

for chill-proofing beer, which has been used successfully for many years in this country and in many others, is probably the outstanding American contribution to brewing technology.

"VITAMINIZED" BEER

Some of the raw materials of brewing contain vitamins, and brewer's yeast is an excellent source of vitamins B and G, but the finished filtered beer contains no nutritionally significant proportion of any vitamin. With the present fad for reinforcing various foods by the addition of vitamins or by irradiation, it is not surprising that processes have been proposed for "vitaminizing" beer. One of these processes (12) utilizes the cell sap separated from yeast by supercentrifugalization or by other methods. The inventor of this method says that the cell-free liquid contains 25 to 30 per cent of soluble yeast proteins, the vitamins and the enzymes. He proposes the addition of definite proportions of this cell sap to the beer after the main fermentation. The inventor asserts that the vitamins and enzymes mix with the beer and pass through the filter.

It is quite likely that this treatment will add vitamins to the beer, but the matter of controlling the vitamin content in practice must be considered. Of still greater significance is the simultaneous addition of yeast proteins which may include unstable compounds, and of a high concentration of yeast enzymes. How the action of this battery of enzymes is to be regulated is not revealed. The importance of regulating their action in order to prevent undesirable changes in the beer constituents is self-evident.

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Alexander, Jerome, *J. Am. Chem. Soc.*, **43**, 434 (1920); *Kolloid-Z.*, **36**, 334 (1925).
- (2) Chrzascz, T., and Janicki, J., *Biochem. Z.*, **263**, 250 (1933); **264**, 192 (1933).
- (3) Embden, Secaho, Deuticke, and Kraft, *Klin. Wochschr.*, **12**, 213 (1933).
- (4) Emslander, F., *Z. ges. Brauw.*, **42**, 127 (1919).
- (5) Geys, *Wochschr. Brau.*, **44**, 145 (1927).
- (6) Harden, A., *J. Inst. Brewing*, **39**, 644-6 (1933).
- (7) Henrici, A. T., "Yeasts, Molds and Actinomycetes," p. 216, John Wiley & Sons, New York, 1930.
- (8) Hopkins, R. L., *J. Inst. Brewing*, **31**, 399 (1925).
- (9) Kolbach, P., and Buse, R., *Wochschr. Brau.*, **50**, 265, 273, 281 (1933).
- (10) Lüers, H., and Leiss, F., *Ibid.*, **50**, 373, 381 (1933).
- (11) Lüers, H., and Rummier, W., *Ibid.*, **50**, 297-301 (1933).
- (12) Lux, Fritz, *Brewers' Tech. Rev.*, **9**, 15 (1934).
- (13) Meyerhof, O., and Kiessling, W., *Biochem. Z.*, **267**, 313 (1933).
- (14) Meyerhof, O., and McEachern, *Ibid.*, **266**, 417 (1933).
- (15) Petit, P., *Brasserie et Malterie*, **16**, 49, 65, 81 (1926).
- (16) Raux, M. J., *Ibid.*, **24**, 65-8 (1934).
- (17) Schlichting, E., and Winther, H., "Practical Points for Brewers," p. 40, National Brewers Academy, New York, 1933.
- (18) Sobotka, H., and Holzman, M., *Biochem. J.*, **28**, 734-9 (1934).
- (19) Wallerstein, Leo, *J. Franklin Inst.*, **183**, 531-56, 715-34 (1917).
- (20) Wallerstein, Leo, U. S. Patents 995,820 and 995,824 (1911).

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Water Purification in the Modern Brewery and Distillery

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WATER forms the greatest portion of all the raw materials used by either breweries or distilleries. In addition, it influences product quality at practically every stage of manufacture because the great majority of process reactions in brewing and distilling take place in aqueous solution and are therefore directly subjected to the effects of chemical characteristics of the water. Finally, water plays another important but entirely independent role in plant operation as utilized for cooling, for washing, or for boiler feed purposes; here water quality has a basic and direct relation to operating and maintenance costs.

One of the outstanding achievements offered to progressive breweries and distilleries is the modern water-purification plant, developed and technically perfected during the time of prohibition. At the inception of prohibition, water purification was just entering its most progressive development stage. In the following decade and a half both chemical and engineering phases have undergone remarkable advancement; practical and theoretical research, together with organized scientific development work, has revolutionized former practices and treatment methods. As a result, the economic and production aspects of plant operation can be benefited in large measure through correct application of modern water-purification methods; this is especially true in brewing and distilling fields at the present time. The importance of these advantages is in some degree indicated by the fact that many plants, which otherwise would have been inoperable because of adverse water conditions, are now producing

beverages of the highest possible quality under efficient conditions solely through the utilization of modern water-purification plants.

