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August 17, 1966

Charles R. Wilke
(M.S. Thesis)

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ABSTRACT

A practical application of the ability of a strain of Desulfovibrio to reduce sulfates to sulfide in concentrated brines is proposed. Using kinetic data from previous studies on the salt-tolerant strain, a continuous process for removal of sulfates from a ten per cent brine is designed, and the economics of the process are determined. A comparison is made with the economics of a conventional process which removes sulfates by precipitation with barium chloride. The results indicate that the bacterial process may be more economical for removing sulfates from brines of ten per cent NaCl or less, especially when large volumes are handled.

A proposal is made for adapting the bacterial reduction process to reclaiming sulfur from seawater, using a cheap carbon source such as sewage, and utilizing the sulfate-free effluent as feed for a seawater conversion plant.

Cost estimates are made based on the proposed design. These are compared with cost estimates for a plant removing sulfate from saturated (26.7%) brine by precipitation with barium chloride. Since the bacteria are not able to grow well in saturated brine, the additional cost of producing saturated brine from 10 per cent brine by evaporation is considered. Costs of the two processes for removing sulfates from brines of 10 per cent and less are estimated and compared.

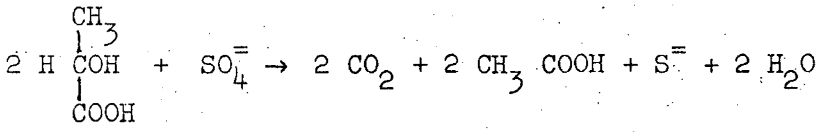
A further application of bacterial reduction of sulfate in recovering sulfur from seawater is hypothesized.

II. PRODUCTION OF SULFATE-FREE TEN PER CENT BRINE BY BACTERIAL SULFATE REDUCTION

A. Description of the Sulfate-Reducing Bacteria

In this study, the term sulfate-reducing bacteria refers to the Gram-negative, obligately-anaerobic vibrio of the genus *Desulfovibrio*. Though several species have been identified it is sufficient in this study to refer merely to the genus or to sulfate-reducing bacteria in general. The particular organism studied by Leban and Wilke,[2] and Edwards,[3] from which kinetic data for this work is taken, was isolated from mud at the bottom of salterns of the Leslie Salt Co. on San Francisco Bay.

Desulfovibrios carry out sulfate reduction as an integral part of an energy-yielding respiratory mechanism analogous to oxidative phosphorylation in aerobic metabolism. A mole of sulfate, as terminal electron acceptor, accepts 8 electrons as it is reduced to sulfide, thereby oxidizing the hydrogen-donating substrate, which may be gaseous hydrogen or any one of a large number of organic compounds. Oxidation of organic compounds is characteristically incomplete, invariably resulting in the formation of acetate. For example, the oxidation of lactic acid follows the relation



$$2\ \mathrm{H}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{COOH}}{\mathrm{COH}}} + \mathrm{SO_4^{=}} \rightarrow 2\ \mathrm{CO_2} + 2\ \mathrm{CH_3\,COOH} + \mathrm{S^{=}} + 2\ \mathrm{H_2O}$$

The cell obtains the carbon for growth from assimilatory reactions. A more complete description of the organism and its isolation, cultivation, and metabolism is given by Leban and Wilke.[2]

B. Growth and Kinetic Experiments

Early experiments[2] on the salt-tolerant Desulfovibrio were carried out on a batch basis, the bacteria being allowed to grow in bottles from which the air was excluded, and samples taken over a period of several days to determine cell concentration, sulfide concentration, and lactate concentration. Media used for the majority of the experiments contained lactic acid as a carbon source.

Later work[3] involved kinetic experiments with a continuous cultivator. The growth medium used was Medium M, described in Appendix E. The fermentation vessel consisted of a 2.3-liter enclosed glass cylinder. Temperature control was accomplished by flowing water through a jacket. Stirring was achieved by a magnetic mixer. Sulfide concentration was controlled by metering H_2S and N_2 through the fermentation broth. Nutrient medium was introduced at a controlled rate with a peristaltic pump and overflowing broth was collected in a waste bottle. A schematic description of the apparatus is shown in Fig. 1. Kinetic data from this apparatus are used in this study and shown in Figs. 3 and 4.

Most experiments performed on the salt-tolerant strain were with media containing 10 per cent NaCl and lactic acid. The bacteria grew well in 10 per cent salt but more slowly in 16 per cent salt. It can be expected that growth would be even less favorable in saturated salt solutions, but quantitative information is lacking. The experiments showed that the addition of yeast extract to the growth medium improved growth rates. Use of this data for design of an industrial-scale fermentation where yeast extract is not added is therefore not strictly valid unless it is assumed that the raw material used as nutrient (molasses) contains some of the growth factors evidently present in the yeast extract.

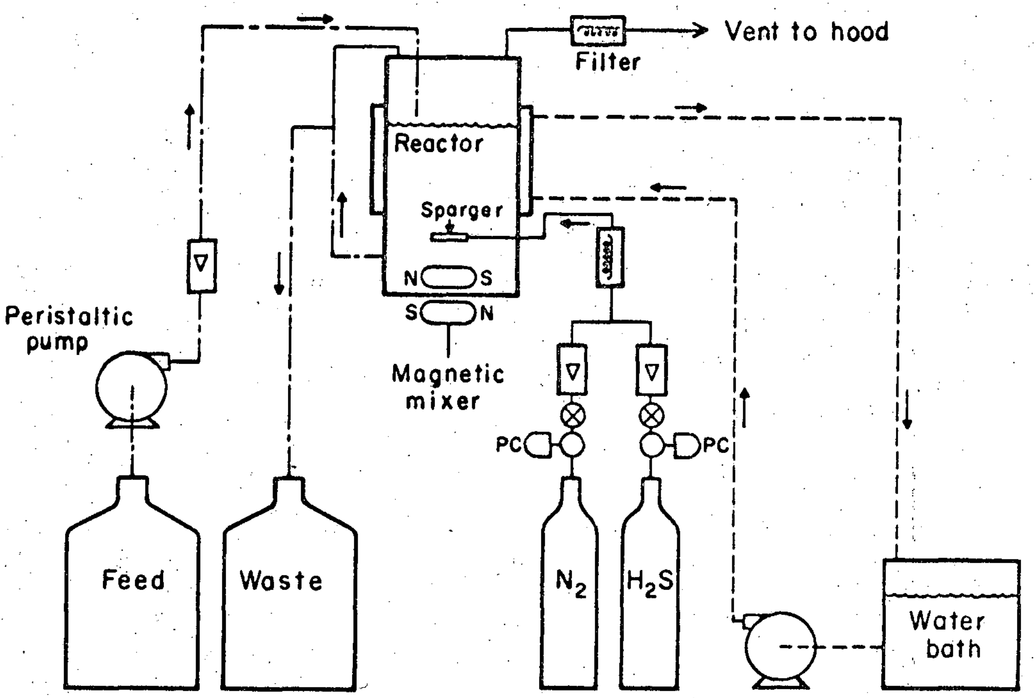


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Fig. 1. Apparatus for kinetic studies on salt-tolerant Desulfovibrio.

Therefore the present study must be regarded as a preliminary assessment to determine whether or not further study of this method for sulfate removal would be justified. For a more accurate assessment, kinetic and yield data should be obtained with substrate and process conditions corresponding more closely to the proposed process.

C. Process Description

1. Design Basis

In order to determine the economic feasibility of bacterial sulfate reduction, the costs involved in removing the sulfate from a given quantity of sulfate-containing rock salt by this method is compared with the costs of removing the sulfate from the same quantity of rock salt by precipitation of barium sulfate from barium chloride. The initial comparison is made between a plant which produces a 10 per cent sodium chloride brine with bacterial sulfate removal and a plant producing saturated brine (26.7 per cent sodium chloride) with barium chloride precipitation. A comparison is then made between the costs for the same barium chloride plant and the costs for a bacterial sulfate reduction plant producing saturated brine concentrated from 10 per cent by evaporation.

The reason for design on the basis of 10 per cent brine in the case of bacterial sulfate removal is that the laboratory studies on which the design is based involved the growth of Desulfovibrio in a 10 per cent sodium chloride medium.[2,3] It is felt that an extrapolation of the kinetic data from a 10 per cent environment to 26.7 per cent would not be warranted but that useful conclusions could still be drawn from the design of a plant processing 10 per cent brine, providing the same quantity of sulfate were processed as that in the barium chloride process.

The plant size chosen for this study is based on a daily chlorine production of 50 tons. With a consumption of 1.7 tons of sodium chloride per ton of chlorine, the amount of rock salt processed is 85 tons per day.

Losses of salt in the purification step are assumed negligible. This plant capacity is probably about the average for the caustic-chlorine industry, although the recent trend is to build plants in excess of 100 tons per day.

No attempt is made in proposing the plant design to choose the most favorable plant location and it is assumed that the cost factors due to location average out to a negligible value. The rock salt used by the plant comes from Kingman, Kansas, and a logical choice for plant site would perhaps be in this area. This particular rock salt was chosen for the study because the relatively high sulfate content would dictate the need for purification in application to the chlorine-caustic process. Advantages of sulfate removal by bacteria would logically be more likely in treatment of brines of high sulfate content, since larger quantities of expensive barium chloride would be required per unit of rock salt processed. The composition of the rock salt of interest is shown in Table 1.[4]

In the design, the following further assumptions are made:

(a) The land necessary for the plant is already owned and available.

(b) Facilities for utilities such as steam and cooling water are available for use, having been built to serve a hypothetical chlorine-caustic complex or other nearby chemical plant.

(c) Storage and handling facilities for the rock salt have been built.

(d) Administrative offices, laboratories, cafeteria, clinic, etc., and attendant personnel are in existence as part of the complex as a whole.

(e) Capital is company-owned.

Table 1. Composition of rock salt from
Kingman, Kansas[4]

Constituent	% by weight
NaCl	97.51
$CaSO_4$	1.51
Na_2SO_4	0.57
$MgCl_2$	0.10
Fe_2O_3	0.11
Insolubles	0.20

Per cent by weight $SO_4^{=}$ = 1.46%

2. General Process Description

The process can be divided into several steps, as illustrated in Fig. 2.

a. Feed preparation. First, the sulfate-containing rock salt must be dissolved in water along with a suitable carbon substrate and other nutrients for growth of sulfate-reducing bacteria.

b. Anaerobic fermentation. This is the main step of the process. Desulfovibrio is allowed to grow in a continuous cultivator under strictly anaerobic conditions. Cellular material is formed at the expense of the carbon substrate while the energy for cellular activity is obtained by reduction of the sulfate in the brine to sulfide.

c. Removal of H_2S. The sulfide formed from the sulfate is partially evolved as H_2S in the fermentor, but the remainder stays in solution. This sulfide must be removed, preferably as H_2S, from the brine stream and suitably disposed of.

d. Removal of organics. Unmetabolized organic material and additional organic matter produced in the anaerobic fermentation must also be removed from the brine before it can be used.

e. Clarification. Finally, the brine stream is freed of all particulate matter and is decolorized, emerging as a clear, sulfate-free effluent.

3. Selection and Design of Process Steps

In this section, the development of the final process is described, as alternative methods of carrying out each process step are discussed and the design of the major processing equipment is carried out. Design calculations for minor and auxiliary equipment for the process are shown in Appendix A.

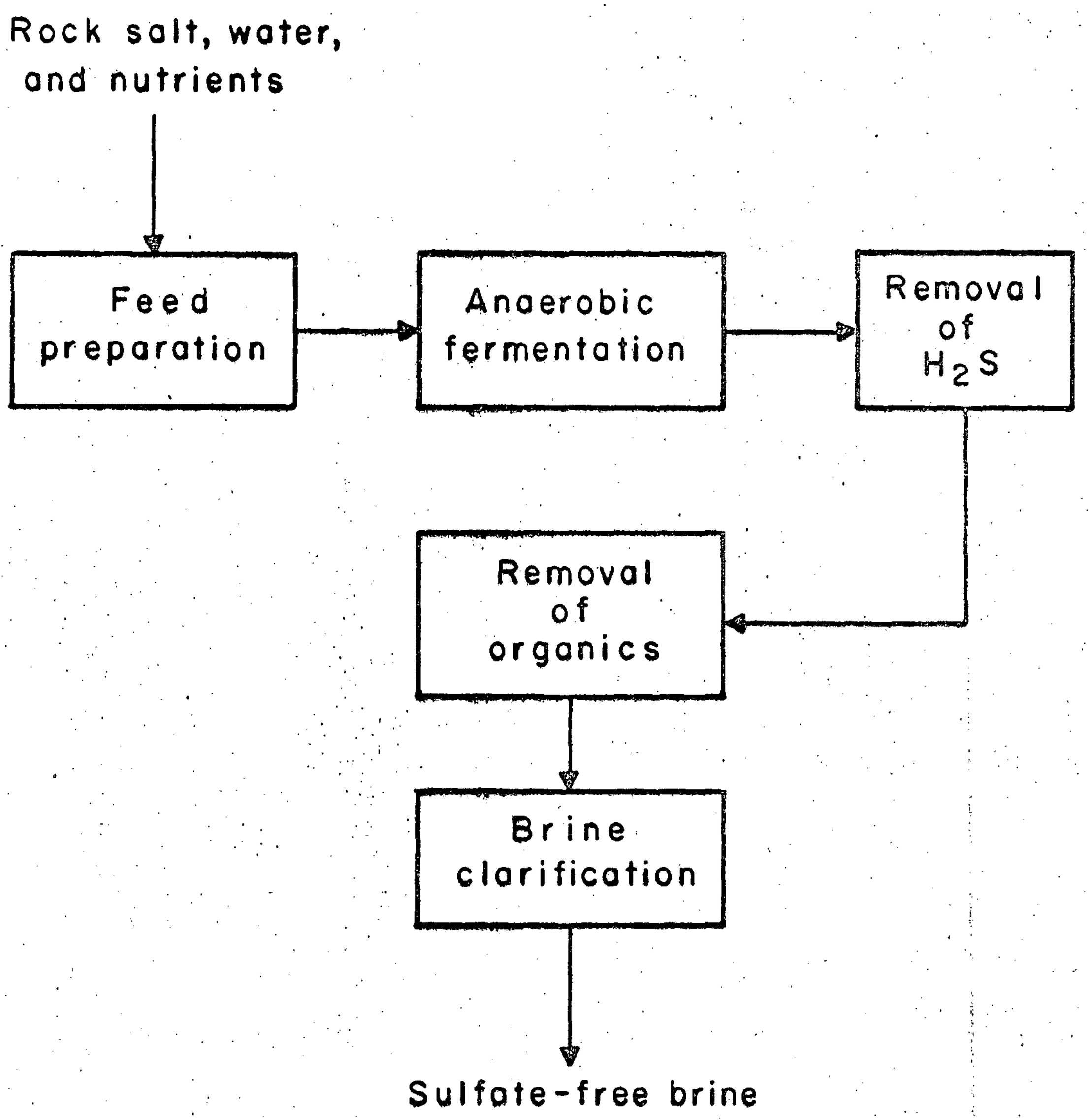

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Fig. 2. Schematic description of a process for removing sulfate from brine by bacterial reduction to sulfide.

a. Feed preparation. The initial design for preparing feed solution for the fermentation involved three large agitated tanks for dissolving rock salt and mixing in nutrients batchwise, each tank discharging its contents alternately after one hour of mixing into a large holding tank. This design proved costly in terms of capital investment and labor requirements and a more economical continuous system was designed. The continuous system is a variation of the method for producing saturated brine from rock salt for the caustic-chlorine industry, namely, the technique of passing water through a bed of rock salt so that it emerges completely saturated in sodium chloride. Rock salt from a large pile or storage bin is fed continuously to a belt conveyor which transfers the salt at a rate of 7,090 pounds per hour to the top of a 20-foot concrete saturation tower. The tower is thus kept full of rock salt while 19,000 pounds per hour of process water flows upward through the salt bed and overflows at the top fully saturated with sodium chloride. The saturated brine flows by gravity to a 2,000-gallon blending tank where it is diluted continuously with 42,800 pounds per hour of process water to a concentration of about 10 per cent sodium chloride. The necessary nutrient, molasses, and the minerals, phosphoric acid, ammonium chloride and sodium sulfide, are pumped at constant flow rate from storage tanks and mixed with the brine in the blender to form a continuous stream of nutrient medium for the microbial sulfate reduction. This method eliminates the need for controlled feeding of rock salt to a dissolving tank that would require a higher residence time than a blending tank which handles fluids only.

The storage tanks for molasses and phosphoric acid are designed for one month's supply, while the mineral storage tank holds approximately one day's supply. Mineral solution is made up daily in a batch mixer. The feed blender is designed for an average residence time of fifteen minutes. Calculations on the design of the feed preparation equipment including conveyor, saturation tower, blending tank, storage tanks and associated pumps are shown in Appendix A.

b. Anaerobic fermentation. Kinetic data by Leban et al.[3] and Edwards and Wilke,[6] are used to design a fermentor for carrying out sulfate reduction by bacteria. A sulfate-removal efficiency of 99 per cent is chosen because it corresponds to a sulfate concentration in the fermentor (and effluent concentration) of 0.2 mM/l, for which data from a continuous laboratory experiment are available, as shown in Figs. 3 and 4. These data, however, most likely do not demonstrate the true dependence of specific growth rate on sulfate concentration. In designing the fermentation system, sulfate concentration is assumed to be the limiting growth factor, while it appears that the curve of Fig. 3 does not pass through the origin as it should for true sulfate limitation. Unfortunately, these are the only kinetic data available for design purposes, since, as Leban and Wilke[2] have pointed out, very little quantitative data on sulfate reduction by bacteria has been published in contrast to the considerable research done on physiology, morphology and ecology of genus Desulfovibrio. Investigation of sulfate-limited growth kinetics is necessary if the economic advantages of sulfate removal from brines or other solutions are to be exploited. The data further suffer from the fact that the laboratory medium for growth contained yeast extract which was shown to be an important factor in the growth rate of Desulfovibrio. Further research would demand the investigation of growth under conditions expected in a large-scale application.

For instance, the utilization of bacteria for recovering sulfur from seawater would require knowledge of growth kinetics in seawater with nutrients such as molasses or even raw sewage as carbon sources. Use of yeast extract to furnish growth factors on a industrial scale would be prohibitive because of high cost. It is possible that these unknown growth factors may be present in molasses or raw sewage, however.

Use of the data from Figs. 3 and 4 will give only an approximate design figure for a fermentor, but if the cost of the fermentor is not the dominating factor in the economics of the process, conclusions may still be drawn concerning the feasibility of the method.

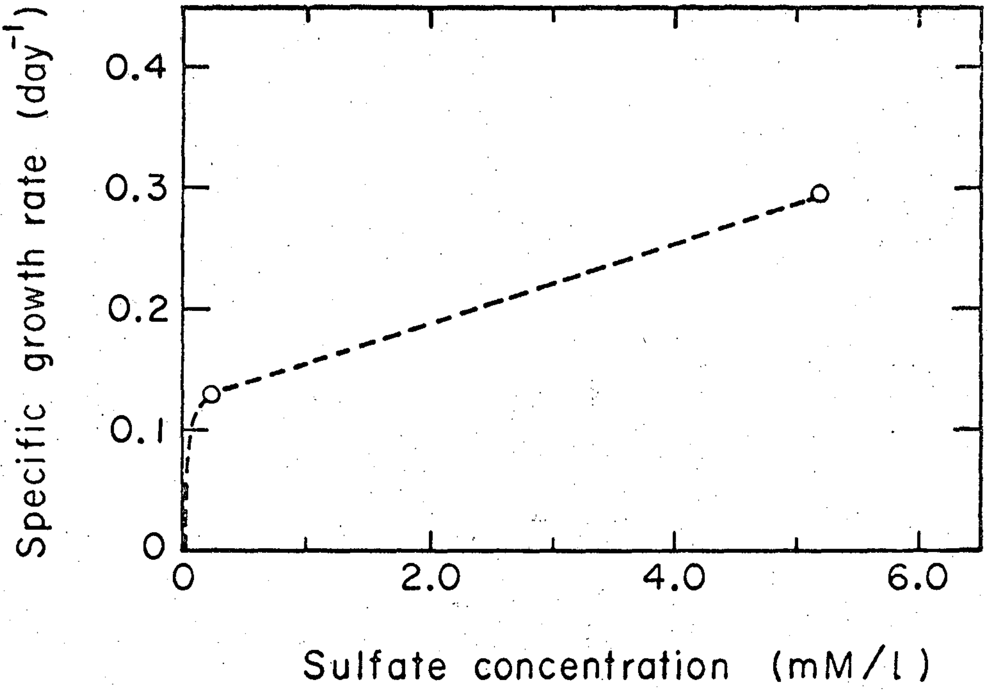

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Fig. 3. Effect of sulfate concentration on specific growth rate of salt-tolerant Desulfovibrio.

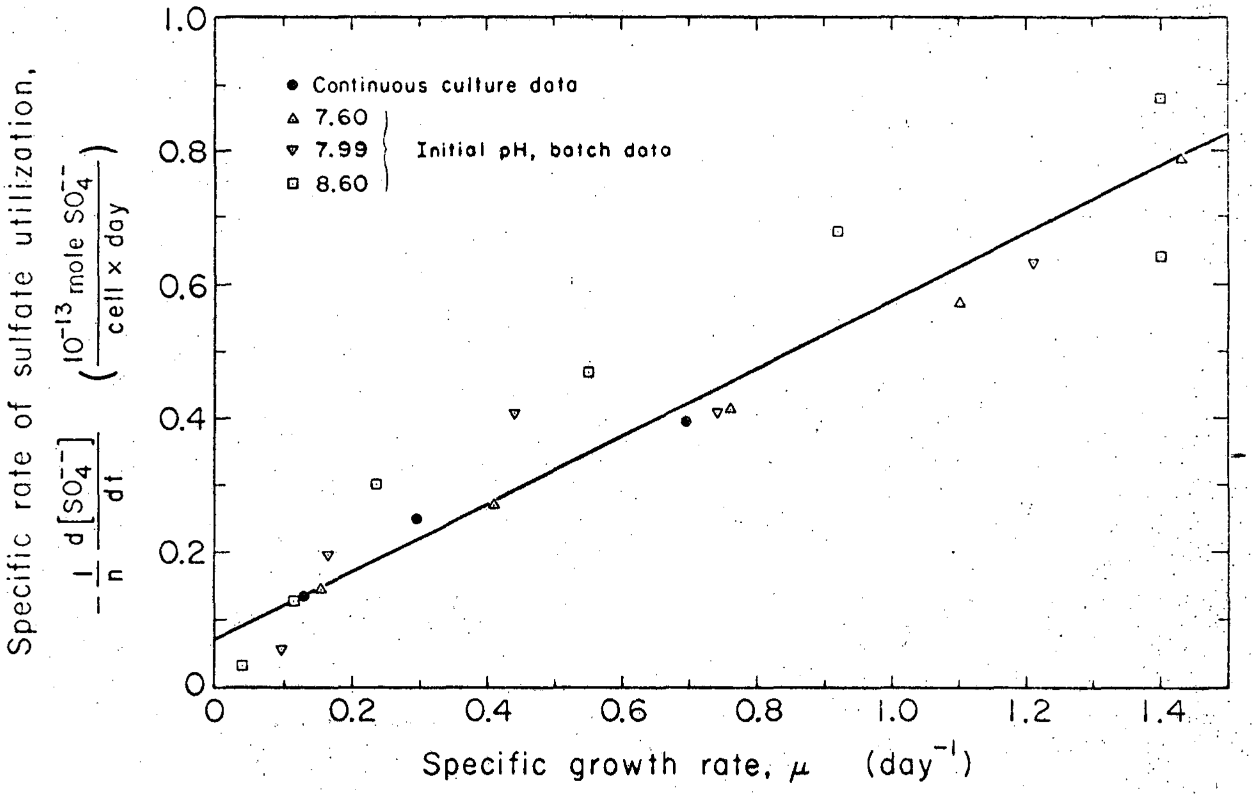

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Fig. 4. Specific rate of sulfate reduction as a function of specific growth rate of Desulfovibrio.

The following fermentor designs were considered for carrying out sulfate reduction:

(a) Single-stage, stirred tank.

(b) Two-stage, stirred tank.

(c) Single-stage, stirred tank with centrifuge recycle.

Of these three alternatives, the single-stage stirred tank with centrifuge recycle shows the most promise on the basis of economy. Approximate installed cost of each alternative design is given in Table 2. The contributing factor to high cost in the first two designs is the tremendously large volume--on the order of 1 million gallons--necessary to carry out the slow fermentation process. With such large volumes, adequate mixing is a definite problem.

By centrifugation of the effluent from the fermentor, the cells are concentrated in a slurry and returned to the fermentor. A high steady-state concentration of cells is maintained in the fermentor in this manner, thereby reducing the required volume by a factor of about 200.

The design calculations for the single-stage and two-stage stirred tank fermentors are shown in Appendix A. Design of the single-stage fermentor with centrifuge recycle is carried out as follows:

(1) Design of fermentor:

Design criteria:

Initial sulfate s_o = 18.3 mM/l (millimoles per liter)

Effluent sulfate s_1 = 0.2 mM/l (99 per cent reduction)

Dry weight of cells = 10^{-12} g/cell

Wet weight of cells = 2.5×10^{-12} g/cell

Volume of cells = 2.5×10^{-12} ml/cell (density 1 g/cc)

Table. 2. Installed costs of various fermentor designs

Design Type	Installed Cost, February 1966
Single-stage stirred tank	$153,000
Two-stage stirred tank	123,000
Single-stage stirred tank, centrifuge recycle	54,000

The maximum practical concentration of dense culture obtained in the fermentor is assumed to be 10 per cent cells by volume.

10% by volume = 0.1 ml cells/ml solution

$$x_1 = (0.1 \text{ ml cells/ml})/(2.5 \times 10^{-12} \text{ml cells/cell}) = 4 \times 10^{10} \text{ cells/ml}$$

This represents a concentration 150 times the normal maximum concentration obtained in a batch culture.

A continuous centrifuge is used to concentrate the effluent and the thickened slurry is recycled back to the fermentation vessel. Assuming the returned slurry is 50 per cent cells by volume, (see following section on design of the centrifuge) the concentration factor, c, will have a value of 5.

Referring to Fig. 5(c), a cell balance over the entire system yields at steady-state:

$$\frac{F}{V_1} x_2 = \mu x_1 \tag{1}$$

where F = volumetric flow rate, gal/day

V_1 = volume of fermentor, gal

x_2 = cell concentration in effluent stream, cells/ml

μ = specific growth rate of the cells, day^{-1}

A sulfate balance over the entire system gives:

$$\frac{F}{V_1}\left[s_o - s_1\right] = \left(\frac{1}{x_1}\frac{ds_1}{dt}\right) x_1 \tag{2}$$

where $\left(\frac{1}{x_1}\frac{ds_1}{dt}\right)$ = specific rate of sulfate reduction,

mM/(cell)(day).

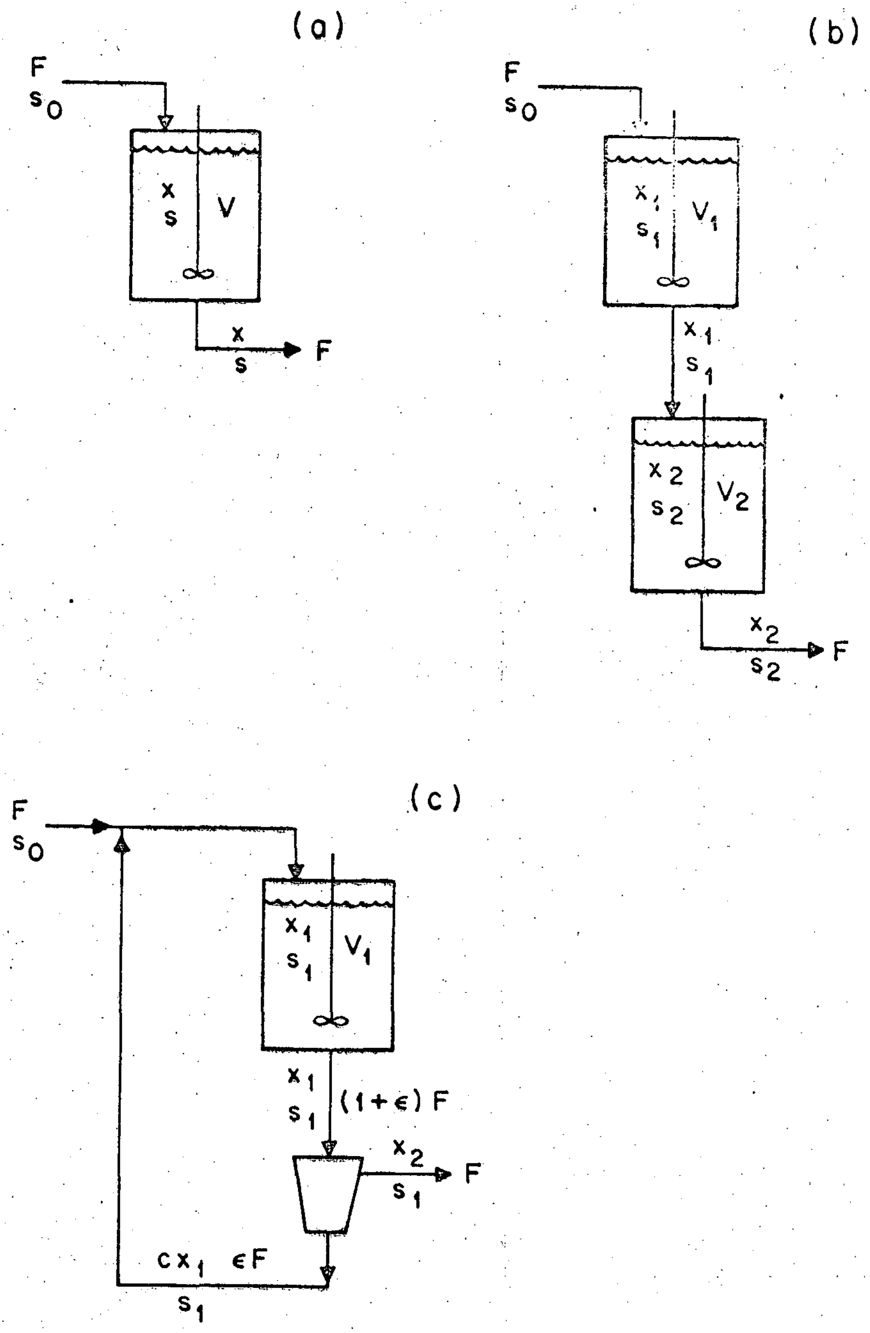

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Fig. 5. Alternative designs of a continuous cultivator for bacterial sulfate reduction.

