporator walls. This was accompanied by the formation of very fine crystals which were sufficiently small to be kept in suspension in the solution within the evaporator. In handling the discharged material it was found necessary to allow longer settling periods preceding decantation. A photomicrograph, figure 8, was taken of a sample of salt from run 11. From a comparison of figures 7 and 8 the difference in average grain size is seen to be quite marked.

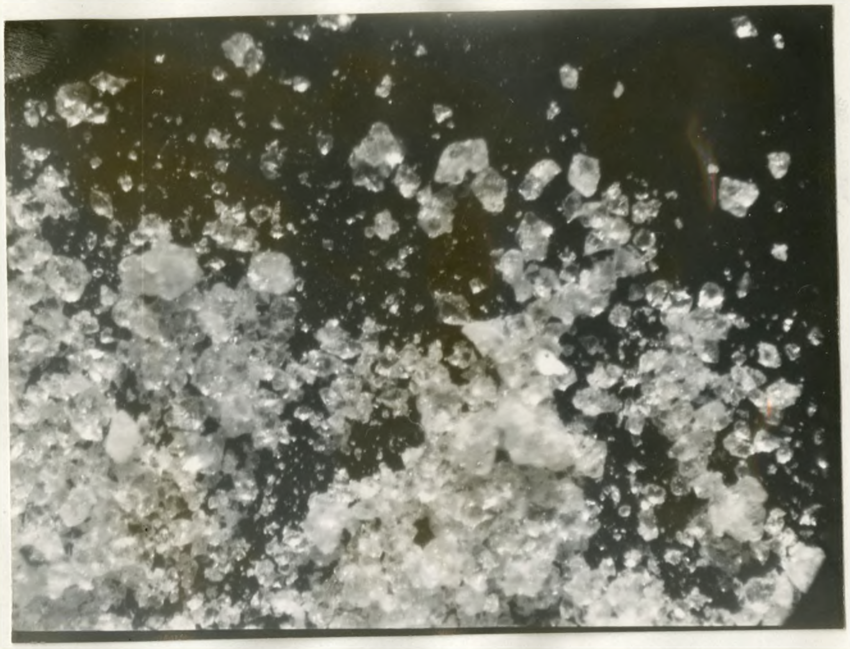


Figure 7

Figure 8

Several factors which might have affected grain size were rate of evaporation, degree of agitation and the presence of impurities in the solutions. Several runs were conducted under similar conditions but with varying results. In some cases scaling occurred but in others none was in evidence. The possibility existed that the matter of grain size was not so much dependent on operating conditions as it was on the presence of impurities in the solutions. Grain size seemed to affect the tendency toward scale formation. In the evaporation of sodium sulfate solutions, a certain amount of supersaturation occurred, the degree of which might well have been altered by the presence of seed crystals. When relatively coarse crystals were formed, a greater portion dropped to the cone of the evaporator but with the formation of a fine-grained product a relatively large percentage remained in suspension thereby avoiding higher degrees of supersaturation. With large grain size and the attending high degree of supersaturation the tendency for scale formation was greater.

In an attempt to determine the effect of impurities on grain size, runs 13 and 14 were conducted with every effort being made to maintain constant operating conditions. Samples were withdrawn from the evaporator periodically and carefully analyzed for iron, calcium and magnesium. The analytical data are shown in the following table.

Table 21

Hours of Operation	Percentage of Impurities		
	Fe	$CaSO_4$	$MgSO_4$
0	0.0556	0.119	0.0794
	0.0572	0.135	0.0792
	0.0573	0.133	0.128
		0.173	0.0813
8	0.0998	0.1050	0.0463
	0.1040	0.0982	0.0430
	0.0894	0.0786	0.0430
20	0.118	0.0969	
	0.123	0.0941	
	0.108		

A brief inspection of table 21 shows that the iron concentration increased with increasing time of operation while the percentages of $CaSO_4$ and $MgSO_4$ decreased. Additional data should be available before any conclusions are drawn regarding the effect of impurities. The samples were taken over a 20 hour period and may not have represented the changes that might have occurred over a longer period.

The estimated operating costs for the experimental plant on a 24-hour basis are shown below:

Item		Cost
Steam (30¢ per 1000 lb.)		
Low pressure	295 lb.	
High pressure	7200	
	7495 lb.	$ 2.25
Electric Power (5¢ per KWH)		
Pumping	5.961 KWH	
Stoker	4.47	
Lights	6.00	
	16.43 KWH	.82
Labor (50¢ per hour)		12.00
Fuel-$4.00 per ton		1.57
Raw material ($1.00 per ton)		
	1695 lb.	.85
		$17.49
Cost per ton of product		$47.00

The process apparently has commercial application but whether or not it will find immediate use is questionable. Figure 9 is a flow diagram for a proposed sodium sulfate plant. Lignite will be automatically fired to the furnace by means of a suitable stoker, probably of the overfeed type. The hot products of combustion will enter the circular evaporator through nozzles spaced about the evaporator circumference and leave the vessel under a slight vacuum produced by a rotary exhauster (not shown). Anhydrous sodium sulfate collecting in the cone of the vessel will be pumped as a 5% to 10% slurry to a settling tank, preferably elevated. A thick slurry, approximately 70% solids, will be removed from the settler and fed to a top-feed filter for further dewatering. The salt will leave the top feed filter with a moisture content of approximately 5% and enter a rotary drier where the salt will pass through the final drying stage. Raw Glauber's salt, conveyed from the deposits, will be fed to a log washer in order to disintegrate the larger lumps and to remove any adhering sand or silt. A saturated solution of sodium sulfate, will be circulated through the log washer to carry away in suspension any foreign matter introduced with the raw salt. A rotary filter will serve as a means of providing clean liquid feed for the log washer. The clean salt emerging from the log washer will be fed to a mixing and melting tank to which the combined liquors from the settler and top feed filter will also be charged. The resulting slurry will be pumped into the evaporator.

Summary

An experimental plant for the production of anhydrous sodium sulfate was successfully built and operated. From the results of a number of experiments the following observations were made:

1. Sharp-edged, horizontal nozzles fitted with scrapers were found satisfactory.
2. Smooth evaporator surfaces were least troublesome.
3. Fly-ash from the lignite furnace gases presented no difficulty.

The highest evaporator efficiency was 92% while the overall efficiency for the same run was calculated as 51%. The evaporation rate was 2.4 lb. of water per lb. of fuel fired.

An attempt was made to determine the cause of grain size variation. Because of the large number of variables encountered in operating the plant it was impossible to draw any definite conclusions in this connection.

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