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CARBON DIOXIDE FOR pH CONTROL

INTRODUCTION:

In recent years carbon dioxide has been used instead of sulfuric acid to control alkalinity in water streams. It has been found economical, abundant, easy-to-apply and safe-to-handle. It has unique advantages in limiting pH to 8.3, a level acceptable for discharge, and providing a source of instrument air if needed at its use location. Cardox, a major supplier, has announced recent technological advances to overcome problems in the storage and solubility to increase its applicability and, of course, their sales.

The major part of the material in this report has been obtained from Cardox or from literature sources. The basic chemistry and its effect on the pH end-point has been confirmed by an SRL Chemist. Cardox is a division of Chemetron Corporation, a member company of Allegheny International Inc. (formerly Allegheny Ludlum Industries, Inc.).

SUMMARY

In recent years carbon dioxide has been used in lieu of sulfuric acid to treat water for high alkalinity. This reagent has the advantage that it can not over acidify and may provide reagent and equipment savings as well.

The major supplier has developed a diffuser to introduce carbon dioxide into a water volume as small bubbles to minimize reagent loss to the atmosphere. This unit is integral to several configurations suggested for treatment.

Users have reported successful applications in the chemical industry and by electric utilities.

CHEMICAL TREATMENT

One of the major advantages claimed for carbon dioxide in pH control is that it cannot over acidify. In discharge streams there is a regulatory standard for minimum pH, 6, as well as the maximum. Sulfuric acid can over acidify very easily because of its non-linear response in neutralization. Much less acid is required between a pH of 6 and 9 than is required between 9 and 11 (for example).

This over acidification cannot occur with carbon dioxide because of the sequence of its reactions. Initially it forms carbonic acid

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

although this acid is hard to isolate in alkaline solutions.

The carbonic acid then reacts with the alkalinity 6 for bicarbonate salts

$$H_2CO_3 + 2OH^- \rightleftharpoons HCO_3^+ + H_2O$$

The pH of these bicarbonate solutions is approximately 8.3. The bicarbonate contains stoichiometrically the maximum quantity of carbon dioxide. Therefore excess CO_2 would force these reactions in the direction of bicarbonate formation. Thus, the claim that over acidification cannot occur when carbon dioxide is used to neutralize is justified by the chemistry of the system.

Cardox has provided pH curves for the neutralization of caustic soda; these curves are attached as Figure 1. Although they imply that, on a weight basis, reagent savings could be obtained by using carbon dioxide, buffering effects are not included. Since buffering agents could respond differently to carbon dioxide and sulfuric acid, pH curves should be rerun using the actual alkaline material to be treated before drawing quantitative conclusions on the acid requirement.

PHYSICAL TREATMENT

Carbon dioxide is widely recognized as a gas at all ambient temperatures in this geographic area. In order to effect a neutralization reaction it is necessary to dissolve this gas into solution with the alkalinity. Simple observation of a carbonated beverage shows how difficult that would be to accomplish. The spontaneous route is for carbon dioxide to leave solution and enter the vapor space above it.

If carbon dioxide were to enter an alkaline solution, it could be expected to react quickly to form a bicarbonate salt. Work has been done to place carbon dioxide gas under a liquid surface in such a configuration that it would diffuse into the solution and by reaction create a concentration gradient from the gas to the liquid. Once this gradient is established the reaction in the liquid could effect net mass transfer from the gas to the liquid to sustain the reaction.

Cardox has designed a diffuser which can be used for introducing carbon dioxide into a liquid volume as bubbles with diameters of 50 microns or less. The diffusion area consists of porous polyethylene film which is formed into a tube and capped. The diffuser dimensions and a more detailed description are given in the attached "tech specs" sheet from Cardox.

The diffuser is suggested for use in batch treatment tanks or in flowing streams as illustrated in Figures 2 & 3 provided by Cardox. The feed-forward implication in Figure 3 is not meant to infer that they advocate that control configuration, but is the draftsman's interpretation.

Carbon dioxide can be stored as a liquid at 0°F, 300 psia. It must be contained in a pressurized refrigerated tank. These units are commercially available in sizes of 5 tons through 45 tons or larger.

If the bubbles from the diffuser are held under a liquid surface for 5 to 6 seconds, they will dissolve into the liquid. Even though the pH of an alkaline solution will not react to a pH below 8.3 at atmosphere pressure, at elevated pressures the solution can be super-saturated and the pH reduced below that, even as low as 3.2. Cardox has taken advantage of these latter properties to develop a technique which they refer to as side stream precarbonation. A small stream from the treated water is pumped under pressure through a pressurized chamber. Excess carbon dioxide enters the chamber through a diffuser and under pressure super saturates the stream. This stream is then introduced into the main body of water where it mixes without perceptible reagent loss. A Cardox sketch of this assemblage is shown as Figure 4.