THE BREWERY

Only occasionally is the water supply available to a brewery suitable for all plant purposes without any treatment whatsoever. The chemical characteristics of a good brewing water are quite different from those of a water satisfactory for boiler feed and cooling purposes; and the water for general washing or rinsing may constitute another individual requirement.

BREWING WATER

The water going directly into the brewing process—forming 85 to 90 per cent of the finished beer—is used for the mashing and sparging operations that extract the desired organic constituents from the grain and hops. Since the physical characteristics of the water, such as suspended matter, taste, or odor, might easily be carried directly into the finished product, it is obvious that the water must be satisfactory in its physical and esthetic characteristics; furthermore, its chemical constituents—both organic and inorganic—must be considered since these may affect the finished beer biologically or chemically.

CLARITY. Although filtration may form a part of the beer-production process at one or more subsequent stages, it is important that the brewing water itself be clear and devoid

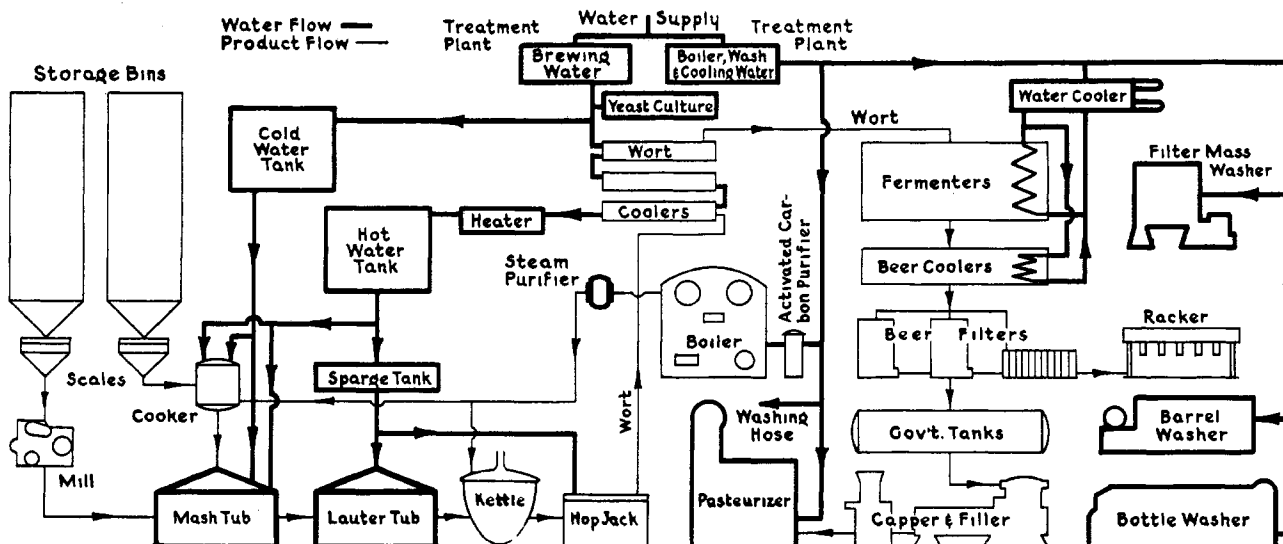


FIGURE 1. WATER FLOW DIAGRAM OF A BREWERY

of suspended matter to assure cleanliness and freedom from unknown suspended substances of a possibly deleterious nature. If not initially clear the water should be filtered; this is best carried out in sand filters of either the pressure or gravity type. In either case, proper consideration must be given to coagulation of the water ahead of the filter beds.

TASTES AND ODORS. The presence of objectionable tastes and odors is obviously undesirable in the manufacture of any food product. Taste and odor in water have become an increasingly important problem because chlorine is used practically universally to sterilize municipal supplies, because increased amounts of industrial trade wastes are entering public supplies, and because recent drought conditions have intensified tastes and odors from natural causes.

Modern activated carbon purifiers make easy work of removing all objectionable tastes and odors from water, and the introduction of this equipment has proved to be one of the most striking recent developments in water purification. The beverage industry in particular has been quick to appreciate the advantages of this reasonably simple, efficient, and economical means of obtaining water of assured palatability, and a remarkably rapid and steadily expanding utilization of this method of purification has taken place in the last five years.

