Liquid Caustic Soda

A Discussion of Advantages of Handling This Essential Chemical in Liquid Form

By ROBERT J. QUINN

DURING the past half-dozen years a change of economic importance has been taking place in the method of distributing caustic soda to large industrial consumers. Many thousands of tons formerly shipped in solid form in drums are now being delivered to the users in tank cars in the form of a solution containing about equal parts of water and caustic soda. Although the tonnage shipped in this liquid form is increasing rapidly every year, it still represents only a part of the total consumption of those users of caustic soda who can be served economically in this manner.

The purpose of this article is two-fold:—first, to present to those interested in a possible change from solid to liquid caustic, facts which will enable them to judge the benefits of such a change in their own plants; and second, to place in the hands of those now using liquid caustic, some useful data on approved methods for its transfer, handling and storage, together with some notes on the dilution, testing and properties of caustic liquors. This material has been selected for its practical value to the plant executive and operating staff and is based upon the wide experience of chemists and engineers and upon information from authoritative reference sources.

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Why Liquid Caustic Soda?

A brief review of the operations in the manufacture and handling of caustic soda, both in solid and in liquid form, will make it clear that the increasing use of liquid caustic is a sound economic development. In the manufacturing process caustic soda is first obtained in the form of a water solution containing from 10% to 25% of sodium hydroxide. To produce solid caustic, it is necessary to drive off *all* the water in this solution by evaporation processes which consume a large amount of fuel. Drums must then be provided for the fused caustic and labor expended in filling, handling and loading these containers for shipment. At the consumer's plant these operations are reversed, the solid caustic being made once more into a water solution with the attendant cost of unloading, handling and cutting open many drums, dissolving the caustic and disposing of the worthless empty drums.

In the case of liquid caustic soda the evaporation process is carried only to the point where the original dilute solution has been "boiled down" to a concentration of approximately 50% by weight of caustic soda. In this form it is shipped to the consumer in tank cars and handled mechanically by means of suitable piping connected to the car. In the consumer's plant the 50% caustic liquor is readily diluted to the desired concentration.

In furnishing liquid caustic the manufacturer's processing and handling costs are reduced to a minimum, permitting him to offer caustic in this form at a lower price. The user thus has the advantage of a substantial reduction in price over caustic soda in solid form, as well as the economy and convenience of handling his caustic entirely by mechanical means.

Who Can Use Liquid Caustic?

Whether or not a plant may profitably use liquid caustic soda is determined by the following factors:—(1) delivered cost on solid and on liquid, (2) yearly consumption, and (3) cost of handling solid caustic.

In discussing delivered costs, there are several facts to be kept in mind regarding solid and liquid caustic soda. First, as to works prices, there is usually a price differential of 35 cents per 100 pounds in favor of caustic soda in liquid form. Second, the freight rate between two given points on solid caustic does not always apply on liquid caustic as well; in some territories both rates are the same and in others a lower rate applies on liquid caustic, with a varying differential between the two rates at different points. Third, in transporting every 100 pounds of caustic soda in the form of 50% liquor, 100 pounds of water are also carried. In other words, for every 100 pounds of caustic soda received in the form of 50% solution, the consumer pays freight charges on 200 pounds of material.

Some examples of delivered costs, will serve to make this clear:

CASE A—Rate on solid caustic 19c; on *liquid* 19c

	Solid	Liquid
Price per 100 lbs. f.o.b. works	$3.00	$2.65
Freight per 100 lbs. caustic soda	.19	.19
Freight per 100 lbs. water	.00	.19
Delivered cost per 100 lbs.	$3.19	$3.03

Differential in favor of liquid caustic—16c per 100 lbs.

CASE B—Rate on solid caustic 38½c; on liquid 25c

	Solid	Liquid
Price per 100 lbs. f.o.b. works	$3.00	$2.65
Freight per 100 lbs. caustic soda	.385	.25
Freight per 100 lbs. water	.00	.25
Delivered cost per 100 lbs	$3.385	$3.15

Differential in favor of liquid caustic—23½c per 100 lbs.

