OxyChem®

OXYCHEM

Caustic Soda Handbook

NaOH

Occidental Chemical Corporation (OxyChem) is a leading North American manufacturer of polyvinyl chloride (PVC) resins, chlorine and caustic soda — key building blocks for a variety of indispensable products such as plastics, pharmaceuticals and water treatment chemicals. Other OxyChem products include caustic potash, chlorinated organics, sodium silicates, chlorinated isocyanurates and calcium chloride. OxyChem's market position is among the top three producers in the United States for the principal products it manufactures and markets. Based in Dallas, Texas, the company has manufacturing facilities in the U.S., Canada and Latin America.

OxyChem has been an active participant in the American Chemistry Council's Responsible Care® initiative since its inception in 1988. Demonstrating their commitment to attaining the highest levels of safety and environmental achievement, Responsible Care companies implement world-class management systems, measure performance based on industry-wide metrics, and are subject to review by independent auditors.

Foreword

This handbook outlines recommended methods for handling, storing, preparing and using caustic soda. It also includes information on the manufacture, physical properties, safety considerations and analytical methods for testing caustic soda. Additional information and contacts can be found on the internet at www.oxy.com/operations/essentials-chemistry/

TABLE OF CONTENTS

INTRODUCTION

Caustic soda (sodium hydroxide or NaOH) is most commonly manufactured by the electrolysis of a sodium chloride (NaCl) solution. OxyChem manufactures caustic soda using either membrane or diaphragm electrolytic cells. OxyChem does not use mercury based electrolytic cells to produce caustic soda. The co-products formed from the electrolytic production of caustic soda are chlorine and hydrogen.

Liquid caustic soda is available as a 50% solution in two main grades. The names of these main grades correspond to the electrolytic cells used to produce the caustic soda; membrane grade and diaphragm grade. OxyChem can also provide dilutions of various concentrations.

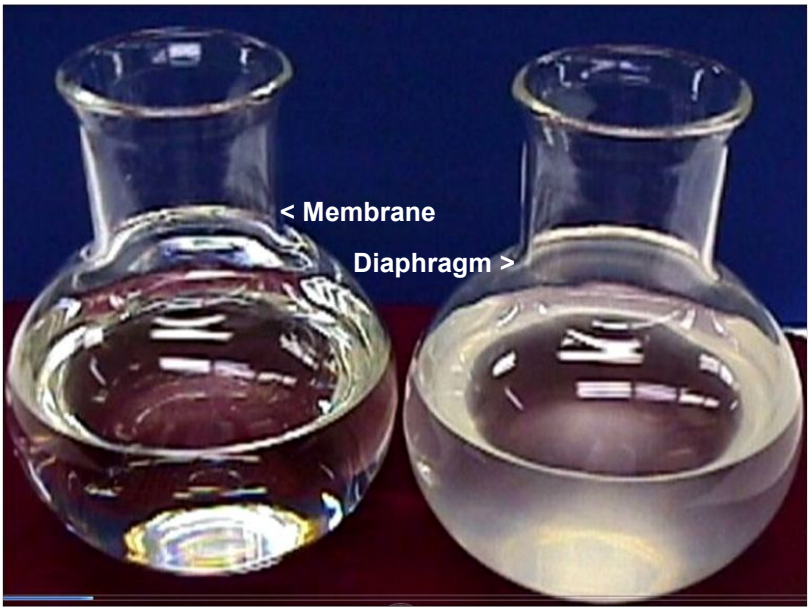
The major difference in the two main grades is the amount of starting material (sodium chloride) remaining in the final product. Membrane grade caustic soda will have less than 100 ppm of the sodium chloride remaining in the product. Diaphragm grade material will have less than 1.1% sodium chloride. Several other differences can be seen in the products when the specification sheets are compared. Specification sheets for each grade can be found on our website at www.oxy.com/operations/essential-chemistry/.

All OxyChem's caustic soda meets the test requirements specified in the Food Chemicals Codex (FCC). Not all OxyChem's caustic soda is produced following all cGMP (current Good Manufacturing Practices) requirements as defined by the FDA (Food and Drug Administration). OxyChem does produce a food grade caustic soda, which is produced following cGMP requirements as defined by the FDA. OxyChem does not represent or warrant general compliance of this product for food use. Each prospective use of a product in a food or food related application must be carefully assessed against appropriate regulations by the user and it cannot be assumed that products meeting FCC test requirements are satisfactory for all uses without such assessment.