By simply flowing water through a properly designed purifier equipped with hard, mechanically strong, and highly activated carbon, all objectionable chlorine and other disagreeable tastes and odors will be removed completely by the carbon bed. The shell of such a purifier must be equipped with a tasteless and odorless dielectric lining to prevent corrosion that would otherwise inevitably result from galvanic action caused by comparatively high differences of potential set up between true activated carbon and all metals when wet.¹ Bone black, wood charcoal, and other carbons of low activity do not show this appreciable potential difference; only true activated carbons, having high adsorption capacity for phenols and other taste- and odor-producing substances (which makes them valuable for purification work), show this necessity for a dielectric, inert lining in the purifier shell.

The water applied to an activated carbon unit should be clear and free from appreciable amounts of suspended matter so that the necessary intimate contact between the water and the highly porous carbon may be obtained. If the water is not clear, the carbon particles will become coated with sus-

pended matter, the pores will become clogged, and the essential contact required for adsorption will be lost. Hence, if water to be purified in an activated carbon unit is not initially clear, it should be properly filtered beforehand.

ALKALINITY AND HARDNESS. Alkalinity of any kind is undesirable in brewing water, since it adversely affects the mashing extraction and tends to produce a harsher, improperly colored, less desirable beer for the American market. Because alkalinity in water includes bicarbonate (temporary) hardness, such hardness is undesirable for mashing water. Noncarbonate hardness, or hardness due to sulfates, chlorides, or nitrates of calcium and magnesium, is unobjectionable and even desirable in moderate amounts.

Generally the most efficient method of removing objectionable alkalinity from mashing or sparging water comprises lime treatment to precipitate the alkaline carbonates, in conjunction with coagulation, settling, and filtration to complete the removal of the precipitated impurities. When sodium carbonate or bicarbonate is present, calcium chloride or sulfate is fed along with the lime in amount sufficient to transform the undesirable sodium carbonate to neutral sodium sulfate or sodium chloride; the carbonate radical precipitates with the lime as calcium carbonate.

This lime treatment reduces alkalinity to an unobjectionable amount, but also raises the pH of the water because of the slight excess of calcium hydroxide; however, the quantitative amount of such hydroxide alkalinity present is negligible, and, when desired, both it and the increased pH may be quickly and easily reduced by lactic or phosphoric acid.

Undesirable alkalinity in brewing water also may be reduced by direct neutralization with lactic or phosphoric acid, but when treating waters containing any appreciable amount of carbonates, these chemicals are so much more expensive than lime that the expense involved is excessive by comparison.

pH CORRECTION. The matter of controlling the pH, or intensity of acidity or alkalinity, as well as the relative quantity of either, has assumed a steadily increasing importance in the treatment of water for brewing. Generally speaking, for best results the pH of the water should be adjusted to neutrality—around 7.0—before mashing. This pH correction may be carried out automatically by simple proportioning feeders that add any predetermined amount of lactic or phosphoric acid to the water, either before or after the hot water storage tank.

The acid also may be fed at the start of the mashing operation, in bulk, but such feeding does not assure accurate

¹ Brandt, Millard (to Darco Corp.), U. S. Patent Reissue 18,967 (Oct. 10, 1933):

measurement, proportioning, or mixing. Scientific control under these conditions is difficult or impossible because during the mashing operation the pH of the mash naturally drops to a value in the neighborhood of 5, thus preventing any check on the amount of acid used for the particular water condition.

IRON. This is a most objectionable impurity because it produces turbidity and undesirable dark color or sediment in the finished beer; in appreciable quantities it may impart a false taste.

Iron may be removed from water by aëration and filtration; the aëration of the water introduces atmospheric oxygen which oxidizes and precipitates soluble ferrous iron as ferric hydroxide, after which it may be mechanically removed by filtration.

Iron removal can be carried out automatically and under pressure if desired, in a unique development made possible by the introduction of activated carbon units for dechlorination. This process, which is covered by pending patent application, utilizes the precipitation of ferrous iron by the oxidation and hydrolysis obtained in the presence of excess chlorine which is automatically proportioned to the raw water. The insoluble iron precipitate thus formed can then easily be removed by filtration (and all excess of chlorine can be removed from the water by means of an activated carbon purifier), yielding an iron-free, palatable, and refreshing effluent. In addition to the advantages of simplicity and automatic pressure operation, this treatment avoids the introduction of undesirable oxygen which usually saturates the water as a result of ordinary aëration, with the attendant possibility of further corrosion which might cause the treated water to acquire more iron from the distribution system than was originally present.

Lime treatment also will remove iron; this is convenient when water requires elimination of objectionable alkalinity in addition to iron removal.