APPLICATIONS

Two examples of large-scale use of carbon dioxides for pH control have been reported. Cardox literature reports a use by Diamond Shamrock at Muscle Shoals, AL and indicate that the system was installed at a capital cost $50,000 less than the alternatives.

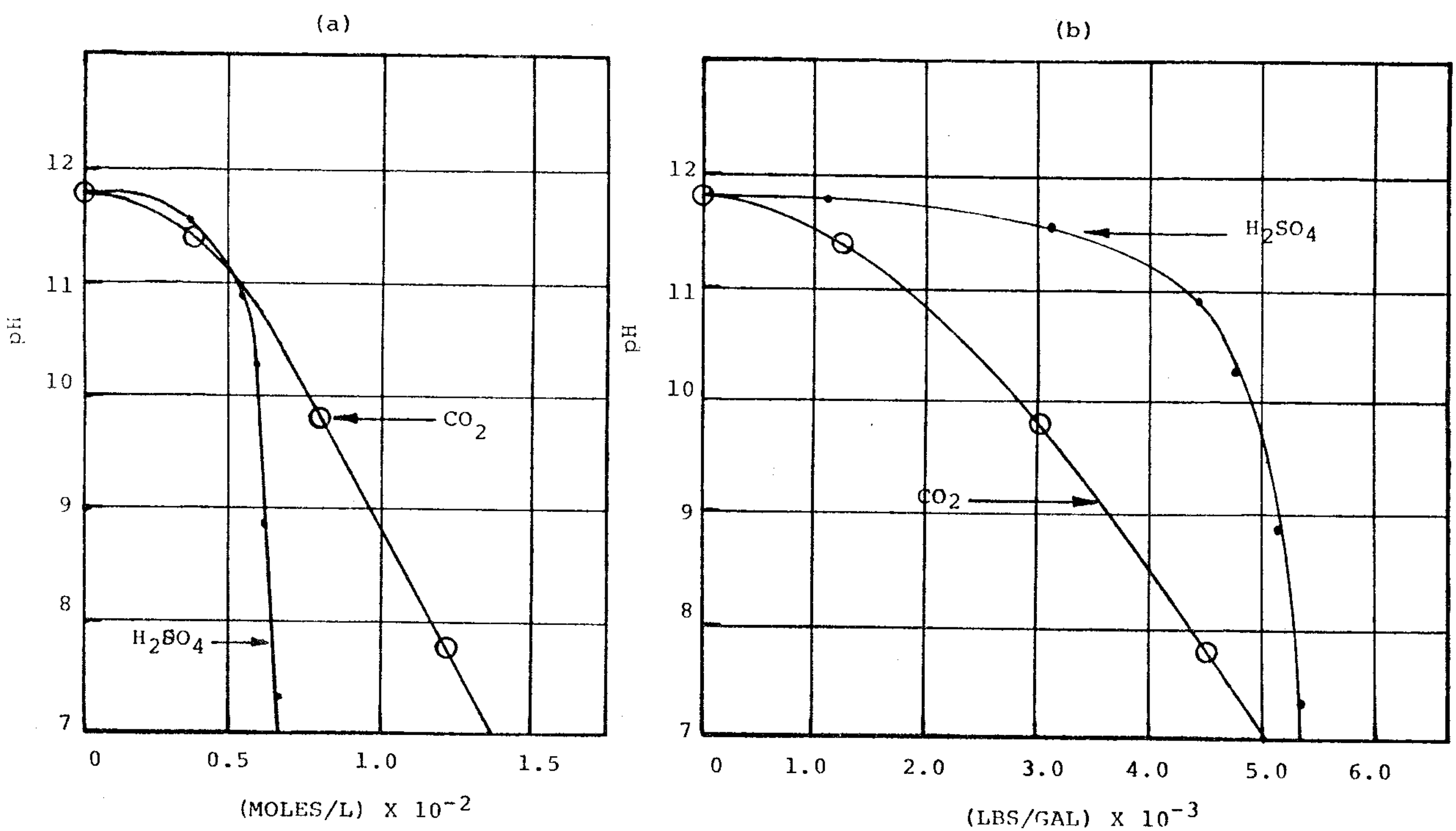
In 1977 Power Engineering published a description of carbon dioxide use by Union Electric Co. to treat the effluent from flyash ponds. The systems were installed at three generating plants including one used for peaking power that did not run continuously. In the latter case the carbon dioxide rate was manually set at the rate required when the plant was operating. Excess reagent was, of course, consumed when the plant was down. They reported that the overfeed penalty was more than offset by equipment and maintenance savings.