OxyChem has played a leading role in providing caustic soda to meet the increasing demands of industry. OxyChem plants are strategically located to conveniently and economically serve industry.

Caustic soda is shipped via pipelines, tank trucks, railcars, barges and ships. Terminals are used to maintain stocks of our caustic soda in many principal cities. Distributor stocks are also available in these and many other cities and form a network of supply for the end user's convenience.

The largest users of caustic soda are the pulp and paper, detergent and chemical industries. Caustic soda is also used in the alumina, oil and gas and textile industries, mostly for its alkalinity value.



PRINCIPAL USES AND CONSUMPTION OF CAUSTIC SODA

Caustic soda is one of the very few chemicals utilized in a very broad range of applications. Some principal products or processes in which caustic soda is used are:

- Acid Neutralization
- Agricultural Chemicals
- Aluminum
- Battery Recycling
- Bleach
- Boiler Compounds
- Cellulose Film
- Detergents
- Drain Cleaners
- Drilling Muds
- Dyestuffs
- Food Processing
- Fruit & Vegetable Peeling
- Glass-Batch Wetting
- Ion-Exchange Resin Regeneration
- Ore Floatation and Processing
- Paint Removers
- Petroleum Refining
- pH Adjustment
- Pharmaceuticals
- Pigments
- Pulp & Paper
- Rayon
- Soap
- Surfactants
- Textile Bleaching
- Vegetable Oil Processing
- Water Treatment

Chemical Manufacture of:

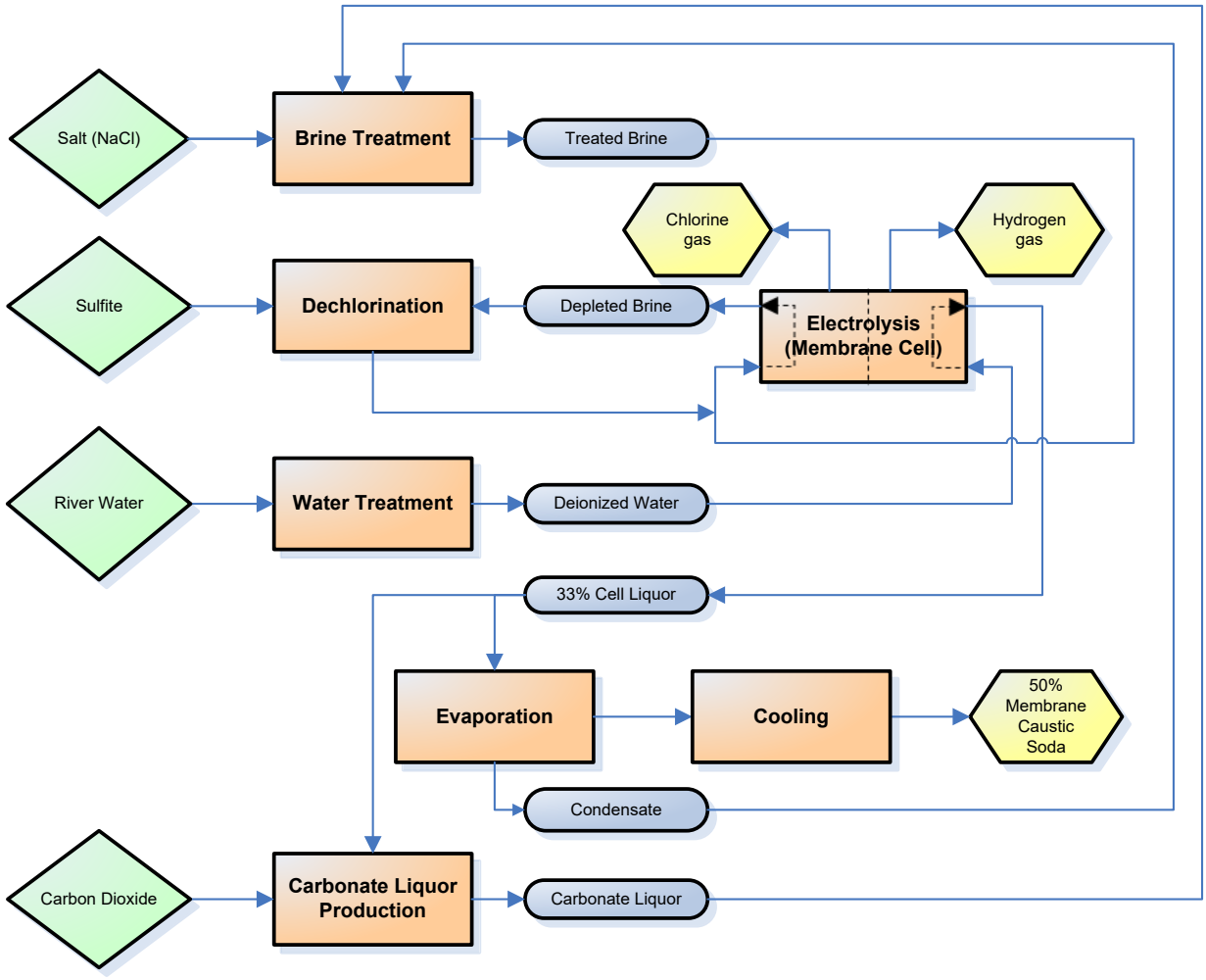
- Ammonia
- Amyl Amines
- Cresol
- Ethylene Amines
- Formic Acid
- Glycerine
- Maleic Anhydride
- Pentaerythritol
- Phenol
- Propylene Oxide
- Polycarbonates
- Salicylic Acid
- Sodium Aluminate
- Sodium Hydrosulfide
- Sodium Hypochlorite
- Sodium Phosphates
- Styrene
- Vinyl Chloride Monomer

