ramine B needed, or at what step the germicide should be added to give maximum benefits. However, it seems that 5.5 ounces for 42.5 gallons or 8 ounces for 60 gallons of rinse water is not far from the optimum, and this should be used in the second clear water rinse. In normal laundry operation this procedure gives approximately 250 p.p.m. available chlorine in the second rinse with enough solution being retained by the load to give about 50 p.p.m. in the sour rinse. Because of the low pH of the sour rinse germicidal action continues through this operation.

As a result of this undertaking the Navy has included a Monochloramine B treatment in their specification covering the renovation of Navy Special Clothing (*2*). This specification calls for 8 ounces of Monochloramine B for each 60 gallons of water used in the second rinse immediately preceding the sour rinse.

Temperature and pH are just as important to the germicidal action of Monochloramine B as is concentration. Excessive amounts of the chemical at low pH values will cause fading (bleaching), and could result in loss of tensile strength. No special studies on the loss of tensile strength were made in this program because of time limitations.

This work suggests the possibility of using Monochloramine B in commercial laundries in cases of emergency, although, under normal conditions commercial laundries rarely need a germicide.

From this investigation the following conclusions were drawn:

Of the chlorine-liberating chemicals studied, only Monochloramine B possessed solubility, pH, and chlorine-liberating characteristics that seemed practical for use in a mobile field laundry.

When Monochloramine B solutions were used at available chlorine levels of 250 p.p.m. at 100° F. and a pH of 8, and 50 p.p.m. at 100° F. and a pH of 5, fading was negligible on olive drab 50:50 cotton-wool knitted fabric after five washing operations lasting 5 minutes each. On 100% cotton fabrics negligible fading occurred under the same conditions at 250 p.p.m. but visible fading was observed at the 50 p.p.m. level at a pH of 5.0. For the 100% cotton fabrics a third rinse would reduce the Monochloramine B content to a safe level in the sour stage.

Laboratory studies on Monochloramine B solutions, containing concentrations of organic material comparable with laundry rinse waters, have indicated sufficient germicidal action to kill *Staph. aureus* in 3 minutes at 23° C. and at pH 5.0 when used at an available chlorine level of 50 p.p.m. If the pH is raised to 6.0, 100 p.p.m. of available chlorine are needed. With a contact time of 5 minutes and at 38° C., 25 p.p.m. of available chlorine kills at pH 5.0, and 50 p.p.m. kills at pH 6.0, 7.0, or 8.0.

Studies in the field with an Army mobile laundry unit yielded data showing a marked reduction of bacterial count when Monochloramine B was used in the laundering operations. This was evidenced on both laundered fabric and in washing and rinsing waters when *E. coli* and even such resistant organisms as *Bacillus subtilis* were the test organisms.

The studies indicate that Monochloramine B is equally effective when the detergent used is soap or anionic synthetic detergent.

Maximum benefit can be expected in bacterial destruction when the chemical is used in the second clear water rinse.

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High Pressure Laboratory Flow Apparatus

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The laboratory flow plant described has given satisfactory results for high pressure reactions, such as the synthesis of methanol from hydrogen and carbon dioxide and the conversion of benzene and benzene-methane into toluene.

IN VIEW of the growing importance of high pressure operation in the process industries, the need for small scale high pressure apparatus for laboratory research is apparent. Such laboratory equipment should be capable of operating under conditions comparable with those employed in industrial practice. The reduction to laboratory scale, however, frequently meets with difficulties in that parts of the apparatus, such as pumps, pressure controllers, etc., tend to operate more erratically when reduced to smaller proportions. This condition imposed by small scale operation requires, in some instances, a departure from the usual commercial or pilot plant practice, as, for example, the delivery of high pressure gas to the reaction system by displacement by liquids from storage cylinders rather than by compressors. The present paper describes a high pressure laboratory flow plant that has given satisfactory results for high pressure reactions, such as the synthesis of methanol from hydrogen and carbon dioxide (*1*) and the conversion of benzene and benzene-methane into toluene (*2*).

DESCRIPTION OF APPARATUS

The high pressure flow plant was designed to process, catalytically or thermally, normally liquid or gaseous materials, or combinations of both, at pressures up to 13,000 pounds per square inch and at temperatures up to 565° C.