Then, $$V_1 = \frac{F\left[s_o - s_1\right]}{\left(\frac{1}{x_1}\frac{ds_1}{dt}\right)x_1} \qquad (3)$$

for $s_1 = 0.2$ mM/l ,

$\mu = 0.13$ day^{-1} from Fig. 3

$\left(\frac{1}{x_1}\frac{ds_1}{dt}\right) = 0.125 \times 10^{-10}$ mM/(cell)(day) from Fig. 4 .

$$V_1 = \frac{(18.3-0.2)(187,000)}{(0.125 \times 10^{-10})(4 \times 10^{13})}$$

$V_1 = 6770$ gallons

From Eq. (1) ,

$$x_2 = x_1\left(\frac{V_1}{F}\right)\mu$$

$$x_2 = (4 \times 10^{10})\left(\frac{6770}{187,000}\right)(0.13) = 1.88 \times 10^8 \text{ cells/ml}$$

A cell balance on the centrifuge yields:

$$x_1(1 + \epsilon)F = cx_1\epsilon F + Fx_2$$

where ϵ is the fraction of feed recycled to the fermentor and c is the concentration factor, having a value of 5 as previously mentioned.

$$\epsilon = \frac{x_1 - x_2}{x_1(c-1)}$$

Since $x_1 >> x_2$.

$$\epsilon = \frac{1}{c-1}$$

$$\epsilon = \frac{1}{5-1} = 0.25$$

The recycle rate ϵF will then be:

$$\epsilon F = (0.25)(7800 \text{ gal/hr}) = 1950 \text{ gal/hr} = 32.5 \text{ gpm}$$

The concentration in the recycle stream cx_1, is:

$$cx_1 = 5(4 \times 10^{10} \text{ cells/ml}) = 2 \times 10^{11} \text{ cells/ml}$$

The reduction in fermentor volume from the case of a single stirred-tank fermentor is more than 200-fold. The investment cost including the centrifuge is lower than for the other designs, as shown in Table 2.

(2) Design of centrifuge:

The design of a continuous centrifuge from theoretical principles alone is not generally possible in the present state of knowledge. The scale-up method of Ambler[15] may be useful when pilot-plant or laboratory data are available but in most cases full-scale test runs by the manufacturer are necessary for determining whether a given separation can be accomplished by centrifugation. This is especially true in the case of the disc-type centrifuge with nozzle discharge, where such variables as the nozzle diameter are determined by trial-and-error in full-scale equipment. Nozzle-discharge centrifuges such as manufactured by DeLaval find use in the separation of yeast "cream" from the fermentation broth in the manufacture of baker's yeast. These centrifuges can handle large volumes of slurry and can concentrate solids up to 50 per cent by weight,[2] and are therefore suitable for the purposes of this design.

Perry[2] and Flood[3] have given a few design criteria from which an appropriately-sized disc centrifuge may be chosen and its cost estimated. Cost data taken from Flood are plotted and shown in Appendix F.

The centrifuge should be able to handle 165 gpm or more of liquid throughput and discharge up to 1.6 tons of dry solids per hour. According to Perry and Flood, a nozzle-discharge centrifuge with a 30-inch bowl would be required for these conditions. This type of centrifuge typically draws 15 to 40 kw hr/ton. With 4 tons/hr of solids (wet basis) the power required is 100 kw hr or 135 hp, which is typical of examples given by Perry. The presence of hydrogen sulfide requires the use of stainless steel for all wetted parts.

Since this design has not been based on experimental work with centrifuges, there is no guarantee that it will work. Neither has the assumption that the kinetics will remain the same for dense cultures as in usual cultures been tested experimentally. At best, it is an adaptation of a design that has found some use, though not extensive, in the fermentation industry. It is proposed in this study because of the economic advantages it offers. Its successful exploitation in industry requires more research into kinetics of dense cultures and centrifugation of bacterial cells.

c. Removal of H_2S. Sulfides in solution are highly corrosive to metals and even concrete and as such are much less tolerable than the sulfates from which they originated. There are several methods which can be used for removal of sulfides:

(1) Oxidation of sulfides to sulfur with Cl_2

(2) Formation of insoluble sulfide, e.g., FeS

(3) Stripping H_2S with air

(4) Steam-stripping H_2S

The first two methods are simple and inexpensive when the level of sulfides is low. But they introduce new contaminants to the brine stream and since precipitates are formed, further processing is required. It is not likely that sulfur or a usable sulfur product can be recovered economically from the first two methods since the precipitates will be mixed with cells and cellular debris from the fermentation and activated-sludge process (which is discussed in the next section dealing with removal of organics). If the pH is 7.0 or less, a majority of the sulfide can be stripped out as

H_2S. Stripping with air is a widely-used technique and is effective in H_2S removal. The major drawback in this case is that the H_2S gas is diluted by a large volume of air, making recovery of the gas for possible sulfur manufacture difficult. Release of the H_2S-containing air to the atmosphere is to be avoided, since it presents an air-pollution problem.

Steam-stripping has the advantage of producing an effluent gas rich in H_2S, making it directly amenable to sulfur recovery and eliminating the pollution problem. A full discussion of various alternatives for disposal of the H_2S is given in Section D of this chapter.

For this study, we will postulate that H_2S is not to be discharged to the air, keeping the process as clean as possible. This dictates that a steam-stripper should be incorporated into the process. The procedure involved in the design of the stripper follows:

(1) Calculation of sulfides in gas and liquid effluents from the fermentor:

Formation of gas in the fermentation generally follows the stoichiometry

$$C_6H_{12}O_6 + SO_4^{=} \rightarrow 2\ CO_2 + 2CH_3COOH + 2H_2O + S^{=}$$

Thus, for every mole of H_2S formed, two moles of CO_2 are also formed.

The flow rate of rock salt is 85 tons per day or 7090 lb/hr. With sulfate at 1.46 per cent, and with a 99 per cent conversion of sulfate to sulfide, the amount of H_2S potentially produced is calculated as (0.0146) (7090)(0.99)(34/96) = 36 lb H_2S/hr. The amount of CO_2 formed will be (2) (36)(44/34) = 93 lb/hr.

Both the H_2S and CO_2 will dissolve to a certain extent in the brine, according to their respective solubilities. Figures 6 and 7 give the solubilities of H_2S and CO_2 in NaCl brines as a function of temperature. The broken curves are extrapolations or interpolations which should be

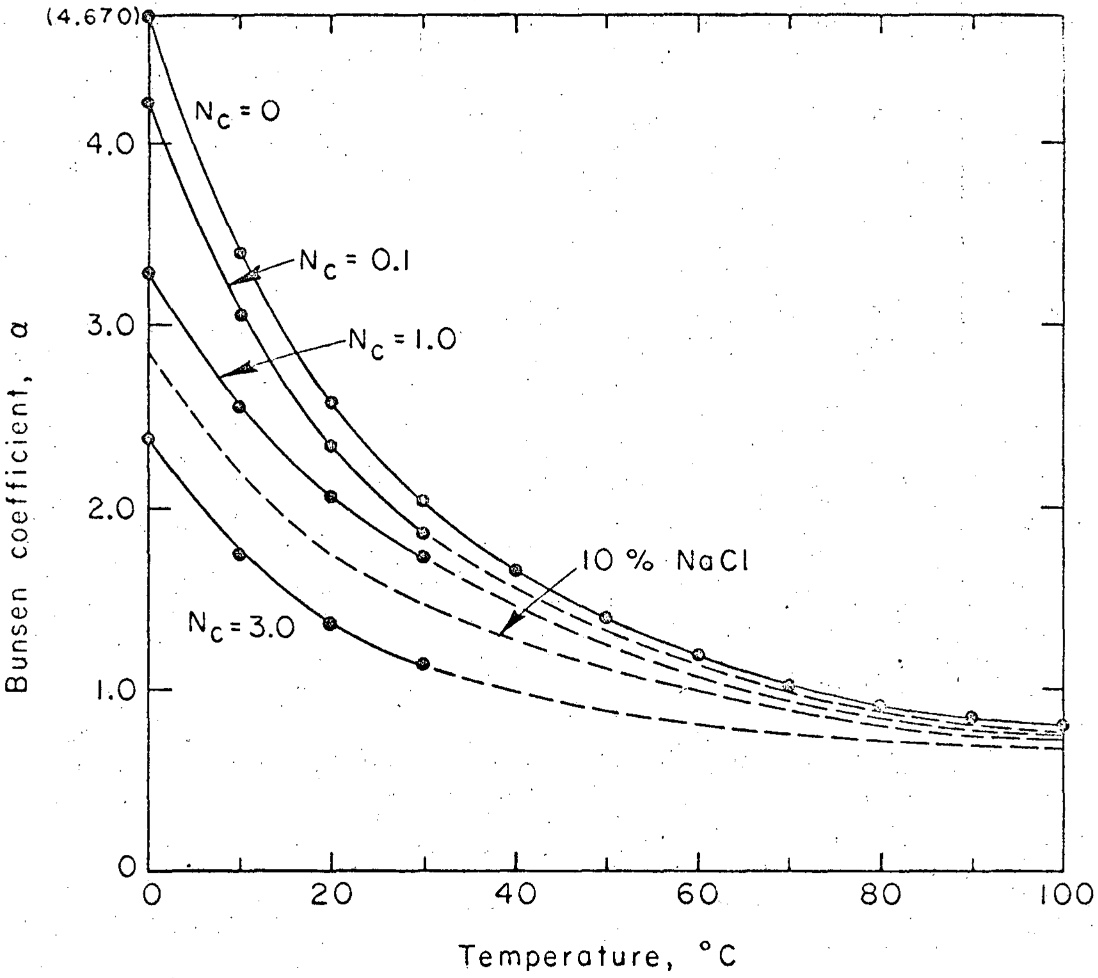

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Fig. 6. Solubility of H_2S in water and NaCl brines.[33,52] N_c = g-equiv. of NaCl per liter. α = volume of H_2S at STP per volume of solution. Partial pressure of H_2S = 1 atm.

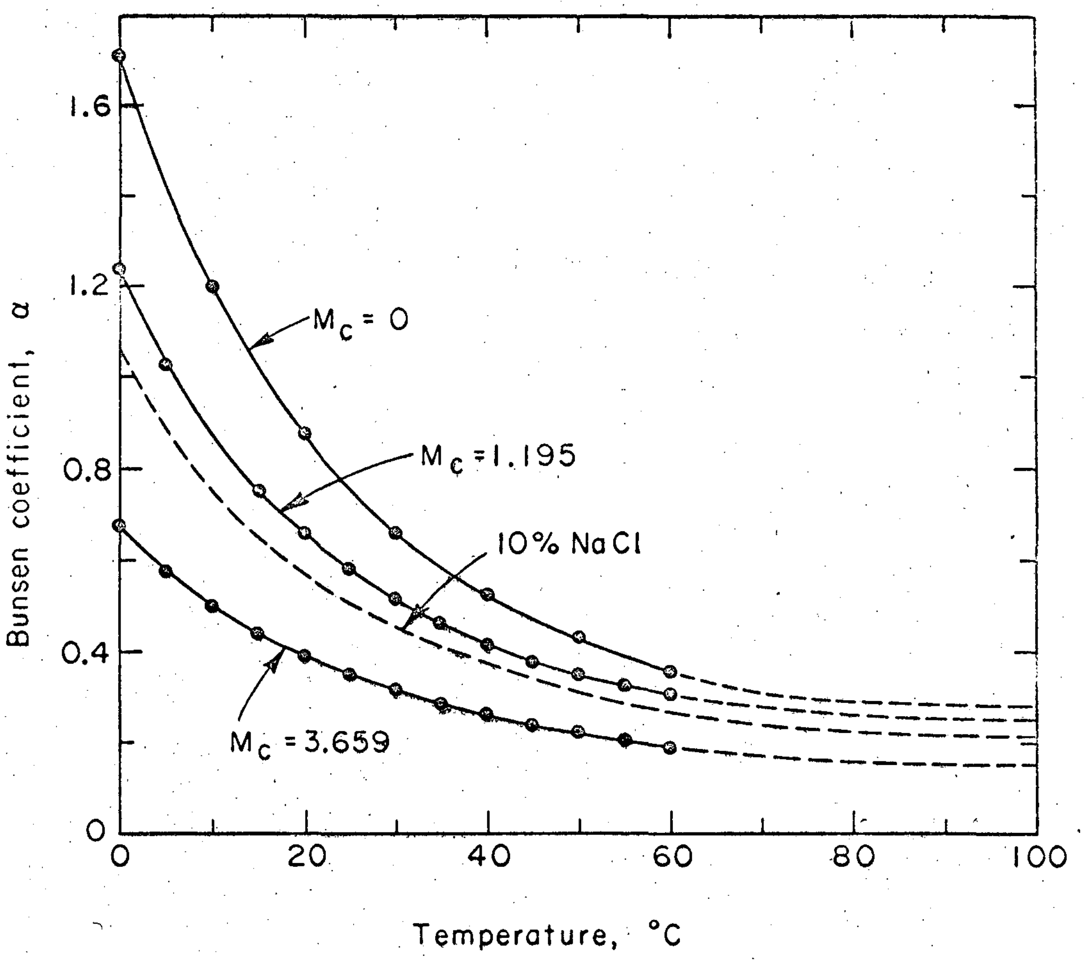

Fig. 7. Solubility of CO_2 in water and NaCl brines.[33,52] M_c = moles NaCl per liter. α = volume of CO_2 at STP per volume of solution. Partial pressure of CO_2 = 1 atm.

reasonably accurate. These curves show that the presence of NaCl lowers the solubilities of the gases.

An H_2S material balance on the fermentor illustrated in Fig. 8 may be written as:

$$x_1L + y_1G = 1.06$$

where x_1 = mole fraction H_2S in liquid

y_1 = mole fraction H_2S in effluent gas

L = total liquid molar flow rate, lb-moles/hr

G = total gas molar flow rate, lb-moles/hr

Similarly for CO_2,

$$x_2L + y_2G = 2.12$$

H_2S and CO_2 in the gas are in equilibrium with the liquid according to Henry's law:

$$y_1 = \frac{H_1x_1}{P}$$

$$y_2 = \frac{H_2x_2}{P}$$

where H_1, H_2 = Henry's law constants for H_2S and CO_2

P = total pressure

An additional equation can be written:

$$y_1 + y_2 = 1$$

Since the gaseous species are very dilute in the liquid, L can be closely estimated as the total molar flow of water and NaCl.

	lb/hr	lb-moles/hr
water	61,900	3440
NaCl	6,910	118

L = 3560 lb-moles/hr

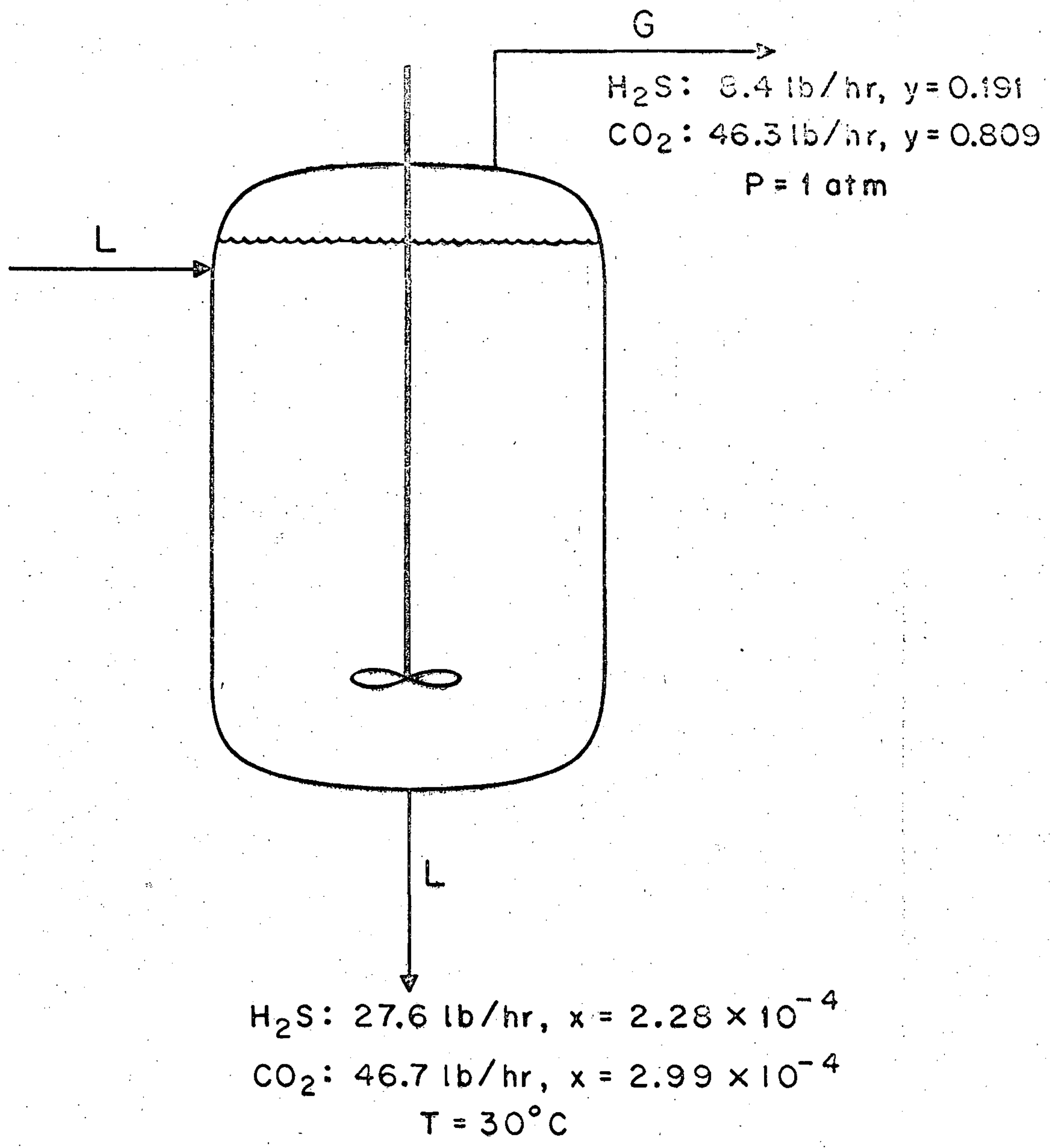

Fig. 8. Distribution of H_2S and CO_2 in liquid and gas effluents from the anaerobic fermentor.

As estimated from Fig. 6 at 30°C, 1 atm partial pressure, $\alpha_1^{30} = 1.48$ l H_2S/l H_2O. For dilute solutions, the Henry's law constant is calculated as follows:

Since $H_1 = p_1/x_1$

$$H_1^{30} = \frac{1 \text{ atm}}{(1.48 \text{ l } H_2S/\text{l } H_2O)/(22.4 \text{ l } H_2S/\text{g-mole})(55.5 \text{ g-moles/l } H_2O)}$$

$$H_1^{30} = 840 \text{ atm/mole fraction}$$

From $\alpha_2^{30} = 0.46$

$$H_2^{30} = 2700 \text{ atm/mole fraction}$$

We have written five equations, and now there are five unknowns, x_1, y_1, x_2, y_2, G, which can be solved for.

Thus, $y_1 = 0.191$

$y_2 = 0.809$

$x_1 = 2.28 \times 10^{-4}$

$x_2 = 2.99 \times 10^{-4}$

$L_1 = 0.81$ lb-moles/hr = 27.6 lb/hr

$L_2 = 1.06$ lb moles/hr = 46.7 lb/hr

$G_1 = 8.4$ lb/hr

$G_2 = 46.3$ lb/hr

(2) Design of steam-stripping column:

Having established the concentrations of H_2S and CO_2 in the brine from the fermentor, a suitable steam-stripping column for removal of the remaining gases can be designed.

Consider the column illustrated in Fig. 9. Overall material balances for H_2S and CO_2 are:

$$L(x_1^F - x_1^1) = G_E Y_1^E \tag{1}$$

$$L(x_2^F - x_2^1) = G_E Y_2^E \tag{2}$$

also, $$y_1 + y_2 + y_S = 1 \tag{3}$$

and $$y_S = \frac{G_S}{G_E} \tag{4}$$

The subscripts 1, 2, S refer to H_2S, CO_2 and steam, respectively. G_E is the total molar flow of gas in the column effluent.

The following assumptions are made about the operation of the column:

(a) The steam flow rate G_S is constant throughout the column.

(b) The column operates isothermally at 212°F and the total pressure in the column is constant at 1 atm (pressure drop is negligible).

(c) The brine molar flow rate, L, is constant.

Writing material balances for H_2S and CO_2 on the n^{th} plate in the column,

$$G_S\left[\frac{y_1^n}{1 - y_1^n - y_2^n} - \frac{y_1^{n+1}}{1 - y_1^{n+1} - y_2^{n+1}}\right] = L\left[x_1^n - x_1^{n+1}\right] \tag{5}$$

$$G_S\left[\frac{y_2^n}{1 - y_1^n - y_2^n} - \frac{y_2^{n+1}}{1 - y_1^{n+1} - y_2^{n+1}}\right] = L\left[x_2^n - x_2^{n+1}\right] \tag{6}$$

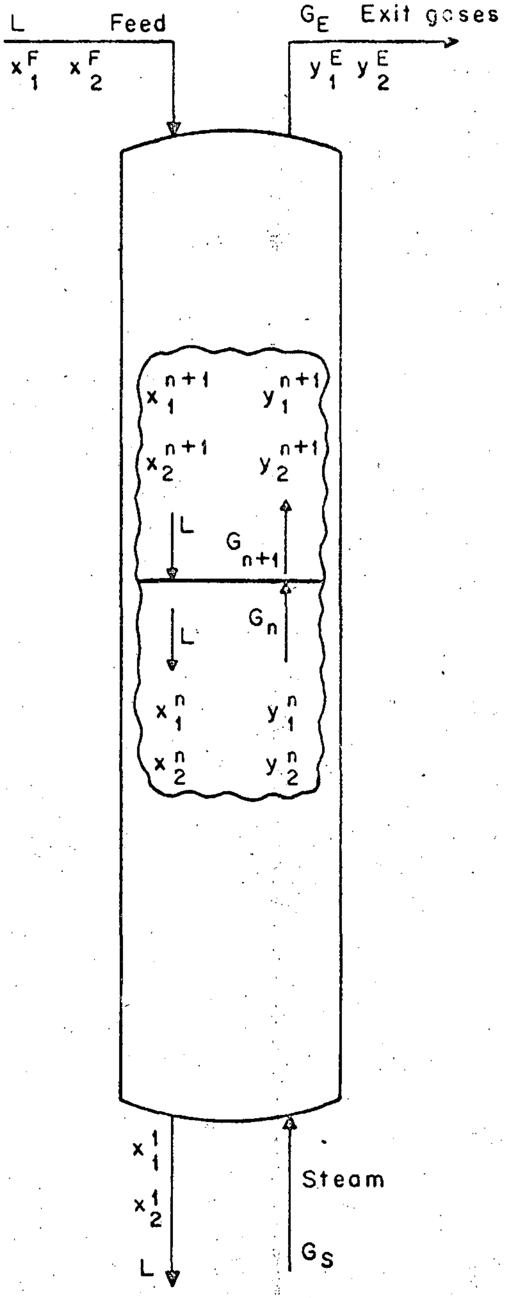

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Fig. 9. Material balances on the nth plate of a bubble-plate steam stripper.

recalling that x_1 and $x_2 << 1$. Equations (5) and (6) describe the operating line of the column on a McCabe-Thiele type diagram. The equilibrium relationships for the n^{th} plate are represented by Henry's law at 1 atm:

$$y_1^{n+1} = H_1 x_1^n \qquad (7)$$

$$y_2^{n+1} = H_2 x_2^n \qquad (8)$$

The Henry's law constants are obtained from Figs. 6 and 7. For H_2S, at 100°C and 1 atm partial pressure,

$$\alpha_1^{100} = 0.975$$

$$H_1^{100} = 1/(0.975)/(22.4)(55.5)$$

$$H_1 = 1280 \text{ atm/mole fraction}$$

similarly,

$$\alpha_2^{100} = 0.215$$

$$H_2^{100} = 1/(0.215)/(22.4)(55.5)$$

$$H_2 = 5790 \text{ atm/mole fraction}$$

The liquid molar flow rate is 3560 lb-moles/hr. The steam rate G_S is specified at 5 lb-moles/hr. This value was obtained by roughly doubling the minimum steam flow rate of 2.11 lb-moles/hr calculated from a McCabe-Thiele diagram (Fig. 10) for the binary system H_2S-H_2O at 100°C. A 95 per cent removal of H_2S is specified and at a steam flow rate of 5 lb-moles/hr, about 3.5 theoretical plates are required, assuming the CO_2 has no effect on the stripping.

A more rigorous design taking into account the CO_2 as well as the H_2S requires the use of Eqs. (1) through (8). For a ternary system, the concentration of only one of the gases in the brine effluent can be specified.

In this case, specifying 95 per cent removal of H_2S, $x_1^1 = (0.05)(2.28 \times 10^{-4}) = 0.114 \times 10^{-4}$. The mole fraction of CO_2 in the effluent brine is then assumed to be a certain value. Using Eqs. (5) through (8), plate-to-plate calculations are made starting with the bottom plate. After n calculations, if it appears that the calculated values of x^{n+1} and y^{n+1} will not coincide with the feed and effluent values of x^F and y^E obtained from the overall material balance, the assumed value of y_2^1 is judged incorrect and a new value assigned, followed by new plate-to-plate calculations. Of course, when the steam flow rate has been specified, the coincidence of values from plate-to-plate calculations and values from the overall material balance may not occur at an integral number of plates.

Application of the trial-and-error procedure described above resulted in the conclusion that essentially all of the CO_2 is removed in the top section of the column. For 95 per cent removal of H_2S, somewhere between 3 and 4 equilibrium plates (ideal) are required at the specified steam flow rate of 90 lb/hr. Essentially the same number of plates was estimated by neglecting the CO_2 and constructing Fig. 10 for a binary system.

To be on the conservative side, 3.5 ideal equilibrium plates are specified for the stripper.

The following final concentrations of H_2S and CO_2 are obtained in the effluent liquid and gas streams:

In the brine stream,

$$x_1^1 = 0.114 \times 10^{-4}$$

$$x_2^1 = 0$$

In the gas stream,

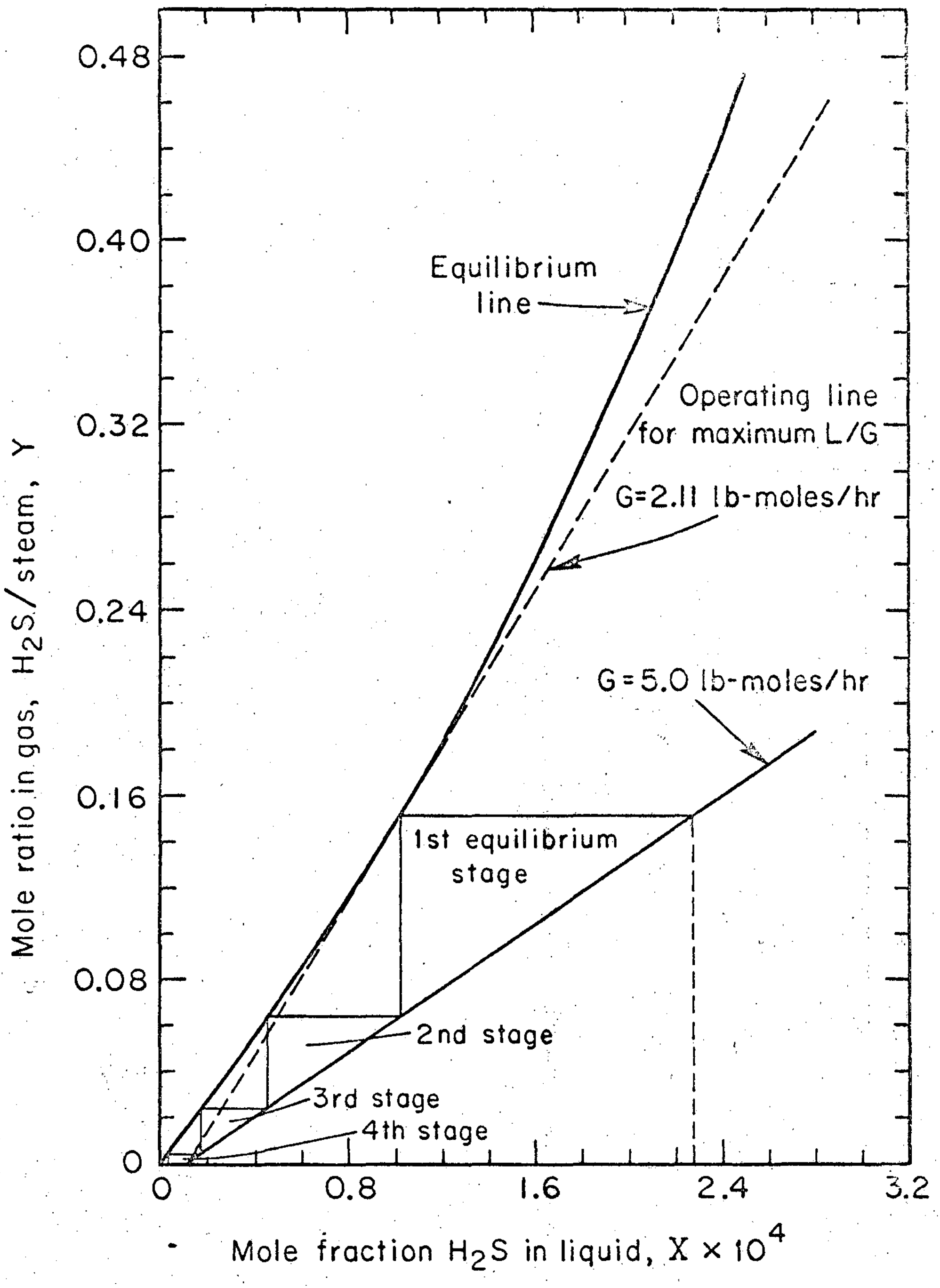

Fig. 10. McCabe-Thiele diagram for the system H_2S-H_2O at 212°F, 1 atm.