OTHER MINERALS. The presence of other minerals in water may have an appreciable effect upon the quality of the finished product. The presence of calcium sulfate and some

sodium chloride, in particular, is desirable to assist favorable extraction and to aid subsequent brewing processes, especially fermentation and clarification. Calcium sulfate, in particular, increases proteolytic cleavage and favors the growth of the proper yeast. However, an excess of these or other minerals may interfere with proper fermentation and lend an objectionable or off-taste to the finished beer. Concentra-

tions of any one substance in excess of 300 parts per million, or total solids above 800 parts per million, may warrant the special consideration of the brewing technologist. Excess of carbonate hardness responds to lime treatment with a reduction in total solids, but other mineral content can be removed commercially only by distillation. Reduction of

total solids by electroosmosis holds much promise, but this treatment is not yet generally practical for industrial capacities.

ORGANIC SUBSTANCES. The organic constituents of the brewing water are usually not so important as the mineral ones, but the water should meet the standard bacteriological requirements for drinking water. If contamination is possible or known to be present, the water

may be sterilized by using automatic hypochlorite or liquid chlorine feeders; after sufficient retention time has been provided for completion of the sterilization reaction, the purified water must then be dechlorinated. Activated carbon purifiers may here be used to excellent advantage for removal of all excess chlorine which would be undesirable for brewing.

Inert organic matter present in brewing water in small amounts is unobjectionable, as the boiling and coagulation taking place in the brew kettle usually precipitate and remove it; however, an excessive amount of organic matter may persist even after the beer filters and may cause difficulty in the finished product by unavoidable deposition of sediment or formation of haze. In such cases, superchlorination (in connection with coagulation), settling, and filtration are indicated, followed by removal of all excess chlorine with activated carbon purifiers. Such treatment has not failed to remove all objectionable organic matter from water.

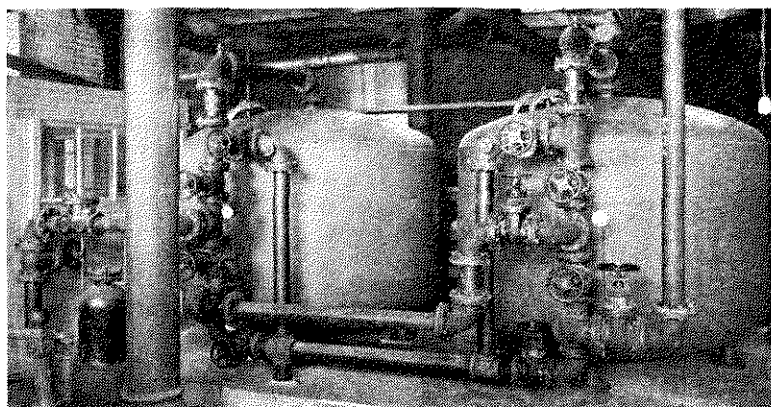


FIGURE 2. PRESSURE FILTER AND ACTIVATED CARBON PURIFIER INSTALLATION IN A BREWERY

Capacity, 2350 gallons per hour

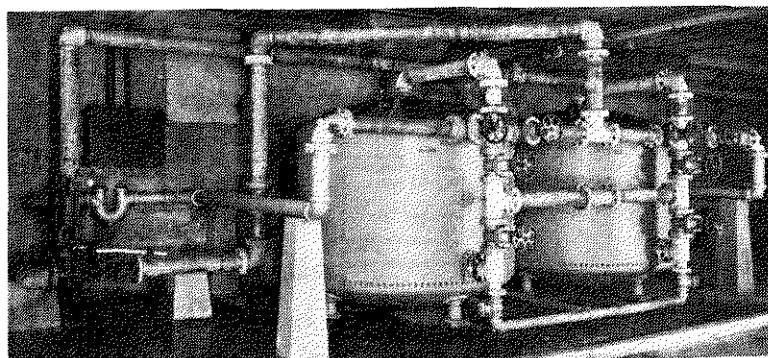


FIGURE 3. ACTIVATED CARBON PURIFIERS FOR TASTE AND ODOR REMOVAL

Capacity, 16,000 gallons per hour

WASH AND RINSING WATER

The water used throughout the plant for general washing and rinsing of beer pipe and equipment must be clean and free from objectionable iron, bacteria, and all possible sources of infection. The water should meet the U. S. Public Health Service requirements for drinking water. In

addition, the water used in bottle washers and pasteurizers and for washing barrels or filter mass should be sufficiently soft to keep this equipment free from scale or other deposition due to hardness. Softening for these purposes is frequently carried out most advantageously by the zeolite method, although zeolite softening is entirely inapplicable to the brewing water itself. The wash water used for barrels and filter mass