That part of the equipment which withstands pressure is enclosed within iron barricades 0.25 inch thick. Peep holes, covered with bulletproof glass, permit the observation of instrument read-

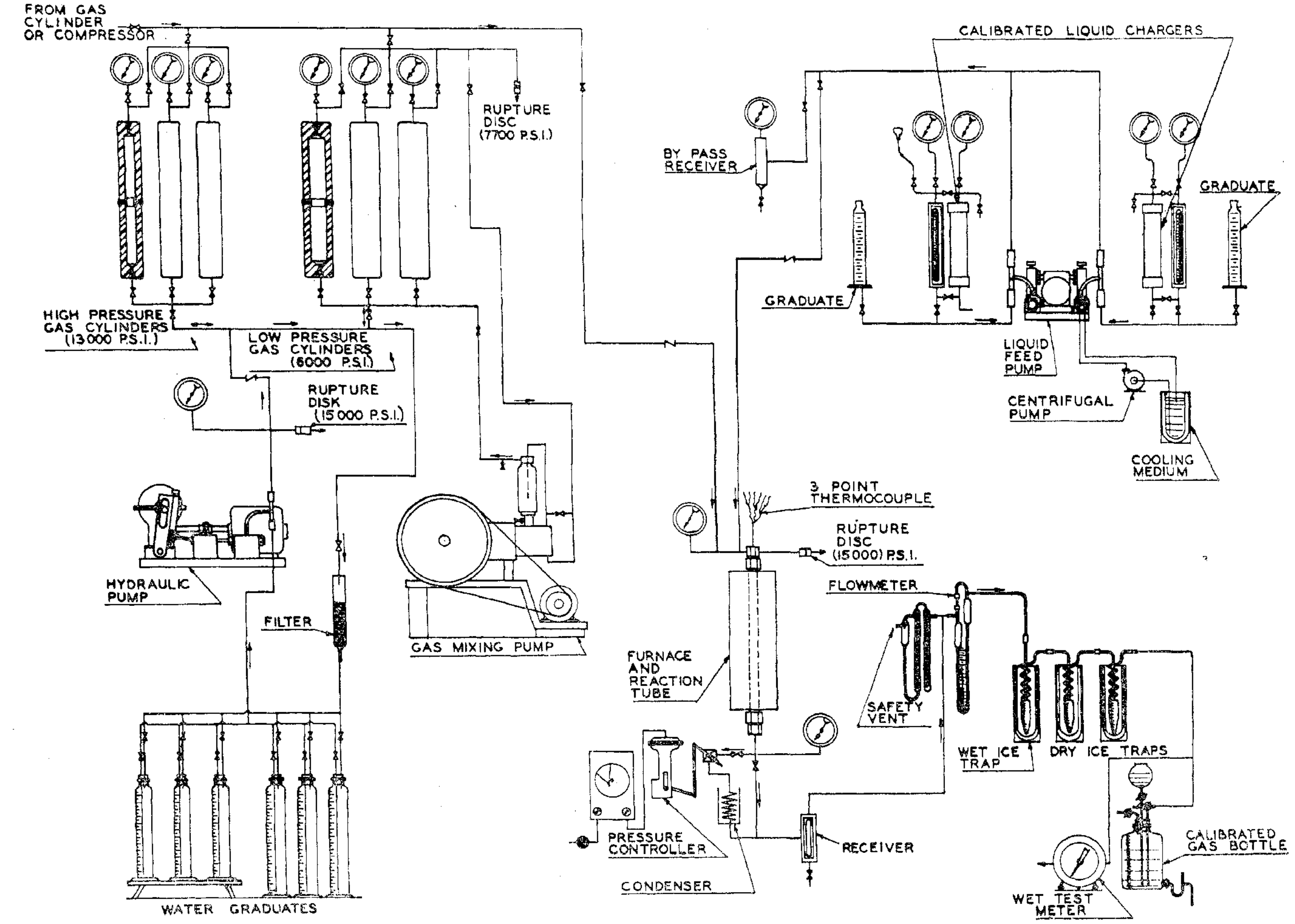

Figure 1. Flow Diagram

ings. All high pressure control valves extend through the barricade walls, so that the plant operation may proceed with due protection.