CONCLUSIONS

Carbon dioxide is an acid reagent which should be considered for reducing the pH of alkaline streams.

It has unique advantages in that over-additions do not drop the pH below 8.3, an allowable value for discharge, and the carbon dioxide itself may be used as instrument air for a pneumatic controller and valve.

Carbon dioxide, however, must be stored at the site of use under pressure and refrigerated. In addition a field trial for the application configuration should be performed to assure that the carbon dioxide is completely solubilized and not lost to the atmosphere when used.



0.0143N NaOH Solutions

FIGURE 1. CO_2 & H_2SO_4 Titration Curves

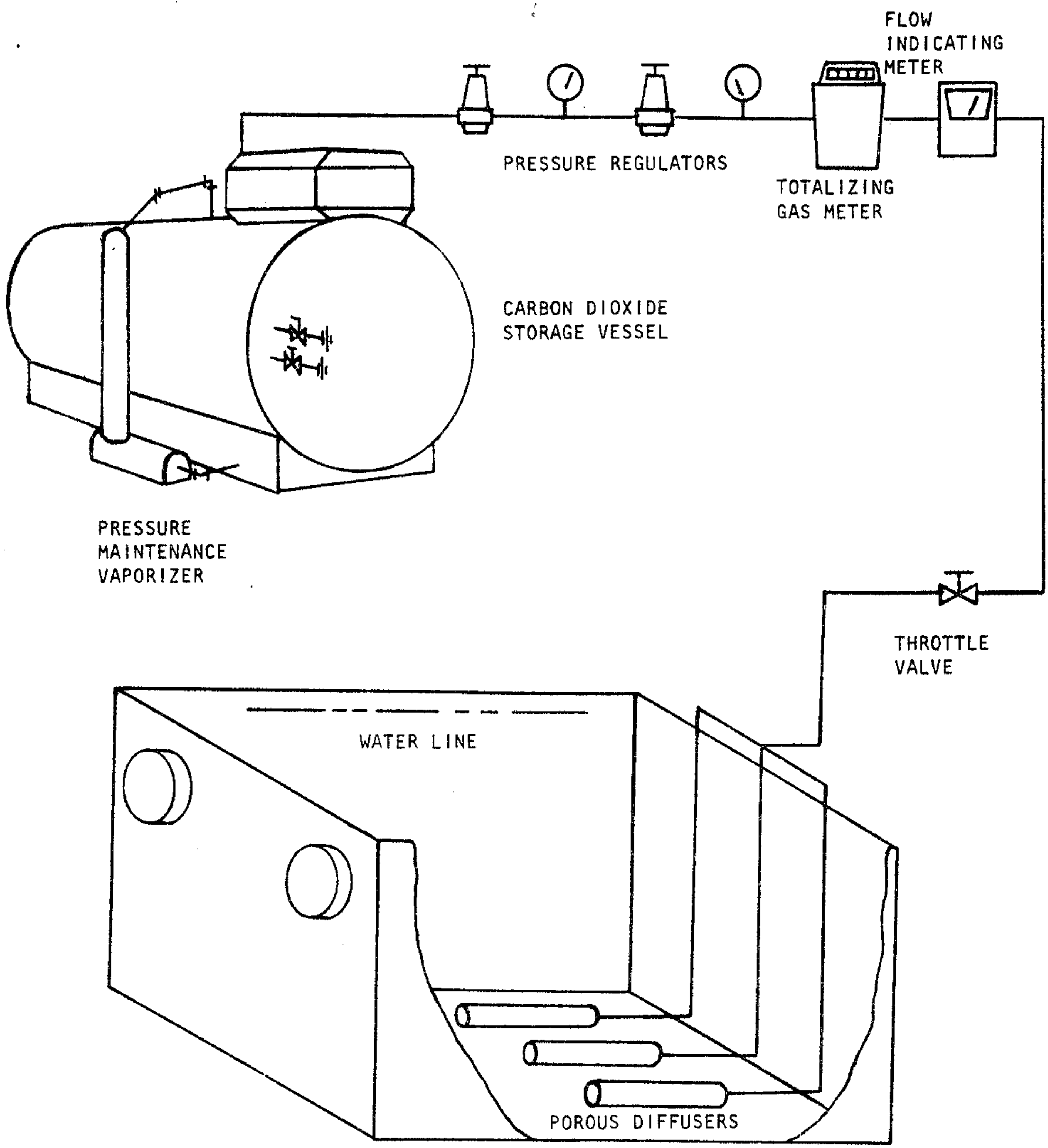


FIGURE 2. Batch Carbonation

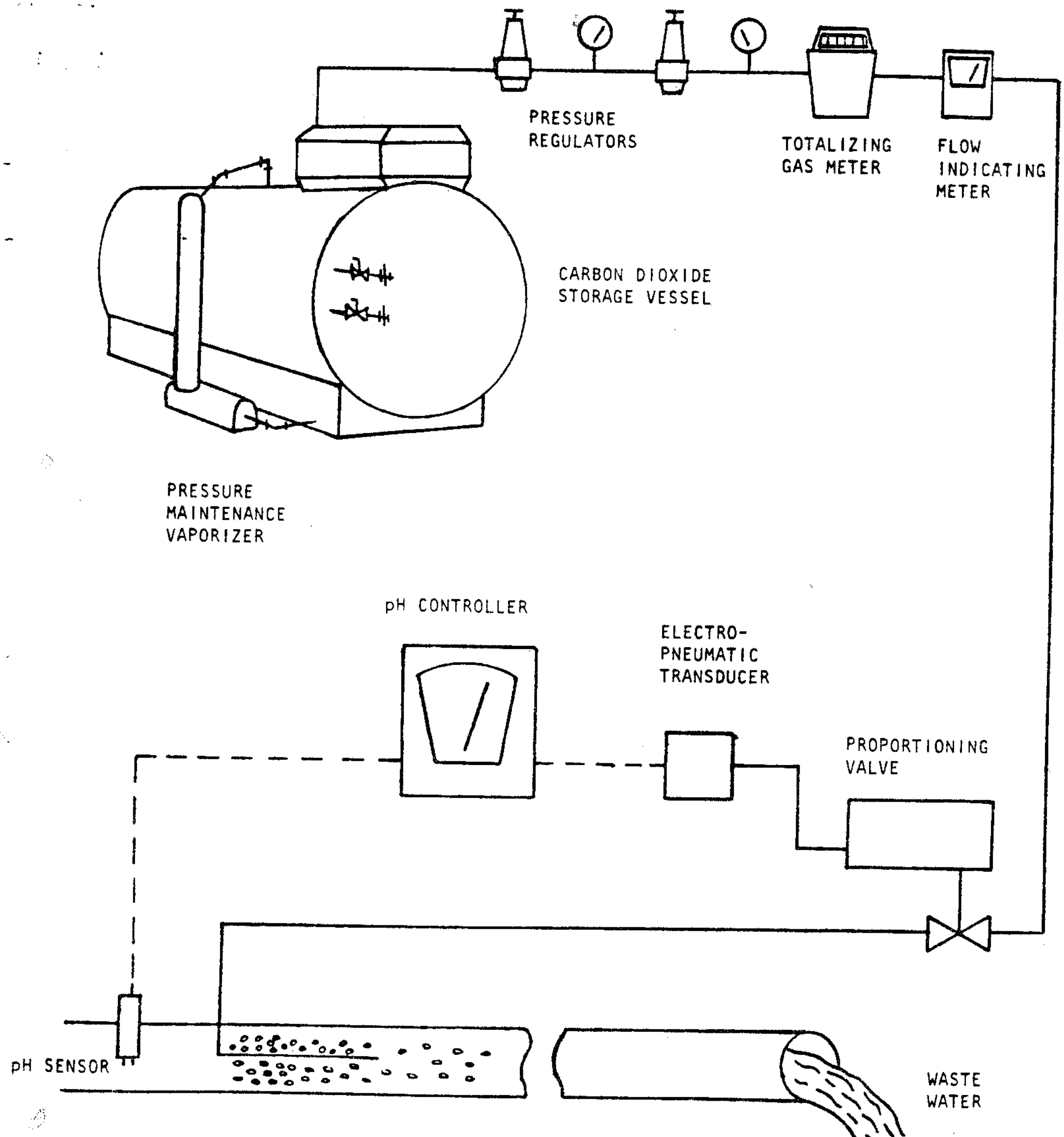
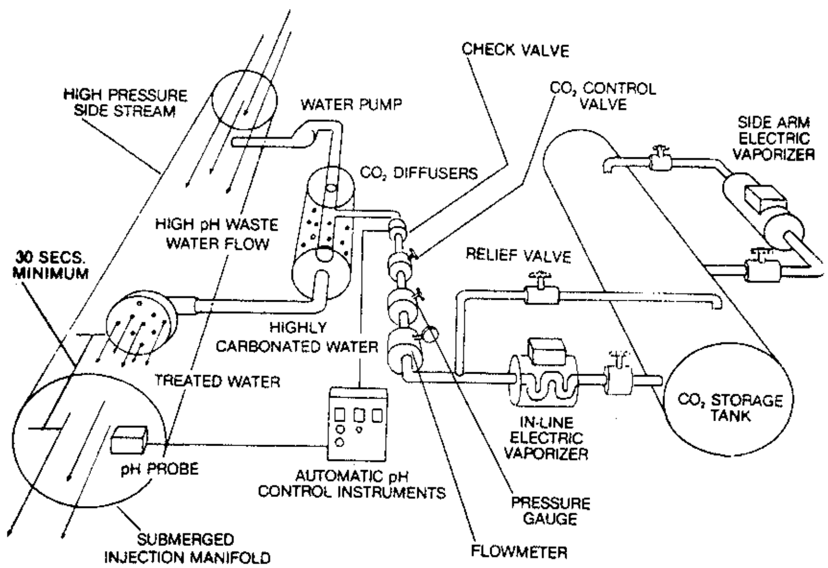