CASE C—Rate on solid caustic 45½c; on liquid 45½c

	Solid	Liquid
Price per 100 lbs. f.o.b. works	$3.00	$2.65
Freight per 100 lbs. caustic soda	.455	.455
Freight per 100 lbs. water	.00	.455
Delivered cost per 100 lbs.	$3.455	$3.560

Differential *against* liquid caustic—10½c per 100 lbs.

It will be noted from these examples that the freight rates on both solid and liquid caustic must be known in order to work out a comparison of the delivered costs in these two forms.

An item in the delivered cost of the solid material, not included in the preceding examples, is that of freight on the tare weight of solid caustic drums. This amount is small, but should not be overlooked. It will vary according to the solid freight rate from a little more than half a cent per 100 pounds in Case A to one and one-third cents per 100 pounds in Case C.

In general, provided the delivered cost is favorable, a consumer purchasing solid caustic, in carload lots, may profitably take deliveries of 50% caustic liquor, in tank cars. An 8,000-gallon tank car of 50% caustic liquor contains approximately 25 tons of caustic soda in solution, or the equivalent of a minimum carload of solid caustic in standard 700-lb. drums. On this basis a buyer of several carloads of solid caustic per year may be considered a potential user of 50% liquid caustic.

It will be obvious that the consumer of liquid caustic soda must have access to railroad siding facilities for the unloading of tank cars. A siding at some distance from the plant may be conveniently used, however, since the liquor is transferred from the car into storage by means of piping. The cost of installing transfer equipment may be offset in a short time by the economy of mechanical handling in place of trucking and manual handling of solid caustic.

Handling solid caustic soda, including unloading and breaking open the containers, dissolving the caustic and disposing of the worthless empty drums, costs approximately 12 cents per 100 pounds in the average plant. This figure is based on conservative estimates and will vary only in accordance with handling methods and local wage-scales on labor. Handling is a very small item with caustic liquor; the change from solid caustic will therefore effect a saving in handling cost of around 10 cents per 100 pounds. This is in addition to any saving that may be obtained in delivered cost.

Even where no money saving can be shown for liquid caustic through a consideration of delivered costs and handling costs, the greater convenience of using caustic soda in liquid form makes it attractive to large consumers. The great increase in shipments of liquid caustic soda within the past few years indicates that growing numbers of progressive consumers are recognizing the economy and convenience of this commodity. Consumers served in this manner represent all the principal industries using caustic soda—soap makers, petroleum and vegetable oil refiners, paper mills, manufactures of chemicals, rayon and liquid bleach, textile bleachers and mercerizers.

Purity of Liquid Caustic

In addition to the advantages it frequently offers from a cost standpoint, caustic soda in liquid form is ordinarily a purer product than the solid material in drums.

At Niagara Falls one large electrolytic plant produces an extremely pure liquid caustic which is known as "cell liquor" because obtained directly from the electrolytic cells without evaporation or processing of any kind. This so-called cell liquor is discharged from the cells at a concentration of from 25% to 30% by weight of caustic soda. Although this solution has a limited radius of distribution due to the greater amount of water that must be transported, it offers a highly desirable form in which to handle the commodity on account of the very high purity of the caustic it contains and because of the low freezing-point of the liquor. It is an interesting fact also that this product is the only caustic liquor that can be shipped as originally produced without subsequent processing. Liquors from some types of electrolytic cells are so low in concentration of caustic and usually contain such large amounts of salt in solution that they cannot be shipped as originally produced. The original liquor obtained from the ammonia-soda process is also too low in concentration of caustic to permit its economical distribution.

The following are typical analyses of the several concentrations of liquid caustic soda as shipped from the two different plants of one producing company, one of the country's largest shippers of caustic.