$y_1^E = 0.113$ $G_1^E = 26.2$ lb/hr

$y_2^E = 0.156$ $G_2^E = 46.7$ lb/hr

$y_S^E = 0.731$

Total molar gas flow, $G_E = 6.833$ lb-moles/hr

(3) Calculation of overall column efficiency:
There are numerous correlations for obtaining the efficiency of a bubble-plate tower in the absence of experimentally-determined efficiencies. The most rigorous of these is that proposed in the A.I.Ch.E. Bubble-Tray Design Manual (1958). Calculations according to this method, shown in Appendix A, give a column efficiency of 0.294. Thus the required number of equilibrium plates will be: 3.5/0.294 = 12 plates.

Appropriate column dimensions would be about 20 feet high by 3 feet wide, allowing 1-foot spacing between plates and about 4 feet for entrance sections. At the operating temperature of the column, wet H_2S is highly corrosive, precluding the use of carbon steel as a material of construction. A 5-7-mil coating of baked-on phenolic for the inside surfaces of the column, including the plates and bubble caps, is adequate for preventing corrosion.[46] The total area to be covered is 470 sq ft. At a 1956 price[13] of $1.70 per sq ft, the cost of the coating is $800 in 1956, or $900 in 1966, applying the CE Plant Cost Index. From Chilton's data,[13] the cost of a carbon-steel bubble-cap tower 3 ft in diameter is $280 per plate, or a total of $3360 in 1947. Updating via the CE Index, the January 1966 installed cost of the carbon-steel tower and plates is $5600. The total installed cost of the tower is therefore $6500.

Of course, there is no way of telling in advance whether the presence of microbial cells in the feed stream will effect the operation of the column. A periodic cleaning of the column will probably be necessary to remove accumulated cellular debris. At 212°F, the column may well be self-cleaning, however. Certainly no bacterial growth will occur at that temperature.

(4) Design of steam condenser:

The exit gas from the stripping tower consists of 73.1 per cent water vapor. This quantity can be reduced by simply condensing the water vapor and subcooling to lower the vapor pressure of the water. The condensation and cooling can be carried out by heat exchange with the incoming brine feed. Cooling and condensing causes the pressure to drop to 5 psia, so that the gases must be removed by a compressor. The exit gas has the composition: 37% H_2S, 50.8% CO_2, and 12.2% H_2O at about 86°F. Cooling still further will remove more H_2O. The design calculations for the condenser are given in Appendix A. For a heat-transfer area of 5.1 sq ft, the 1966 cost is $470.

(5) Other auxiliary equipment:

In addition to a condenser and compressor, a pump for the feed to the column is required, as is a heat exchanger for recovering heat from the tower bottoms for preheating the incoming brine. In addition, further heating is required to make up for heat losses and inefficiency of the economizer. Steam is used for this purpose, exchanging heat with the brine in a heat exchanger. Direct-steam-injection has the disadvantage of diluting the brine stream by about 1 per cent, since 770 lb/hr of steam are required. Calculations for the design of this auxiliary equipment appear in Appendix A. The feed economizer requires 2700 sq ft of heat-transfer area and has a 1966 cost of $13,800. The steam-heater requires 43 sq ft and costs $780.

A flow diagram of the H_2S stripping unit is shown in Fig. 11.

d. <u>Oxidation of organic material</u>. The removal of organic matter suspended or dissolved in water is a problem common to the sanitary engineer. Aerobic biological oxidation, sometimes in conjunction with anaerobic digestion, has been used in sewage treatment and is finding some use in the treatment of industrial wastes. The most widely-used method of biological oxidation is the activated-sludge process. In this process, the organic-containing stream is brought into a large vessel, either open or closed and usually made of concrete, where it is aerated vigorously by passing air through

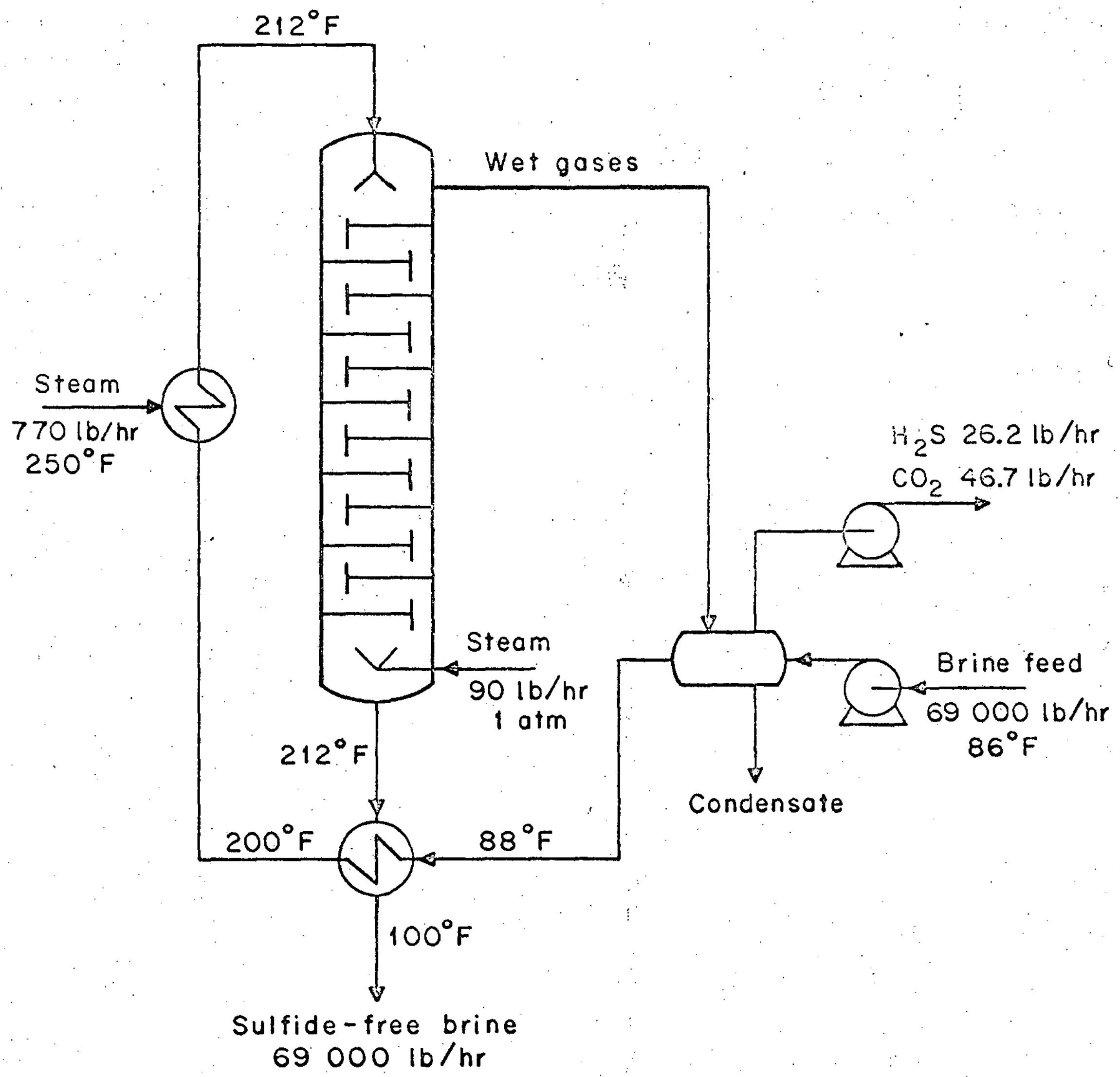

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Fig. 11. Flow diagram for H_2S stripping tower.

diffusers at the bottom of the vessel. The usual residence time in the aerator is 6-8 hours. At the high aeration rate the growth of aerobic bacteria, fungi, and protozoa is stimulated at the expense of the excess organic material, and the mass of cells, including non-viable anaerobic organisms, forms a floc which is then allowed to settle in a large settling tank. Part of the settled solids, the so-called activated sludge, is recycled to the aeration tank to keep the population density of microorganisms at a high level. The unrecycled solids are allowed to dry on dewatering beds and incinerated or sold as fertilizer. About 90-94 per cent of B.O.D. (Biological Oxygen Demand) is removed by the activated-sludge process.[5]

The Chemical Oxygen Demand (C.O.D.) of Medium M (Appendix E) after anaerobic growth of Desulfovibrio has occurred has been determined by the chromate method[5] to be 15.6 g O_2/l. This is adequate for the support of an activated sludge and it is assumed that the C.O.D. level of spent molasses medium will be equally favorable. An attempt was made to determine whether an activated sludge would develop in a 10 per cent salt solution containing Engose-127 in shake cultures inoculated with soil. After several days considerable growth had occurred but only a few species of microorganisms devloped, including yeasts, and no flocculation occurred. The results are not surprising, however; a satisfactory sludge could probably be developed from a raw-sewage inoculum.

For the design study, a conventional activated-sludge system is incorporated. The aeration tank has a residence time of 7.7 hours (60,000 gal), and the final settling tank a residence of 3.2 hours (25,000 gal). Concrete is the material of construction. Investment costs are estimated from published sources[9] which conveniently give installed costs of several types of sewage treatment systems plotted against the design flow rate (million gallons per day). Though there is considerable scatter in the gathered data used to develop these cost curves, they probably give a much more reliable estimate than could be gotten from calculating the amount and costs of concrete, steel, labor, etc., needed to build an activated-sludge unit. Rowan et al.[10] have published information on operating and maintenance costs for activated-sludge plants. For a brine flow rate of 7800 gal/hr, the design flow rate for the activated-sludge plant is 0.2 MGD (million gallons per day). The investment cost, not including engineering, legal and administrative costs, is $100,000 in 1959 dollars.[9] The operating and maintenance costs for a plant of this size are $8700 per year, not including capital maintenance (depreciation) costs.[10]

Other methods of removal of organic material involve chemical oxidation or wet combustion. The first method is not feasible on a large scale because of the high cost of oxidizing agenst such as potassium permanganate.

Air-oxidation of organic materials is carried out in the Zimmermann process,[11] where a feed stream such as concentrated sewage sludge is contacted with air in a high-temperature, high-pressure reactor and the organics actually burn like fuel and are reduced to a non-active ash. This latter method is generally not applicable to relatively small flow rates such as in this design, or streams of less than 25 g/l C.O.D. Investment costs are high because of the need for high-pressure, high-temperature equipment.

e. Brine clarification. If the activated-sludge plant is operating as it should be, the greater bulk of the cellular material and other solids will settle out rapidly as a floc in the settling basin. Nevertheless, a certain amount of solids will be present in the overflow, as well as some dissolved organic material which was not oxidized by the microorganisms to CO_2 and cellular material. An efficient way of removing particulates and disposing of organic matter in low concentrations is to pass the liquid through a sand filter. Better results may be obtained by adding an adsorbent such as carbon to the bed. In addition to removal of solid particles, dissolved organics are removed by a layer of microbial growth which develops on the upper part of the sand bed, and by adsorption by the carbon. For a bed with no adsorbent, virtually complete removal of solids is possible, with 50 per cent reduction of dissolved organics and 20 per cent color removal.[47]

Very often a sand-type filter is enclosed in a vessel and operated under pressure to obtain a desired throughput of liquid. Such a pressure filter is proposed for this design study. To facilitate the periodic cleaning of the filter, two units are installed in parallel, each of which can handle the total brine flow rate. A typical design criteria[5] for a sand filter is 4 gpm/sq ft. With a brine flow rate of 130 gpm, 32.5 sq ft of bed area are required. The bed is 6 feet deep, consisting of 2 feet of fine sand, 1 foot of coarse sand, 2 feet of crushed anthracite, and 1 foot of crushed rock. The installed cost of pressure filters varies from about $17 to $40 per gallon of water per minute.[12] An average of about $28 per gpm is chosen.

4. Process Flow Diagram

The process is best described by a diagram showing the major pieces of equipment and giving quantitative information on the flow rates of the process streams, as in Fig. 12.

5. Material Balances

Table 3 gives the overall material balance for the sulfate reduction process. Table 4 lists flow rates and percentages of components in the inlet and product brine streams. Impurities from the molasses are not significantly high in the product stream. Flow rates for the materials in the brine stream are calculated as follows:

a. Rock salt: 85 tons per day design capacity

b. NaCl: $(0.975)(85)(200)/24 = 6900$ pounds/hour

c. Water for a 10 per cent brine: $(6900)(\frac{9}{1}) = 62{,}000$ pounds/hour

d. Molasses: As a carbon source, molasses is widely used in the fermentation industry because it is relatively cheap and contains a fairly high percentage of fermentable sugars. The typical composition of molasses[18] is given in Appendix D.

The amount of glucose necessary to reduce a given amount of sulfate to sulfide is governed by the following relation:

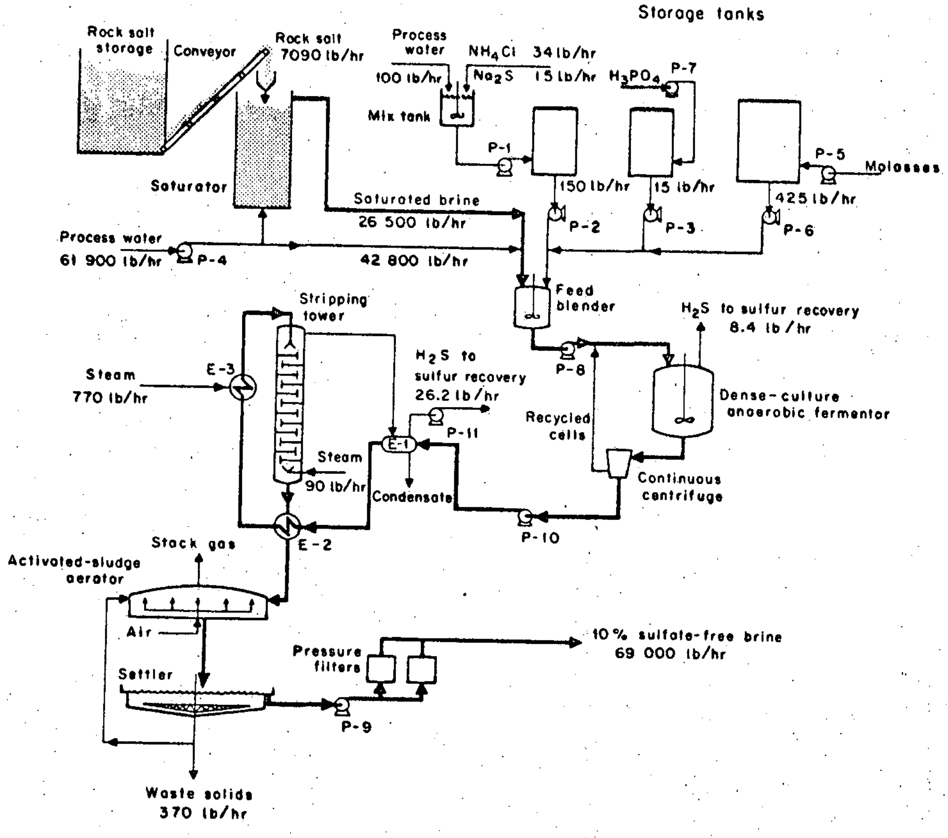

Fig. 12. Process flow diagram for removal of sulfate from 10 per cent brine by bacterial reduction.

Table 3. Overall material balance--bacterial-reduction process

Materials	Input lb/hr	Output lb/hr
Brine solids (see Table 4)	7,490	6,960
Process water	62,000	62,000
Reaction products		
H_2S		36
CO_2		96
H_2O		39
Dry sludge		370
	69,500	69,500

Table 4. Flow rates and percentages of components in the brine stream

Component	Input		Output	
	Flow lb/hr	Wgt.% solids	Flow lb/hr	Wgt.% solids
NaCl	6910	92.24	6910	99.09
$CaSO_4$	104	1.43	1.07	0.02
Na_2SO_4	40.4	0.54	0.41	0.01
$MgCl_2$	7.1	0.09	7.1	0.10
Fe_2O_3	7.8	0.10	7.8	0.12
Insolubles	14.2	0.19	0	0
NH_4Cl	34.0	0.45	1.7	0.03
H_3PO_4	15.0	0.20	0.8	0.01
$Na_2S \cdot 9H_2O$	15.0	0.20	0	0
Sugars	264	3.52	3.3	0.05
SiO_2	2.1	0.03	0	0
K_2O	14.9	0.20	14.9	0.22
CaO	6.4	0.09	6.4	0.09
MgO	0.4	0.01	0.4	0.01
P_2O_5	0.8	0.01	0.8	0.01
H_2SO_4	6.8	0.09	0.7	0.01
Cl_2	1.7	0.02	1.7	0.03
Organics	42.5	0.57	0.5	0.01
Acetic acid	0	0	1.3	0.02
	7490	100.00	6960	100.00

$$C_6H_{12}O_6 + SO_4^= \rightarrow 2CO_2 + 2CH_3COOH + 2H_2O + S^=$$

One mole of glucose is necessary to convert one mole of sulfate to sulfide via the respiratory system of <u>Desulfovibrio</u>. The bacteria derive their energy from the above reaction but need additional glucose for growth and production of new cells. This additional amount of glucose necessary is estimated at 30 per cent by calculating the ratio of carbon source to sulfate in Medium M (Appendix E) used in laboratory experiments. Amount of sulfate in rock salt: 1.46 per cent (see Table 1)
Percentage of conversion: 99 per cent

e. <u>Glucose flow rate</u>: (0.0146)(7090)(.99)(180/96)(1.3) = 250 pounds per hour. Molasses contains 59 per cent fermentable sugars (glucose equivalent).

f. <u>Molasses flow rate</u>: 250/0.59 = 425 pounds per hour.

g. <u>Minerals and impurities</u>. In addition to a carbon source, the organisms need a source of nitrogen and phosphate for proteins, nucleic acids and other cell materials. Also, since the organisms are strict anaerobes, they grow best in a reducing environment. The addition of sulfide to the growth medium keeps the redox potential at a low enough value to encourage growth. Other elements such as iron, potassium, and magnesium are required in trace amounts and are present in sufficient quantities as rock salt and molasses impurities. The required flow rates of ammonium chloride, phosphoric acid, and sodium sulfide are calculated from their respective concentrations in Medium M.

The use of molasses as a carbon source invariably increases the impurity content of the brine and it is difficult to estimate how much of these impuritities are metabolized. The sugars used as energy source by the bacteria are converted to acetic acid, which acts as carbon source, along with unmetabolized glucose, in the activated-sludge system.

The rate of production of acetic acid is:

(2)(250/1.3)(60/180) = 128 pounds per hour.

If it is assumed that one pound of glucose goes into one pound of cells, since the concentration of cells in the centrifuge effluent is 1.88×10^{8} cells/ml and the cells weigh 10^{-12} g/cell, the amount of glucose going into cells will be:

$$(1.88 \times 10^{8})(10^{-12})(7800)(1000/454) = 12.2 \text{ pounds per hour.}$$

The unused glucose is thus:

$250 - (250/1.3) - 12.2 = 46$ pounds per hour. Ninety-five per cent of this is removed in activated sludge and assuming absorption reduces it another 80 per cent, the glucose in the final brine will be:

$$(46)(0.05)(0.20) = 0.5 \text{ pounds per hour.}$$

Using the same figures for acetic acid, its flow rate will be:

$$(128)(0.05)(0.20) = 1.3 \text{ pounds per hour.}$$

The amount of NH_4Cl and H_3PO_4 remaining in the brine is estimated by assuming 95 per cent removal by bacterial processes. The $Na_2S \cdot 9H_2O$ is assumed to be completely converted to H_2S or oxidized to sulfur in aeration.

6. Design Specifications

a. Materials of construction. Despite the corrosive nature of brines, cast iron and carbon steel are generally satisfactory for ambient temperatures and these materials are used for most pumps and piping. Cathodic protection is useful for prolonging the lifetime of iron and steel equipment. The mixing and storage tanks for ammonium chloride and sodium sulfide with associated piping and pumps is made of stainless steel because of the corrosive nature of these materials. The storage tank for 75 per cent phosphoric acid is lined with rubber while pumps and piping are stainless steel. The molasses storage tank and feed blending tank are of carbon steel. The hydrogen sulfide formed in the anaerobic fermentation dictates the use of stainless steel for the fermentation vessel and continuous centrifuge. The concrete used for the rock salt saturator and activated-sludge system combines low cost with corrosion resistance. Standard carbon-steel design is used for the pressure anthrafilt filters. The carbon-steel shell and plates of the steam-stripper are coated with phenolic to arrest corrosion from the wet H_2S gas.

b. Process control. Since the process is a continuous one, a certain amount of control instrumentation is necessary. The following represent the major process controls:

(a) Control of rock salt level in saturator by on-off control of conveyor.

(b) Control of process water flow rate to saturator and blending vessel. This may be done by installing a controlling throttle valve in the inlet line to the saturator and the inlet line to the blender.

(c) Control of flow rates of nutrients by use of positive-displacement pumps.

(d) Level control on the feed blender by throttling the outlet stream.

(e) Level control on the fermentation vessel by throttling the fermentor oulet stream.

(f) Control of pH in the fermentor by feedback control of correcting reagent flow rate.

(g) Control of recycle rate to the fermentor by throttling bypass to centrifuge effluent.

c. Equipment list and specifications. Table 5 lists the major pieces of equipment in the design of a process for removal of sulfate from 10 per cent brine by reduction with bacteria and gives the January 1966 installed cost of each. This list does not include the activated-sludge plant and a sulfur-conversion plant (discussed in section D).

Tables 6(a) through 6(o) outline the specifications for each piece of equipment and show the source and date of cost data.

Table 5. List of major equipment for the process of sulfate removal from 10 per cent brine by bacterial reduction

Equipment	Installed Cost, January 1966 CE Plant Cost Index = 105.6
Rock salt conveyor	$ 3,100
Brine saturator	1,200
Mineral dissolving tank	4,500
Mineral solution transfer pump (P-1)	1,540
Mineral solution storage tank	2,860
Mineral solution metering pump (P-2)	2,800
Phosphoric acid metering pump (P-3)	2,000
Ten per cent brine blender	5,850
Process water pump (P-4)	1,670
Molasses storage tank	7,850
Molasses transfer pump (P-5)	930
Molasses feed pump (P-6)	670
Phosphoric acid storage tank	1,740
Phosphoric acid transfer pump (P-7)	890
Ten per cent brine feed pump (P-8)	1,670
Agitated anaerobic fermentor	18,000
Continuous centrifuge	36,000
Anthrafilt pressure filters (2)	10,360
Pressure filter pump (P-9)	2,080
H_2S stripping tower	6,500
Tower condenser (E-1)	470
Tower feed economizer (E-2)	13,800
Tower feed heater (E-3)	1,300
Tower feed pump (P-10)	1,750
Tower gas compressor (P-11)	670
Total installed equipment cost	$130,200

Table 6. Equipment specifications for the process of sulfate removal from 10 per cent brine by bacterial reduction

(a) Pumps

Pump	Type	Cap. (gpm)	Hp	Material of construction	Installed cost, year, source
Mineral solution transfer pump	centrif.		1	SS	$920 1947, 13
Mineral solution metering pump	recipr.	18	1	SS	$1700 1947, 13
Phosphoric acid metering pump	recipr.	2	1/2	SS	$1200 1947, 13
Process water pump	centrif.	123	5	CI	$1000 1947, 13
Molasses transfer pump	rotary	83	5	CS	$750 1954, 14
Molasses feed pump	rotary	36	1	CI	$570 1954, 14
Phosphoric acid transfer pump	centrif.	33	1	SS	$720 1954, 14
10% brine feed pump	centrif.	127	5	CI	$1000 1947, 13
Pressure filter pump	centrif.	130	10	CI	$1250 1947, 13
Stripping tower feed pump	centrif.	130	5.5	CI	$1050 1947, 13

Table 6. (continued)

(b) Storage tanks

Tank	Type	Cap. (gal)	Material of construction	Installed cost, year, source
Molasses storage	vertical cylinder	25,500	carbon steel	\$4700 1947, 13
Phosphoric acid storage	vertical cylinder	1,000	rubber-lined steel	\$1400 1954, 13
Mineral solution storage	vertical cylinder	500	stainless steel	\$2700 1958, 13

(c) Rock salt conveyor

Purpose: To convey rock salt from storage bin to top of saturator.

Type: Continuous belt

Length: 45 feet

Belt width: 14 inches

Capacity: 7090 pounds per hour

Materials of construction: Steel welded frame, steel pulleys and idlers, rubber-covered duck belt.

Auxiliaries: Steel discharge chute

Drive motor: 1 hp

Total purchase cost:[13] \$2,540 (1957)

Installation cost:[13] \$375 (1966)

Total installed cost: \$3,100 (1966)

(d) Rock salt saturator

Inside dimensions: 20' × 6' × 6'

Wall thickness: 6 inches

Material of construction: Poured concrete walls. Reinforced concrete floor.

Installed cost:[14] \$760 (1954)

Table 6. (continued)

(e) Mineral dissolving tank

Purpose: Preparation of solutions of NH_4Cl and Na_2S

Type: Vertical, cylindrical, with open top, top-mounted agitator

Capacity: 350 gallons

Material of construction: Stainless steel

Agitator power: 2 hp

Installed cost:[13] $2,700 (1947)

(f) 10 per cent brine blending tank

Purpose: Blending of saturated brine, water and nutrients

Type: Vertical, cylindrical, totally enclosed, agitator mounted through top.

Capacity: 2,000 gallons

Material of construction: Carbon steel

Agitator power: 10 hp

Installed cost:[13] $3,500 (1947)

(g) Anaerobic fermentation vessel

Type of vessel: Vertical, cylindrical, totally enclosed, agitator mounted through top, vented to stack

Capacity: 6,770 gallons

Material of construction: Stainless steel

Agitator power: 35 hp

Operating temperature: 30°C

Operating pressure: Atomospheric

Installed cost:[13] $11,000 (1947)

Table 6. (continued)

(h) Continuous centrifuge

Purpose: Concentrate 10 per cent cells effluent from fermentor to 50 per cent and recycle to fermentor.

Type: Nozzle-discharge disc centrifuge

Bowl diameter: 30 inches

Liquid throughput: 165 gpm

Solids throughput: 1.6 tons per hour

Materials of construction: Stainless steel

Drive power: 135 hp, 3,600 rpm

Purchase cost of motor:[17] $3,100 (1963)

Purchase cost of centrifuge:[16] $26,000 (1955)

Total installed cost: (106% of total purchase cost)[13] $36,000 (1966)

(i) Activated-sludge system

Design flow rate: 0.2 million gallons per day

Efficiency: 95 per cent B.O.D. removal

Aeration Tank:

Volume: 60,000 gallons

Type of construction: Enclosed, circular, concrete basin, top level with ground. Fitted with air distribution pipes along bottom and gas vents on top

Aeration rate: 1 scfm/gal of volume

Settling tank:

Volume: 25,000 gallons

Type of construction: Circular concrete basin with conical bottom. Equipped with mechanical sludge rake and sludge pumps.

Total installed cost:[9] $100,000 (1959)

Table 6. (continued)

(j) Anthrafilt pressure filters

Number required: 2

Description: Vertical cylindrical tanks, totally enclosed, containing a filter bed consisting of 2 feet of fine sand, 1 foot of coarse sand, 2 feet of crushed anthracite, and 1 foot of crushed rock

Design flow rate: 130 gpm

Filtration area: 32.5 sq ft

Vessel dimensions: 9 ft high, 6.45 ft diameter

Material of construction: carbon steel

Installed cost (each):[12] \$3,600 (1950), at \$27.7 per gpm

(k) H_2S stripping tower

Purpose: Removal of H_2S from brine stream

Type: Bubble-cap plates, steam stripping

Number of plates: 12

Dimensions: 20 ft high, 3 ft diameter

Operating conditions: 212°F, atm.

Materials of construction: carbon-steel shell and plates, with 5-7-mil baked-on phenolic lining

Installed cost of tower:[13] \$3,360 (1947)

Installed cost, phenolic lining:[13] 470 sq ft at \$1.70/sq ft = \$800 (1956)

Total installed cost: \$6,500 (1966)

(l) Stripping tower condenser

Purpose: Condensation of water vapor in exit gas from stripper

Type: Horizontal shell-and-tube

Required heat-transfer area: 5.1 sq ft

Operating conditions: 5 psia shell side, 15-20 psia in tubes, 90°F on tubes

Table 6. (continued)

Materials of construction: carbon-steel shell, 3/4" OD × 16BWG copper tubes
Purchase cost:[13] $350 (1958)
Installed cost: (1.25 × purchase cost) $440 (1958)

(m) Tower feed economizer

Purpose: Recover heat for incoming brine from hot tower bottoms
Type: Shell-and-tube heat exchanger
Required heat-transfer area: 2700 sq ft
Materials of construction: Steel shell, steel tubes
Installed cost:[13] $8,300 (1947)

(n) Tower feed steam-heater

Purpose: Bring feed up to tower operating temperature of 212°F
Type: Shell-and-tube, steam condensing on shell side
Required heat-transfer area: 43 sq ft
Steam consumption: 770 lb/hr at 250°F
Materials of construction: Steel shell, steel tubes
Installed cost:[13] $780 (1947)

(o) Tower exit gas compressor

Purpose: Removal of low-pressure gases in condenser, discharging at 1 atm to sulfur-recovery plant
Type: Reciprocating, single-stage
Capacity: 39 cu ft/min
Drive horsepower: 2 hp
Operating conditions: suction pressure: 5 psia
discharge pressure: 15 psia
gases handled: H_2S: 26.2 lb/hr
CO_2: 46.7 lb/hr
H_2O: 4.6 lb/hr

Table 6. (continued)

Materials of construction:	Stainless steel
Installed cost:[13]	$400 (1947)

D. Disposal of H_2S

1. Releasing H_2S to the Atmosphere

a. Air pollution regulations. There are no nationwide regulations on emission of odorous gases such as H_2S. In Los Angeles and neighboring counties, the permissible limit on sulfur compounds in stack gases is 0.2 per cent (as SO_2). In New York State, emissions are limited to a certain percentage of emission potential. In some areas were there are no regulations on emission, the concentration of gases such as H_2S or SO_2 at ground level can not exceed a specified level over a given period of time.[8] This latter regulation can present a problem in design, since it is difficult to predict in advance whether the tolerable ground level concentration of a pollutant will be exceeded, given a certain emission rate and stack concentration.

