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FUNDAMENTALS OF CARBON DIOXIDE ABSORPTION AS THEY APPLY TO CONTROLLED-ATMOSPHERE STORAGES

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REMOVAL OF EXCESS carbon dioxide is essential for the operation of a controlled-atmosphere (CA) fruit storage. Most storages employ special equipment for this purpose, yet little information is available regarding the suitability, theory of operation and operating characteristics of the carbon dioxide absorption equipment used.

Several researchers (Comstock and Dodge, 1937; Furnas and Bellinger, 1938; Spector and Dodge, 1946; and Tepe and Dodge, 1943) have extensively studied the absorption of carbon dioxide with either sodium hydroxide or sodium carbonate solutions under laboratory conditions. Their findings, unfortunately, are not directly applicable to carbon dioxide removal from CA fruit storages.

This paper presents some of the theoretical considerations gained through 3 years of intensive study of the problem of the absorption of carbon dioxide with caustic soda solutions and discusses the practical aspects of carbon dioxide removal from controlled-atmosphere storages.

PROPERTIES AND REACTIONS OF CAUSTIC SODA

Caustic soda is the commercial designation (Solvay Tech. and Engineer. Ser., 1956) of sodium hydroxide (NaOH). All forms of commercial caustic soda are marketed on the basis of their equivalent sodium oxide (Na_2O) content. Pure caustic soda, which is 100 percent sodium hydroxide, contains 77.48 percent sodium oxide. Dry,

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solid, commercial grade caustic soda (commonly known as "78 percent caustic soda") contains at least 98.90 percent NaOH and is available as regular flake, fine flake, crystal flake and powder. All forms are readily soluble in water.

Caustic soda (sodium hydroxide) solution absorbs carbon dioxide by chemical reaction in two steps:

I. 1.0 lb. NaOH + 0.55 lb. $CO_2 \rightarrow$ 1.325 lb. Na_2CO_3 + 0.225 lb. H_2O

II. 0.55 lb. CO_2 + 1.325 lb. Na_2CO_3 + 0.225 lb. $H_2O \rightarrow$ 2.1 lb. $NaHCO_3$

As shown by these equations, 1 pound of pure sodium hydroxide will absorb 1.1 pounds of carbon dioxide. One-half is absorbed in each step; however, step I takes place much faster than II. Obviously, each reaction has special characteristics which may affect the operation of an absorber; for example, reaction II is reversible in that sodium hydroxide will react with sodium bicarbonate to form sodium carbonate.

FACTORS THAT AFFECT RATE OF CO_2 ABSORPTION

The rate of absorption of carbon dioxide is affected by such variables as the state of completion of the chemical reaction, the liquid flow rate, the absorbing surface area, the liquid temperature, and the concentration of carbon dioxide gas in the atmosphere.

Characteristics of Caustic Soda Absorbing Solutions

Fig. 1 illustrates the rate of carbon dioxide absorption in the M.S.U. absorber (Pflug, et al., 1957) operated with a liquid flow rate of 60 gallons per minute (g.p.m.), an airflow rate of 60 cubic feet per minute (c.f.m.), the absorbing solution temperature shown in Fig. 2, the carbon dioxide level shown in Fig. 3, and an absorbing solution containing 10 pounds of caustic soda per 100 gallons of water.

In general, the portion of the curve between points A to B of Fig. 1 reflects the great affinity of sodium hydroxide for carbon dioxide. The decreasing rate from A to B is due to the increased concentration of sodium carbonate as reaction I nears completion. At point B (Fig. 1), the sodium hydroxide has been completely neutralized to sodium carbonate. As more carbon dioxide is absorbed, the rate of absorption is further reduced as the sodium carbonate is