FIGURE 3. Continuous Carbonation



This typical side stream pre-carbonation system with electric vaporizer meets customer requirements.

FIGURE 4. Side Stream Precarbonation

CARDOX

tech specs

number: 1036-A

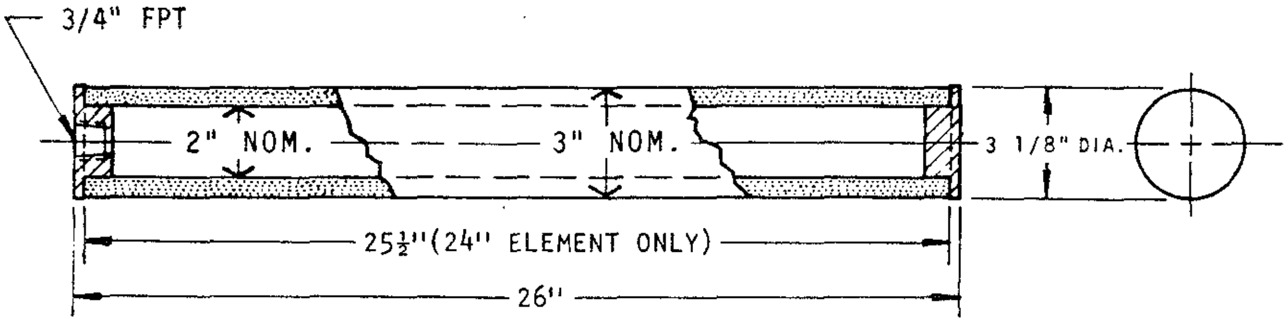
date: 2-15-79

Subject: PLASTIC DIFFUSER TUBE ASSEMBLY
Stock No. 7-937-0002

PLASTIC DIFFUSER TUBE (ELEMENT ONLY)
Stock No. 7-937-0001

<u>PURPOSE</u>: To promote efficient diffusion of a gas, such as CO_2, into a surrounding liquid medium so that the maximum amount will be absorbed by the liquid.

<u>APPLICATIONS</u>: Wastewater, pH neutralization
Potable water, pH neutralization and recarbonation



<u>DESCRIPTION</u>: Two styles of diffusers are available.

Stock No. 7-937-0002 is a complete assembly including PVC end caps cemented in place, one of which has a 3/4" female pipe thread connection. The porous element is made of white ultra high molecular weight polyethylene plastic with an approximate pore size of 50 microns.

Stock No. 7-937-0001 is the porous plastic element without end caps, 24" long. It is for use as a replacement in installations originally equipped with diffusers with removable end caps.

<u>FLOW RATE</u>: Each assembly is capable of flowing 600 SCFH of carbon dioxide vapor with less than 1 psi differential pressure. To obtain larger flows, groups of assemblies should be manifolded together.

<u>ADVANTAGES</u>: UHMW polyethylene plastic is inherently tough and will not shatter if accidently bumped or dropped. The tube assembly is a complete unit, so no gaskets are required and installation is simplified.