Percentage Content of:	Electrolytic Cell Liquor	Caustic Liquor Concentrated	Soda Process Caustic Liquor
Sodium Hydroxide	27.5	49.8	50.07
Sodium Carbonate	0.10	0.25	0.35
Sodium Chloride	0.05	0.10	0.29
Sodium Sulphate	0.008	0.016	0.21
Sodium Sulphide	(None)	(None)	(None)
Silica	0.005	0.007	0.14
Iron Oxide & Alumina	0.002	0.008	0.034
Calcium Oxide	0.003	0.005	0.005
Magnesium Oxide	0.001	0.002	0.007

The figures in the first column represent an average analysis of cell liquor. In the second column is shown an analysis of the 50% caustic solution obtained through partial evaporation of this cell liquor. It is of interest to note the low salt content of these liquors. In both the cell liquor and the concentrated solution, the sodium hydroxide content of the caustic soda is in excess of 99%. The figures in the third column represent an average analysis of the liquid caustic produced by the ammonia-soda process.

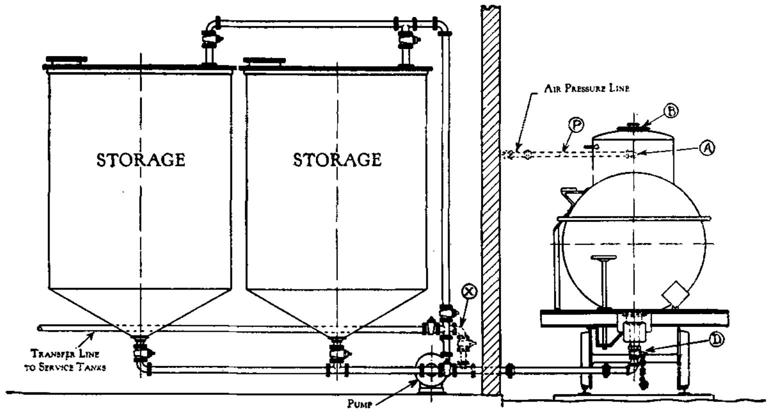
Tank Car Equipment

Liquid Caustic Soda is shipped in tank cars of 8,000 gallons capacity (equivalent to approximately 100,000 pounds of 50% caustic liquor). This equipment is of the latest type, conforming to A.R.A. Specifications for Class III Tank Car and to I.C.C. Specification No. 103.

All tank cars for caustic liquor should be equipped with steam heating coils, for use during the winter months, and with an auxiliary bottom outlet valve. Steam heating coils should be of 2-in. extra-heavy steel pipe, with 2-in. connections, and all joints welded throughout to prevent leakage sometimes experienced with threaded joints.

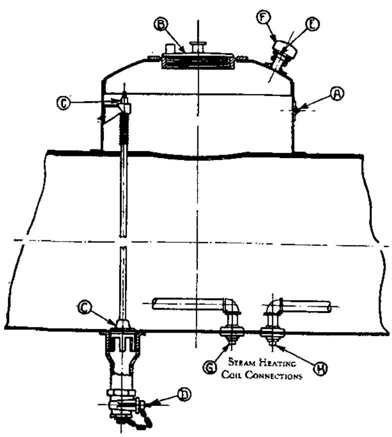
The auxiliary bottom outlet valve mentioned above was adopted several years ago by a large shipper as a protective measure for users of caustic liquor. It had been found next to impossible to maintain the regulation Tank Car Bottom Outlet Valves tight against leakage be-

Approved Methods for Unloading Liquid Caustic Soda



Typical Layout for Unloading Liquid Caustic by Pump and by Air Pressure

NOTE Additional Equipment for Unloading by Air Pressure Indicated by Dotted Lines, Marked "P" and "X"



Longitudinal Section Through Dome and Bottom of Car

Instructions for Unloading

By Pump.