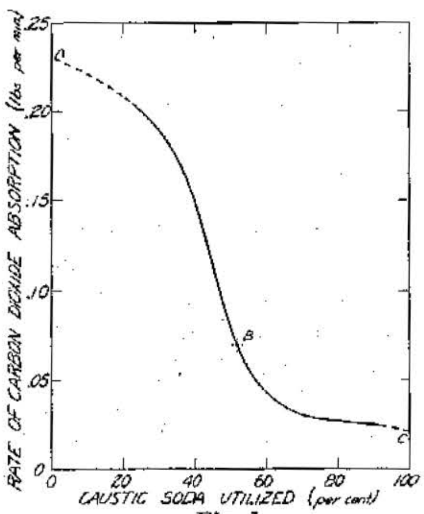

Fig. 1

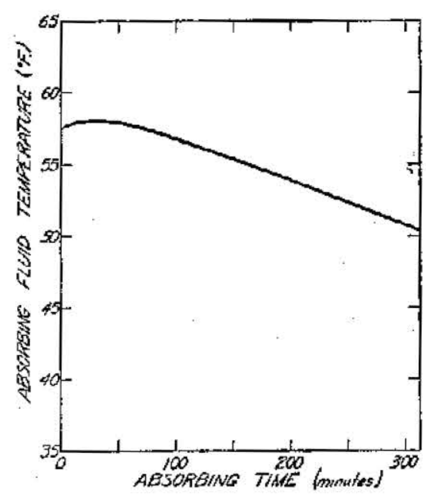

Fig. 2

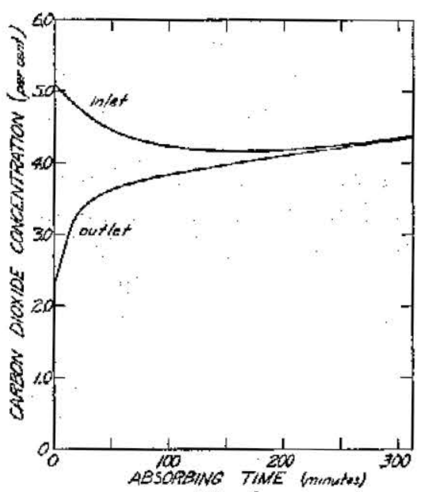

Fig. 3

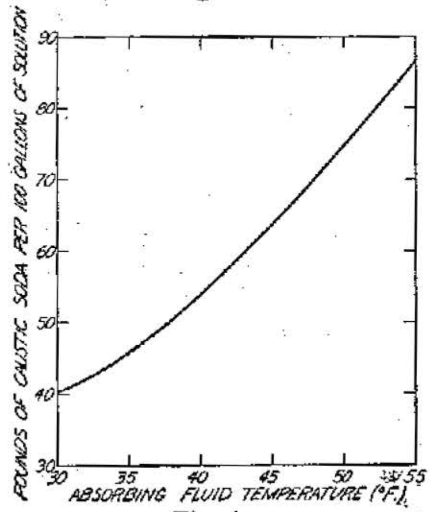

Fig. 4

These four graphs show characteristics of carbon dioxide absorbers.

neutralized to sodium bicarbonate. The absorption rate at point C of Fig. 1 is about one-third of the rate at point B.

Liquid Flow Rate

The effect of liquid flow rates on carbon dioxide absorption from commercial CA apple storages have been studied by Pflug, Dewey and Brandt (1957). The length of time required to utilize 90 percent of the caustic soda (using a charge of 10 pounds per 100 gallons of solution at flow rates of 20, 40, 60 and 80 g.p.m.) was 343, 223, 167 and 142 minutes, respectively. Under these conditions, the rates of carbon dioxide absorption were directly proportional to the rates of liquid flow.

Absorbing Surface Area

Carbon dioxide absorption is a surface phenomena; consequently, the contact area between the absorbing fluid and the gas has an important effect on the rate of absorption. In general, the rate of absorption is proportional to the surface contact area. The "brine-spray" type absorber (Kedenberg, 1953) utilizes the spray droplet surface, plus the surface of the evaporator coil, to provide contact of the liquid and the gas. The packed column absorber utilizes the large surface area of the packing for this purpose.

Liquid Temperature

Increasing the temperature of the absorbing fluid increases the rate of absorption; however, temperature has a greater effect on reaction II than on reaction I (Furnas and Bellinger, 1938; Tepe and Dodge, 1943).

The temperature of the absorbing fluid is a function of the design of the absorbing system. In the integral absorber-evaporator ("brine-spray") system, the temperature of the absorbing fluid will approximate the temperature of the storage room air. In the M.S.U. absorber, the heat of reaction plus the fan and pump energy exceeds the heat loss during the early phase of the absorption cycle, causing a rise in the temperature of the absorbing solution. The temperature of the solution levels off and then gradually decreases as the rate of absorption decreases during the latter part of the absorption cycle (Fig. 2).