MANUFACTURING PROCESS

Caustic soda is produced by OxyChem by an electrolytic process as shown in the following diagrams. Brine, prepared from sodium chloride (NaCl), is electrolyzed in either a membrane cell or a diaphragm cell. The production of caustic soda (NaOH) also results in the co-products of chlorine and hydrogen.

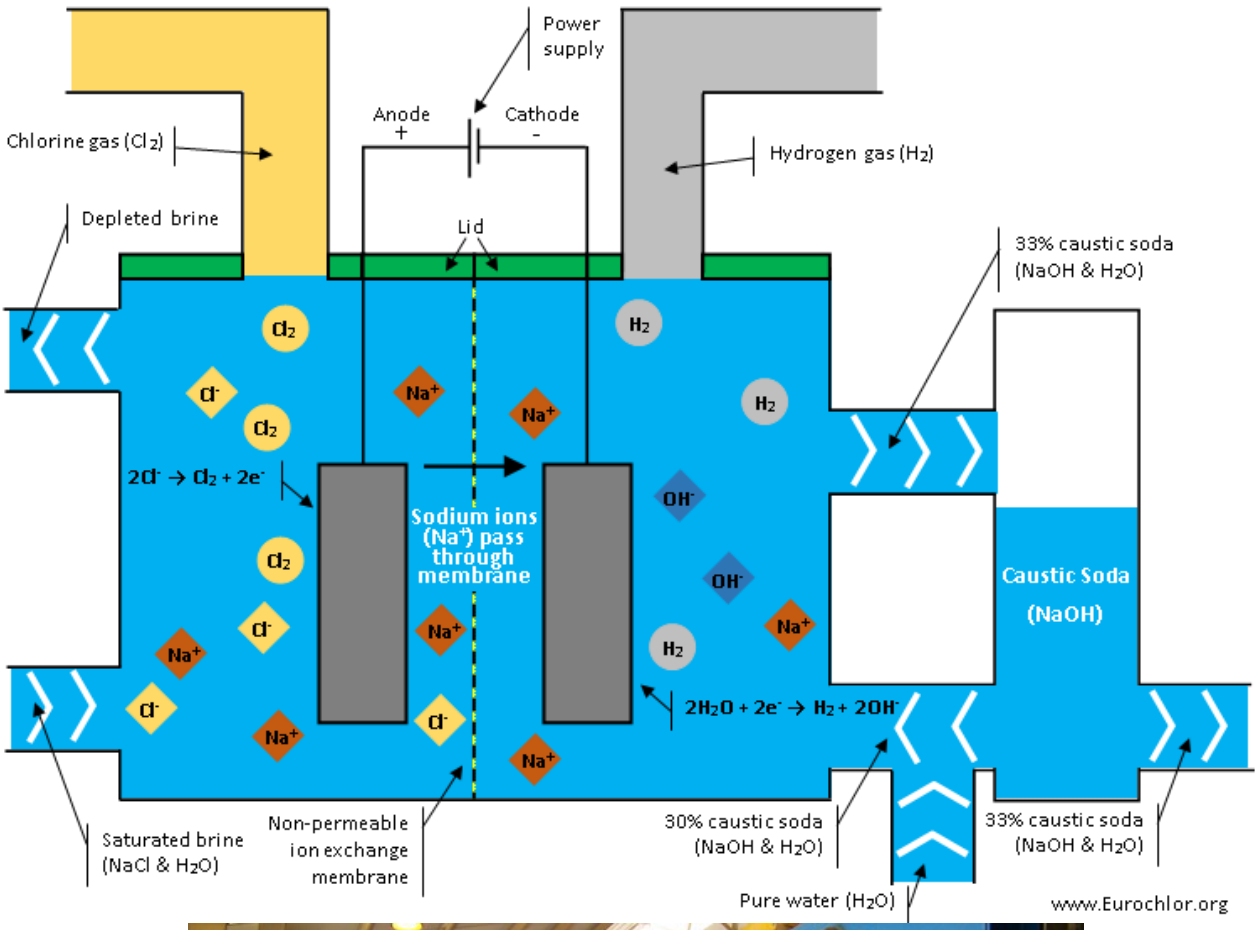
In the membrane process, a solution of approximately 33% in strength is formed. The solution is then sent to evaporators, which concentrate it to a strength of 50% by removing the appropriate amount of water.