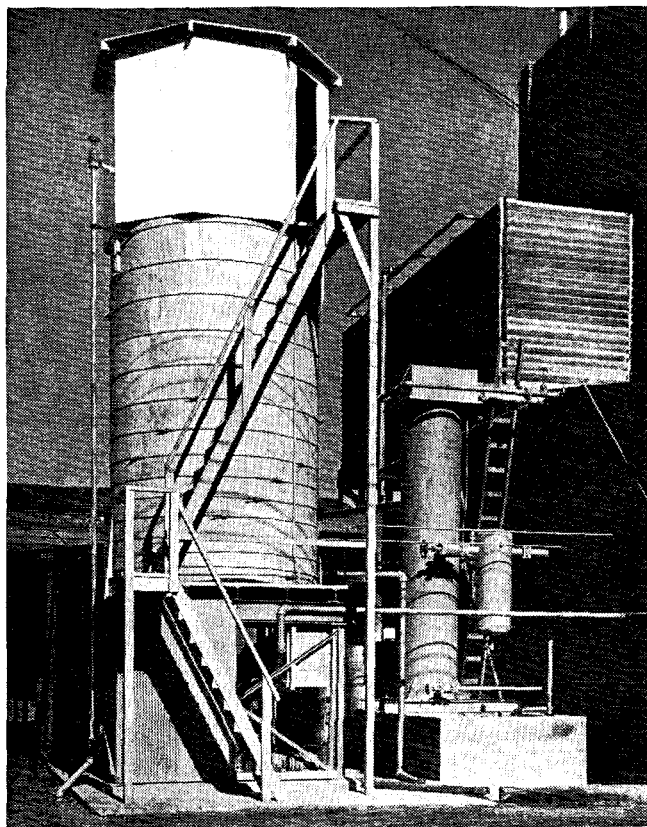


FIGURE 4. MODERN CONTINUOUS LIME TREATMENT AND FILTRATION PLANT IN A BREWERY
Capacity, 1250 gallons per hour

should be free from iron that might contaminate the finished beer.

BOILER FEED WATER

The usual requirements for boiler feed water must be met in the brewery—i. e., clarity, freedom from scale-forming hardness, suitable sulfate-carbonate ratio to inhibit caustic embrittlement of boiler metal, absence of corrosive qualities, and freedom from high total solids or excessive organic matter that might induce foaming or priming. In addition, boiler

feed water for the brewery must also be free from objectionable chlorine or other tastes and odors if process steam comes in contact with the product.

COOLING WATER

The circulating water used in cooling applications throughout the plant should be noncorrosive and free from hardness that will deposit scale on heat-exchange surfaces. It should not contain suspended matter, algae, or iron in appreciable quantities that might collect and obstruct flow of the water or transmission of heat. The cooling water requirements are in many respects similar to those for boiler feed, but they are less stringent, and the question of objectionable volatiles is not important in the usual closed cooling system. Generally, cooling water is most conveniently softened by the zeolite process.

THE DISTILLERY

Inasmuch as the mashing operations in a distillery follow the same principles as in the brewery, the mash water requirements of both are much alike. The boiler feed and cooling water treatments are also essentially alike in principle; however, the latter requirements in the distillery are larger and more critical, and therefore place increased importance on water characteristics. In addition, the distillery requires special water for cutting, reducing to proof, and perhaps for blending and for rectifying purposes in subsidiary locations.

BOILER FEED WATER

Boiler feed requirements in the distillery are similar to those in the brewery. More attention and control would be justified in handling distillery requirements because they usually involve higher pressures and ratings; greater emphasis therefore must be placed on the exactness and completeness of water treatment.

COOLING WATER

Distilleries necessarily use large volumes of cooling water in coolers and condensers, and the large amount of heat units thus passed into the cooling water represents a considerable portion of the heat energy and operating cost expended in the power plant. Any means of creating and maintaining higher heat-transfer efficiencies is therefore of fundamental importance; likewise, every possible means of recovering