Many industries are imposing their own control limits in the interest of maintaining a clean public image or even for pure humanitarian reasons. In some cases, economic gains are realized by the recovery of a potential pollutant. Everyone will agree, though, that the wanton emission of polluting gases and particulates is harmful to all concerned, and there is developing a willingness on the part of industry to play an active role in the control of environmental pollution.

b. Air-stripping in a packed tower. An alternative method of removing the H_2S from the brine other than steam-stripping is to flow the brine countercurrent to air in a packed tower. Piester[48] has determined mass-transfer coefficients for desorption of H_2S from brine with air in a tower packed with 1-inch Raschig rings. Using Piester's data, the design of a packed tower to remove 95 per cent of the H_2S from the brine in this study was carried out. An L/G ratio similar to Piester's was used and the flooding velocity of 1000 lb/hr ft^2 was determined using Leva's correlation (Fig. 18.51 of Perry[7]). Operating at half the flooding velocity, the following tower variables were determined:

Air flow rate: 5560 lb/hr
Tower diameter: 3.77 ft (45 in.)

Height of packing: 36 ft

The installed cost of a phenolic-lined tower with packing, pump and blower is approximately $20,000 in January 1966, compared with $24,500 for the steam-stripping equipment. The operating costs for the packed tower can be expected to be lower than for steam-stripping.

c. Stripping in activated-sludge aerator. At the typical aeration rate of 1 cu ft of air per gallon of aerator volume,[49] a total of 290,000 lb/hr of air is bubbled through the aerator. It is conceivable that this volume of air would be sufficient to strip out H_2S from the brine. Three equations can be written describing the desorption of H_2S from the aerator:

$$\frac{y^* - y_1}{y^* - y_2} = e^{N_{OG}} \quad \text{(mass-transfer efficiency)}$$

$$L(x_1 - x_2) = G(y_2 - y_1) \quad \text{(material balance)}$$

$$y^* = Hx_2 \quad (H_2S\text{-}H_2O \text{ equilibrium})$$

where y^* = mole fraction H_2S in gas in equilibrium with the liquid
y_1 = mole fraction H_2S in entering air (0.0)
y_2 = mole fraction H_2S in leaving air
N_{OG} = number of gas-phase mass-transfer units
L = liquid molar flow rate (3560 lb moles/hr)
G = gas molar flow rate (10,000 lb moles/hr)
x_1 = mole fraction H_2S in entering brine (2.28×10^{-4})
x_2 = mole fraction H_2S in aerator brine

These equations assume complete mixing in the aerator. N_{OG} may be determined from

$$\frac{1}{N_{OG}} = \frac{1}{N_G} + m\left(\frac{G}{L}\right)\left(\frac{1}{N_L}\right)$$

where N_G = mass-transfer units in the gas film

N_L = mass-transfer units in the liquid film

m = slope of the equilibrium curve = Henry's law constant at 1 atm = 840

N_G and N_L may be estimated by assuming the aerator to be one equilibrium plate and using the correlations of the A.I.Ch.E. Bubble-Tray Design Manual which are used for calculating the efficiency of the steam-stripper in Appendix A. The calculated values are

$$N_G = 14.9$$

$$N_L = 1050$$

$$N_{OG} = 0.432$$

Only three quantities are unknown: y^*, y_2, x_2

Solution of the equations yield

$$x_2 = 2.76 \times 10^{-7}$$

which indicates essentially all of the H_2S is removed by the air. Carbon dioxide and other gases would presumably be stripped out at the same time.

If the sole objective were to remove the H_2S from the brine stream, then it would not be necessary to install an external stripper to do the job.

If air-stripping were employed the H_2S would be too dilute to recover and would have to be emitted to the atmosphere. Including the H_2S evolved in the fermentor, the H_2S concentration in the air from the aerator would be 0.01 per cent or 100 ppm. This is well under the allowable 0.2 per cent. Nevertheless, H_2S at this concentration is highly dangerous. Hydrogen sulfide is more lethal than carbon monoxide, but its strong odor promotes a feeling of false safety.

2. Recovery of Sulfur

The chief advantage of steam-stripping is that the H_2S is made available in a concentrated gas stream which can be processed for its sulfur content. The pollution problem is substantially reduced by this operation.

In the petroleum industry it is becoming common practice to remove the H_2S from flue gases by a method such as the Girbotol process with possible subsequent conversion of H_2S to sulfur by a modified Claus process. A typical flow diagram for producing elemental sulfur from H_2S is given in Fig. 13. In the Claus process, about one-third of the hydrogen sulfide gas feed is burned in a special furnace with air to sulfur dioxide. Heat is recovered in a waste-heat boiler as steam. The sulfur dioxide and remaining two-thirds of the hydrogen sulfide feed is passed through a single or multi-stage converter containing a catalyst such as activated bauxite. The reactions with regard to H_2S conversion are:

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2\ H_2O$$

Elemental sulfur is produced as a gas which is then scrubbed and condensed with recycled cooled sulfur, and either pumped to tank cars or allowed to solidify in storage. Yields of sulfur are generally 85-95 per cent, depending on the number of catalyst beds.[35,36]

In this design, the amount of H_2S produced from the rock salt containing 1.46 per cent sulfate, and with 99 per cent reduction and 95 per cent H_2S recovery, is calculated as $(0.0146)(7090)(0.95)(0.99)(34/96) = 34.2$ lb H_2S/hr. This represents a plant capacity of $(34.2)(24)(32/34)(0.90)/2240 = 0.31$ long tons of sulfur per day, assuming a 90 per cent conversion of H_2S to elemental sulfur (1 long ton = 2240 lb).

Parker,[35] Kohl and Fox,[36] Hays and Barber,[37] and Reed and Updegraff[38] have published data on the economics of sulfur production from H_2S. Their data for investment and operating costs for the period 1950-54 are plotted in Figs. 14 and 15.

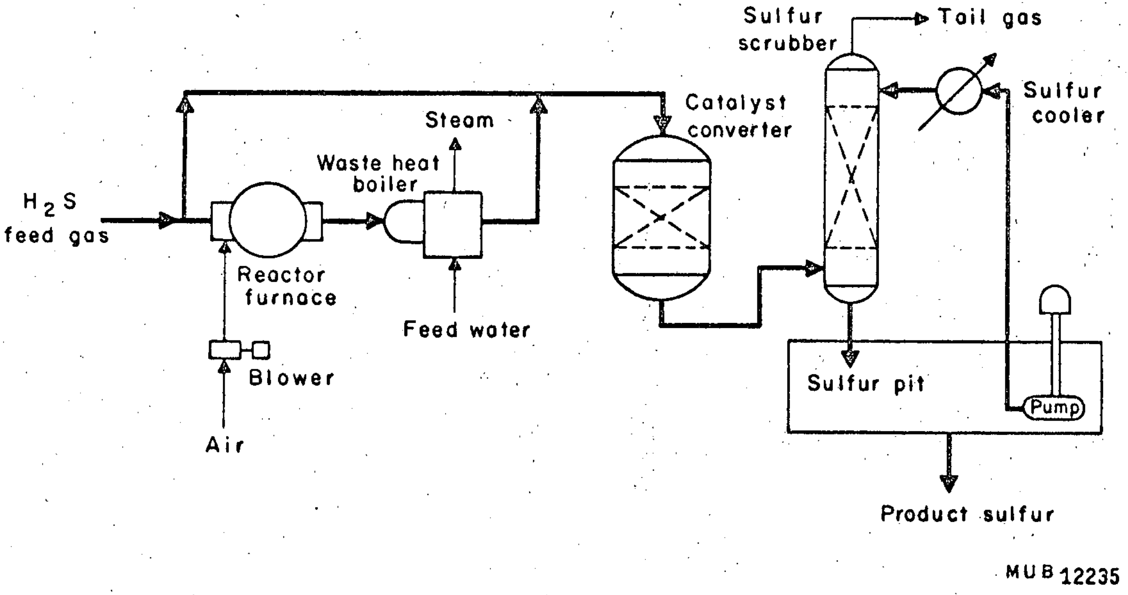

Fig. 13. General flow diagram of a plant for processing H_2S to elemental sulfur.

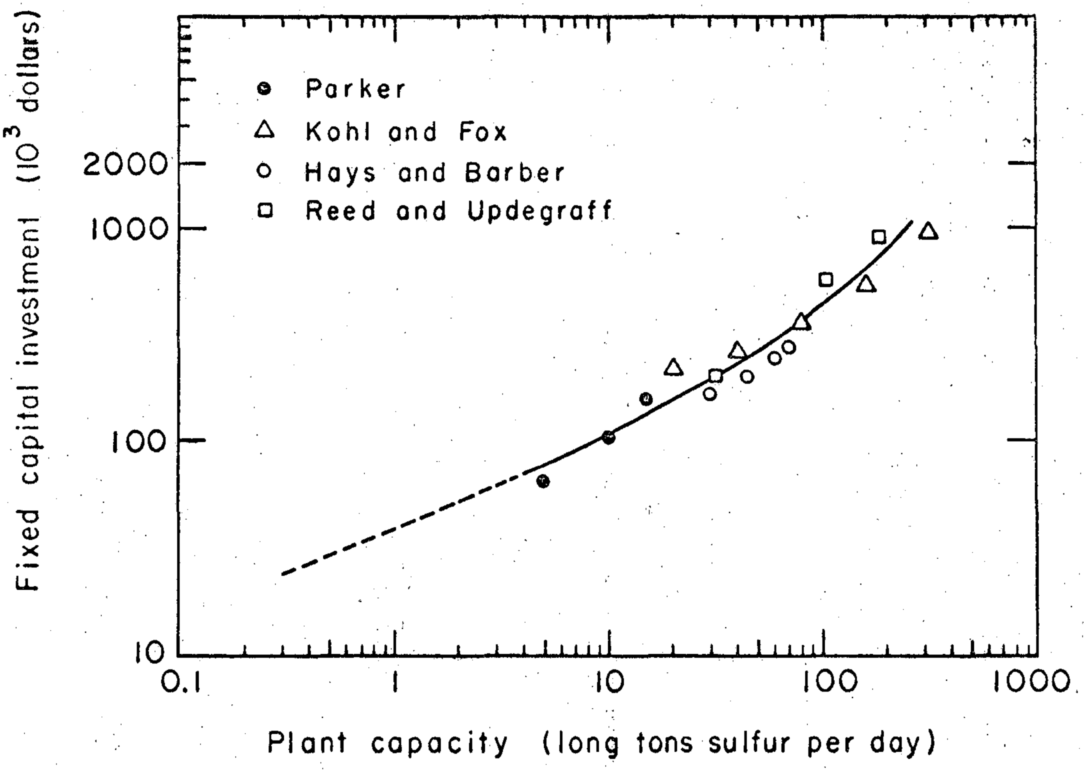

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Fig. 14. Investment costs for sulfur recovery from H_2S (1950-1954).

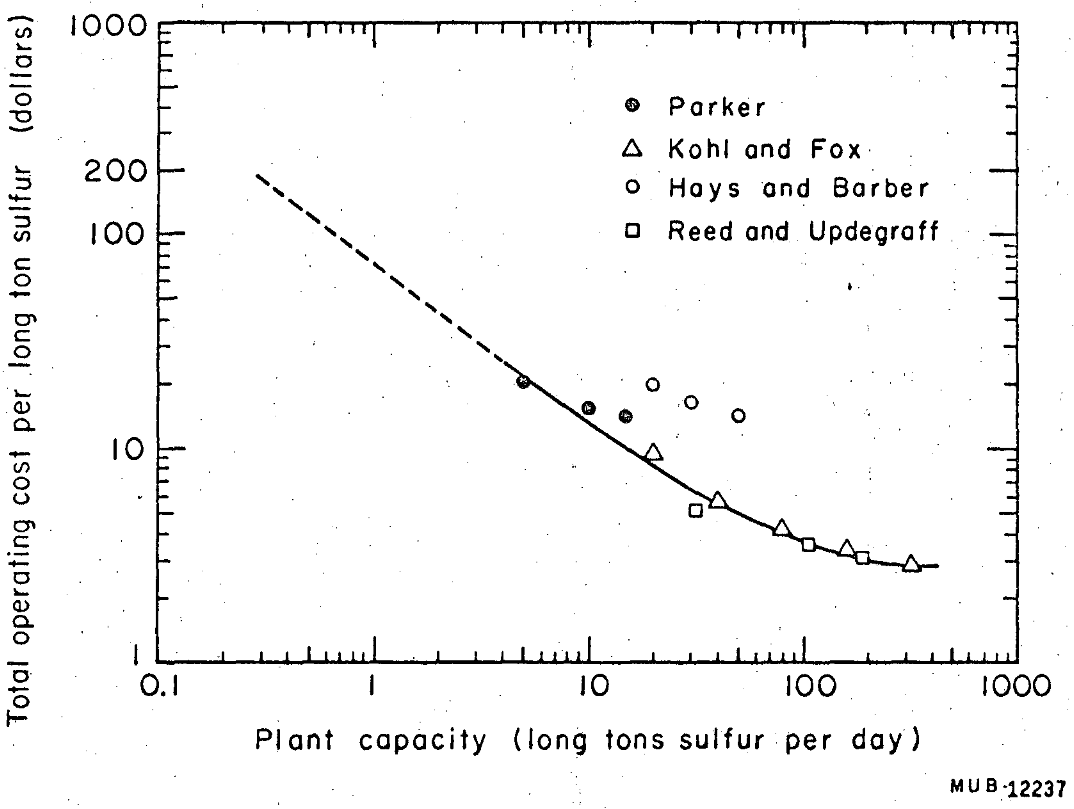


Fig. 15. Operating costs for sulfur recovery from H_2S (1950-1954).

Referring to Fig. 14, the capital investment for the period 1950-54 for a plant capacity of 0.31 LT/day of sulfur is only $\$$25,000. The total operating cost for a plant of this size, however, is quite high--being approximately $\$$170 per long ton of sulfur produced--according to Fig. 15. These figures are only approximate, of course, since they are obtained from an extrapolation of curves which themselves are based on scattered data. Nevertheless, the definite upward trend of operating costs for low-capacity plants is very evident in Fig. 15. Assuming the operating costs for 1966 to be the same as those for 1950-54 (they will most likely be higher), with a 1966 price of sulfur of $\$$27.00 per long ton, the break-even plant capacity will be at about 4 LT/day.[21] It appears, then, that the recovery of sulfur from H_2S produced by the bacterial sulfate reduction process will hardly be economical for the design capacity of this study. Assuming 5 LT/day of sulfur were being produced, 5.9 LT/day of H_2S (90 per cent conversion) would be required from 16.8 LT/day of sulfate (99 per cent conversion) which would be equivalent to processing 1150 LT/day of rock salt (1.46 per cent of $SO_4^=$). This would furnish enough sodium chloride for 760 tons per day of chlorine--a capacity far beyond any plant in existence today.

But the purpose of the plant is to dispose of H_2S, not necessarily to make a profit. The expense of converting the H_2S from the steam-stripper to sulfur is to be carried as an operating cost for the bacterial sulfate-removal process and is discussed in section E under manufacturing costs.

3. Other Alternatives

One alternative to converting the H_2S to sulfur is to produce SO_2. The market for SO_2 is small compared to sulfur, however, and little economic data on SO_2 conversion has appeared in the literature. The advantage of sulfur over SO_2 is its ease of handling and storage.

Another alternative would be to produce sulfuric acid--one step further than SO_2. Small quantities of sulfuric acid are of little value, however.

E. Investment and Manufacturing Costs

No economic study of this type is complete without a discussion of the methods used to estimate the capital and manufacturing cost. This particular section deals with the cost estimate for sulfate removal by bacteria producing 10 per cent brine.

Cost estimates vary in detail and accuracy from the order-of-magnitude estimate to the firm or contractor's estimate, and in the design of a new chemical facility it is not unusual for several cost estimates to be made before the plant is built, providing the economics are favorable. The feasibility of a proposed project is determined by a predesign cost estimate or study estimate which generally is accurate to within ± 30 per cent. Perry[7] has outlined the required information necessary to make such an estimate. The methods of cost estimation are discussed in detail by Aries and Newton,[14] Chilton,[13] Perry,[7] Peters,[19] and Zimmerman and Lavine.[12]

The methods for obtaining a predesign cost estimate have not changed substantially since 1947-48 when Lang first proposed the factor method for fixed-capital investment. In the absence of previous experience and information on the design of a particular project, it is usually necessary to estimate a particular cost item by assuming a certain percentage of the equipment cost to be attributed to that item. The equipment cost is estimated from published data or private sources. Selection of the proper percentage or factor will depend on the type of plant, the objectives of the design and other circumstances demanding the best judgment of the estimator. The term "guesstimation" often used to describe a predesign cost estimate, though harsh, nevertheless has a certain amount of truth in it.

1. Investment Cost Estimates

a. Installed equipment. Much of existing cost data for process equipment appeared in the literature before 1950. More information began to appear in the latter part of the 1950's, with Weaver's[20] excellent review in Industrial and Engineering Chemistry on chemical cost and profitability estimation from 1955 to 1958, and with the inauguration in 1958 of the CE

Cost File as a standard feature of Chemical Engineering. Chilton's[13] book is a compilation of most of the articles on costs that have appeared in Chemical Engineering from 1947 to 1959.

Unfortunately, new data have not yet replaced much of the early cost data and the latter in many cases must still be relied upon. Out-of-date cost data must be brought up to date in order for any estimate to be meaningful. Cost indexes such as the Engineering News-Record Construction Cost Index (EN-R Index) and the Marshall and Stevens Index of Comparative Equipment Costs (M & S Index) are widely used for updating costs. A new index, the Chemical Engineering Plant Cost Index (CE Index) shows the most promise of providing reliable up-to-date cost estimates for the chemical industry.

Since much of the equipment cost data for this study is in terms of installed equipment cost, an appropriate index for updating has been devised from the CE Plant Cost Index, making use of the weight factors for equipment and machinery costs and erection and installation labor costs.[45] Calculation of this modified index and its value for several years is shown in Appendix G. The values do not differ greatly from the overall CE index.

It is interesting to compare the results obtained from use of the EN-R, M & S, and CE indexes. Using the EN-R index, costs will have risen by a factor of 2.5 from 1947 to 1966, while the M & S index predicts a rise of 1.61 and the CE index a rise of 1.67. Surely, use of the EN-R index in updating costs for the chemical industry is open to serious doubt.

Table 5 shows that the total updated installed equipment cost amounts to $130,200. This cost does not include the cost of equipment for the activated-sludge system and sulfur-recovery plant, which are complete entities in themselves, and which are not included in the following estimation of piping, instrumentation, and other capital items.

b. Piping. This is perhaps the most difficult capital cost to estimate and it is a significant cost in most cases. The most accurate estimate, of course, comes from detailed piping layouts and specifications, but in the absence of these, piping costs are estimated as a percentage of equipment cost. Chilton[13] suggests the following ranges of percentage of installed process equipment cost for piping:

Low: Solids-processing plants = 7 to 10%
Average: Mixed-processing plants = 10 to 30%
High: Fluids-processing plants = 30 to 60%

For the case of sulfate removal by bacteria, we are using 30 per cent of installed equipment cost.

Piping = (0.3)($130,200) = $39,000

c. Insulation. Aries and Newton[14] suggest using 8 per cent of the purchased equipment cost. If installation costs are assumed to be 43 per cent of purchased equipment costs,[14] then insulation cost is 5.5 per cent of installed equipment cost.

Insulation = (0.055)($130,200) = $7,200

d. Instrumentation. For an average chemical plant having some automatic controls, instrumentation cost is 5 to 10 per cent of installed equipment cost.[13] Choosing 10 per cent,

Instrumentation = (0.1)($130,200) = $13,000

e. Electrical installations. Costs for electrical installations include labor and materials for substations, feeders and major wiring. Aries and Newton[14] use 10 per cent of purchased equipment cost, which amounts to 7 per cent of installed equipment cost.

Electrical installations = (0.07)($130,200) = $9,100

f. Buildings and services. The cost for buildings and services is assumed to be the same for both the bacterial reduction process and barium chloride process, which is considered in Chapter IV. The cost is estimated as 35 per cent of the installed equipment cost for the barium chloride process, from Chilton's[13] figures of 20 to 60 per cent for mixed outdoor and indoor construction.

Buildings and services = (0.35)($81,800) = $32,700

g. Yard improvements. We have assumed that land for the plant is available; however, some expenditures for clearing, grading, installation of sewers, utility lines, fencing, roads, etc. will be necessary. According to Peters,[19] yard improvements cost between 10 to 15 per cent of purchased equipment cost. Using 10 per cent, the cost will be 7 per cent of the total installed cost.

Yard improvements = (0.07)($130,200) = $9,100

h. Total physical plant cost. The sum of items a. through g. gives the physical plant cost for bacterial reduction of sulfate--a total of $240,300. The activated-sludge system is a complete plant including piping and other auxiliaries, with a physical plant cost of $104,000. The total physical plant cost is thus $344,300.

i. Engineering and construction. For a project requiring only straightforward engineering and an average labor/materials ratio, engineering and construction costs are 20 to 35 per cent of the total physical cost.[13] Using 20 per cent,

Engineering and construction = (0.2)($344,300) = $69,000.

j. Total direct plant cost. The sum of the total physical plant cost and the cost for engineering and construction is the direct plant cost for sulfate removal by bacteria. This amounts to $413,300. An additional capital expense is for recovery of sulfur from H_2S produced in the process. A plant adequate for this purpose has been shown to have a plant cost of $36,000. The sum of direct plant costs for sulfate removal and sulfur recovery gives a total direct plant cost of $449,300.

k. Contractor's fee. Peters[19] suggests 4 to 10 per cent of the direct plant cost for the fee. A value of 4 per cent is chosen here. The contractor's fee for the sulfur-recovery plant is assumed to be included in its direct plant cost.

Contractor's fee = (0.04)($413,300) = $16,500

l. Contingency. This factor is usually included in a capital investment estimate to compensate for unpredictable events and errors in cost estimation. Because of the speculative nature of the design, a fairly high contingency of 25 per cent of the total direct plant cost is used.[13,14]

Contingency = (0.25)($449,300) = $112,000

m. Fixed capital investment. The sum of the total direct plant cost, contractor's fee and contingency gives the fixed capital investment for the complete process of removal of sulfate from 10 per cent brine by bacteria. To the nearest $1,000, this sum is $578,000.

2. Manufacturing Cost Estimates

Manufacturing costs are those costs incurred in the day-to-day operation of the plant by virtue of the consumption of raw materials, labor, utilities and from other expenses. The direct manufacturing cost of the activated-sludge plant which includes all costs other than plant overhead, depreciation, and taxes and insurance has been estimated from the literature, as discussed earlier. The fixed manufacturing cost for the sulfur recovery plant, which includes all costs, is found from extrapolation of Fig. 15. All other costs are computed and itemized below.

a. Raw Materials. The yearly cost of raw materials is estimated from the required flow rates and the price of each material as listed in the Oil, Paint and Drug Reporter.[21] The prices are not adjusted for freight. Table 7 summarizes the raw materials costs for the bacterial sulfate-reduction process.

Table 7. Costs of raw materials for removal of sulfate by bacteria in 10 per cent brine

Raw material	Flow rate lb/hr	Cost/unit[21]	Cost/year
NH_4Cl, granular	34	$0.06 /lb	$17,600
H_3PO_4, 75 per cent	15	0.056/lb	7,300
$Na_2S \cdot 9H_2O$, flake	15	0.065/lb	8,400
Molasses, blackstrap	425	0.12 /gal	36,700
			$70,000

b. Labor. Since the entire plant runs continuously, there is no need for a large labor force and one operator is most likely sufficient for running the plant. This cost will not include any labor associated with operation of the activated-sludge unit and the sulfur-recovery plant. Labor is estimated as follows:

Men/shift	Man hr/day	Cost/man hr	Cost/day	Cost/year
1	24	\$3.50	\$84.00	\$30,200

c. Supervision. At the most, one supervisor is all that would be necessary, working 8 hours per day and 40 hours per week. The supervisor's salary is estimated at \$8,000 per year.

d. Maintenance. Maintenance requirements vary widely with each piece of equipment and are dependent on the nature of the process. If maintenance requirements are not known for each piece of equipment, the usual approach to estimating is to assume the yearly cost is a certain percentage of the fixed capital investment. According to Perry,[7] 4 per cent per year of the fixed capital investment is a minimum for new installations, but the estimate can go as high as 20 per cent[19] for corrosive service. For this study, it is assumed that maintenance labor and materials can be estimated at 2 per cent each of the fixed capital investment less the investment for activated-sludge and sulfur-recovery, and that maintenance overhead costs are 1 per cent of the adjusted fixed capital investment, for a total of 5 per cent.[22] The adjusted fixed capital investment is computed as follows:

Total fixed capital investment = \$578,000.

Fixed capital investment of sulfur-recovery plant =
(1.25)(\$36,000) = \$45,000.

Fixed capital investment of activated-sludge plant =
(1.2)(\$104,000)(1.29) = \$161,000.

Adjusted fixed capital investment = \$578,000 -\$45,000 -\$161,000
= \$372,000.

Maintenance labor = (0.02)($372,000) =	$ 7440
Maintenance materials = (0.02)($372,000) =	7440
Maintenance overhead = (0.01)($372,000) =	3720
Total maintenance cost =	$18,600

e. Plant supplies. These include items such as gaskets, charts, lubricants, etc., used by plant personnel in the normal operation of equipment. It is approximated as 15 per cent of annual maintenance costs.[14]

Plant supplies = (0.15)($18,600) = $2,800

f. Utilities. The utilities required for the continuous removal of sulfate from brines with bacteria are process water, electric power, and steam. The amount of process water required comes from the material balance. Table 8 lists the users of electric power (not including activated-sludge and sulfur-recovery). The continuous centrifuge consumes 64 per cent of the total power, making it a significant factor in yearly costs. The H_2S stripping tower consumes 860 lb/hr of steam in removing 25.6 lb/hr of H_2S from the brine stream.

Utility	Consumption	Cost/unit[7]	Cost/year
Process water	7430 gal/hr	$0.20/1000 gal	$12,800
Power	3770 kw hr/day	0.01/kw hr	13,500
Steam	860 lb/hr	0.40/1000 lb	3,000
Total cost of utilities			$29,300

g. Total direct manufacturing cost. Summing the above items gives the direct manufacturing cost for the bacterial sulfate removal as $158,900. From the literature,[9] the direct manufacturing cost (operating and maintenance) for the activated-sludge unit is found to be $8,700 per year. The total direct manufacturing cost is thus $158,900 + $8,700 = $167,600.

h. Plant overhead. Plant overhead normally includes costs for general plant upkeep and overhead, payroll overhead, medical, restaurants, salvage, laboratories, storage facilities and packaging.[19] Since most of these

Table 8. Electric power requirements for the removal of sulfate by bacteria in 10 per cent brine

User	Hp	Kw	Kw hr/day
Mineral mix tank agitator	2	1.5	1.5
Mineral metering pump	1	0.75	18
Rock salt conveyor	1	0.75	18
Phosphoric acid pump	0.5	0.375	9
Blending tank agitator	10	7.5	180
Process water pump	5	3.75	90
Molasses feed pump	1	0.75	18
10% brine feed pump	5	3.75	90
Anaerobic fermentor agitator	35	26.2	630
Centrifuge	135	100	2,400
Pressure filter pump	10	7.5	180
Stripper feed pump	5.5	4.12	99
Stripper gas compressor	2	1.5	36
Total power			3,770

items are assumed already available and considering the small number of personnel needed to run the plant, overhead will not be large. Peters[19] recommends using 50 to 70 per cent of operating labor, supervision, and maintenance labor. We will choose 50 per cent.

Operating labor:	\$30,200
Supervision:	8,000
Maintenance labor:	7,440
Total:	\$45,640

Plant overhead = (0.5)(\$45,640) = \$22,800

i. Indirect manufacturing cost. Plant overhead is the only cost of importance under this heading, amounting to \$22,800.

j. Depreciation. The operating costs for the sulfur-recovery plant includes depreciation charges. For the remainder of the plant, including the activated-sludge unit, depreciation is estimated as 10 per cent of the fixed capital investment. This gives the plant a lifetime of 10 years assuming straight-line depreciation. The fixed capital investment less the sulfur recovery plant is \$578,000 -\$45,000 = \$533,000.

Depreciation = (0.1)(\$533,000) = \$53,300

k. Taxes and insurance. Generally, 2 to 3 per cent of the fixed capital investment is used for estimating taxes and insurance on property and equipment.[22] In this case the capital investment does not include that for sulfur recovery, as for depreciation. As 2 per cent,

Taxes and insurance = (0.02)(\$533,000) = \$10,700

l. Fixed manufacturing cost. The sum of depreciation and taxes and insurance is the fixed manufacturing cost, amounting to \$64,000.

m. Manufacturing cost--sulfate removal. Addition of direct manufacturing costs, indirect manufacturing cost, and fixed manufacturing cost gives the manufacturing cost for removal of sulfate by bacteria from 10 per cent brine. The yearly cost is \$254,400.

n. Manufacturing cost--sulfur recovery. A description of the operation and economics of the Claus Process for sulfur recovery was given in section D of this chapter. From Fig. 15, the total operating cost for a plant of 0.31 long tons per day capacity is $170 per long ton of sulfur for the period 1950-1954. Updating this cost to 1966 is not straightforward as is the case for investment cost, since some important factors in operating cost, such as utilities and raw materials, may remain constant or even decrease in cost, while other items such as maintenance and depreciation vary with capital investment, which generally increases year-to-year. Labor costs, generally independent of capital investment, have been increasing as well. For a plant of small capacity, as in this study, investment-dependent costs, such as depreciation, taxes, maintenance, and costs for labor, supervision and overhead, are dominant over utilities costs, which are independent of plant size on a per-pound-of-product basis. The economic breakdown given by Kohl and Fox[36] shows that utilities costs represent only 4.6 per cent of the total operating cost for a 20-long-ton-per-day plant, while these costs amount to 21 per cent for a plant producing 320 long tons per day.