MEMBRANE CELL FLOW DIAGRAM



MANUFACTURING PROCESS

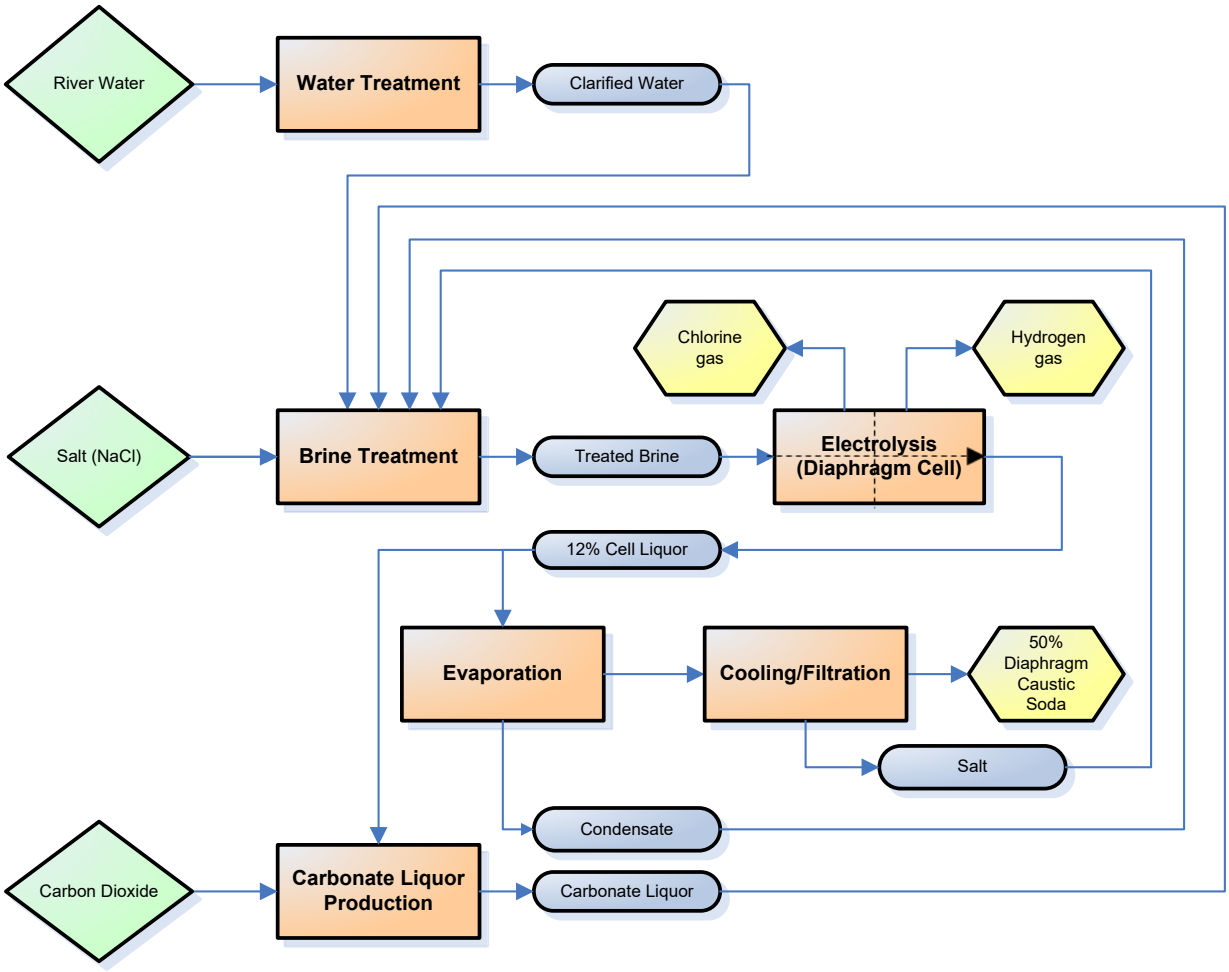
MEMBRANE CELL



MANUFACTURING PROCESS

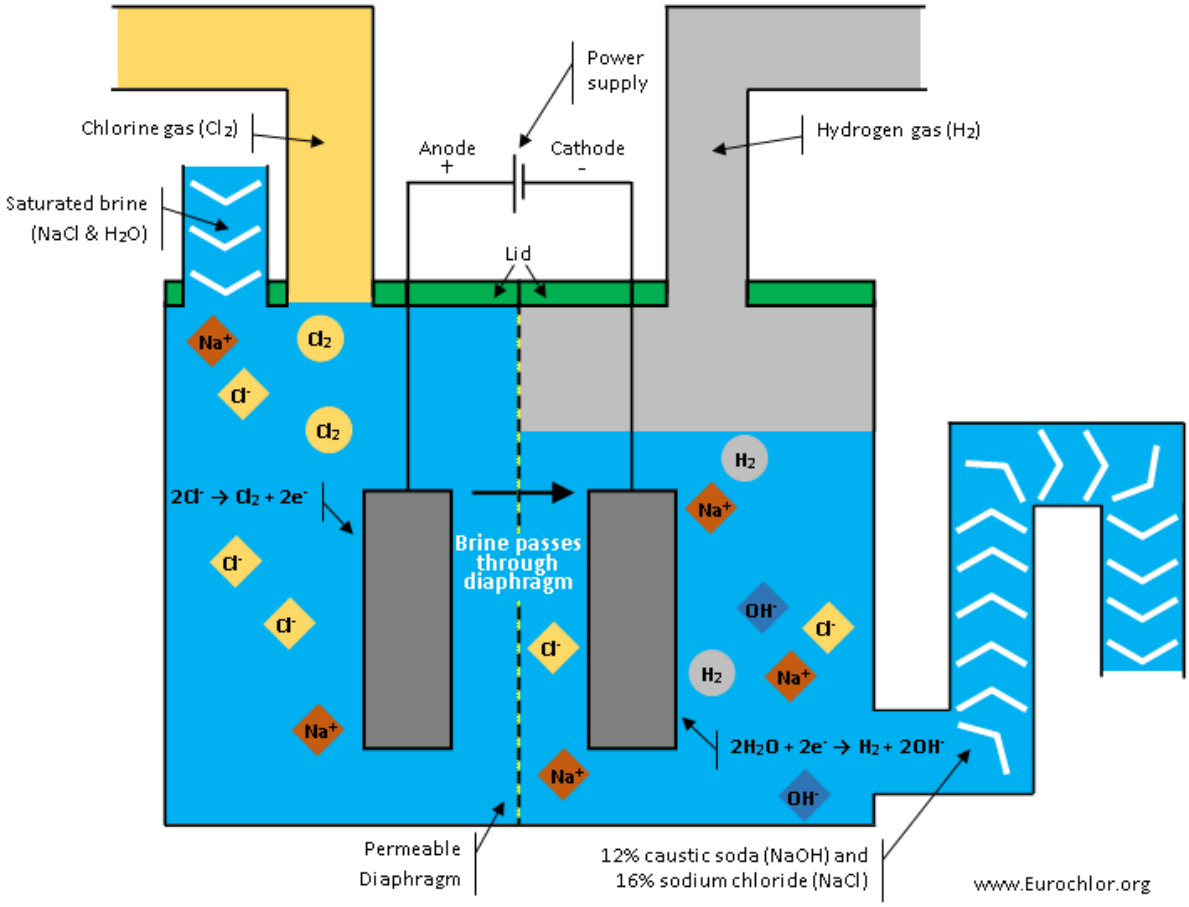
The diaphragm process is similar to the membrane process except that a solution of only 12% is formed in the cell. Again, additional evaporation is required to reach the saleable concentration of 50%.