Carbon Dioxide Concentration

The rate of carbon dioxide absorption is a function of the concentration of the carbon dioxide in the atmosphere as it comes in contact with the absorbing solution (Leva, 1953). The carbon dioxide concentration in the air exhausted from the absorber during the early part of the absorption cycle should not be less than one-half of the concentration of the carbon dioxide in the air at intake.

Since the rate of absorption is variable (Fig. 1) and the rate of airflow constant, the carbon dioxide concentration of the exhaust air will be at a minimum level at the start of the absorption cycle and highest at the end of the cycle.

The inlet and outlet carbon dioxide concentrations for the M.S.U. absorber are shown in Fig. 3. Toward the end of the absorption cycle, the carbon dioxide is absorbed less rapidly than it is produced within the storage by the fruit. It is for this reason there is an increase in the carbon dioxide level toward the end of the absorption cycle (Fig. 3).

Airflow Rate

The results reported by Perry (1950) indicate that the airflow rate does not affect the rate of absorption, except that very low airflow rates may excessively reduce the carbon dioxide concentration in the absorber. The air exerts a cooling effect on the absorbing solution which is proportional to the rate of flow, and high airflows consume excessive energy; therefore, a minimum amount of airflow is desirable to maintain the highest possible temperature in the absorber.

OPERATING THE ABSORBER

Although the operation of the carbon dioxide absorber is relatively simple, problems often arise which are not readily solved because of the large number of variables involved. The following suggestions are therefore included as aids to CA-storage operators.

Comparison of Absorbers Now in Use

There are three types of absorbing systems commonly used in the United States to remove carbon dioxide from CA-storages: the barrel type (Smock and VanDoren, 1941), the brine-spray type (Kedenberg, 1953), and the packed tower (Pflug, et al., 1957). All operate on the same principle in that a solution of caustic soda is recirculated through a system that brings the CA-storage room atmosphere in contact with a large surface area of the absorbing fluid.

This is accomplished in the barrel absorber with a simulated plate tower; in the brine-spray with a spray plus surface area, and in the packed tower with a large surface area plus a high flow rate of liquid per cross section area. Observations and experiments (Angelini, 1956) with these absorbers have shown that the time required to utilize 90 percent of the caustic soda was more than 60 minutes per pound for barrel units, 12 to 22.5 minutes per pound for brine-spray units, and 18 minutes per pound for the packed tower.

Caustic Soda Per Charge

The quantity of caustic soda used each time the absorber is charged is important in that it should be small enough to avoid the formation of a precipitate when the caustic soda is neutralized to sodium carbonate. In Fig. 4, the maximum permissible amount of caustic soda per 100 gallons of absorbing solution that can be used without producing a sodium carbonate precipitate is shown as a function of absorbing fluid temperature.

A sodium carbonate precipitate may plug pipelines and drains if present in appreciable quantities. Absorbers operating with a solution temperature of 50° F. have a capacity of 75.4 pounds of caustic soda per 100 gallons of water without forming a precipitate; absorbers with a solution temperature of 35° F. will handle only 47.2 pounds of caustic soda per 100 gallons of water before a precipitate forms.

The Absorption Schedule

Daily removal of carbon dioxide from the storage room is desirable to prevent wide fluctuations of the carbon dioxide level of the atmosphere. When carbon dioxide is removed daily, the storage operator has an opportunity to adjust the quantity of caustic soda and the operating time of the absorber, thereby regulating the carbon dioxide level with minimum effort. Furthermore, the fruits in the storage tend to exert a flywheel effect on the gas concentration of the room atmosphere because of the accumulation of carbon dioxide within the fruit tissues.

When the level of carbon dioxide becomes excessive in the free atmosphere of the room, a like increase gradually occurs in the fruit. Subsequently, when the gas level is decreased in the atmosphere, the carbon dioxide will slowly diffuse from the fruit until an equilibrium is reestablished. Such changes disrupt the normal pattern of gas level fluctuations to a serious extent under a sporadic program of absorption, and, no doubt, would cause considerable difficulty to the operator in regulating the proper level of carbon dioxide.

Recharging the Absorber

The nature of the absorption reaction is such that it is important that the entire charge of caustic soda be loaded at the start of the absorption operation. If additional caustic soda is needed, the reservoir should be drained, refilled with fresh water, and recharged.

If this procedure is not followed, the rate of carbon dioxide absorption will be considerably reduced. For example, if 10 pounds of caustic soda were added to the absorbing solution after an initial charge of 10 pounds was completely neutralized to sodium bicarbonate, the caustic soda would immediately react with the sodium bicarbonate to produce sodium carbonate.