1–Attach two-inch pipe at valve (D) by means of flanged connections.
2–Remove plug (A) for release of internal pressure.
3–Remove dome cover (B).
4–Open valve (C) (Inside dome).
5–Open valve (D) and start transfer pump.

By Compressed Air.

1–Attach two-inch pipe at valve (D) by means of flanged connections.
2–Remove plug (A) and connect compressed air line (P) at this point.
3–Remove dome cover (B).
4–Open valve (C) (Inside dome).
5–Replace dome cover (B) (Tight gasket).
6–Apply air pressure (not to exceed 30 lbs. per sq. inch).
NOTE: Lead disc (E) in vent (F) ruptures at 30 lbs. per sq. inch air pressure. This is sufficient to lift 50% caustic liquor 35 ft. above R.R. track level.
7–Open valve (D) and other valves in line to storage.
NOTE: When unloading by means of compressed air, by-pass connection (X) with valve must be provided.

cause of their location and the requirements imposed by I.C.C. specifications. Such leakage resulted in the discharge nipple becoming filled with caustic liquor, which very often spilled over the workmen when the cap was removed. To prevent this, a change in the I.C.C. specifications was obtained permitting the installation of the auxiliary bottom discharge valves on tank cars for caustic liquor service. All caustic liquor cars are inspected on the completion of each trip, washed out, tested, and the valves ground when necessary. During the cooler months the steam heating coils are tested on the return from each trip.

This careful maintenance of tank

car equipment insures the customer against transportation delays and against contamination or loss of material.

Transfer Equipment

Liquid caustic is transferred to storage tanks by means of a pipe line connected to the car at a point on the consumer's railroad siding. The two approved methods for unloading into storage are by means of pump and compressed air. These methods are shown in connection with the sectional drawings on the previous page. In rare cases where storage tanks are located below the siding track level, caustic liquor may be transferred by gravity, with the same procedure as for unloading by pump. It is also possible to unload by suction, through the manhole opening, but this practice is not recommended.

Lubricated plug cocks or valves, transfer pumps and pipe lines should be of all-iron construction.

Storage Equipment Specifications

CAPACITY:
To conform with consumer's requirements; minimum capacity approximately 16,000 gallons.

PLATES:
Of flange steel having ultimate strength of 55,000 lbs. per sq. in.

RIVETS:
Of boiler rivet steel driven hot.

JOINTS:
To be double riveted and calked inside and outside.

Winter Handling and Storage

Concentrated solutions of caustic soda (25% to 50% NaOH content) will deposit crystals of the solid hydrates of sodium hydroxide under normal winter weather conditions. At abnormally low temperatures, around 0° F., and depending upon the concentration of the solutions, complete solidification may take place.

This consideration necessitates the use of steam coils in tank cars and in storage tanks exposed to winter weather. Outside pumps, transfer lines, etc., must be effectively protected from the cold.

During the winter months the physical condition of liquid caustic should be noted before transfer from car or storage is attempted. An examination can readily be made by probing the liquid with an iron rod for indications of solid hydrates or to determine the extent to which solidification has progressed. If a top crust has formed, it must be broken before steam is applied in the heating coils in order to provide for expansion of the heated liquid. The steam pressure applied should not exceed 10 lbs.

Where storage is provided within heated buildings steam coils inside the tanks are not required. Caustic liquor of 50% concentration is more conveniently handled in this type of storage. When 50% liquor is stored in outside tanks, it is necessary to maintain heat in the coils almost continuously during the winter months. Less difficulty is experienced with outside storage in the case of more dilute solutions of 25% concentration or less. Shipments usually consist of 50% liquor which requires a dilution with 1.4 volumes of water to reduce the concentration to 25% sodium hydroxide. A tank of 20,000 gallons capacity would be required for storing the contents of one tank car (8,000 gallons) of 50% liquor after such a dilution.