DIAPHRAGM CELL FLOW DIAGRAM



MANUFACTURING PROCESS

DIAPHRAGM CELL



SHIPPING METHODS

Liquid caustic soda is available from OxyChem's many plants and terminals in tank truck, rail tank car, barge and ship quantities. Each form of transportation has its own advantages. The type of service selected will depend upon such factors as size and location of storage, rate of consumption, plant location, freight rates, etc.

Liquid caustic soda is regulated by the U.S. Department of Transportation (DOT) and is classified as a corrosive material. The DOT identification number is UN I824 for liquid caustic soda.

SAFE HANDLING CAUSTIC SODA

***Caustic soda* in any concentration must be respected by everyone who handles and uses it. Before starting to work with it, the user should be aware of its properties, know what safety precautions to follow, and know how to react in case of contact. Accidental exposure to caustic soda may occur under several conditions. Potentially hazardous situations include handling and packaging operations, equipment cleaning and repair, decontamination following spills and equipment failures. Employees who may be subject to such exposure must be provided with proper personal protective equipment and trained in its use. Some general guidelines follow:**

1. Read and understand the latest Safety Data Sheet.
2. Provide eyewash fountains and safety showers in all areas where caustic soda is used or handled. Any caustic soda burn may be serious. DO NOT use any kind of neutralizing solution, particularly in the eyes, without direction by a physician.
3. Move the patient to a hospital emergency room immediately after first aid measures are applied.

FIRST AID MEASURES

INHALATION: If inhalation of mists, vapors, or spray occurs and adverse effects result, remove to uncontaminated area. Evaluate ABC's (is Airway constricted, is Breathing occurring, and is blood Circulating) and treat symptomatically. GET MEDICAL ATTENTION IMMEDIATELY.

SKIN CONTACT: Immediately flush contaminated areas with water. Remove contaminated clothing, jewelry and shoes. Wash contaminated areas with large amounts of water. GET MEDICAL ATTENTION IMMEDIATELY. Thoroughly clean and dry contaminated clothing before reuse. Discard contaminated leather goods.

EYE CONTACT: Immediately flush contaminated eyes with a directed stream of water for as long as possible. Remove contact lenses, if present, then continue rinsing. GET MEDICAL ATTENTION IMMEDIATELY.

INGESTION: If swallowed, do not induce vomiting. For definite or probable ingestion, do not administer oral fluids. If vomiting occurs spontaneously, keep airway clear. Monitor airway. Volume resuscitation (IV fluids) and circulatory support (CPR) may be required. Never give anything by mouth to an unconscious or convulsive person. GET MEDICAL ATTENTION IMMEDIATELY.

PROTECTIVE EQUIPMENT

OSHA requires employers to supply suitable protective equipment for employees. When handling caustic soda, the following protective equipment is recommended:

Wear suitable chemical splash goggles for eye protection during the handling of caustic soda in any concentration. The goggles should be close fitting and provide adequate ventilation to prevent fogging, without allowing entry of liquids. The use of a face shield may be appropriate when splashing can occur, including loading and unloading operations.

Wear rubber gloves or gloves coated with rubber, synthetic elastomers, PVC, or other plastics to protect the hands while handling caustic soda. Gloves should be long enough to come well above the wrist. Sleeves should be positioned over the glove.

Caustic soda causes leather to disintegrate quite rapidly. For this reason, wear rubber boots. Wear the bottoms of trouser legs outside the boots. DO NOT tuck trouser legs into boots.

Wear chemical resistant clothing for protection of the body. Impregnated vinyl or rubber suits are recommended.

Wear hard hats for some protection of the head, face and neck.

If exposures are expected to exceed accepted regulatory limits or if respiratory discomfort is experienced use a NIOSH approved air purifying respirator with high efficiency dust and mist filters.

PROTECTIVE PRACTICES

Keep equipment clean by immediately washing off any spill or accumulation of caustic soda.

Weld pipelines where practical. Use flanged joints with gaskets made of caustic soda resistant material such as rubber, PTFE, or EPDM rubber. If a screwed fitting is used, apply Teflon® tape to the threads.

When disconnecting equipment for repairs, first verify that there is no internal pressure on the equipment and the equipment has been drained and washed.

Provide storage tanks with suitable overflow pipes. Overflow pipes should be directed to a protected overflow area away from operations.