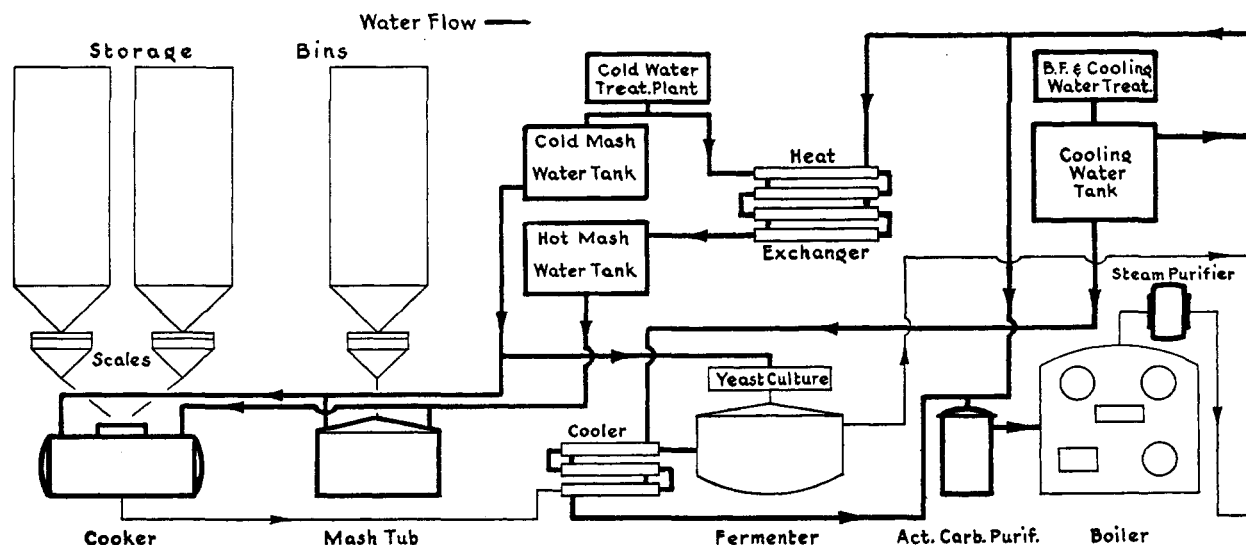


FIGURE 6. WATER FLOW

heat units within the cycle of plant operation should be utilized to reduce operating costs.

Therefore proper cooling water treatment, when necessary, becomes an essential, since heat exchangers, cooling coils, and condensers must be kept free from scale incrustations or accumulation of sediment in order to operate as originally designed and to prevent expensive maintenance or replacement costs. Zeolite softening is widely used for hard, scale-causing cooling water; previous filtration is indicated if the water is appreciably turbid. Excessive iron or algae content may cause objectionable deposit on heat-exchange surfaces or obstructions to normal water flow; aëration or chlorination followed by filtration will remove iron, and simple chlorination—either alone or in conjunction with the feeding of ammonia compounds to form the more lasting chloramine—generally prevents objectionable algae growths.

Large distilleries frequently collect used cooling water in hot water storage tanks from which it is taken as needed for processes requiring heated water. This creates an important heat saving; but, as previously pointed out, the water characteristics and treatment methods used for the cooling supply are generally undesirable for process water. This is especially true of the mash supply. For instance, the proper treatment of water for cooling might be just the opposite of that required for mashing, and obviously it would be unwise to utilize spent cooling water for mashing under these circumstances; the same considerations apply to other hot water requirements.

This does not create an impasse, however, for a simple installation of heat exchangers will make an efficient heat balance possible, conserving all possible heat energy while still keeping the process water and cooling water systems separate, each with its individual, correct type of water treatment.

DISTILLED WATER

Reducing or blending water mixed with the final product must not only be free from excess mineral matter but also devoid of objectionable tastes and odors. Commercial distillation will remove practically all mineral matter and solids from water, but it does not necessarily follow that the distilled water will be free from objectionable tastes and odors if such volatiles are present in the raw water.

Such impurities may volatilize in the still with the steam, pass over into the condensing chambers, and be redissolved