Therefore, for a small plant producing a mere 0.31 long tons of sulfur per day, operating costs over the years will follow investment costs reasonably closely, and the CE Plant Cost Index can be applied to updating operating costs. The index for 1952 is 81.3, and has a value of 105.6 for January 1966. Yearly manufacturing cost for sulfur removal in January 1966 is calculated as: ($170/long ton)(0.31 long tons/day)(360 days/year)(105.6/81.3) = $26,200.

o. Credit for sulfur. Part of the operating costs for H_2S disposal via conversion to sulfur is recovered in the value of the sulfur produced. The March 1966 price of crude sulfur is $27.00 per long ton;[21] neglecting distribution, packaging, and other costs, the yearly revenue from sale of the sulfur will be:

(0.31)(27.00)(360) = $3200.

p. Total manufacturing cost. Adding the manufacturing costs for sulfate removal and sulfur recovery, and allowing for sulfur credit, the total manufacturing cost for removing sulfates from 10 per cent brine with bacteria is $277,000, to the nearest $1000.

q. Cost per pound of rock salt. At a consumption rate of 7090 lb/hr of rock salt, the cost for removal of sulfate will be: $277,000/(7090)(24)(360) = $0.0045/lb rock salt.

r. Accuracy of cost estimate. The accuracy of the estimates of capital investment and manufacturing cost are judged to be about ±25 per cent.

3. Summary of Investment and Manufacturing Costs.

Tables 9 and 10 provide summaries of investment and manufacturing costs for the removal of sulfate from 10 per cent brine with bacteria.

Table 9. Estimated capital-investment statement for producing 10 per cent sulfate-free brine by bacterial reduction

Basis: Capacity = 85 tons rock salt/day

Operating time - continuous, 360 days/year

CE Plant Cost Index:[1] 105.6

Installed equipment	$130,200		
Piping	39,000		
Insulation	7,200		
Instrumentation	13,000		
Electrical installations	9,100		
Buildings and services	32,700		
Yard improvements	9,100		
PHYSICAL PLANT COST - BACTERIAL REDUCTION		$240,300	
PHYSICAL PLANT COST - ACTIVATED SLUDGE		104,000	
Engineering and construction	$ 69,000		
DIRECT PLANT COST - SULFATE REMOVAL		$413,300	
DIRECT PLANT COST - SULFUR RECOVERY		36,000	
Contractor's Fee	$ 16,500		
Contingency	112,000		
FIXED CAPITAL INVESTMENT			$578,000

Probable accuracy of estimate: ±25%

Table 10. Estimated manufacturing-cost statement for producing 10 per cent sulfate-free brine by bacterial reduction

Basis: Capacity = 85 tons rock salt/day
Operating time - continuous, 360 days/year

Raw materials	$70,000		
Labor	30,200		
Supervision	8,000		
Maintenance	18,600		
Plant supplies	2,800		
Utilities	29,300		
DIRECT MANUFACTURING COST - BACTERIAL REDUCTION		$158,900	
DIRECT MANUFACTURING COST - ACTIVATED SLUDGE		8,700	
Plant overhead	$22,800		
INDIRECT MANUFACTURING COST		$ 22,800	
Depreciation	$53,300		
Taxes and insurance	10,700		
FIXED MANUFACTURING COST		$ 74,000	
MANUFACTURING COST - SULFATE REMOVAL			$254,400
MANUFACTURING COST - SULFUR RECOVERY			26,200
CREDIT FOR SULFUR			3,200
TOTAL MANUFACTURING COST			$277,000
COST PER POUND OF ROCK SALT			$0.00455

Probable accuracy of estimate: ±25%

III. PRODUCTION OF SULFATE-FREE SATURATED BRINE BY BACTERIAL SULFATE REDUCTION

A. Process Description

1. Design Basis

Saturated brine is the desired raw material in the chlorine-caustic industry. Unfortunately, sulfate-reducing bacteria do not grow well in saturated brine since they must expend a good deal of energy keeping water within their cells and NaCl out. Direct removal of sulfates from saturated brines by bacteria is probably not feasible.

In the manufacture of chlorine and caustic soda by diaphragm cells, a slurry of NaCl is recovered from the caustic evaporators and is recycled to the process input. An undersaturated brine can thus be used for initial feed, although a 10 per cent brine is still too dilute and would require concentration. In the mercury-cell process, which is rapidly overtaking the diaphragm-cell process, a dilute brine stream is recovered and recycled, so that solid rock salt is necessary as initial feed. If sulfate were to be removed by bacteria from a 10 per cent brine it would be necessary to remove water before it could be used in either of the above processes, the mercury-cell process requiring considerably more water removal than the diaphragm-cell process.

It would be of some interest to determine what additional investment and operating costs would be required to concentrate a 10 per cent brine, from which the sulfate has been removed, to a saturated condition. The simplest approach to removal of the water is by evaporation.

The design flow rate of rock salt is again 85 tons per day, equivalent to producing 50 tons per day of chlorine. The process assumptions for the discussion of Chapter II hold here as well.

2. Design of Evaporator

Design criteria:

Inlet stream water content = 9/1 = 9 lb H_2O/lb NaCl

Outlet stream water content = 100/36.2 = 2.76 lb H_2O per lb NaCl

Water removal rate = (0.975)(7090)(9.00-2.76) = 43,000 lb/hr

Available steam: 50 psig, 298°F, λ = 912 Btu/lb

Available cooling water: 70°F

Pressure, temperature in condenser: 4 in. Hg, 125°F

In the design of an evaporator for removing substantial quantities of liquid, it is desirable to find the optimum number of effects. The method developed by Reinhold and Connelly[34] is useful for obtaining a rapid estimate of this optimum number. The procedure is as follows:

If C_1 represents the cost of a single-effect evaporator for evaporating a given quantity of liquid, the non-capitalized cost of an N-effect evaporator, V_1, with a payout time of A years for the same evaporation is approximated by

$$V_1 = C_1 N^{0.75}/A$$

Operating costs, including labor, cooling water, power and maintenance can be represented by

$$V_2 = \frac{hWC_2}{S} + V_0$$

where h = annual operation time in hours

W = water evaporated, lb/hr

C_2 = steam cost, \$/lb

S = steam economy, lb water/lb steam

V_0 = operating costs other than steam

Expressing the steam economy as a geometric series,

$$S = s_1 + s_1s_2 + s_1s_2^2 + \text{---------} + s_1s_2^{N-1}$$

or, $$S = \frac{s_1(1-s_2^N)}{(1-s_2)}$$

where s_1 and s_2 are limits of the range of steam economy for a single-effect evaporator. The total annual cost is then

$$V = V_1 + V_2 = \frac{C_1}{A}N^{0.75} + \frac{(1-s_2)hWC_2}{s_1(1-s_2^N)} + V_0$$

The optimum cost will occur when $dV/dN = 0$. Performing the differentiation with V_0 assumed constant, Reinhold and Connelly obtain what they call the cost factor, $P = (AhWC_2)/(C_1)$, as a function of N and then plot the relation for different values of s_1 and s_2. This plot is shown in Fig. 16; it gives the optimum N for a given calculated P.

In order to determine the single-effect cost, C_1, the required heat-transfer area must be calculated. A heat balance on the evaporator shown in Fig. 17 satisfies the relation:

$$Q = UA\Delta T$$

where Q = total heat transferred, Btu/hr

U = overall heat-transfer coefficient, Btu/hr ft^2 °F

A = heat-transfer area

ΔT = temperature difference for heat transfer, °F .

The temperature of the boiling liquid is higher than the saturation temperature of 125°F because of the dissolved salt. Boiling-point rise for salt solutions may be estimated from Figs. 11.19 of Perry.[7] Condensed vapor is used to preheat the incoming feed to an estimated temperature of 100°F. The heat load Q will be

$$Q = (69{,}000)(0.88)(135-100) + (43{,}000)(1017) = 45{,}600{,}000 \text{ Btu/hr.}$$

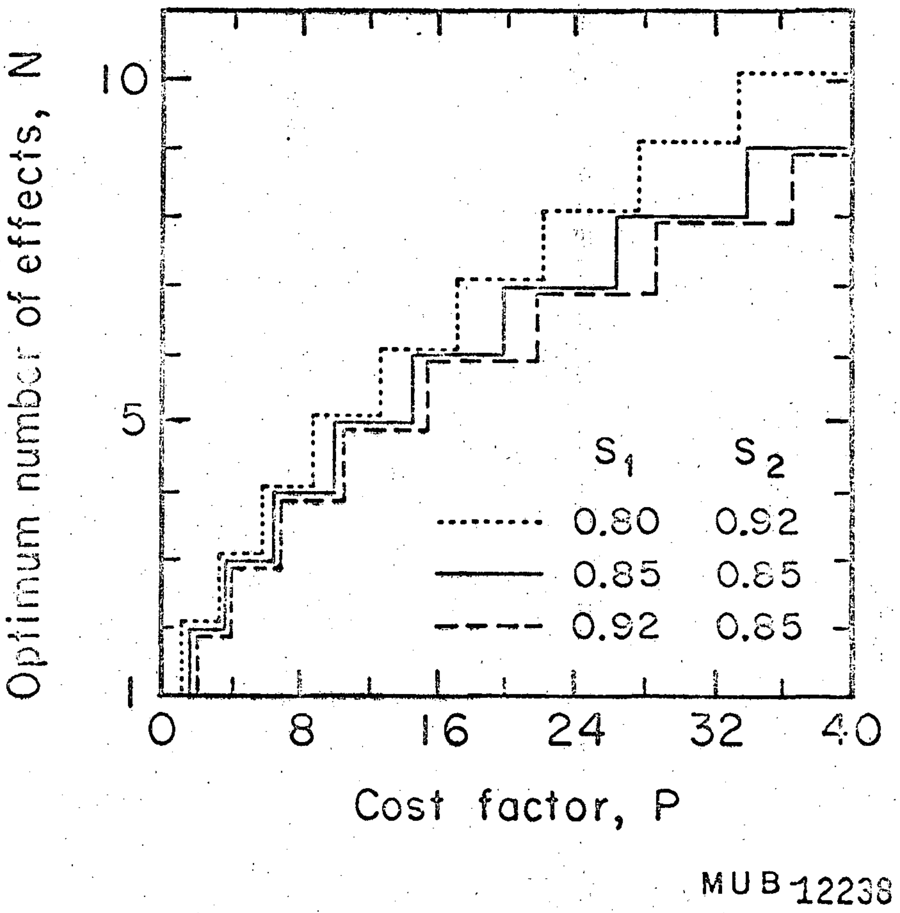


Fig. 16. Variation of optimum number of effects with cost factor, according to Reinhold and Connelly.[34]

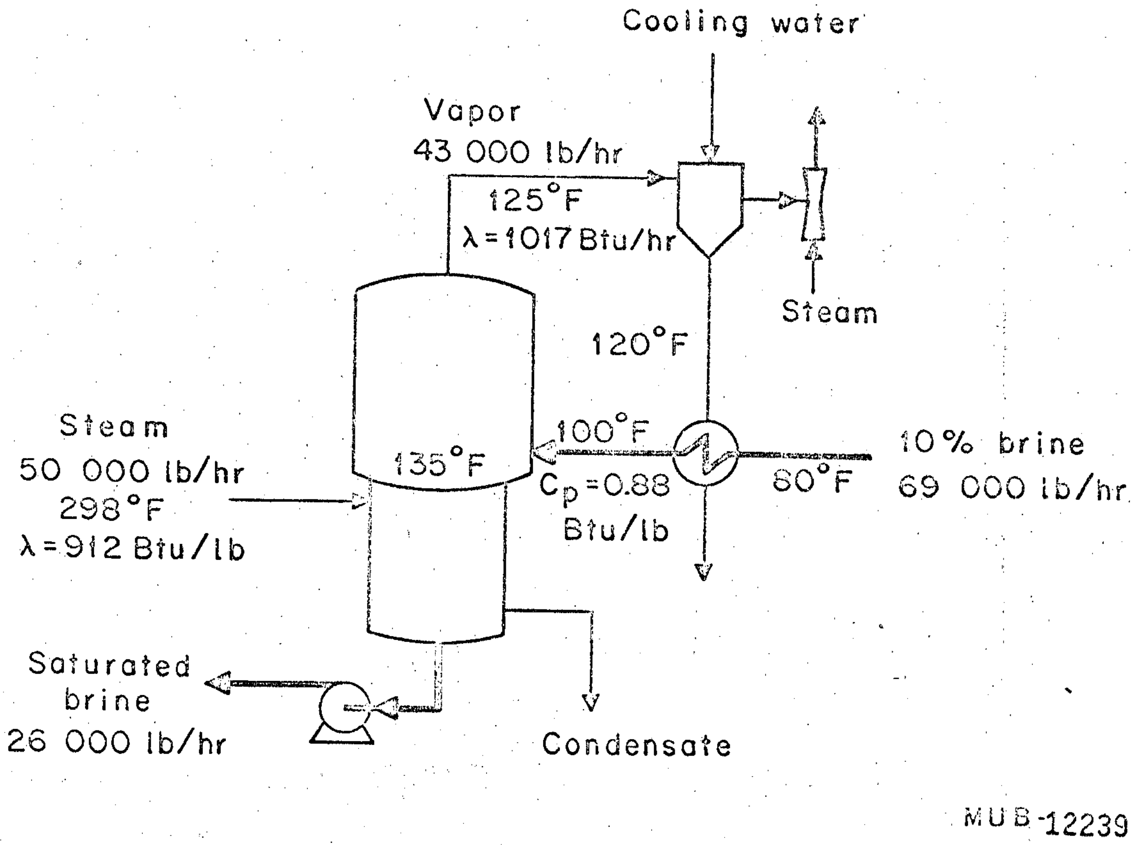


Fig. 17. Heat and material balances on a single-effect evaporator.

Steam requirement = 45,600,000/912 = 50,000 lb/hr.

Steam economy = 43,000/50,000 = 0.86.

The overall heat-transfer coefficient is estimated from Fig. 11.20 of Perry[7] which gives heat-transfer coefficients in salt evaporators as a function of boiling temperature. A value of $V = 500$ Btu/hr ft^2 °F is thus obtained. Then,

$$A = Q/U\Delta T = 45{,}600{,}000/(500)(298-135) = 560 \text{ sq ft.}$$

Perry[7] has given cost data for various types of evaporators as a function of total heat-transfer surface. For a Monel body, 90/10 Cu-Ni tubes, forced-circulation evaporator, the installed cost for 560 sq ft of surface including foundation, steelwork, evaporator assembly, pumps, instrumentation and auxiliary equipment is C_1 = \$55,000 in 1960, or C_1 = \$56,000 in February, 1966.

Values of other parameters are:

Annual operation (h)	= 8200 hours
Steam cost[7] (C_2)	= \$0.40/1000 lb
Payout time (A)	= 2 years

$$P = \frac{AhWC_2}{C_1} = \frac{(2)(8200)(43{,}000)(0.00040)}{56{,}000} = 5.0$$

From Fig. 16, the optimum number of evaporators, $N = 3$ for all values of s_1 and s_2 shown.

In the design of the triple-effect evaporator, the following assumptions are made in order to determine the temperature in each effect:

(1) Heat-transfer area is the same for each effect

(2) $V = 500$ Btu/hr ft^2 °F for each effect

(3) Amount of vapor evaporated is the same for each effect.

Then, the amount of vapor from each effect is 43,000/3 = 14,500 lb/hr.

Concentration in effect #3 = 12.8% by weight
Concentration in effect #2 = 17.5%
Concentration in effect #1 = 26.7%
Boiling point rise[7] in effect #3 = 3°F
Boiling point rise in effect #2 = 6°F
Boiling point rise in effect #1 = 18°F
Total BPR 27°F

Total available ΔT = 298-125-27 = 146°F

Therefore, if $A_1 = A_2 = A_3$ and $V_1 = V_2 = V_3$, $T_1 = T_2 = T_3 = 49°F$. Knowing the ΔT's, the temperature of the boiling liquid and vapor for each effect can be calculated.

The steam, cooling water and heat-transfer areas required can now be calculated from heat and material balances. The symbols used in the calculations refer to Fig. 18.

Data:

$(C_p)_F$ = 0.88 Btu/lb°F

$(C_p)_{L_3}$ = 0.86 Btu/lb°F λ_{L_3} = 1021 Btu/lb λ_{V_3} = 1023 Btu/lb

$(C_p)_{L_2}$ = 0.83 Btu/lb°F λ_{L_2} = 989 Btu/lb λ_{V_2} = 993 Btu/lb

λ_{L_1} = 946 Btu/lb λ_{V_1} = 985 Btu/lb

Heat balance on effect no. 3:

$$993V_2 = (69{,}000)(0.88)(128-100) + 1021V_3$$

Heat balance on effect no. 2:

$$958V_1 = (69{,}000-V_3)(0.86)(182-128) + 989V_2$$

Heat balance on effect no. 1:

$$912S = (69{,}000-V_3-V_2)$$

Overall material balance:

$$V_1 + V_2 + V_3 = 43{,}000$$

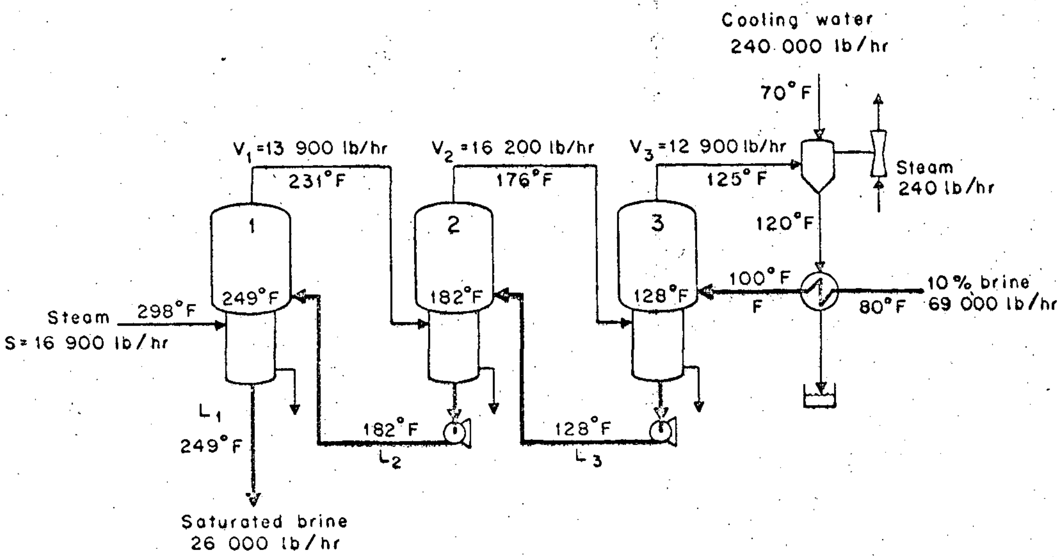


Fig. 18. Heat and material balances on a triple-effect evaporator.

Solution of the above simultaneous equations yields:

V_3 = 12,900 lb/hr

V_2 = 16,200 lb/hr

V_1 = 13.900 lb/hr

S = 16,900 lb/hr

Steam economy = 43,000/16,900 = 2.54.

Cooling water requirement is calculated as follows:

Cooling water temperature = 70°F

Vapor condensed = 12,900 lb/hr

Latent heat = 1023 Btu/lb

$W(1)(125-70) = (12,900)(1023)$

W = 240,000 lb/hr.

Steam requirement for single-stage jet ejector:

Required pressure = 100 mm Hg abs. (4 in. Hg)

Assuming a capacity (air-vapor mixture) of 30 lb/hr, steam consumption[12] at 100 psig is 240 lb/hr.

Heat-transfer areas are calculated from:

$Q = UA\Delta T$

$Q_1 = (912)(16,900)$; U_1 = 670 Btu/(hr)(sq ft)(°F); T_1 = 49°F

A_1 = 470 sq ft

$Q_2 = (958)(13,900)$; U_2 = 590 Btu/(hr)(sq ft)(°F); T_2 = 49°F

A_2 = 460 sq ft

$Q_3 = (993)(16,200)$; U_3 = 500 Btu/(hr)(sq ft)(°F); T_3 = 49°F

A_3 = 660 sq ft

Total area = 1600 sq ft

For more accurate calculations, the new values of U and A are used to recalculate T's, V's and still other A's. The iteration may be carried out until calculated values remain constant. The above calculations are assumed sufficiently accurate for this study, however.

3. Process Flow Diagram

Figure 19 illustrates the process of sulfate removal by bacteria with evaporation to produce a saturated brine.

4. Evaporator Specifications

Specifications for the design of the triple-effect evaporator are given in Table 11.

B. Investment and Manufacturing Costs

1. Investment Cost Estimates

Only the more important features of the cost estimate need be discussed, since the same percentage factors employed in the process involving no evaporation apply here as well.

a. Installed equipment. In addition to the installed equipment cost of $130,200 for the 10 per cent brine process, the following costs are added:

Item	Installed Cost February, 1966
Triple-effect evaporator	$134,000
Condensate collection tank	2,860
Cooling water pump (P-12)	1,550
Hotwell pump. (P-13)	1,550
Evaporation equipment cost	$139,960
Sulfate removal equipment cost	$130,200
Total equipment cost	$270,160

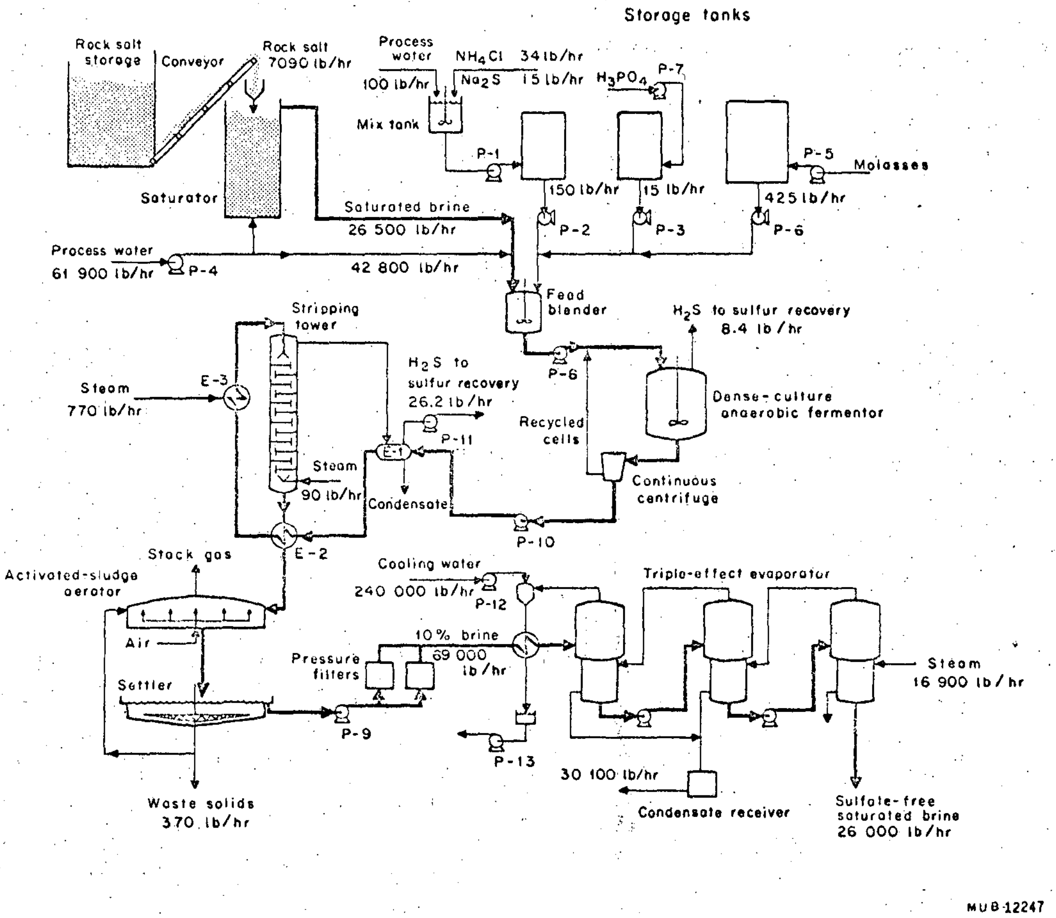


Fig. 19. Process flow diagram for production of sulfate-free saturated brine by bacterial reduction.

b. Buildings and services. The same cost of $32,700 used for the 10 per cent brine process and barium chloride process is again assumed.

2. Manufacturing Cost Estimates

Table 11. Specifications for a triple-effect evaporator

Purpose:	To concentrate 10 per cent brine to saturation
Type:	Forced-circulation, three effects
Required heat-transfer area:	1600 sq ft total
Materials of construction:	Monel body, 90/10 Cu-Ni tubes
Auxiliary equipment:	Foundation, steelwork, pumps, barometric condenser, hotwell, feed preheater, steamjet ejector.
Steam economy:	2.54
Installed cost:[7]	$130,000 (1960)

a. Labor. The addition of an evaporation step to the process does not necessitate an increase in the operating and supervisory manpower, since the continuous nature of the operation makes it amenable to automatic control.

b. Utilities. Evaporation normally requires a large amount of steam and cooling water. In this case, 16,900 lb/hr of steam for evaporation and 240 lb/hr for the jet ejectors are needed. For condensation of vapors from the third effect, 240,000 lb/hr of cooling-tower water are required. Collection of condensate from the first two effects allows a reduction of process water requirements from 61,900 lb/hr for the 10 per cent process to 31,800 lb/hr. Additional power needed for evaporation is shown below. The summary below clearly shows that steam costs are a major factor in the manufacturing cost of the evaporation process.

User	Hp	Kw	Kw hr/day
Evaporator pump	3	2.25	54
Evaporator pump	6	4.5	108
Cooling water pump	7.5	5.62	135
Hotwell pump	7.5	5.62	135
Total for evaporation			432
Total for sulfate removal			3770
Grand total			4200

Utility	Consumption	Cost/unit[7]	Cost/year
Steam	18,000 lb/hr	\$0.40/1000 lb	\$62,300
Tower water	29,000 gal/hr	0.02/1000 gal	5,000
Process water	3,810 gal/hr	0.20/1000 gal	6,600
Electric power	4,200 kw hr/day	0.01/kw hr	15,100
Total cost of utilities			\$89,000

3. Summary of Capital Investment and Manufacturing Costs

Tables 12 and 13 summarize the costs for removing sulfates from 10 per cent brine with bacteria with additional evaporation to saturate the brine. The costs are considerably higher with evaporation than without.

Table 12. Estimated capital-investment statement for producing sulfate-free saturated brine by bacterial reduction and evaporation

Basis: Capacity - 85 tons rock salt/day

Operating time - continuous, 360 days/year

CE Plant Cost Index:[1] 105.6

Installed equipment	$270,200	
Piping	81,000	
Insulation	14,800	
Instrumentation	27,000	
Electrical installations	18,900	
Buildings and services	32,700	
Yard improvements	26,200	
PHYSICAL PLANT COST - BACTERIAL REDUCTION		$471,000
PHYSICAL PLANT COST - ACTIVATED SLUDGE		104,000
Engineering and construction	$115,000	
DIRECT PLANT COST - SULFATE REMOVAL		$690,000
DIRECT PLANT COST - SULFUR RECOVERY		36,000
Contractor's fee	$ 22,000	
Contingency	181,000	
FIXED CAPITAL INVESTMENT		$929,000

Table 13. Estimated manufacturing-cost statement for producing sulfate-free saturated brine by bacterial reduction and evaporation

Basis: Capacity - 85 tons rock salt/day

Operating time - continuous, 360 days/year

Raw materials	$70,000		
Labor	30,200		
Supervision	8,000		
Maintenance	36,100		
Plant supplies	5,400		
Utilities	89,000		
DIRECT MANUFACTURING COST - BACTERIAL REDUCTION		$38,700	
DIRECT MANUFACTURING COST - ACTIVATED SLUDGE		8,700	
Plant overhead	$26,300		
INDIRECT MANUFACTURING COST		26,300	
Depreciation	$87,400		
Taxes and insurance	17,500		
FIXED MANUFACTURING COST		$104,900	
MANUFACTURING COST - SULFATE REMOVAL			$378,600
MANUFACTURING COST - SULFUR RECOVERY			26,200
CREDIT FOR SULFUR			3,200
TOTAL MANUFACTURING COST			$402,000
COST PER POUND OF ROCK SALT			$0.00661

IV. PRODUCTION OF SULFATE-FREE SATURATED BRINE BY BARIUM CHLORIDE PRECIPITATION

A. Process Description

1. Design Basis

The design capacity of the plant is 85 tons of rock salt per day, supplying NaCl for a 50-ton-per-day chlorine plant. Plant operation is continuous, 360 days per year. Plant location is assumed not important, though a logical choice of location is near the source of rock salt. The assumptions concerning land for the plant, utilities, storage and handling, auxiliary buildings, and capital are the same as outlined in Chapter II.

2. General Process Description

A process for barium chloride precipitation of the sulfate from brine may be divided into several unit operations. These are illustrated in Fig. 20.

a. Brine saturation. Sulfate-containing rock salt is contacted with water to produce a saturated brine.

b. $BaCl_2$ preparation. Barium chloride in solid form is dissolved in water to provide a reagent solution for precipitation of barium sulfate.

c. Precipitation of $BaSO_4$. Saturated brine and barium chloride solution are mixed in a vessel and $BaSO_4$ is allowed to precipitate from the brine.

d. $BaSO_4$ filtration. Slurried $BaSO_4$ is passed through a filtration unit to clarify the brine.

e. $BaSO_4$ drying. Wet $BaSO_4$ is dried and packed for sale.

3. Selection and Design of Process Steps

Here a description and design of the major processing units for the precipitation of barium sulfate from brines is given. For routine design calculations for some of the process equipment, the reader may refer to Appendix C.