Referring to the curve in Fig. 1, the rate of carbon dioxide absorption would then start at point B and continue to C. It would be necessary to absorb 11 pounds of carbon dioxide at this low absorption rate. If the reservoir were drained and charged with fresh solution, the higher absorption rate from points A to B (Fig. 1) would be utilized in absorbing 5.5 pounds of carbon dioxide, leaving only 5.5 pounds to be absorbed at the slower rate, B to C.

Foaming, Air Carryout, Liquid Carryover

Drying oils, paint, pipe dope, caulking compounds, and other materials used around the absorber of a CA-storage contain fats and oils that react with caustic soda and cause foaming. Very small concentrations of fatty acids will produce enough soap or emulsifying agent to form stable bubbles which will carry the storage room air out of the absorption tower to be released in the reservoir and lost to the atmosphere outside of the storage room.

Other bubbles will be carried by the airstream into the storage room where caustic may be dropped on the fruit. The addition of 15 milliliters (half a teaspoon) of a defoaming agent to the absorbing solution at each charging will prevent this difficulty and help assure trouble-free operation.

SUMMARY

Some pertinent factors affecting the absorption of carbon dioxide from storage atmospheres are presented as aids to better understanding and accomplishing carbon dioxide removal from CA-fruit storages.

1. The rate of carbon dioxide absorption decreases throughout the period of operation of the absorber. It is initially high when a large concentration of caustic soda (sodium hydroxide) is present in the solution and steadily decreases until all of the caustic soda has been converted to sodium bicarbonate.
2. The rate of absorption increases as the rate of solution flow through the absorber increases.

3. The rate of absorption is proportional to the surface contact area of the solution with the atmosphere containing carbon dioxide.
4. The rate of absorption increases as the temperature of the absorbing solution is raised.
5. The rate of absorption increases with increases in carbon dioxide concentration.
6. The rate of airflow through the absorber does not materially affect the absorption coefficient. High airflow rates are undesirable since they waste power and cool the absorbing solution.
7. Carbon dioxide should be absorbed daily from the CA-storage.
8. The absorber reservoir should be drained and flushed each time it is recharged with caustic soda.
9. The addition of 15 milliliters (half a teaspoon) of defoaming agent to 100 gallons of solution will reduce foaming of the solution, thereby minimizing liquid carryover into the storage room and air loss from the storage.

LITERATURE CITED

Angelini, Pio (1956). A study of carbon dioxide absorption equipment for controlled-atmosphere fruit storages. Thesis for degree of M.S., Mich. State Univ., East Lansing. (Unpublished)

Comstock, C. S., and B. F. Dodge (1937). Rate of carbon dioxide absorption by carbonate solutions in a packed tower. Ind. and Eng. Chem. 29: 520-529.

Furnas, C. C. F., and F. B. Bellinger (1938). Operating characteristics of packed columns. I. A new method of correlating gas absorption data. Am. Instit. Chem. Engr. Trans. 34: 251-286.

Kedenberg, Frank Jr. (1953). This improved CO_2 control cuts apple storage costs. Food Engineering 25 (3): 126-127.

Leva, Max (1953). Tower packings and packed tower design. U. S. Stoneware Company, Akron, Ohio. 214 pp.

Perry, J. H. (1950). *Chemical Engineers' Handbook.* 3rd ed. McGraw-Hill Co., N.Y. 1942 pp.

Pflug, I. J.; D. H. Dewey and M. W. Brandt (1957). An absorber for the removal of carbon dioxide from CA-storages. Mich. Agr. Expt. Sta. Quart. Bul. 40: 139-146.

Smock, R. M., and A. VanDoren (1941). Controlled-atmosphere storage of apples. Cornell Univ. Agr. Expt. Sta. Bul. 762. 45 pp.

Solvay Technical and Engineering Service (1956). Caustic soda. Solvay Process Div., Allied Chemical and Dye Corp. Bul. No. 6. 84 pp.

Spector, N. A., and B. F. Dodge (1946). Removal of carbon dioxide from atmospheric air. Am. Inst. Chem. Engr. Trans. 42: 827-848.

Tepe, J. B., and B. F. Dodge (1943). Absorption of carbon dioxide by sodium hydroxide solutions in a packed column. Am. Inst. Chem. Engr. Trans. 39: 255-276.