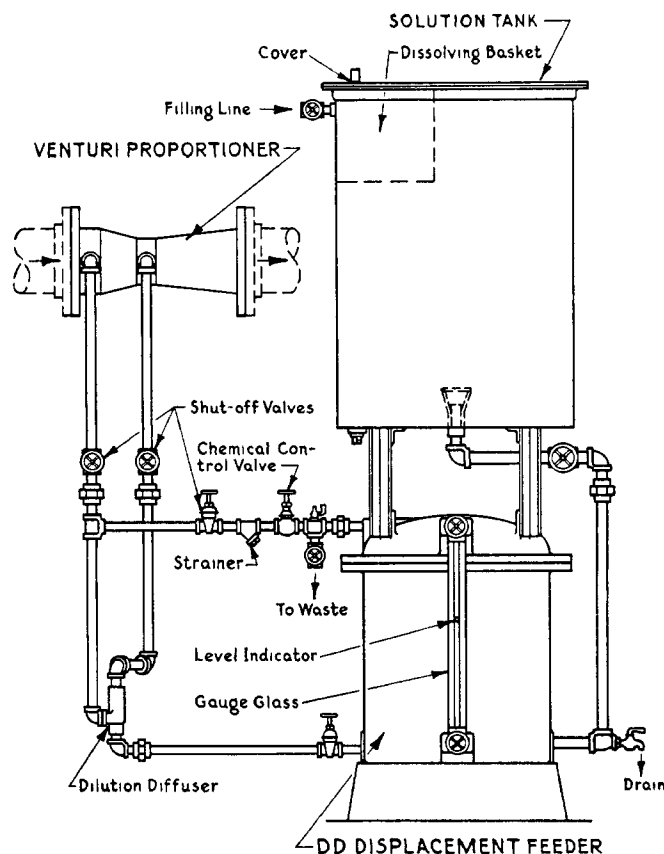


FIGURE 5. AUTOMATIC PRESSURE SOLUTION FEEDER FOR LACTIC OR PHOSPHORIC ACID

in the distillate. The extent of such volatile recontamination of the distilled water may vary widely; a pronounced odor or taste may be evident in the distilled water, or the trace of impurity may be so slight that its effect is not directly obvious. In any case, activated carbon purifiers are of great advantage in removing such off-tastes and odors in all concentrations, and this method of final purification for distilled water has already met with wide acceptance.

Although the water obtained from a still is usually clean and clear, occasional particles of sediment may appear or be picked up from pipe lines or equipment; it is therefore ad-

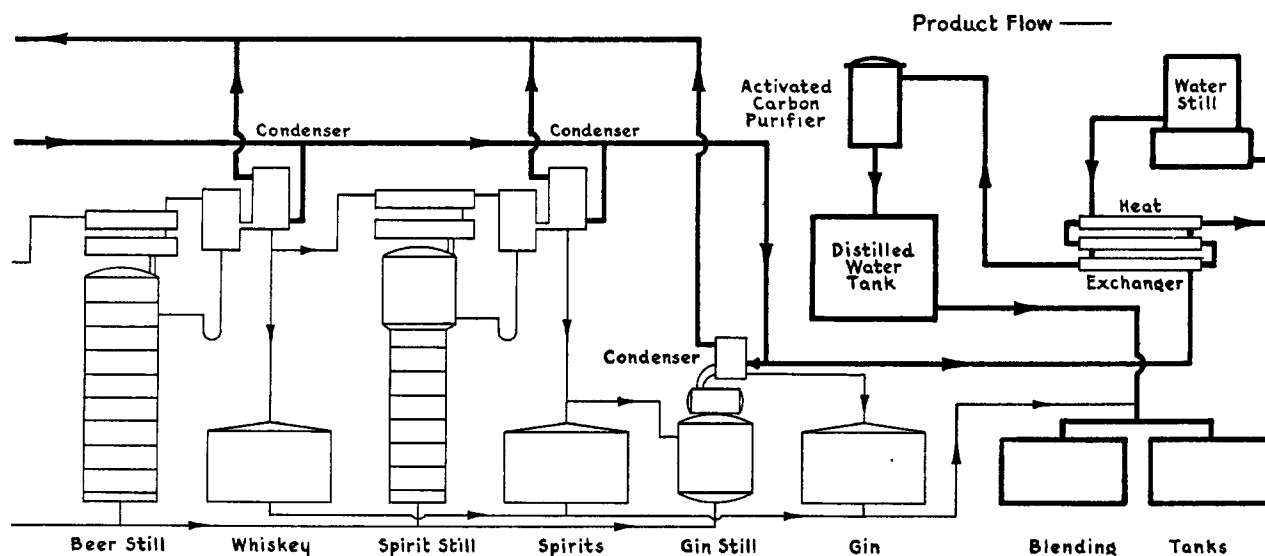


DIAGRAM OF A DISTILLERY

vantageous to pass the distilled water through a disk filter for rapid filtration through compressed cotton fiber disks, giving brilliancy and perfect clarity to the distilled water just before it goes into the product.

UNDISTILLED BLENDING WATER

In addition to the advantages of lower first cost and lower operating cost, the use of undistilled blending water may be advantageous from an esthetic standpoint, inasmuch as it has been widely observed that fresh, palatable, natural water without excessive mineral content is more refreshing and pleasant than the most carefully aerated distilled water.

When the amount of dissolved mineral matter in water is not great enough to cause precipitation of minerals or pectins or otherwise produce a haze when the water is mixed with the beverage in the correct proportion, then the primary reason for distillation—removal of mineral matter—is obviated and proper chemical treatment of the water, instead of distillation, will frequently yield an equal if not superior supply.