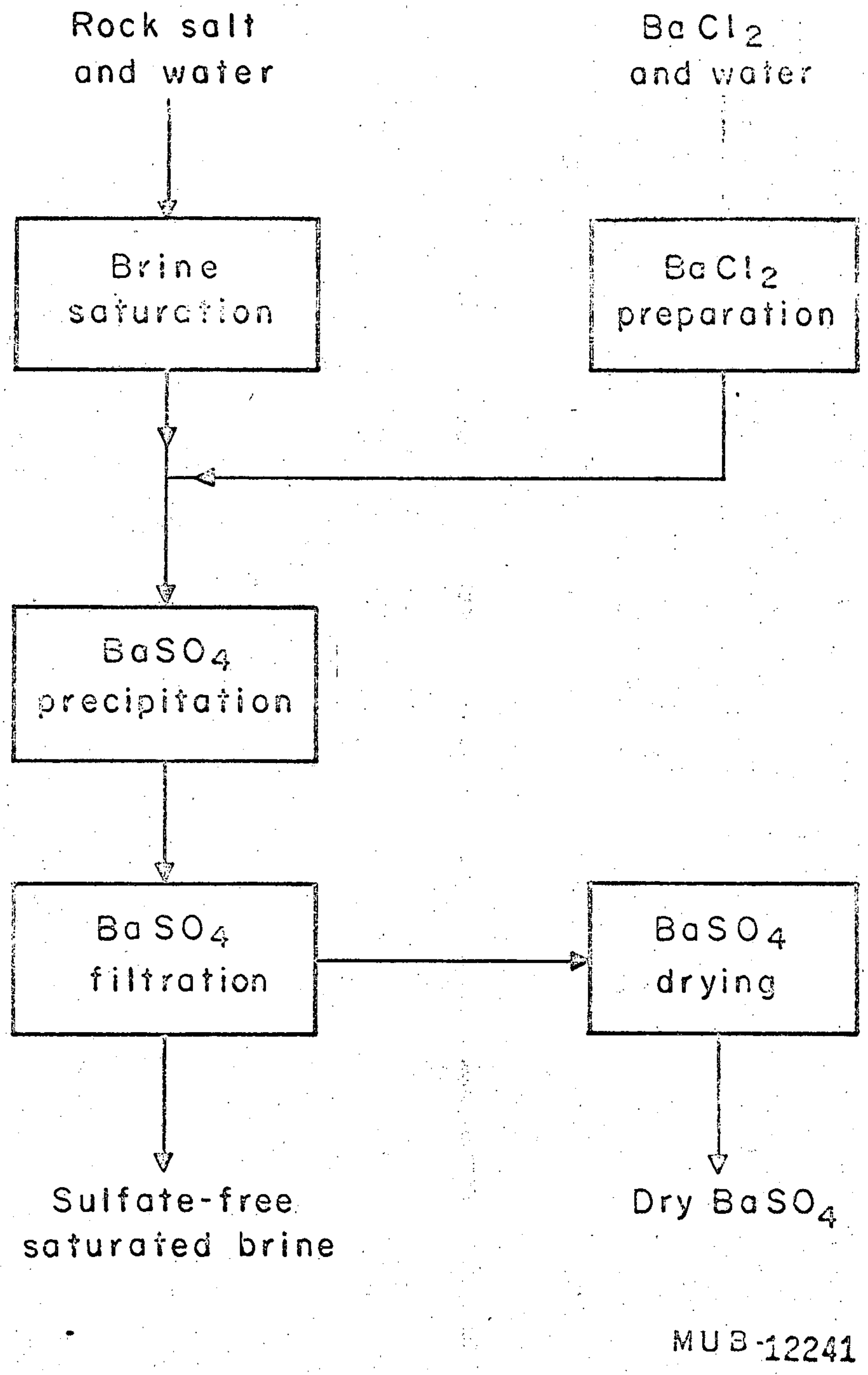


Fig. 20. Schematic description of a process for removing sulfates from brine by barium chloride precipitation.

a. Literature on $BaSO_4$ precipitation. There is little information in the literature on processes for removing sulfates from brine, mainly because precipitation with barium chloride or other barium salt is a straightforward process long practiced. Equipment for carrying out barium sulfate precipitation does not seem to merit description in the literature and the process has not been described in detail.

Hengerer[23] has proposed using the bed of rock salt for treatment of brines by adding suitable precipitating agents such as barium chloride in solid form to the rock salt or introducing them into the process water. The water is allowed to flow through the bed by gravity. Precipitated impurities are removed by the lower portion of the salt bed which acts as a filter. This method is quite economical but removes less sulfate than the bacterial reduction method and less sulfate than that theoretically possible considering the low solubility of barium sulfate. Hirsch[24] recommends the use of calcium chloride and a calcium sulfate "seed" to precipitate calcium sulfate from the brine, but reports only 67 per cent sulfate removal.

Most other approaches are the quite logical one of mixing the sulfate-containing stream with a precipitating agent such as barium chloride for a certain period of time, and then removing the precipitated barium sulfate. The process proposed in this study is the author's own version of this rationale.

b. Brine saturation. Saturated brine is made up in the same manner as in the bacterial sulfate reduction process, viz., by passing water upwards through a bed of rock salt contained in a 20-foot concrete tower. The brine overflows at the top saturated with NaCl. The bed is maintained at a constant level by a controlled conveyor.

c. BaCl$_2$ preparation. The quantity of BaCl$_2$ needed is such that a saturated solution can be made up batchwise twice a day and transferred to a storage tank. To dissolve 2810 pounds of BaCl$_2$ in 960 gallons of water, a 1200-gallon tank is adequate. To hold 1 1/2 days' supply of BaCl$_2$ solution, a 3000-gallon storage tank is required.

d. Barium sulfate precipitator. The design of this vessel is on a somewhat arbitrary basis. A literature search on barium sulfate precipitation did not turn up any useful kinetic equation which could be used in the design of a suitable precipitator. A correlation developed by O'Rourke and Johnson[25] shows excellent agreement with data for precipitation of barium sulfate from very dilute solutions. Their experiments show that the precipitation is a surprisingly slow process in solutions of concentration on the order of 1 mM/l. About 1.5 hours elapse before precipitation is complete. They also found that temperature has very little effect on the rate of precipitation. The concentration of sulfate in the saturated brine is about 50 mM/l, so that the kinetics probably will not follow the O'Rourke-Johnson model which was developed from experiments on solutions of less than 1 mM/l.

In discussing his process for the purification of alkali metal halides, Hay[26] suggests that after addition of barium chloride to precipitate sulfates the solution should be boiled for 1 to 10 hours to obtain complete precipitation. In the gravimetric determination of sulfate in analytical chemistry, a 1-hour period of digestion below the boiling point is recommended in order to promote formation of large particles and to prevent co-precipitation of sodium chloride.[27]

In the absence of usable kinetic data, the precipitation vessel is designed on an estimated basis of 1 hour's residence time with the slurry maintained at 90°C with steam in a surrounding jacket. With a flow rate of 26,200 pound per hour of brine which has a density of 9.94 pounds per gallon, and with a flow of 84.5 gallons per hour of saturated barium chloride solution, the required volume is about 2800 gallons. Glass-lined steel is chosen for corrosion-resistance because it is actually cheaper than a stainless-steel or stainless-clad jacketed vessel.[13]

Calculations of the requirements for steam and heat-transfer area for the jacket are shown in Appendix C.

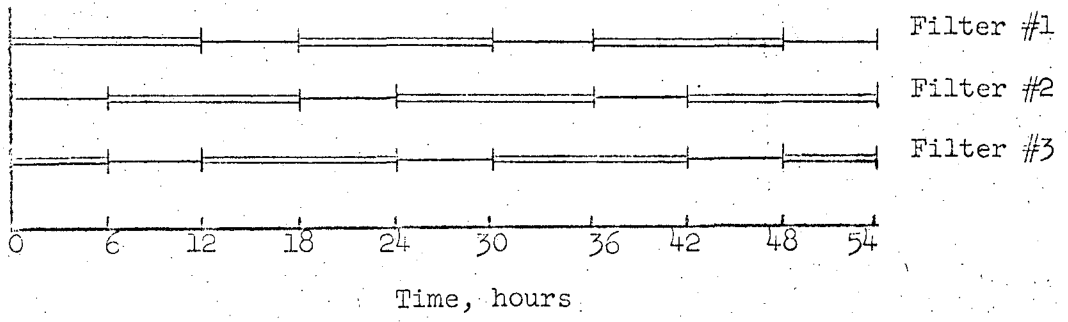
e. Feed preheater. Considerable savings on steam is possible by preheating the incoming feed with the hot effluent from the precipitator. Since both streams are alike and both are liquid, a double-pipe exchanger is chosen rather than the shell-and-tube type. Stainless steel is used because of the hot brine being handled. Calculation of required heat-transfer area is shown in Appendix C.

f. Barium sulfate filter. Selection of a solids-liquid separator is a more difficult problem than selection of most other pieces of process equipment. To make a proper choice, detailed information on the process variables are usually required. Laboratory or pilot-plant tests on the material involved are essential for determining the best approach.

However, it is possible to make a reasonably good choice of the type of equipment to use by consideration of the properties of the material being filtered and the process conditions prevailing. For example, Smith[28] suggests that in dewatering less than 300 pounds per hour of solids, continuous filtration or centrifugation probably are not economical. If complete separation is desired and recovery of the solids also desired, filtration would be better than settling. If the recovered solids are to be further processed, washing should be incorporated into the separation process. Chalmers, et al.[29] indicate that for filtering suspensions of low solids concentration (less than 1 per cent by weight), pressure filters such as the plate-and-frame type should be considered.

In this design, the production of barium sulfate is 250 pounds per hour. Its concentration in the brine stream is 0.92 per cent by weight. It is assumed that the barium sulfate is to be recovered and then dried in a subsequent process step. These conditions indicate that a thorough-washing plate-and-frame filter press is a logical choice for solids removal.

In designing the filter press, constant-flow-rate filtration at 100 psig is assumed. Calculations in Appendix C show that a filter area of 1000 sq ft is required. If a continuous flow of filtrate is to be maintained with a single filter press, it would be necessary to have storage tanks before and after the press and to have a filter area larger than 1000 sq ft. If two presses were used alternately for a calculated filling time of 24 hours each, the tanks could be eliminated but each filter would have to have 1000 sq ft of area and would stand idle for quite a few hours after it had been washed and emptied of cake. A more economical approach is to employ 3 filters in parallel, each with 500 sq ft of area, with filtration carried out in two presses while the third is put through a 6-hour wash and cleaning step. The filling time in each press is 12 hours. The diagram below shows that at any given time, 2 filters are in operation while one is being washed, emptied and reset. The double bar represents the filling step while the single bar represents the washing and emptying step.



Charts devloped by D. L. Sperry and Co.[30] indicate that for 500 ft^2 of filter area, a 32-inch press with 40 plates is most economical.

g. Barium sulfate dryer. If the barium sulfate is to be recovered and sold, it must first be dried. The product will be crude barium sulfate, which sells for $30 per ton.[21]

Filter cakes may be dried in several ways but a common and efficient method is by use of a rotary drum dryer. For this study, it is assumed that the filter cake is charged manually to a screw-type feeder which breaks up the cake and feeds it to a direct-type rotary dryer. Solids travel countercurrent to a stream of steam-heated air and are discharged directly into drums for shipping.

For estimating the required size, air flow rate, steam and power for a rotary dryer, the empirical methods given by Perry[7] are satisfactory. Costs are estimated from one of the articles appearing in Chilton's book.[13] Calculations of the above design requirements are given in Appendix C.

4. Process Flow Diagram

A flow sheet illustrating the process for removal of sulfates from brine with $BaCl_2$ is shown in Fig. 21.

5. Material Balances

The overall material balance for the barium chloride process is shown in Table 14. Table 15 gives the flow rates and percentages of components in the inlet and effluent brine streams. The barium chloride added for precipitation of sulfate presents an added impurity, though small, in the effluent brine stream.

As before, the basis for design is a 50 tons-per-day chlorine plant, which requires 85 tons per day or 7090 pounds per hour of rock salt. Sulfate represents 1.46 per cent by weight of the rock salt. This represents a sulfate-removal rate (100 per cent removal) of (0.0146)(170,000)/24 = 103 lb $SO_4^=$ per hour. If a 5 per cent excess of barium chloride is used for precipitation, the required amount is (103)(208/96)(1.05) = 235 lb $BaCl_2$ per hour. The amount of barium sulfate thus produced is (235)(233/208)/1.05 = 250 pounds per hour.

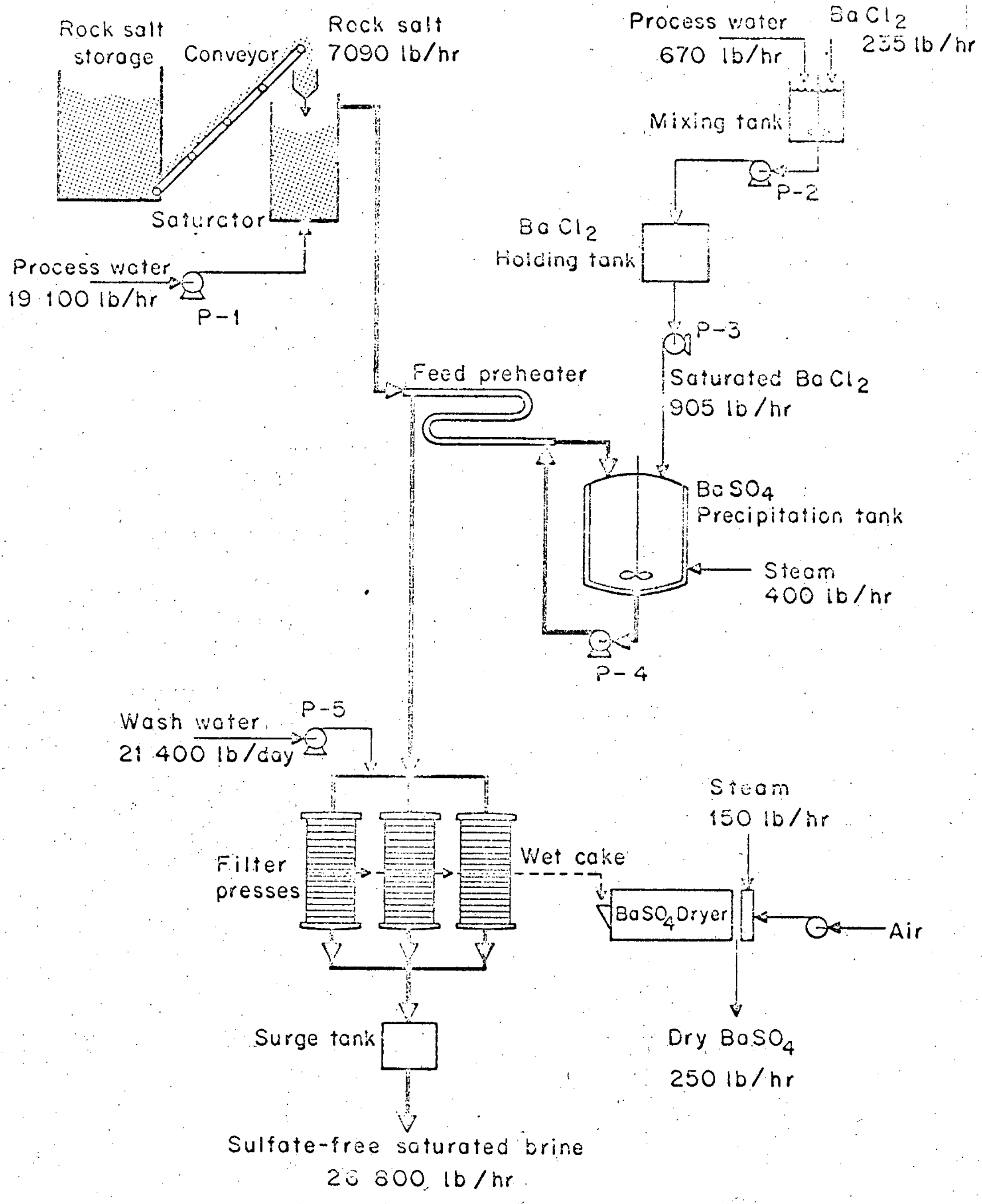


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Fig. 21. Process flow diagram for removal of sulfate from saturated brine by precipitation with $BaCl_2$.

Table 14. Overall material balance - barium chloride process

Materials	Input lb/hr	Output lb/hr
Rock salt	7,090	7,060
Process water	19,770	19,710
Barium chloride	235	12
Cake moisture		60
Dry barium sulfate		250
	27,090	27,090

Table 15. Flow rates and percentages of components in the brine stream - barium chloride process

Component	Input Flow lb/hr	Input Wgt. % Solids	Output Flow lb/hr	Output Wgt. % Solids
NaCl	6910	94.39	6943	98.37
$CaSO_4$	107	1.46	nil	0
Na_2SO_4	40.4	0.55	nil	0
$MgCl_2$	7.1	0.10	7.1	0.10
Fe_2O_3	7.8	0.11	7.8	0.11
Insolubles	14.2	0.19	nil	0
$BaCl_2$	235	3.20	12	0.17
$CaCl_2$			88	1.25
	7321	100.00	7058	100.00

The solubility of sodium chloride in water at 25°C is 36.2 grams per 100 grams of water.[33] The process water requirement is thus (7090)(.975)(100/36.2) = 19,100 pounds per hour. Since saturated salt solution has a density of 9.94 pounds per gallon, the brine stream flow rate is 2640 gallons per hour.

Since barium chloride has a solubility[33] of 35 grams per 100 grams of water at 25°C, the amount of water necessary for its solution is (235)(100/35) = 670 pounds per hour. With a density of 10.7 pounds per gallon, the volumetric flow rate of saturated barium chloride is (235 + 670)/10.7 = 84.5 gallons per hour.

The solubility of barium sulfate is extremely small, on the order of 2.5×10^{-4} grams per 100 grams of water, therefore, essentially all of the sulfate is assumed removed from the brine stream.

6. Design Specifications

a. Materials of construction. Because of corrosion problems with hot brines, the precipitation tank is constructed of glass-lined steel while the heat exchanger is of stainless-steel pipe. The slurry pump is also stainless steel. All other equipment and piping is of carbon steel or cast iron except the saturation tower which is concrete.

b. Process control. The following are the major controls assumed necessary for operation of the process:

(a) Control of rock salt level in the saturator
(b) Control of process water flow rate
(c) Control of saturated $BaCl_2$ solution flow rate
(d) Level control in the precipitator
(e) Flow control of filter effluent

c. Equipment list and specifications. A list of major process equipment and their January 1966 costs is shown in Table 16. Tables 17(a) through 17(h) provide the essential specifications for each piece of equipment and give the sources and dates of cost data.

B. Investment and Manufacturing Costs

1. Investment Cost Estimates

The methods employed in determining capital and manufacturing costs for the barium chloride process are the same as for the bacterial reduction process, i.e., by use of percentages and factors of equipment cost, capital investment or other known cost.

a. Installed equipment. Costs for equipment are obtained from the literature. The method of updating costs has been described in Chapter II, Section E-1.

b. Piping. Chilton's[13] suggestion of 30 per cent of installed equipment cost for a fluids-processing plant is used.

Piping = (0.3)($92,100) = $27,600

c. Insulation. As before, 5.5 per cent of installed equipment[14] cost is assumed.

Insulation = (0.055)($92,100) = $5,100

d. Instrumentation. For an average amount of instrumentation, 10 per cent of installed equipment cost is assumed.[13]

Instrumentation = (0.10)($92,100) = $9,200

e. Electrical installations. Aries and Newton[14] suggest an estimate of 7 per cent of installed equipment cost.

Electrical installations = (0.07)($92,100) = $6,400

f. Buildings and services. The need for buildings for this process is not large. Most of the equipment will be indoors, but the brine saturator and storage facilities need very little protection. From the values of 20 to

Table 16. List of major equipment for the process of sulfate removal by barium chloride precipitation

Equipment	Installed Cost, January 1966 CE Plant Cost Index = 105.6
Rock salt conveyor	$ 3,100
Process water pump (P-1)	1,500
Brine saturator	1,200
Barium chloride mix tank	4,700
Barium chloride transfer pump (P-2)	1,240
Barium chloride holding tank	3,400
Barium chloride metering pump (P-3)	840
Feed preheater	16,700
Barium sulfate precipitation tank	27,600
Barium sulfate slurry pump (P-4)	2,170
Filter press	5,200
Filter press	5,200
Filter press	5,200
Wash water pump (P-5)	1,670
Brine surge tank	970
Barium sulfate dryer	11,400
Total installed equipment cost	$92,100

Table 17. Equipment specifications for the process of sulfate precipitation from saturated brine with barium chloride

(a) Pumps

Pump	Type	Cap. (gpm)	Hp	Material of Construction	Installed cost, year, source
Process water pump	centrif.	44	10	CI	$1210 1954, 14
Barium chloride transfer pump	centrif.	106	1 1/2	CI	$ 740 1947, 13
Barium chloride metering pump	recipr.	2	1/2	CS	$ 500 1947, 13
Barium sulfate slurry pump	centrif.	44	13	CI	$1300 1947, 13
Wash water pump	centrif.	11	4 1/2	CI	$1000 1947, 13

(b) Barium chloride mix tank

Purpose: preparation of saturated barium chloride solution

Type: vertical, cylindrical, open top, top-mounted agitator

Capacity: 1200 gallons

Material of construction: carbon steel

Agitator power: 3 hp

Installed cost:[13] $2800 (1947)

(c) Barium chloride holding tank

Purpose: Storage of saturated barium chloride solution

Type: Vertical, cylindrical, totally enclosed

Capacity: 3000 gallons

Material of construction: Carbon steel

Installed cost:[13] $3,200 (1958)

Table 17. (continued)

(d) Feed preheater

Purpose: Preheat incoming brine with effluent from precipitator

Type: Double-pipe heat exchanger

Required heat-transfer area: 450 square feet

Design pressure: 150 psig

Material of construction: Both tubes of stainless steel

Installed cost:[13] $10,000 (1947)

(e) Barium sulfate precipitation tank

Purpose: Blending of brine stream with barium chloride to precipitate barium sulfate

Type: Totally enclosed, cylindrical, jacketed vessel, with agitator mounted through top

Capacity: 2800 gallons

Operating temperature: 90 to 100°C

Agitator power: 5 hp

Jacket heat-transfer area: 215 square feet

Materials of construction: Interior of vessel is glass-lined steel. Jacket and exterior is carbon steel.

Installed cost:[13] $26,000 (1958)

(f) Barium sulfate filters (3 identical)

Purpose: Removal of precipitated barium sulfate from brine stream.

Filter type: Plate-and-frame pressure type, hydraulic closing, thorough washing

Filtration area: 500 square feet

Plate size: 32 inches

Number of plates: 40

Operating pressure: 100 psig

Materials of construction: Cast iron plates and frames, steel framework and piping

Purchase cost:[31] $3,700 (1960)

Installation cost: 35 per cent of purchase cost[14]

Installed cost: $5,000 (1960)

Table 17. (continued)

(g) Brine surge tank

Purpose: To maintain a constant flow of purified brine for subsequent processing

Type: Totally-enclosed cylindrical tank, vented to atmosphere

Capacity: 660 gallons

Material of construction: Carbon steel

Purchase cost:[32] $700 (1960)

Installation cost: 30 per cent of purchase cost[14]

Installed cost: $900 (1960)

(h) Barium sulfate dryer

Purpose: To dry filter cake to a low moisture content

Type of dryer: Direct rotary

Capacity: 250 pounds dry solids per hour

Air flow rate: 240 pounds per hour per sq ft

Steam requirements: 150 pounds per hour

Dimensions: 16 feet long, 3 feet in diameter

Total power requirement: 6.8 hp

Operating temperature range: 110 to 250°F

Material of construction: Insulated steel shell, steel framework

Auxiliary equipment: Feeder, drives, fan, heater

Purchase cost:[13] $6,700 (1954)

Installation cost: 38 per cent of purchase cost[13]

Installed cost: $9,200 (1954)

60 per cent of installed equipment cost for mixed outdoor and indoor construction given by Chilton,[13] 35 per cent is chosen. It has already been assumed that buildings and services costs for the bacterial reduction process will be the same as for this case.

Buildings and services = (0.35)($92,100) = $32,700

g. Yard improvements. Seven per cent of installed equipment cost is used as before.[19]

Yard improvements = (0.07)($92,100) = $6,400

h. Total physical cost. The sum of the items a. through g. represents the total physical plant cost and amounts to $179,500.

i. Engineering and construction. Twenty per cent of the total physical cost[13] should be adequate.

Engineering and construction = (0.20)($179,500) = $35,900

j. Direct plant cost. When engineering and construction costs are added to the total physical plant cost, the direct plant cost is obtained. In this case it is $215,400.

k. Contractor's fee. This item is estimated to be 4 per cent of the direct plant cost.[19]

Contractor's fee = (0.04)($215,000) = $8,600

l. Contingency. The 25 per cent of direct plant cost assumed for contingnecy is somewhat higher than the average suggested by Aries and Newton.[14]

Contingency = (0.25)($215,400) = $53,800

m. Fixed capital investment. The fixed capital investment is the sum of the total physical cost, direct plant cost, contractor's fee and contingency. The fixed capital investment for the process of sulfate removal from brines by $BaCl_2$ precipitation is thus $278,000.

2. Manufacturing Cost Estimates

a. Raw materials. Cost of barium chloride is a major item in the total manufacturing cost of the barium chloride process.

Material	Flow rate	Cost/unit[21]	Cost/year
$BaCl_2$	5620 lb/day	$176/ton	$178,000

b. Labor requirement and cost. An operator will definitely be necessary for handling the filtration system. With a washing and cleaning time of 6 hours one man should have time to run the rotary dryer and make up a batch of barium chloride solution. One man, then, is assumed sufficient to operate the plant at any one time. Labor cost is thus the same as for the bacterial reduction process, i.e., $30,200 per year.

c. Supervision. As in the bacterial reduction process, supervision for 8 hours per day, 40 hours per week is assumed sufficient, at an annual cost of $8,000.

d. Maintenance. A breakdown of 2 per cent annually of fixed capital investment for maintenance labor, 2 per cent for materials and 1 per cent for overhead is again assumed.[22]

Maintenance labor = (0.02)($278,000) = $5,600
materials = (0.02)($278,000) = $5,600
overhead = (0.01)($187,000) = $2,800
Total maintenance cost : $14,000

e. Plant supplies. Estimate at 15 per cent of maintenance.[14]

Supplies = (0.15)($14,000) = $2,100

f. Utilities. Steam, process water, and electric power are the utilities required in this process. Steam is required in the jacket of the precipitator at a flow rate of 400 pounds per hour and for heating air in the dryer at a rate of 150 pounds per hour. Process water flows to the saturator at a rate of 19,100 pounds per hour. In addition, 16,100 pounds per day of water are required for preparation of barium chloride solution, and 21,400 pounds per day are used for washing filter cake. The electric power requirements are listed in Table 18.

Utility	Consumption	Cost/unit[7]	Cost/year
Steam	550 lb/hr	$0.04/1000 lb	$1,900
Process water	2480 gal/hr	$0.20/1000 gal	$4,100
Electric power	637 kw hr/day	$0.01/kw hr	$2,300
Total cost of utilities			$8,300

g. Direct manufacturing cost. Addition of items a. through f. gives the direct manufacturing cost associated with operation of the process. The total is $240,600.

h. Plant overhead. From Peters'[19] recommended range of 50 to 70 per cent of operating labor, supervision and maintenance labor, a value of 52 per cent is chosen, to include overhead for packaging the barium sulfate.

Operating labor:	$30,200
Supervision:	8,000
Maintenance labor:	5,600
Total:	$43,800

Plant overhead = (0.52)($43,800) = $22,800

i. Indirect manufacturing cost. The only indirect cost is plant overhead.

j. Depreciation. Assuming that the plant has a 10-year lifetime, with straight-line depreciation, cost is 10 per cent of fixed capital investment annually.

Depreciation = (0.10)($278,000) = $27,800

k. Taxes and insurance. Two per cent of fixed-capital investment is assumed.[22]

l. Fixed manufacturing cost. Fixed costs are those which must be paid out regardless of whether the plant is operating or not. Depreciation and taxes and insurance are fixed costs, amounting to $33,400.

Table 18. Electric power requirements for the removal of sulfate from saturated brine with barium chloride

User	Hp	Kw	Kw hr/day
Process water pump	10	7.5	180
Rock salt conveyor	1	0.75	18
Barium chloride tank agitator	3	2.25	14
Barium chloride metering pump	0.5	0.38	9
Precipitation tank agitator	5	3.75	90
Barium sulfate slurry pump	10	7.5	180
Wash water pump	5.5	4.0	24
Barium sulfate dryer	6.8	5.1	122
Total power			637 kw hr/day

m. Barium sulfate credit. If the removal of sulfates from the brine stream is carried out separately from other purification steps as it is in this design, the byproduct barium sulfate is amenable to recovery and the credit in its sale may be used to partially defray manufacturing costs. The barium sulfate recovered will be contaminated with insolubles from the brine stream, and residual salts not removed by washing. As such, the selling price of \$30 per ton for off-color, crude southern barytes is assumed.[21]

$$\text{Sales revenue} = \frac{(250\ \text{lb/hr})(24\ \text{hr/day})(360\ \text{day/yr})(\$30/\text{ton})}{2000\ \text{lb/ton}} = \$32{,}400\ \text{per year}$$

A major expense in the sale of a product is the packaging cost. Assuming the barium sulfate is packaged in 200-pound fiberboard drums, the packaging cost (materials only) is 0.5¢ per pound of product, or \$1.00 per drum. It is assumed that packaging does not require additional labor, since at the rate of 250 pounds per hour, a simple automatic weighing system is easily incorporated.

Packaging cost = (250 lb/hr)(\$0.005/lb)(24 hr/day)
(360 days/yr) = \$10,800 per year

Miscellaneous sales expense depends on the product, but an estimate of 2 to 4% of sales revenue may be used.[7]

Sales expense = (0.03)(\$32,400) = \$ 1,000

Sales revenue:	32,400
Packaging cost:	10,800
Sales expense:	1,000
Net barium sulfate credit	\$20,600

n. Total manufacturing cost. Summing direct, indirect, and fixed manufacturing costs, and allowing credit for barium sulfate recovery, the total manufacturing cost comes to \$276,000 annually.

o. Cost per pound of rock salt. If rock salt is consumed at a rate of 7090 lb/hr, the cost of removing the sulfate from it will be $276,000/(7090)(24)(360) = $0.00451 per pound.

p. Accuracy of cost estimates. As it was for the bacterial reduction process, the probable accuracy of cost estimates for the barium chloride process is ± 25 per cent.

3. Summary of Capital Investment and Manufacturing Costs

Summaries of the above discussion of capital and operating costs are provided in Tables 19 and 20.