The apparatus consists essentially of six parts:

1. A high pressure gas charging system consisting of six high pressure cylinders, three for pressures up to 6000 pounds per square inch and three for pressures between 6000 and 13,000 pounds per square inch, the top outlets of all six cylinders being manifolded to the gas feed line to the reaction tube and the bottom outlets to the discharge side of a motorized, variable-stroke hydraulic pump, the intake of which connects any one of six water graduates.
2. A gas mixing pump, connecting the top and bottom manifolding systems of low pressure (6000 pounds per square inch) gas cylinders, for making up composite gas charges.
3. A liquid charging system consisting of two calibrated heavy duty chargers for liquids of high vapor pressures and two calibrated glass cylinders for liquids of low vapor pressures, one of each type being manifolded to each of the suction ends of a two-unit variable-stroke liquid feed pump which discharges into the preheater section of the reaction tube.
4. A copper-lined high pressure reaction tube supported in an electrically heated stainless steel block furnace with an automatic temperature regulator.
5. A pressure controller attached to the exit end of the reaction tube, releasing the products to atmospheric pressure before condensation.
6. A cold water condenser and receiver, or gas separator to collect the liquid product. The gas from the receiver, or gas separator, is led consecutively through a wet ice and dry ice–acetone trap to a wet-test meter.

HIGH PRESSURE GAS CHARGING SYSTEM. Each of the three high pressure (13,000 pounds per square inch) gas cylinders has a capacity of 1400 ml. and each of the low pressure cylinders (6000 pounds per square inch) a capacity of 3600 ml. They were fabricated by boring out two steel blocks and welding together the two bored ends. Pressure gages are provided and thermocouples contact the outside walls midway between the top and bottom of the cylinders.

The hydraulic pump is motorized and has a variable cam for changing the stroke and varying the pumping rate. At maximum stroke the pumping rate is 11.6 liters per hour. The hydraulic pump has two functions: pressuring the process gas to the operating level and forcing the gas into the reaction tube during the runs. If a dry gas is desired, a dryer (omitted from Figure 1) may be installed in the gas feed line to the reaction tube.

The gas mixing pumps is a motorized, belt-driven Hofer recycling or circulation pump.

LIQUID CHARGING SYSTEM. The heavy duty liquid chargers, used for liquids of high vapor pressures, are made of heavy steel pipe and provided with calibrated gage glasses. Glass graduates with holes bored through the bottoms and provided with connectors for the pump suction lines serve for liquids of low vapor pressures.

The liquid feed pump, though smaller, is similar in construction to the hydraulic pump, with the exception that two pumping units are provided for pumping two separate liquid streams simultaneously into the reaction tube when it is not feasible to make up a composite liquid charge. One of the pumping units has its cylinder, or pump body, chambered to accommodate circulating liquid coolant for liquids that tend to cause vapor lock—e.g., carbon dioxide with a critical temperature of 31° C. By diverting the liquid stream to the by-pass receiver and holding the pressure therein at the operating level by manual control of the pressure release valve, the stroke of either pumping unit may be adjusted to give the desired feed rate before starting the run.

Reaction Tube. The reaction tube consists of stainless steel (18–8 molybdenum Type 316) and is provided with a push-fit copper liner.

The top 5-inch section has a copper spacer. The next 10-inch section, which serves as a preheater, is filled with copper punchings, porcelain beads, or other inert material. Following this is the catalyst zone with a capacity of 50 ml. and length of 10 inches. The lower 9 inches below the catalyst contain a loose-fitting copper filler which serves as a support for the catalyst, at the same time reducing the volume of the lower part of the tube and hastening the exit of the reaction products.

A thermocouple well, sheathed with Duronze tubing, extends downward through the center of the reaction tube into the catalyst bed. This arrangement makes possible the installation of fixed thermocouples near the top and bottom and at the center of the catalyst zone to determine the catalyst temperatures at these positions (see Figure 2).