An installation that will assure undistilled blending water of ideal quality (if the mineral matter content is satisfactory) consists of pressure units providing superchlorination and coagulation, with sufficient retention time to complete these processes, followed by a pressure sand filter and activated carbon purifier. This will remove all precipitated iron and suspended matter and all objectionable tastes and odors, including any excess of chlorine. A disk filter, as the last unit on the line, is often included for final filtration to assure brilliant clarity.

SUMMARY

Water treatment plants, like many another industrial process, have evolved from the old batch treatment methods utilizing laborious manual dosing and mixing of chemicals, to the modern continuous treatment plants employing the unit processes of chemical engineering in some of their most efficient forms.

Automatic, proportional feed of improved treating chemicals is combined with highly efficient mixing, flocculation, and settling methods to eliminate practically all manual supervision, with attendant savings in space requirements and treatment costs. Chemicals are handled dry, in solution, or as slurries according to the most advantageous operation; improvements in sludge disposal systems help to shorten the amount of reaction time formerly required and yield a clearer settled water that imposes less load on filtration equipment.

Filters are furnished with hydraulically operated single-control valves to eliminate the conventional multivalve filter front, greatly simplifying the labor and time required for filter operation, without any possibility of leaking, sticking, or necessity of lubrication such as occurred with plug cocks formerly proposed for this service. Rate-of-flow indicators and controllers indicate or maintain proper flow rate through the equipment, visualizing operating conditions with the units or eliminating the human element and possibility of errors in functioning.

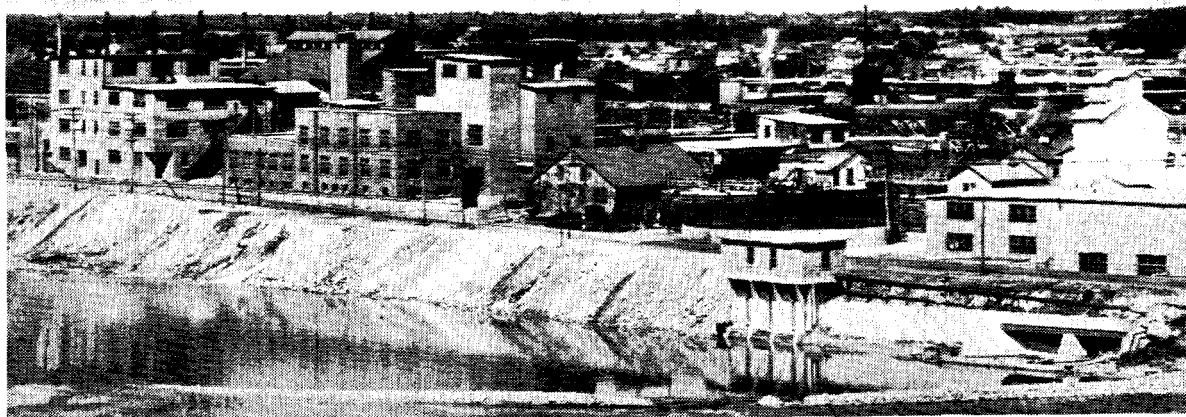
The latest developments in many phases of chemical research—including adsorption, colloid chemistry, and reactions at the interface—enter into important roles in modern water treatment plants, as well as the more familiar and fundamental reactions of general chemistry. With advantages resulting from the application of developments in pure chemistry, combined with improvements in continuous treatment equipment and process control, our modern water purification methods evince truly impressive progress, and must be considered as fundamental, not accessory, phases of present-day efficient plant operation.

It is imperative, however, that each application of water purification equipment should be planned for its own particular set of requirements. A complete analysis of the water should be made if any type of chemical treatment is considered or if there is any possibility that treatment might be advantageous. The possibility of seasonal variation in the water supply should be considered; surface supplies—particularly rivers and streams—may vary widely from one season of the year to another, requiring a different form of treatment at different times. The size and type of the equipment selected, even after the nature of treatment has been determined, should be in part governed by the economic as well as the engineering questions involved.

The economic advantages of modern continuous treatment are particularly important in both the brewery and the distillery, not only because present processes offer improvements and savings over older systems, but also because water quality exerts a direct influence on the character of product. As a result of this immediate effect on product quality and salability, properly applied treatment pays large dividends.

The services of trained consultants and analytical laboratories familiar with modern water purification possibilities are frequently of the greatest assistance in determining the desiderata for each application, and in fixing the allowable limits of impurities.

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