Table 19. Estimated capital-investment statement for producing sulfate-free saturated brine by barium chloride precipitation

Basis: Capacity - 85 tons rock salt per day

Operating time - continuous, 360 days per year

CE Plant Cost Index:[1] 105.6

Installed equipment	$92,100		
Piping	27,600		
Insulation	5,100		
Instrumentation	9,200		
Electrical installations	6,400		
Buildings and services	32,700		
Yard improvements	6,400		
TOTAL PHYSICAL COST		$179,500	
Engineering and construction	$35,900		
DIRECT PLANT COST		$215,400	
Contractor's fee	$ 8,600		
Contingency	53,800		
FIXED CAPITAL INVESTMENT			$278,000

Probable accuracy of estimate: ±25%

Table 20. Estimated manufacturing-cost statement for producing sulfate-free saturated brine by barium chloride precipitation

Basis: Capacity - 85 tons rock salt per day
Operating time - continuous, 360 days per year

Raw materials	$178,000		
Labor	30,200		
Supervision	8,000		
Maintenance	14,000		
Plant supplies	2,100		
Utilities	8,300		
DIRECT MANUFACTURING COST		$240,600	
Plant overhead	$ 22,800		
INDIRECT MANUFACTURING COST		$ 22,800	
Depreciation	$ 27,800		
Taxes and insurance	5,600		
FIXED MANUFACTURING COST		$ 33,400	
BARIUM SULFATE CREDIT		20,600	
TOTAL MANUFACTURING COST			$276,000
COST PER POUND OF ROCK SALT			$0.00451

Probable accuracy of estimate: ± 25%

V. DISCUSSION OF RESULTS

The fixed capital investment for a plant to remove sulfates from a 10 per cent brine with bacteria ($578,000) is more than double the capital investment for removal with barium chloride ($278,000). Comparing the two flow diagrams, Figs. 12 and 21, this is not surprising, since considerably more equipment is necessary to carry out the former process. If an evaporation step is added to the bacterial process in order to produce a saturated brine, the investment cost increases to $929,000.

Comparison of Tables 10 and 20 indicates, however, that the bacterial process compares quite favorably with the barium chloride process in terms of manufacturing costs, which represent a more conclusive criteria in making a choice among alternative processes. The estimated costs, $277,000 for the former process, and $276,000 for the latter, are almost identical, though somewhat fortuitously so to be sure. On the other hand, if the 10 per cent brine is evaporated to saturation, operating costs of the bacterial reduction process rise to $402,000.

Cost improvements quite possibly can be made on the process of sulfate removal by bacteria. For example, if the anaerobic reduction of sulfates is allowed to proceed in the lower depths of large earthen basins over the course of several days' residence time rather than in a dense-cell cultivator, savings in investment and operating costs may be realized. On the other hand, it may be expensive to cover the basins in order to collect evolving H_2S. Also, poor mixing may result in incomplete sulfate reduction. Another area in which costs can be reduced is in stripping H_2S from the brine. If air pollution were of no concern, the H_2S could merely be stripped with air from the aerator and no attempt to recover it need be made. An earlier cost estimate showed that the manufacturing cost is $252,000 if H_2S is not recovered, giving a saving of 9 per cent. Other important savings could be made if the bacteria could be made to grow efficiently on a cheap carbon source such as sewage sludge or wood pulp liquors.

The proposed design for precipitation of barium sulfate may not be the most economical in terms of capital investment. Nevertheless, a look at Table 20 shows the direct manufacturing cost to be dominated by raw materials and labor which will remain essentially the same regardless of design. Indirect costs and fixed charges related to the capital investment are not large compared to the direct costs. It is felt, therefore, that the proposed design will give an adequate estimation of the economics of sulfate removal with barium chloride.

It should be kept in mind that a direct comparison of the two processes is not perfectly valid based on the information presented in Tables 10, 13 and 20. The reason for this, of course, is that the bacterial process in this study removes sulfate from a 10 per cent brine, while the barium chloride process removes the same amount of sulfate from a saturated brine.

Nevertheless, some important conclusions can still be made. First, it is apparent that it is not economical to produce a sulfate-free saturated brine by initially removing the sulfate with bacteria in a 10 per cent brine and then evaporating the excess water. Evaporating costs are high, as reflected in the utilities and depreciation charges of Table 13. A corollary of this first conclusion is that in removal of sulfate from saturated brine, barium chloride precipitation is more economical, simply because the bacteria will not grow well under those conditions. But on the other hand, an advantage is enjoyed by the bacterial reduction process in removal of sulfates from more dilute brines of 10 per cent or less salt.

This last point can be illustrated by the following argument: Suppose we wished to remove the sulfate from a 10 per cent brine by precipitating with barium chloride. Instead of handling about 27,000 lb/hr of brine when it is saturated, 69,000 lb/hr of 10 per cent brine would have to be handled. Assuming the six-tenths factor method[13] of cost estimating to be reasonably valid, the investment cost for the plant will be approximately

$(\$278,000)(69,000/27,000)^{0.6} = \$495,000$. Manufacturing costs directly proportional to fixed-capital investment such as maintenance, supplies, overhead, depreciation, and taxes and insurance would increase by \$41,000, in addition to an increase in utilities cost. Manufacturing costs would thus be about \$320,000, about 16 per cent higher than for the bacterial reduction process.

Using the six-tenths factor method, investment costs for sulfate removal from a 3 per cent brine for both processes may be estimated. By estimating the increase in manufacturing cost due to investment-dependent charges such as depreciation and maintenance, the manufacturing costs may also be approximated. Results are shown in Fig. 22. In all cases, 85 tons per day of rock salt is being processed and the same amount of sulfate is removed. The manufacturing costs curve does not take into account the increasing growth rate of the bacteria with decreasing salt concentration on the one hand, and the decreasing growth rate with decreasing sulfate concentration on the other. The calculations for neither process take into account the effect of investment costs on utilities. The calculations on which Fig. 22 is based are approximations at best, but serve to show the trend of costs with percentage of NaCl in brine and indicate that sulfate removal by bacteria from undersaturated brines compares quite favorably with the older method of precipitation with barium chloride.

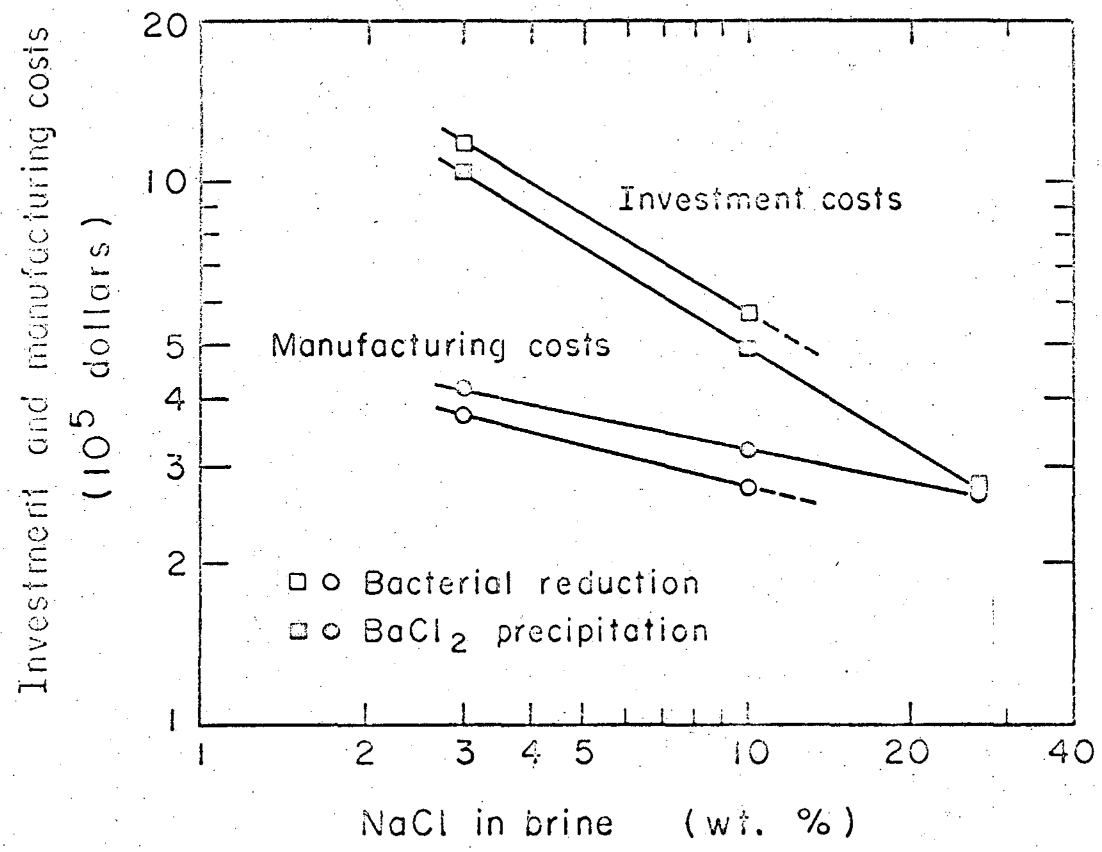

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Fig. 22. Estimated trends of investment and manufacturing costs for bacterial reduction and $BaCl_2$ precipitation processes as a function of per cent NaCl in the brine.
Basis: 85 tons/day of rock salt containing 1.46% sulfate.

VI. SULFUR FROM SEAWATER

The oceans have long been recognized as an unlimited potential source of a wide variety of chemicals. Other than Na^+ and Cl^-, the table below shows that the most abundant ionic constituents in ocean water are Mg^{++} and $SO_4^=$.

Ions	Grams per liter of ocean water
Cl^-	19.68
Br^-	0.07
$SO_4^=$	2.74
$CO_3^=$	0.08
Na^+	10.89
K^+	0.40
Mg^{++}	1.33
Ca^{++}	0.43
Total	35.62

The oceans are the major source of magnesium and bromine at present and have the very obvious potential of being an important supplier of sulfur to bolster the world's shrinking supply of Frasch-process sulfur. A preliminary literature survey has indicated that the sea has yet to be exploited for its sulfur to any significant extent, presumably because prevailing methods of sulfate removal such as treatment with barium salts, or the direct reduction of sulfate to sulfide by chemical means, are not economically attractive.

With the concentration of sulfate in seawater at 28.6 m M/l, compared to 18.3 m M/l in the 10 per cent brine of this design study, a halophilic strain of <u>Desulfovibrio</u> would grow quite well, converting most of the sulfate to sulfide, providing a suitable carbon source were supplied.

The British workers, Butlin, Selwyn and Wakerley, have successfully grown Desulfovibrio in raw sewage sludge to which sulfate was added.[41,42] The object of their investigations was to determine whether sufficient quantities of sulfide could be produced, with raw sewage as nutrient, for the possible conversion of H_2S to sulfur. They did not mention the possibility of supplementing a sulfate-containing raw material such as seawater with raw sewage, rather than adding the sulfate in solid form to the sewage. In their studies, they enriched the sewage with $CaSO_4$ to as high as 0.34 M/l and obtained 1.2-1.9% w/v sulfide as H_2S in 28 days' fermentation and 1% in 7 days.

The studies by Leban, Wilke, and Edwards[2,3] show that a halophilic strain of Desulfovibrio will grow well with concentrations of sulfate on the order of 10 m M/l, with subsequent reduction of most of the sulfate to sulfide. It is proposed then, that a process for reducing sulfates in seawater to sulfide by microbial action, with an inexpensive nutrient such as raw sewage, and with the ultimate aim of converting the sulfide to sulfur by conventional means, would warrant some study.

A flow diagram for a hypothetical process for recovering sulfur from seawater is shown in Fig. 23. Assuming the plant is located close to a large sewage treatment facility, a concentrated sewage sludge from the primary settling tanks is readily available for nutrient for the sulfate-reducing bacteria. Seawater is pumped directly from the ocean and mixed with the sewage sludge. The anaerobic sulfate reduction is allowed to proceed in a large enclosed basin with a residence time of a day or more. A proposed design for a suitable fermentation vessel is shown in Fig. 24. This design incorporates mixing sections at the entrance and exit of the vessel with flow channels constituting the major volume. There may be problems with the solids settling out in the channel, in which case it would be necessary to provide more complete mixing throughout the vessel. Hydrogen sulfide and other gases (methane is likely to be formed by methane bacteria) evolved from the liquid are collected by manifold pipes for

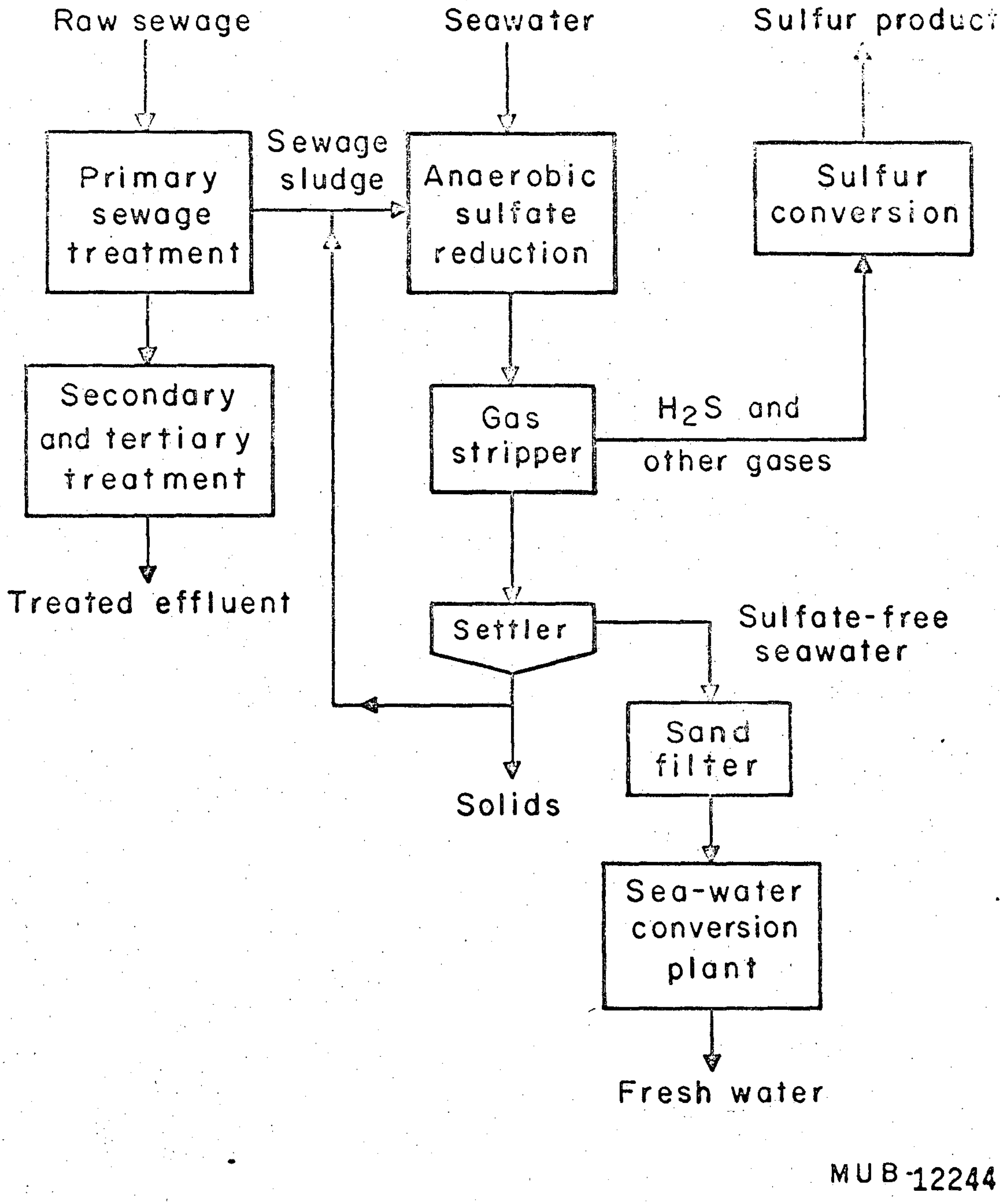

Fig. 23. Hypothetical process for recovering sulfur from seawater.

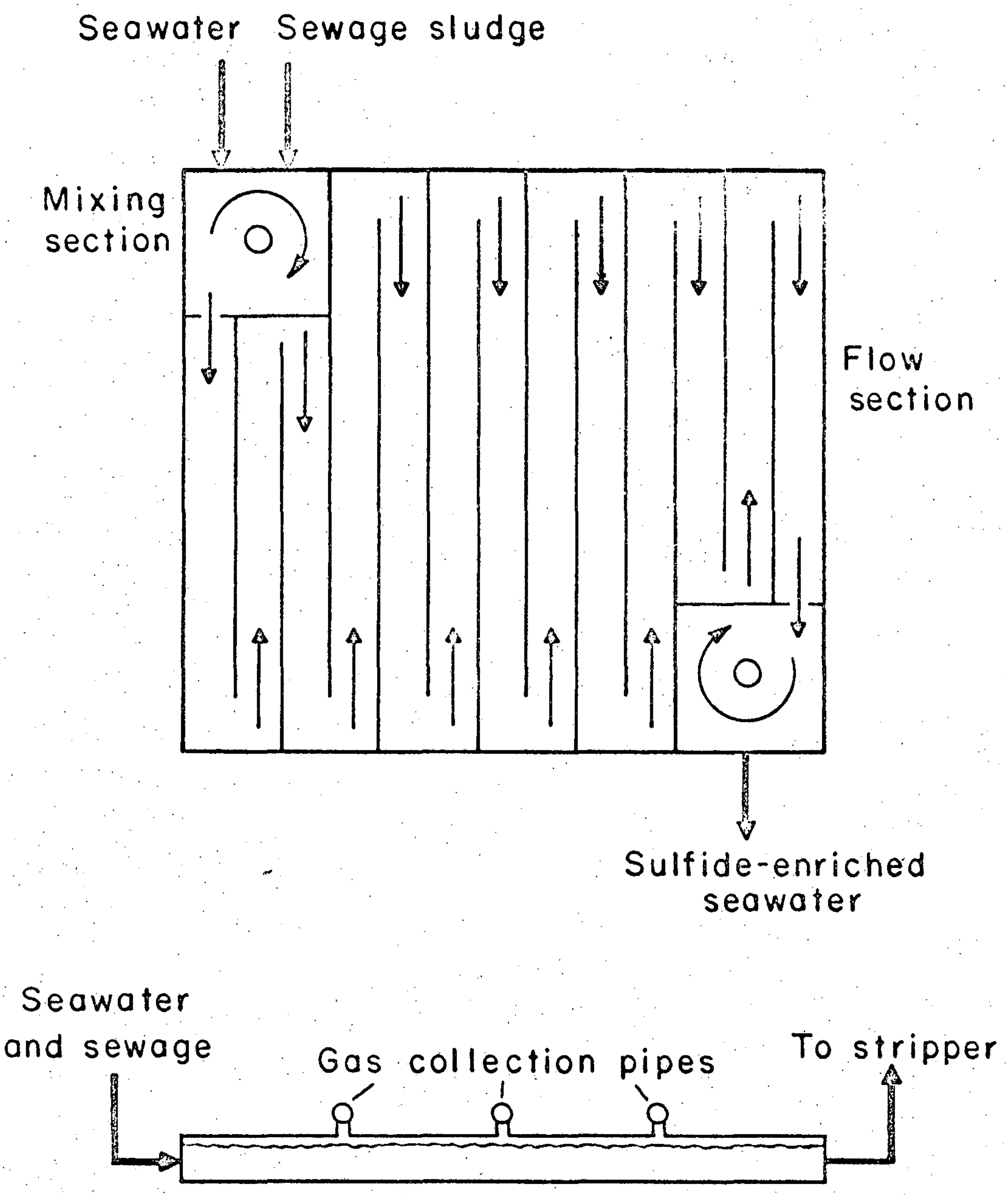

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Fig. 24. Proposed design of a large vessel for bacterial sulfate removal from seawater.

subsequent treating. Sulfide-enriched seawater is passed through a stripper to remove the dissolved H_2S. The stripping may be accomplished with steam, as described earlier in Chapter II, section C, if the amount of other gases such as CO_2 and CH_4 is not too large. In that case, the gases from the stripper may be used directly as raw material for production of sulfur by the Claus or other process.

Solids, including bacteria to some extent, are settled out of the effluent from the stripper. The bulk of the solids may be dried and incinerated or sold as fertilizer, while a portion is recycled to the anaerobic digester to help maintain a stable bacterial population.

The sulfate-depleted seawater is returned to the sea, or alternatively may be further processed to provide fresh water as shown in Fig. 23, or may be used for other purposes. In the case of seawater conversion, a real advantage is gained in having a sulfate-free feed stream, thereby avoiding the problem of fouling evaporators and heat exchange equipment with $CaSO_4$.

The main economic advantage of this process is that the raw materials, seawater and sewage, are both available in large quantities at essentially zero cost. Operation of the anaerobic digestion system is expected to be low in cost, and providing the plant has a fairly large sulfur capacity, say 50 long tons per day or more, it is conceivable that sulfur may be produced at a profit from this process. With sulfate-free seawater available, the operating costs of an adjacent seawater conversion plant may be reduced as well.

Shortly after the above proposal for recovery of sulfur from seawater with concomitant fouling-abatement for desalination plants was written, a news brief appeared in a recent issue of Chemical Engineering[50] which expressed the same ideas presented above, but based on a different process for removal of sulfates. The news brief reads:

> Great Salt Lake may yield its mineral riches at lower cost, thanks to a new desulfation process developed by the U. S. Bureau of Mines. Economical desulfation of the brine will facilitate recovery of the potassium and magnesium salts present in high concentrations in the lake. The Bureau's Salt Lake City Metallurgy Research Center, which developed the new process, says there is even a good chance for future recovery of lithium values present at much lower concentrations. The process also shows promise as a scale-control method in water desalting plants.
>
> The process is based on precipitation of the sulfate as barium sulfate. Economics depend on recovery and recycling of the barium and on production of salable byproducts.
>
> Sulfate-bearing brine is contacted with a cation-exchange resin in the barium form, simultaneously precipitating the sulfate as barium sulfate and converting the resin to the sodium form. The barium sulfate is recovered and roasted with carbon to form barium sulfide, which is dissolved to yield a strong solution of $Ba(OH)_2$ and $Ba(HS)_2$ that is in turn used to regenerate the spent resin, completing the cycle. Effluent liquor from regeneration is a solution of NaOH and NaHS that can be further and economically treated to yield soda ash and sulfur.

On the basis of this study, it would appear that the bacterial reduction process proposed may be competitive with this new development. Nevertheless, the feasibility of recovering sulfur from seawater or rock salt or any other sulfate-containing raw material, can only be determined from a detailed economic study based on data obtained on the actual behavior of sulfate reducers under the proposed conditions of operation.

VII. SUMMARY AND CONCLUSIONS

This work is a continuation of the study of the sulfate-reducing bacteria, Desulfovibrio, particularly a salt-tolerant strain isolated from salterns of San Francisco Bay. The previous investigators, Leban, Wilke, and Edwards, have given a complete description of the isolation and ecology of this microorganism and have provided kinetic data on its growth in batch and continuous culture.[2,3] The ultimate object of the research was, in addition to contributing to the general understanding of sulfate-reducers, to obtain a basis from which the economic importance of sulfate reduction by bacteria could be evaluated.

A possible economic utilization of sulfate-reducing bacteria is in the removal of sulfates from salt brines. A plant design and economic study was carried out for a process to remove sulfate from a 10 per cent rock salt brine which was presumed to be a raw material in the manufacture of chlorine and caustic soda. The plant capacity was based on a 50-ton-per-day chlorine plant. To obtain a basis for comparison of relative economic advantages, a plant for removal of the sulfate from a saturated rock salt brine stream by precipitation with barium chloride was designed, and operating costs were determined. The latter process is the common technique for removal of sulfates from industrial process streams. The additional expense of concentrating the 10 per cent brine by evaporation was determined by design and cost estimate procedures for the purpose of comparison on the basis of a saturated brine product. Sulfate-reducers are not expected to grow very well in saturated brine (26.7%), although it was possible to acclimatize them to salt concentrations up to 16 per cent.[2]

Important features of the bacterial reduction process include a dense-culture anaerobic fermentation system utilizing a continuous centrifuge for recycling cells, and an activated-sludge system for removal of organic matter from the process stream. Both of these unit operations deserve more research than has been carried out in the past, particularly in application to biochemical engineering practice. In addition, a steam-stripper is employed for removing H_2S from the brine stream, and a Claus process facility converts the H_2S to sulfur, thus eliminating the air pollution problem.

The principal operations in the barium chloride process involve precipitation and digestion of barium sulfate in a steam-heated vessel with subsequent filtration and drying of the solids. The evaporator designed for concentrating 10 per cent brine was found to require an optimum number of three effects, according to the method of Reinhold and Connelly.[34]

The results of the cost estimates gave the following indications:

1. Removal of a given quantity of sulfate from a 10 per cent brine stream by bacterial reduction is economically comparable to removal of the same quantity of sulfate from a saturated brine by barium chloride precipitation.

2. The costs required for concentrating a 10 per cent brine to saturation (26.7 per cent) make the barium chloride process more economical than the bacterial process in producing sulfate-free saturated brine. The bacteria are not expected to grow well in brines more concentrated than about 16%.

3. For brines of 10 per cent or less salt, removal of a given quantity of sulfate with bacteria is more economical than removal with barium chloride.

Microbial sulfate reduction shows some promise as a means for converting sulfates in seawater to H_2S, which can then be processed by conventional pathways to sulfur. The oceans have yet to be challenged for their sulfur content in spite of the abundant supply and the fact that anaerobic sulfate reduction by bacteria takes place quite naturally in ocean water.

The process proposed in this study employs an extremely cheap growth nutrient, namely sewage sludge. In addition to obtaining sulfur from H_2S produced in the process, the sulfate-free seawater obtained may be used to advantage in a seawater conversion plant.

Further research under the design operating conditions is necessary in order to assess more accurately the feasibility of sulfate removal and sulfur recovery via anaerobic sulfate reduction by Desulfovibrio.

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APPENDICES

A. Design Calculations- Bacterial Reduction Process

The design of the agitated anaerobic fermentor, continuous centrifuge, activated-sludge system and the sand and anthrafilt filters has been discussed in the text. Below, the design of the remaining major pieces of equipment is presented.

1. Rock Salt Conveyor

Since the saturation tower is 20 to 25 feet high, a conveyor at 30° to the horizontal would be about 45 feet in length.

Design capacity: 8000 lbs/hr
Density of rock salt: 190 lb/ft^3
Void fraction: 0.64
Volume per pound = 1/(190)(0.36) = 0.0136 ft^3/lb
Designing for a belt width of 14 inches, and a bed depth of 2 inches, the average belt speed will be:
Average belt speed = (8000)(0.0146)(144)/(2)(14)(60) = 10 ft/min
Power requirement: 1 hp is judged adequate

2. Rock Salt Saturation Tower

Rogers, in his Manual of Industrial Chemistry, describes the preparation of saturated brine for the chlorine-caustic industry as follows:[43]

> If the starting material is solid rock salt, the brine is prepared in a saturator, a tall, square concrete tank about 6 ft square × 20 to 25 ft high. The tank is kept full of salt. Water is introduced from the bottom of the tank, and the flow is so regulated that as it forces its way up it becomes sautrated and flows from the outlet at the top as saturated brine. Salt is constantly added to keep the tank full, and the mud that accumulated in the saturator may be flushed out at intervals through the outlet opening at the bottom.

The tank is designed for an inside height of 20 ft and is 6 ft square on the inside. Walls and floor are 6 inches thick. Wall area is (20)(6)(4) = 480 sq ft, while the floor area is (7)(7) = 49 sq ft.

3. Mineral Dissolving Tank

A batch is made up once a day, requiring 2400 lb of water. The minimum volume necessary is thus 2400/8.35 = 288 gal. A volume of 350 gal is adequate, and using a rule of thumb of 5 hp/1000 gal for mixing, about 2 hp for the agitator will be needed.

4. Brine Blending Tank

A residence time of 15 minutes is specified. At a volumetric flow rate of 7400 gal/hr, the required volume is (7400)(15)/60 = 2000 gal. A 10 hp agitator is adequate for this volume, assuming 5 hp/1000 gal.

5. Process Water Pump

The pump capacity is 7400 gal/hr or 123 gpm. Calculations showed that the pressure drop due to the bed of rock salt is negligible. Assuming an average head of 25 ft, including friction losses, the theoretical power requirement is:

$$W_0 = \frac{(25)(123)(62.4)}{(60)(7.48)(550)} = 0.8 \text{ hp}$$

A centrifugal pump with this power requirement has an efficiency of 16 per cent, according to Braca and Happel in an article appearing in Chilton's book.[13] Therefore, the actual power requirement is 0.8/0.16 = 5 hp.

6. Molasses Storage Tank

Molasses is required at the rate of 10,200 lb/day. Specifying one month's storage, (30 days) the storage capacity must be (10,200)(30)/12 = 25,500 gal. Density of molasses is 12 lb/gal.

7. Phosphoric Acid Storage Tank

The requirement for this nutrient is 15 lb/hr. To hold a 30 days' supply, the necessary capacity is (15)(24)(30)/(1.58)(8.35) = 820 gal. The specific gravity of 75 per cent H_3PO_4 is 1.58.

8. Brine Feed Pump

The same design conditions apply as for the process water pump, giving a power requirement of 5 hp.

9. Pressure Filter Pump

Assuming an operating pressure of 50 psi, the head will be approximately (50)(34)/15 = 115 ft. Flow rate is 130 gpm. Minimum power is:

$$W_0 = \frac{(115)(130)(62.4)(1.067)}{(60)(7.48)(550)} = 3.5 \text{ hp}$$

The brine specific gravity is 1.067.

The efficiency of a centrifugal pump with the above power requirements is 37 per cent. The actual power requirement is thus 3.5/0.37 = 10 hp.

10. Mineral Solution Storage Tank

A storage capacity of 5 shifts or 40 hours is assumed. The volume necessary is then (288 gal/day) (40 hr)/(24 hr/day) = 500 gal.

11. Single-Stage, Stirred Tank Fermentor

This design was one of the rejected alternatives discussed in Chapter II, section C-3. The design is carried out as follows:

A cell balance on the fermentor in Fig. 5(a) gives:

$$\frac{dx}{dt} = -Dx + \mu x$$

where μ = specific growth rate, day^{-1}

D = dilution rate, $\frac{F}{V}$, day^{-1}

x = cell concentration, cells/l

F = flow rate, gallons per day

V = volume, gallons

At steady state,

$$D = \frac{F}{V} = \mu$$

Since $\mu = f(s)$ (Fig. 3), where s is the concentration of sulfate in the fermentor and is known, the fermentor volume V can be calculated directly from the above equation. Specifically, when

$s = 0.2$ mM/l
$\mu = 0.13 \text{ days}^{-1}$
F = 187,000 gallons per day
V = 187,000/0.13 = 1,440,000 gallons

This tremendous volume presents a problem in obtaining sufficient mixing and requires a high investment cost (see Table 2).