Heat of Dilution

When water is added to liquid caustic soda, heat is evolved and a rise in the temperature of the solution takes place. This is due to the heat of reaction in the formation of the various hydrates of sodium hydroxide, and is generally termed heat of dilution. This heat effect is considerable and allowance should be made for it in diluting caustic liquor, particularly if the diluted solution is to be used in the preparation of bleach liquor.

In general, a sharp rise of temperature will be noted until a volume of water has been added about equal to the original volume of the liquor. From this point on, further dilution results only in a decrease in temperature. The extent of these temperature changes is indicated by the results of the following dilutions in a Dewar flask.

One volume of a solution containing 50% NaOH by weight was diluted with successive portions of distilled water each equal to one-half the original volume of 50% solution. The initial temperature of both solution and water was 14.5°C. (58.1°F.), and the temperature of the solution was observed following each dilution. After dilution (1) the temperature was 38.5°C. (101.3°F); (2) 45.5°C. (113.9°F.); (3) 46.5°C. (115.7°F.); (4) 44.8°C. (112.6°F.); (5) 42.5°C. (108.5°F.); (6) 40.0°C. (104.0°F.).

Data based upon laboratory experiments is only of value, however, in estimating the temperature increase that may be expected upon diluting caustic liquor in the plant. The size and shape of dilution tanks, their heat capacities and their heat radiations, all exert such an important influence that theoretical figures cannot be applied in actual practice. It is advisable for the operating man to determine this factor by observation under plant conditions.

Sampling of Caustic Liquor

Careful sampling is absolutely essential to the accurate analysis of tank car shipments of liquid caustic. Particularly in cold weather, it is important that heating be continued until all crystals have gone into solution and the entire contents of the car has been converted into a liquid condition. Samples containing crystals of hydrates of sodium hydroxide will obviously not be representative of the liquor in the tank car. Since some of these hydrates may form in concentrated liquors even under mild weather conditions, it is desirable that 50% liquid caustic be warmed until a surface temperature of approximately 75° F. has been reached.

Samples should be taken at three different depths in cars of cell liquor (27.5% caustic soda) and at five different depths in more concentrated liquors. The best method of sampling is by means of an iron or wooden rod, fitted at one end with a basket in which is fastened a small-necked 16 oz. bottle. This is provided with a cork attached to a wire, so that it can be removed when the bottle has been submerged to the proper level. Separate samples are thus taken at various depths in the car.

Analysis of Caustic Liquor

TOTAL ALKALI:

If no determination for carbonate is to be made, weigh out directly in a closed weighing bottle about 1.5 grams from the sample of 50% liquor, or a correspondingly larger amount for liquors of less concentration.

The weighed sample is transferred to a beaker and titrated with N/2HCl in the presence of methyl orange. This titration (A) is a measure of the total alkali present and may be expressed in terms of Na_2O and NaOH.

$$\frac{A \times 3.1}{\text{Wt. of sample} \times 2} = \text{\% Total Alkali as } Na_2O$$

$$\frac{A \times 4.0}{\text{Wt. of sample} \times 2} = \text{\% Total Alkali as NaOH}$$

SODIUM HYDROXIDE AND SODIUM CARBONATE:

When a determination for carbonate is to be made, a larger sample of from 14 to 16 grams of the 50% liquor is used. The weighed sample for analysis is diluted to the mark in a 500 cc. volumetric flask with water free from CO_2. Air should be excluded as much as possible during this operation.