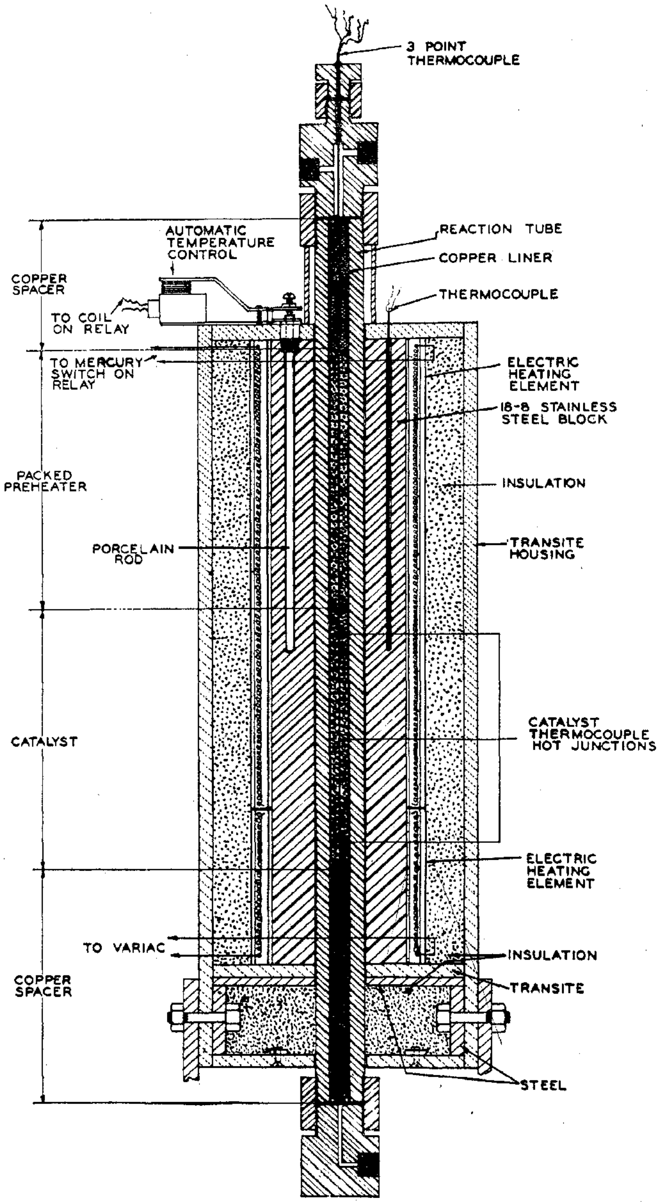

Figure 2. Furnace and Reaction Tube

Furnace. The furnace consists of an electrically heated cylindrical stainless steel block with a hole in the center extending coaxially the length of the block to accommodate the reaction tube. The temperature regulation is automatic and depends on the difference in thermal expansion between the block and a porcelain rod which extends downward in an off-centered hole into the interior of the block. The porcelain rod engages an adjustable lever arm which operates a microswitch which in turn opens and closes a relay in the circuit of the upper heating element surrounding the block. The furnace block is provided with a thermocouple well. A separate heating element with Variac control surrounds the lower end of the furnace block below the larger heating element to compensate for the heat loss at the exposed lower end of the reaction tube.

Pressure Control System. The pressure controller operates a diaphragm motor which in turn actuates, by means of a lever arm, the valve handle extension of the pressure release valve (Hofer type needle valve). The release of the pressure from operating levels up to 13,000 pounds per square inch to atmospheric pressure in one stage proceeds smoothly with this type of valve with little or no pulsation even at very low feed rates. No erosion of the valve parts has been observed.

Valves, Fittings, and Accessories. The valves, which together with various fittings such as connectors, nipples, tees, couplings, and check valves were fabricated at the laboratory's machine shop at Riverside, are right-angle, stainless steel, Hofer type needle valves with armored packing around the stems. The tubing connectors are of the cone-closure type and welded to the tubing. All high pressure lines connecting parts of the apparatus consist of iron tubing of capillary bore with the exception of the lines to the gas mixing pump, which are 0.125-inch pipe size heavy stainless steel tubing. Lines in which the pressure never exceeds a few hundred pounds per square inch, such as the liquid charger feed lines to the pumps, are copper tubing.

OPERATION

Preparation of Gas Charge. When the process gas consists of a single constituent and the operating pressure is not in excess of 6000 pounds per square inch, the low pressure (6000 pounds per square inch) gas cylinders are employed. By alternately charging gas into one of these cylinders at the available supply pressure and forcing the gas into another by water displacement by means of the hydraulic pump, the gas pressure may be raised to any desired level in the latter, which becomes the source of gas supply for the experiment. Two cylinders are required for this operation. The third shown in the flow diagram (Figure 1) is used for storage. The quantity (weight or moles) and the density of the high pressure gas may be calculated from *P-V-T* data.

When the process gas is a synthetic mixture, each component is charged into a separate low pressure (6000 pounds per square inch) gas cylinder to the pressure level required by *P-V-T* data to give the quantities required for the composite gas charge. The valves connecting the respective gas cylinders with the upper and lower manifolds are opened and the gas is cycled by the gas mixing pump, 1 hour being sufficient for complete mixing. After mixing, the composite gas is raised to desired pressure level as previously outlined. The residual gas left behind in the gas mixing pump and other parts of the apparatus after transfer of the major portion to the gas supply cylinder may be determined by metering at atmospheric pressure, the correction applied, and the quantity and density of the composite gas in the supply cylinder determined.