12. Two-Stage, Stirred Tank Fermentor

Design criteria:

F = 7800 gallons/hour = 187,000 gallons/day
$s_1 = 5.0$ m M/l
$s_2 = 0.2$ m M/l
$s_0 = 18.3$ m M/l

A cell balance on first stage of Fig. 5(b) at steady-state gives:

$$\frac{F}{V_1} = \mu_1 \qquad (1)$$

A sulfate balance at steady-state results in:

$$0 = D_1 \, [s_0 - s_1] \left(\frac{1}{x_1} \frac{ds}{dt}\right) x_1$$

for $s_1 = 5.0$ m M/l
$\mu_1 = 0.29 \text{ day}^{-1}$ (Fig. 3)
$\left(\frac{1}{x_1} \frac{ds}{dt}\right) = 0.24 \times 10^{-10}$ m M/cell -day (Fig. 4)

$$V_1 = 187{,}000/0.29 = 645{,}000 \text{ gallons}$$

$$x_1 = \frac{(0.29)(18.3-5.0)}{(0.24\times10^{-10})} = 1.61 \times 10^{11} \text{ cells/l}$$

A cell balance on the second stage at steady-state yields:

$$0 = D_2(x_1-x_2) + \mu_2 x_2$$

$$D_2 = \frac{F}{V_2} = \frac{\mu_2 x_2}{x_2-x_1} \qquad (2)$$

A sulfate balance at steady-state results in:

$$0 = D_2\left[s_1-s_2\right] - \left(\frac{1}{x_2}\ \frac{ds}{dt}\right) x_2 \qquad (3)$$

Substituting Eq. (2) into Eq. (3),

$$\frac{\mu_2(s_1-s_2)}{x_2-x_1} = \left(\frac{1}{x_2}\ \frac{ds}{dt}\right)$$

$$x_2 = \frac{\mu_2(s_1-s_2)}{\left(\frac{1}{x_2}\ \frac{ds}{dt}\right)} + x_1$$

for $s_2 = 0.2$ mM/l

$\mu_2 = 0.13 \text{ day}^{-1}$ (Fig. 3)

$\frac{1}{x_2}\ \frac{ds}{dt} = 0.125 \times 10^{-10}$ m M/cell-day (Fig. 4)

$$x_2 = \frac{(0.13)(5.0-0.2)}{0.125 \times 10^{-10}} + 1.61 \times 10^{11} = 2.11 \times 10^{11} \text{cells/l}$$

$$V_2 = \frac{(187{,}000)(2.11 \times 10^{11}-1.61 \times 10^{11})}{(0.13)(2.11 \times 10^{11})} = 340{,}000 \text{ gallons}$$

$V_1 + V_2 = 985{,}000$ gallons

The total volume required is less than in the case of a single-stage fermentor, but the difference in cost is not significant. Again, mixing requirements remain an uncertainty.

13. Stripping Tower Condenser

Steam-containing gases from the stripper enter the condenser and are cooled by the incoming brine stream passing through the tubes to about 88°F. H_2S enters at a partial pressure of 1.85 psia, CO_2 is at 2.54 psia, and the partial pressure of water vapor at 88°F is 0.615 psia. The total pressure is then 5.01 psia.

Water vapor enters at 212°F at 90 lb/hr. Brine is at 86°F at a flow rate of 69,000 lb/hr. The amount of water vapor leaving the condenser is 4.6 lb/hr. Neglecting sensible heat of the gases,

Heat duty $Q = (90-4.6)(970) + (1)(90-4.6)(212-87)$

$Q = 94{,}400$ Btu/hr

$Q = (69{,}000)(0.88)\Delta T$

$\Delta T = 1.5°F$; leaving brine is at about 88°F.

The film coefficient for condensation is affected by the presence of non-condensibles. The film heat-transfer coefficient may be estimated by the correlation developed by Othmer:[51]

$$\log f = \log \Delta T\,[1.213-0.00242T] + \left[\frac{\log T}{3.439} - 1\right] \times$$

$$[\log (c + 0.505) - 1.551-0.009T]$$

where f = film coefficient, Btu/hr ft^2°F

ΔT = temp. drop, steam to film = 125°F

T = steam temp. = 212°F

c = % non-condensibles = 11.2 + 15.6 = 26.8%

therefore,

$$\log f = 2.26$$

$$f = 182 \text{ Btu/hr ft}^2 \text{ °F}$$

For calculating the liquid-side coefficient,[7]

$$\frac{hD}{k} = 0.023\left(\frac{Dv\rho}{\mu}\right)^{0.8}\left(\frac{C_p\mu}{k}\right)^{1/3}$$

$C_p = 0.88$ Btu/lb°F

$\mu = 1.5$ cp $= 3.63$ lb/ft hr

$k = 0.35$ Btu/hr ft^2 (°F/ft)

For brine flowing through 1-inch tubes at 5 fps,

$D = 1/12$ ft

$v = 5$ ft/sec $= 18{,}000$ ft/hr

$\rho = (1.067)(62.4) = 70.5$ lb/ft^3

Performing the calculations,

$h = 738$ Btu/hr ft^2 °F

$$\frac{1}{U} = \frac{1}{f} + \frac{1}{h} = \frac{1}{182} + \frac{1}{738}$$

U = overall coefficient = 146 Btu/hr ft^2 °F

$Q = UA\Delta T$

$A = (94{,}400)/(146)(125)$

$A = 5.1$ ft^2 = required heat-transfer area.

14. Tower Feed Economizer.

The economizer is a heat exchanger which allows the heat from the tower bottoms to be transferred to the feed brine stream. Both streams flow at a rate of 69,000 lb/hr. Entering feed brine is at 88°F, and specifying a ΔT at both ends of the exchanger of 12°F, the feed will emerge at 200°F, since the bottoms brine is at 212°F. With $C_p = 0.88$ Btu/lb °F,

$Q = (69{,}000)(0.88)(200-88)$

$Q = 6.8 \times 10^6$ Btu/hr

$Q = UA\Delta T$

$\Delta T = 12°F$

$U = 250$ Btu/hr ft^2 °F, estimated from Table 6 of Peters,[19] for aqueous solutions on both sides of exchanger.

$A = (6.8 \times 10^6)/(250)(12)$

$A = 2700$ ft^2 = required heat-transfer area.

15. Tower Feed Heater

Since the economizer cannot possibly exchange all the heat from the bottoms brine to the feed, additional heat will be required to elevate the feed from 200°F to 212°F, the operating temperature of the stripper. The heating may be done by condensing steam in a shell-and-tube heat exchanger, using 30 psia steam at 250°F.

$Q = (69{,}000)(0.88)(12) = 730{,}000$ Btu/hr

Steam requirement, S:

$\lambda = 945$ Btu/lb

$S = 730{,}000/945 = 770$ lb/hr

$Q = UA\Delta T_{lm}$

$U = 400$ Btu/hr ft^2 °F estimated from Table 15.1 of Foust et al.[44]

$$\Delta T_{lm} = \frac{(250-200) - (250-212)}{\ln \frac{(250-200)}{(250-212)}} = 43°F$$

$A = (730{,}000)/(400)(43) = 43$ ft^2 = required heat-transfer area.

16. Tower Feed Pump

The height of the tower is about 25 ft including the base. With an estimated pressure drop of 10 ft in piping and exchangers, the total head is about 35 ft.

$$\text{Output hp} = \frac{(35)(69{,}000)}{(3600)(550)} = 1.22$$

Efficiency[13] = 22%

Required hp = 1.22/0.22 = 5.5 hp.

17. Tower Exit Gas Compressor

Conditions of operation:

Intake pressure = 5.01 psia

Intake temperature = 90°F

Discharge pressure = 15 psia

Gas molar flow rate = 2.03 lb moles/hr

For isothermal compression, the theoretical hp requirement is given by:

$$hp = 3.03 \times 10^{-5} p_1 q_1 \ln \frac{p_2}{p_1}$$

where p_1 = intake pressure = 720 lb/ft^2

p_2 = delivery pressure = 2160 lb/ft^2

q_1 = cubic feet of gas per min at intake conditions.

Assuming an ideal gas,

$$q_1 = \frac{(2.03)(359)}{(60)} \left(\frac{15}{5.01}\right) \left(\frac{530}{492}\right) = 39.1 \text{ cfm}$$

$$hp = (3.03 \times 10^{-5})(720)(39.1) \ln \frac{2160}{720}$$

$$hp = 1.12$$

Isothermal efficiencies are generally[19] 50-60%. Using 60%

Actual hp = 1.12/0.6 = 2

18. Calculation of Stripping Tower Efficiency

According to the method developed by the AIChE, two equations are recommended for calculating the number of gas and liquid film-transfer units for bubble-cap plates:

$$N_G = (0.776 + 0.116W - 0.290F + 0.0217L)/(Sc)^{0.5}$$

$$N_L = (1.065 \times 10^4 D_L)^{0.5}(0.26F + 0.15)t_L$$

where W = weir height, in.

F = F factor $(v(\rho_G)^{0.5})$ based on the bubbling area of the plate

L = liquid flow rate, gal/(min)(ft width)

Sc = gas-phase Schmidt number

D_L = liquid diffusivity, ft^2/hr

t_L = liquid contact time, sec., calculated as $t_L = 37.4\ Z_c Z_L/L$

Z_L = length of liquid travel between inlet and outlet weirs (ft)

Z_C = liquid holdup on plate, in^3/in^2, which is correlated by the equation

$$Z_C = 1.65 + 0.19W - 0.65F + 0.02L$$

The gas-phase Schmidt number, $\mu/\rho D_{AB}$, is calculated from the following data:

$\mu = 0.0125$ cp (water vapor at 100°C, 1 atm)

$\rho_g = 7.2 \times 10^{-4}$ g/cm^3 (from steam table)

$D_{AB} = 0.15$ cm^2/sec (estimated for the binary system H_2S-H_2O by the Chapman-Enskog correlation)

$$N_{Sc} = (1.25 \times 10^{-4})/(7.2 \times 10^{-4})(0.15) = 1.16$$

The bubble-caps and trays have the following dimensions:

$W = 2$ in

Diameter of column = 3 ft (specified)

Tray bubbling area = 66% of total area = $(0.66)\pi$

$$(1.5)^2 = 4.6 \text{ ft}^2$$

l = average column width = 66% of tray width =

$$(0.66)(3) = 2 \text{ ft}$$

Z_L = 75% of tray width = (0.75)(3) = 2.25 ft

From an average gas molar flow rate of 5.91 lb moles/hr,

$$u_g = 0.151 \text{ ft/sec}$$

$$F = u_g(\rho_g)^{0.5} = 0.032$$

with a brine flow rate of 7800 gal/hr,

$$L = (7800)/(60)(2) = 65 \text{ gpm/ft}$$

$$N_G = (0.776 + 0.116(2) + 0.290(0.032) + 0.0217(65))/(1.16)^{0.5}$$

$$N_G = 2.22$$

$$Z_c = (0.19)(2) + (0.65)(0.032) + (0.02)(65) + 1.65$$

$$Z_c = 3.35 \text{ in}^3/\text{in}^2$$

$$t_L = (37.4)(2.25)(3.35)/(65) = 4.35 \text{ sec}$$

$D_L = 1.61 \times 10^{-5}$ cm^2/sec 25°C (H_2O-H_2S system from Table 14-51 of Perry)[7]

Assuming $\frac{D\mu}{T}$ = constant,

$$D_L = 4.0 \times 10^{-5} \text{ cm}^2\text{/sec} = 15.5 \times 10^{-5} \text{ ft}^2\text{/hr at } 100°\text{C}$$

$$N_L = (100)(1.55 \times 10^{-4})^{0.5}(0.26(0.032) + 0.15)(4.35)$$

$$N_L = 0.86$$

$$-\frac{1}{\ln(1-E_{OG})} = \frac{1}{N_G} + \frac{\lambda}{N_L}$$

where E_{OG} = gas-phase point efficiency

λ = ratio of slope of equilibrium curve (y/x) to slope of operating line (L/G)

$L/G\ (\text{bottom}) = (3.56 \times 10^3)/(5.0) = 0.7 \times 10^3$

$L/G\ (\text{top}) = (3.56 \times 10^3)/(6.833) = 0.52 \times 10^3$

$\text{Average } L/G = 0.62 \times 10^3$

$y/x = H/P$

$y/x = (1.28 \times 10^3)/(1.0) = 1.28 \times 10^3$

$\lambda(\text{avg}) = 1.28/0.62 = 2.08$

These calculations are based on the operating and equilibrium lines for H_2S only.

$$-\frac{1}{\ln(1-E_{OG})} = \frac{1}{2.22} + \frac{2.08}{0.86} = 0.45 + 2.42 = 2.87$$

$$\ln(1-E_{OG}) = -0.348$$

$$-E_{OG} = -1 + 0.706$$

$$E_{OG}(\text{avg}) = 0.294$$

B. Design Calculations - Evaporator Auxiliaries

1. Evaporator Pumps

a. Pump for effects 3-2. From the temperatures in effects 3 and 2,

$p_3 = 1.94$ psia

$p_2 = 6.87$ psia

The flow rate of brine between the two effects is 56,100 lb/hr. The specific gravity is 1.08.

Pumping head = $\frac{(6.87-1.94)}{(15)} \left(\frac{34}{1.08}\right)$ = 10 ft of brine

Pump output = $\frac{(10)(56,100)}{(3600)(550)}$

Efficiency[13] = 10 per cent

Required hp = 2.8 = 3 hp

b. Pump for effects 2-1

p_2 = 6.87 psia

p_1 = 21.2 psia

Flow rate = 39,900 lb/hr
Specific gravity = 1.10

Pumping head = $\frac{(21.1-6.87)}{(15)} \left(\frac{34}{1.10}\right)$ = 30 ft of brine

Pump output = $\frac{(30)(39,900)}{(3600)(550)}$ = 0.61 hp.

Efficiency[13] = 10 per cent

Required hp = 6 hp

2. Cooling Water Pump

Flow rate of water = 480 gpm

Estimated head = 20 ft

Pump output = $\frac{(20)(480)(62.4)}{(60)(7.48)(550)}$ = 2.4 hp

Efficiency[13] = 32 per cent

Required hp = 7.5 hp

3. Hotwell Pump

Flow rate of water = 520 gpm

Estimated head = 20 ft

Pump output = $\frac{(20)(520)(62.4)}{(60)(7.48)(550)}$ = 2.6 hp

Efficiency[13] = 33 per cent

Required hp = 7.5 hp

C. Design Calculations - Barium Chloride Process

1. Barium Chloride Mix Tank

Saturated barium chloride is made up twice a day. Water required is 16,050 lb/day, while $BaCl_2$ required is 5620 lb/day. At a density of 10.7 lb/gal, the volumetric flow rate is (16,050+5620)/10.7 = 2120 gal/day. A 1200-gal tank is adequate for making each batch. A 3 hp agitator is sufficient.

2. Feed Preheater

Conditions of cold brine:
Flow rate = 2550 gal/hr
Inlet temperature = 25°C
Outlet temperature = 80°C
Heat capacity = 0.83 Btu/lb °F
Conditions of hot brine:
Flow rate = 2640 gal/hr
Inlet temperature = 90°C
Outlet temperature = 35°C

The heat transferred from the hot brine to the cold brine is

$$Q = FC_p\Delta T = UA\Delta T_m$$

$$\Delta T = 55°C = 99°F$$

$$\Delta T_m = 10°C = 18°F$$

$$F = (2600\text{ gal/hr})(1.13)(8.35\text{ lb/gal}) = 24{,}500\text{ lb/hr}$$

$$C_p = 0.83\text{ Btu/lb}$$

$U = 250$ Btu/hr ft^2°F, estimated from Table 6 of Peters,[19] for aqueous solutions on both sides of exchanger.

The required heat-transfer area is calculated as:

$$A = \frac{(24{,}500)(0.83)(99)}{(250)(18)} = 450\text{ sq ft.}$$

3. Barium Sulfate Precipitation Tank

Brine stream flow rate = 24,500 lb/hr

Inlet temperature = 80°C

Outlet temperature = 90°C

Heat capacity = 0.83 Btu/lb °F

The steam requirement, F_s, is calculated from:

$$F_s \Delta H_v = FC_p \Delta T$$

ΔH_v = 970 Btu/lb at 100°C, atm pressure

$$F_s = \frac{(24,500)(0.83)(18)}{970} = 400 \text{ lb/hr}$$

Using an overall kettle heat-transfer coefficient of U = 100 Btu/hr ft^2 °F estimated from Table 11-15 of Perry,[7] the jacket heat-transfer area is calculated from

$$F_s \Delta H_v = UA\Delta T_m$$

$$A = \frac{(400)(970)}{(100)(18)} = 216 \text{ sq ft}$$

The agitator power requirement can be estimated using the power-number correlation given in Perry.[7] From this method,

$$P = KN^3 D_a^5$$

where P = agitator hp

K = correlation coefficient = 0.32 for a propellor-type agitator with 3 blades, square pitch

N = agitator rpm = 1150

D_a = propellor diameter = 1 ft

Thus, $P = (0.32)(1150)^3(1)^5 = 5$ hp

This method is good when such things as propellor size and shape and the agitator speed are specified, but the rule-of-thumb approach and common engineering sense are still indispensable for quick estimates without specific information.

4. Barium Sulfate Slurry Pump

Operating pressure = 120 psi = 270 ft H_2O

Capacity = 44 gpm

Slurry density = 1.2 g/cc

$$W_o = \frac{(270)(44)(62.4)(1.2)}{(60)(7.48)(550)} = 3.7 \text{ hp}$$

Pump efficiency[13] = 28%

$W = 3.7/0.28 = 13$ hp

5. Wash Water Pump

Operating Pressure = 100 psi = 230 ft H_2O

Capacity (1 hour at 1/4 filtrate rate) = 11 gpm

$$W_o = \frac{(230)(11)(62.4)}{(60)(8.48)(550)} = 0.92 \text{ hp}$$

Pump efficiency[13] = 20%

$W = 0.92/0.2 = 4.5$ hp

6. Barium Sulfate Filter Presses

Mode of operation: The slurry is pumped through at a constant rate until a pressure of 100 psi is reached, at which point the slurry is diverted to another filter press.

Assuming laminar flow through the filter cake, the equation of Carman-Kozeny applies:[44]

$$\frac{-\Delta P g_c}{L} = 180 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu v_s}{D_p^2}$$

since v_s = fluid velocity = $V/A = \frac{\text{volumetric flow}}{\text{filtration area}}$,

$$\frac{-\Delta P g_c}{L} = 180 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu V}{D_p^2 A}$$

or, $$A = \frac{180L}{\Delta PG_c} \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu V}{D_p^2}$$

The volumetric flow rate is a constant in this case, while filtration pressure, ΔP, will increase as filtration progresses. Setting the upper limit for ΔP at 100 psi, the filtration area, A required to maintain the volumetric flow rate at a given value may be calculated.

ΔP = filtration pressure = 100 psi = 14,400 lb_f/ft^2

L = cake thickness = 1 inch = 0.083 ft

ϵ = cake porosity = 0.5 (assumed)

V = volumetric flow rate = 2640 gal/hr = 0.098 ft^3/sec

μ = filtrate viscosity = 2.5 cp = 16.8×10^{-4} lb/ft sec

D_p = particle diameter = 10μ = 3.28×10^{-6} ft (observed microscopically)

g_c = gravitation constant = 32.2 ft-lb_m/lb_f sec^2

$$A = \frac{(180)(8.3 \times 10^{-2})}{(1.44 \times 10^4)(32.2)} \frac{(0.5)^2}{(0.5)^3} \frac{(16.8 \times 10^4)(0.98)}{(3.28 \times 10^{-6})^2}$$

A = 1000 sq ft

A 32-inch metal filter press with 40 plates has a filtering area of 496 sq ft, according to the data furnished by Sperry.[30]

With 1-inch chambers, the total capacity of each press is 20.65 cu. ft.

Since ϵ = 0.5,

(0.5)(20.65) = 10.33 cu ft solids per fill.

Density of $BaSO_4$ = (4.5)(62.4) = 281 lb/ft^3.

Weight of solids per fill = (281)(10.33) = 2900 lb.

Flow rate of $BaSO_4$ = 250 lb/hr.

Filling time of filter press = 2900/250 = 12 hr.

7. Barium Sulfate Dryer

Solids flow rate = 250 lb $BaSO_4$/hr.

Cake void fraction = 0.5.

Assuming voids to be filled with water, there will be 1 cu ft H_2O/cu ft $BaSO_4$ in the wet cake.

Specific gravity of $BaSO_4$ = 4.5.

Thus the initial cake moisture content = 1/4.5 = 0.22 lb H_2O/lb $BaSO_4$, or 18.2 per cent by weight.

Assuming that the air used for drying has a dry-bulb temperature of 80°F and a wet-bulb temperature of 60°F, from psychrometric charts the inlet moisture content will be 0.0067 lb H_2O/lb dry air.

Further assuming that the air is heated to 250°F with steam and then cools adiabatically as it picks up moisture to 70 per cent relative humidity, the outlet moisture content of the air will be 0.0394 lb H_2O/lb dry air, according to psychrometric charts.

Moisture pickup = 0.0394 - 0.0067 = 0.0327 lb H_2O/lb dry air

Water input = (0.22)(250) = 55 lb H_2O/hr

Required air flow = 55/0.0327 = 1680 lb dry air/hr

Inlet air conditions:

250°F dry bulb

$$\Delta T_1 = 190°F$$

60°F wet bulb

Outlet air conditions:

110°F dry bulb

$$\Delta T_2 = 11°F$$

99°F wet bulb

$$\Delta T_{lm} = \frac{190 - 11}{\ln 190/11} = 63°F$$

Design calculations for a rotary dryer can be made following the procedure presented in Chapter 20 of Perry.[7] The following equations are from that source.

$$N_t = \frac{T_1 - T_2}{\Delta T_{lm}}$$

where N_t = no. of heat-transfer units

T_1 = inlet gas temperature, 250°F

T_2 = outlet gas temperature, 110°F

ΔT_{lm} = log-mean-temperature driving force, 63°F

$$N_t = \frac{250-110}{63} = 2.2$$

Since, according to Perry, rotary dryers are most economically operated when N_t is between 1.5 and 2.5, the above design conditions seem appropriate.

The total heat transferred from the air to the water is expressed by

$$Q_t = Ua\ V(\Delta T)_{lm}$$

where Q_t = total heat transferred, Btu/hr

Ua = volumetric heat-transfer coefficient, Btu/(hr)(cu ft dryer volume)(°F)

V = dryer volume, cu ft

ΔT_{lm} = log-mean-temperature driving force = 63°F

Neglecting heating of the solids and sensible heating of the water, the heat transferred can also be expressed as

$$Q_t = W\lambda$$

where W = moisture-removal rate = 55 lb/hr (assuming 100% removal)

λ = latent heat of vaporization = 1049 Btu/lb (80°F)

therefore,

$$Q_t = (55)(1049) = 57{,}700 \text{ Btu/hr}$$

For a conservative design estimate, Perry[7] recommends

$$Ua = \frac{10G^{0.16}}{D}$$

Assuming the dryer diameter, D, to be 3 ft, the air mass velocity, G, is calculated as

$$G = (1680)(4)/(\pi)\ (3)^2 = 240 \text{ lb/hr ft}^2,$$

and $$Ua = (10)(240)^{0.16}/3 = 8 \text{ Btu/hr ft}^3\ ^\circ\text{F}.$$

The dryer volume can be estimated from

$$V = \frac{Q_t}{Ua(\Delta T)_{lm}} = \frac{57{,}700}{(8)(63)} = 114 \text{ cu ft.}$$

For a diameter of 3 ft, the length, L, will be

$$L = (114)(4)/(\pi)\ (3)^2 = 16 \text{ ft.}$$

The L/D ratio is 5.3, which is between the recommended range of 4 to 10 given by Perry.[7]

For the purpose of cost estimation the peripheral area = $(16)(\pi)\ (3)$ = 150 sq ft.

The thermal efficiency of a steam-heated air dryer is 30 to 55 per cent, according to Perry.[7] Using an efficiency of 40 per cent, the steam requirement when the latent heat of steam is 945 Btu/lb is:

$$\text{steam requirement} = \frac{(55)(1046)}{(0.4)(945)} = 150 \text{ lb/hr}$$

Electric power to rotate the dryer and operate the blower and feeder can be estimated from the relation:[7]

$$\text{Power} = 0.75\ D^2$$
$$\text{Power} = 0.75(3)^2 = 6.8 \text{ hp}$$

8. Brine Surge Tank

Brine from the filters flows at a rate of 44 gpm. A tank with a 15-minute residence time to damp out fluctuations in flow would require a volume of (44)(15) = 660 gallons.

D. Composition of Molasses

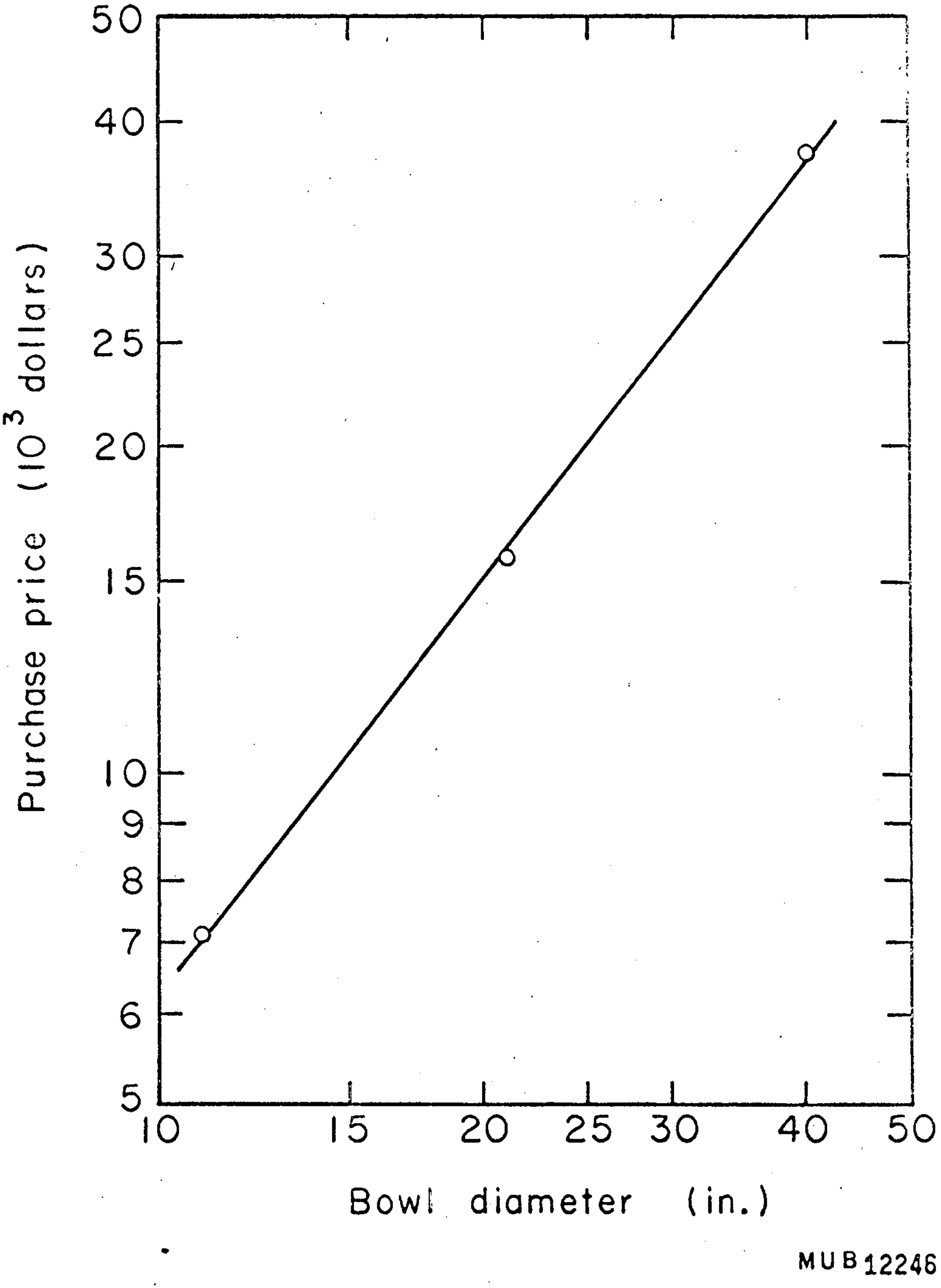
For the purpose of this study, blackstrap molasses is considered to have the following composition:[18]

Substance	Per Cent by weight
Water	20
SiO_2	0.5
K_2O	3.5
CaO	1.5
MgO	0.1
P_2O_5	0.2
SO_3	1.6
Cl	0.4
Other minerals	0.2
Sugars	62.0
Nitrogenous substances	3.0
Gums	2.0
Free acids	2.0
Combined acids	3.0

E. Composition of Medium M

This medium was used for some of the growth experiments conducted on the halophilic Desulfovibrio,[2,3] and is used in this study as a basis for estimating the required amount of nutrients for the bacterial sulfate-reduction process. Weights given are grams required for 1 liter of medium.

Component	Weight (grams)
Lactic acid (100% basis)	7.66
KH_2PO_4	0.340
$CaCl_2$	0.111
$MgSO_4 \cdot 7H_2O$	0.123
Na_2SO_4	4.26
NH_4Cl	0.535
Yeast extract	2.5
Sodium chloride	100.0
$FeSO_4 \cdot 7H_2O$	0.007
$Na_2S \cdot 9H_2O$	0.240



F. Costs of Nozzle-Type Disc Centrifuges.[16]

G. Installed Equipment Cost Index

Most of the equipment cost data obtained for this study was in terms of installed cost. To obtain an index that would allow updating of installed costs, the Chemical Engineering Plant Cost Index was modified as follows: the CE Index is made up of four major components each of which is weighted.[45] Two of the components and their weight factors are:

Equipment, machinery and supports	61%
Erection and installation labor	22%

An index made up of these two components would have weight factors of 61/(61 + 22) = 0.735 for equipment and 22/(61 + 22) = 0.265 for installation.

Therefore, the installed equipment index (I_e) = 0.735 equipment index + 0.265 installation index. For example, in February 1966, the equipment index is 103.5 while the installation index is 110.9;[45] then, $I_e = (0.735)(103.5) + (0.265)(110.9) = 105.5$. The installed equipment cost index for several years is given below.

Year	Index
1966 (Feb.)	105.0
1963	102.3
1960	102.2
1959	101.8
1957	98.5
1954	85.3
1950	72.5
1947	63.3

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