Transfer a 50 cc. aliquot of the sample and add 10 cc. of a 10% solution of $BaCl_2$. Using one drop of phenolphthalein for an indicator, titrate with N/2HCl to almost an end point. After washing down flask with distilled water (free of CO_2), an additional drop of the indicator solution is added and the titration then continued to the end point. For extreme accuracy, air free of CO_2 should be introduced into the flask during titration. This titration (B) is a measure of the alkalinity due to sodium hydroxide.

$$\frac{B \times 4.0}{\text{Wt. of sample in aliquot} \times 2} = \text{\% Actual NaOH}$$

The difference between the two titrations (A) and (B) is a measure of the Na_2CO_3 present.

$$\frac{(A - B) \times 4.3}{\text{Wt. of sample in aliquot} \times 2} = \text{\% } Na_2CO_3$$

The figure for total alkali as Na_2O, calculated from the preceding method of analysis is the true or actual sodium oxide (Na_2O) content. To obtain the percentage of total alkali as Na_2O according to the New York and Liverpool test, multiply the figure for total alkali as Na_2O, as determined from analysis, by the factor 1.0323.

Selling Basis on Liquid Caustic

During the first few years after caustic soda in liquid form was placed on the market, there were many different practices in use as regards specifications and prices. Much confusion existed in the minds of consumers, who found it difficult to compare the product and price offered by one producer with that offered by another. The situation was further complicated by the fact that liquid caustic was demanded by consumers in a variety of concentrations ranging from 25% to 50%, none of which was a standard article of commerce.

Through the co-operation of progressive manufacturers and consumers, liquor of 50% concentration has now been established as the standard for the commodity liquid caustic soda.

It was also desirable that some standard practice be adopted in marketing and invoicing liquid caustic, and that this practice be based as far as possible on terms familiar to the buyer. Most caustic liquor is now sold on the basis of its caustic soda content expressed in terms of solid caustic soda of standard test, that is, 76% actual Na_2O. Contracts usually specify a given tonnage of "solid caustic soda (76% actual Na_2O) to be shipped in the form of 50% solution." Buyers can now compare on a common basis their quotations from various producers, or check their price on caustic in liquid form against past market levels on solid caustic.

The following rule may be used for computing the value of a car of liquid caustic:

$$\text{Wt. of liquor} \times \frac{\%\ \text{Total Alkali as NaOH}}{\%\ \text{Purity of Caustic}} \times \text{Price} = \text{Value of Car}$$

For example: A shipment consisting of 100,000 lbs. of liquor is found by analysis to contain 49.00% NaOH. The market price on solid caustic (76% actual Na_2O) is $3.00 per 100 lbs.; liquid caustic is 35 cents lower in price, or $2.65 per 100 lbs.

$$100{,}000 \times \frac{49.00}{98.00} \times \$0.0265 = \$1{,}325.00$$

The average 76% solid caustic soda contains approximately 98% NaOH and 2% of solids other than NaOH. In the above rule, the term "% Purity of Caustic" refers to this average figure 98%. In special cases where the purity of the caustic furnished averages above or below this figure, the actual percentage purity of such caustic should be inserted.

President Trevithick Names Additional Committees

Neutral Oil and Detergent Bodies to be Headed by McLean and Howells Respectively

PRESIDENT TREVITHICK of the American Oil Chemists' Society, in a communication to the Editor of OIL & FAT INDUSTRIES, announces the personnel of the following committees of the Society for the year 1927-1928:

Refining Sub-committee A
(Neutral Oil Committee)
Claude E. McLean, Chairman,
c/o Choctaw Cotton Oil Co.
Ada, Oklahoma.
George S. Jamieson
M. G. Boulware
E. C. Ainslie
A. S. Richardson
F. R. Robertson

Detergents Committee
F. H. Guernsey, Chairman,
c/o Cowles Detergent Co.
Lockport, N. Y.
L. T. Howells, Vice-chairman
H. C. Bennett
C. P. Long
W. T. Reese
J. S. Boulden
E. T. Marceau
A. S. Richardson
V. K. Cassady
E. R. Millard
F. H. Rhodes
A. K. Church
H. S. Mitchell
F. W. Smither
T. G. Vail
L. F. Hoyt
W. C. Preston

Due to the fact that Mr. Hoyt will be exceptionally busy this year, he found it necessary to decline re-appointment as chairman of the Detergents Committee.