When the operating pressure is between 6000 and 13,000 pounds per square inch, the gas charge, single or multicomponent, is made up in the low pressure cylinders (6000 pounds per square inch) as described above and transferred by water displacement into the high pressure (13,000 pounds per square inch) cylinders and the pressure raised to the required level in the manner described for operation at 6000 pounds per square inch or below.

During the experiment the compressed gas is discharged at the desired pressure level into the preheater section of the reaction tube, likewise by water displacement. From the amount of water pumped from the graduated cylinders, the quantity of gas charged and the flow rate may be determined.

Liquid Charge. Liquid materials of low vapor pressure are charged from the graduated glass cylinders into the reaction tube by means of the liquid feed pump. Liquids of high vapor pressure or normally gaseous substances which have critical temperatures above the room temperature are also charged by the liquid feed pump from the heavy duty chargers; at all times there must be a sufficient quantity in the charger to ensure the presence of the liquid phase.

In the preheater section of the reaction tube, which is filled with copper punchings or porcelain beads, the gaseous charge and the vapors of the liquid charge mix and pass down through the catalyst zone. The products, after release to atmospheric pressure through the pressure release valve on the exit end of the reaction tube, pass on to the condenser. Liquid product separates out in the receiver, and the gas passes on through a wet ice trap and dry ice–acetone trap in tandem arrangement to remove any entrained material and condense low boiling products, and finally through a wet-test meter.

Weight Balances. The weight of the total products obtained from runs of 2 to 4 hours' duration, after a line-out period of 1 to 2 hours, will usually fall within the range of 95 to 103% of the weight of the total charge.

The reaction products are investigated by the usual procedures.

ACKNOWLEDGMENT

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PICKLE LIQUOR NEUTRALIZATION

Economic and Technologic Factors

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The various economic factors that should be considered in designing a pickle liquor neutralization plant are discussed in some detail. The advantages and disadvantages of low and high cost alkaline agents are compared quantitatively by means of tabulated data and graphs. Preliminary data are presented on the operation of a pilot neutralization plant operated by the Warner Company.

THIS is the fourth paper in a series (*1, 2, 3*) dealing with the treatment of waste pickle liquor with alkaline agents. The earlier papers were concerned chiefly with reaction rates and sludge characteristics. The major emphasis of the present contribution is on economic factors and the potentialities of alkaline agents normally considered to be wastes by their producers.

Spent pickle liquor can be used successfully in a variety of applications—e.g., water purification, sewage treatment, and treatment of many industrial wastes. Unfortunately, however, economy requires that it be used relatively near the plant producing it. Its corrosive nature and high water content result in costly transportation charges, although it has been hauled in ordinary steel tanks for distances of 15 miles or more; as the tanks corroded, they were replaced, and, over a period of years, the costs were not excessive. Its most desirable component, copperas, can be separated easily, but this compound contains 45% of water of crystallization, and this limits the distance it can be shipped. If this product is dried to ferrous sulfate monohydrate, its solution rate is reduced materially. The cost of the additional operation prevents it from competing with other low-cost coagulants.

This combination of circumstances necessitates treating pickle liquor as a waste product in most instances, and such treatment is most economically effected by neutralization with lime or some other cheap alkaline agent.

SELECTION OF ALKALINE AGENT

The choice of the best neutralizing agent in any instance will be governed by the economic position of any given plant. Waste treatment practice varies so widely, because of the inherent complexity of the problems involved, that each installation must be designed to fit the particular situation of the plant for which it is intended. Although neutralization procedures have become more or less standardized, pickle liquor neutralization plants also must be properly adapted to local conditions. Where there is a choice of alkaline agents, it is important that the one best suited to the purpose be selected.

Two types of factors affect the choice of agent: (1) those fixed by the agent itself, such as basicity factor, delivered price, and reactivity; and (2) those set by conditions prevailing at a given mill, such as operating schedule, area available for the treatment plant, and character of the receiving stream or sewer system. Generally, the last-mentioned group of factors will be relatively unalterable and an agent must be selected to meet those requirements. Choice of an agent should be based on the following considerations.

Cost. It is axiomatic that the cheapest agent capable of fulfilling the requirements should be used. Delivered cost per ton is not usually a sound criterion of actual cost, and wherever possible even cheap agents should be held to specifications by routine analysis of each shipment.

Space Available. Where little or no land is available for lagooning the sludge from the treatment plant, the agent that yields the most settleable (or dewaterable) sludge must be used, even though its costs be comparatively high. Sludge handling may cost several times as much as the actual neutralization, and any agent that will substantially reduce sludge volume will permit the payment of a correspondingly higher price for it.

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