Shield the seal area of pumps to prevent spraying of caustic solutions in the event of a leak.

When releasing air pressure from a pressurized system, take every precaution to avoid spurts or sprays of caustic solution.

In case of a spill or leak, stop the leak as soon as possible. After containment, collect the spilled material and transfer to a chemical waste area. Remove large liquid spills by vacuum truck. Neutralize residue with dilute acid. Flush spill area with water and follow with a liberal covering of sodium bicarbonate or other acceptable drying agent.

SAFE HANDLING CAUSTIC SODA

HANDLING LIQUID CAUSTIC SODA

In handling caustic soda solutions, care must be taken to avoid solidification which will plug pipelines and equipment. Graph 1 on page 31 shows the freezing points for solutions of caustic soda at various concentrations.

Should a caustic soda solution become frozen in process equipment or piping, care must be taken when thawing the material. The use of atmospheric pressure steam is suggested. Accelerated corrosion can occur in areas where equipment is subjected to extremely high temperatures.

UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

GENERAL INFORMATION

Liquid caustic soda has a markedly corrosive action on all body tissue. Even dilute solutions may have a destructive effect on tissue after prolonged contact. Inhalation of mists can cause damage to the upper respiratory tract, while ingestion of liquid caustic soda can cause severe damage to the mucous membranes or other tissues where contact is made.

It is important that those who handle caustic soda are aware of its corrosive properties and know what precautions to take. In case of accidental exposure, immediately flush the exposed area with large amounts of water and seek medical attention. For more specific information refer to the Safe Handling section of this handbook and in the OxyChem SDS for liquid caustic soda.

PLACEMENT OF THE RAILCAR FOR UNLOADING

1. After the car is at the loading spot, DOT regulations require that the hand brake be set and the wheels blocked (chocks).
2. DOT regulations require caution sign(s) be placed on or next to the rail track to warn persons approaching the car from the access track end(s). Caution signs must be left up until the railcar is completely unloaded and disconnected from the customer's connections. Signs must be made of metal or other suitable material, at least 12x15 inches in size, and bear the words, "STOP-TANK CAR CONNECTED", or "STOP-MEN AT WORK."
3. It is recommended that a *locked* switch or derail device be placed at the access track end(s), a minimum of one car length away from the railcar to be unloaded.
4. A railcar of caustic soda should only be unloaded when adequate lighting is available.
5. A suitable ramp should be used to access the railcar top operating or safety platform. The access ramp chosen should accommodate a variety of platform widths because of variations in rail car manufacturers, and railcar heights since the railcar will rise while unloading.

UNLOADING PRECAUTIONS

- Before making any connections, verify the content of the railcar is caustic soda.
- Test the nearest eyewash and safety shower per your facility procedure.
- Only responsible and properly trained personnel should unload liquid caustic soda. Unloading operations must be monitored while the car is connected.

UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

- Since serious burns can result from contact of caustic soda with the eyes and skin, the personal protective equipment (PPE) listed below is recommended when handling equipment for caustic soda. Based on a job task analysis or job hazard assessment more PPE may be appropriate.

  Hard hat
  Mono-goggles
  Face shield
  Rubber, steel-toed boots
  Chemical gloves
  Chemical resistant suit
  Respiratory protection

- Make certain the storage tank is vented and has sufficient room available for the contents of the entire railcar.
- Consider restricting access to the area around the railcar and transfer line to the storage during the actual transfer operation.
- If a railcar needs to be moved when partially unloaded, DOT regulations require that all unloading lines must be disconnected and railcar closures must be replaced.
- A railcar may be sampled either from the top manway, or from the top eductor line using a suitable procedure. Sampling from the bottom unload piping is not recommended. If a railcar has partially frozen and has been thawed, special sampling techniques may be required due to stratified concentrations that may be present.
- A tank truck may be sampled either from the top manway, or from the rear discharge valve. When sampling from the valve, a customer provided sampling device is required to control product flow. Flush the sample device with 1-2 gallons of product prior to taking the sample. Repeat as required. Sampling from the airline purge connection is not recommended.
- OxyChem's liquid caustic soda is shipped in insulated and lined railcars. Typical linings have an upper temperature limit of 225°F. Therefore, recommended 'trapped steam' pressure used in the coils to heat up a rail railcar is limited to 15 psig max. Most customers use atmospheric steam in the coils.
- Unloading lines should insulated and heated when used to transfer liquid caustic soda to storage in cold climates. The preferred method of heating is to provide electric or steam heat tracing around the unloading line, under the insulation. An alternate method is to provide tees in the unloading line so that steam (or hot water) can be run through the unloading line just prior to its use. Use caution using this method so as to NOT put water or steam directly into the railcar of caustic soda. **NOTE: *Running steam through unlined steel piping systems can result in increased corrosion and iron pickup in the product.***
- A properly designed and equipped padding system must be used if the railcar will be pad pressure unloaded. Compressed air is the most common padding gas. Nitrogen can also be used but it is more costly and it has the additional hazard of being an **asphyxiant gas**, thus extra precautions are required. All fittings used for padding a railcar should be inspected for defects before each use.
- The air supply system should be oil free, and have a pressure relief valve set at 25 psig, and a pressure

UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

General purpose caustic railcars are structurally constructed to a 100 psig design and with a burst rating of approximately 500 psig. Per 49 CFR 179.15, caustic railcars can have a pressure relief device installed that is set for 75 to 165 psig. The lower rated relief devices are sometimes hydraulically activated during rough transport handling, and can release some liquid onto the jacket area.

Even though they are designed and equipped as stated, these are NOT pressure railcars and should not be padded above the **OxyChem and the Chlorine Institute recommended range of 20 to 25 psig max.**

At OxyChem after a railcar is loaded with product, it is padded up to approximately 30 psig and leak checked to meet the DOT shipping requirement. That test pad pressure is released prior to shipping.

Because of inherent shaking and jarring experienced by the railcar and contents during the shipping process, gaskets and joints can loosen up and customers should be cautious of that possibility. If pressure unloading, particular areas to watch are the manway gasket, the bottom flange gasket (when bottom unloading), and the top operator stuffing box gland area for the bottom outlet valve (BOV) if so equipped.

Additionally, the top operated bottom outlet valve reach rods can, in rare instances, come detached during transit. There have been reports that these detached rods can be *pushed up* from a railcar if unloading pressures greater than 30 psig are used.

HANDLING IN COLD WEATHER

Since OxyChem tank cars are well insulated and liquid caustic soda is loaded hot (~100F), product usually arrives at its destination in a liquid state. However, since 50% liquid caustic soda begins to crystallize at 54°F, in cases of unusual delays in transit, partial freezing may take place in cold weather.

A temperature measurement of the caustic soda is the best indication if steaming is required. If the railcar product is 65°F or cooler, heating is recommended prior to unloading. Even if all liquid, it may flow poorly due to its higher viscosity.

If a railcar temperature is over 65°F but product will not flow from the BOV (bottom unloading), try applying a steam lance for a few minutes to the BOV and auxiliary valve. This uninsulated piping area is prone to freezing. If freezing has occurred, the following procedure should be used:

1. Vent the railcar – OxyChem recommends opening the railcar manway cover.
2. Connect a steam line to the bottom jacket connection pipe, and/or at the BOV connection. Connect a condensate return line at the steam condensate outlet pipe. If a steam trap is used on the exit of a railcar, OxyChem recommends regulating the steam pressure into the coils to a maximum of 15 psig. This is to protect the lining from excessive spot heating, which will damage the lining. If a condensate return line is not used, the condensate must be disposed of or otherwise utilized in a manner compliant with all environmental regulations.

UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

The amount of material that is frozen in a caustic soda rail car is dependent upon the outside temperature, wind chill, and the time elapsed between when the railcar was loaded and is unloaded. In very cold winter conditions, it is possible for a caustic soda railcar to be totally frozen. For this case, it may be necessary to steam the rail car for as long as three days (72+ hours) to fully liquefy all of the contents.

A temperature measurement is the best indication as to when the contents have liquefied and the caustic soda is ready for unloading. ***The recommended minimum unloading temperature of 50% caustic soda is 70°F. At 70°F through 90°F steaming may be desirable to reduce viscosity.***

If the above measures do not liquefy the contents on the railcar, contact your OxyChem technical representative.

ADDITIONAL NOTES FOR HEATING RAILCARS:

Do not exceed a steam pressure of 15 psig on the jacket. Certain railcar linings can be damaged using steam pressure above15 psig.

Do not keep steam on while emptying the railcar. Exposing the steam coils without fluid present to dissipate the heat can damage the lining due to local heating.

Do not heat the product over 120°F to minimize corrosion of unlined steel piping systems and equipment.

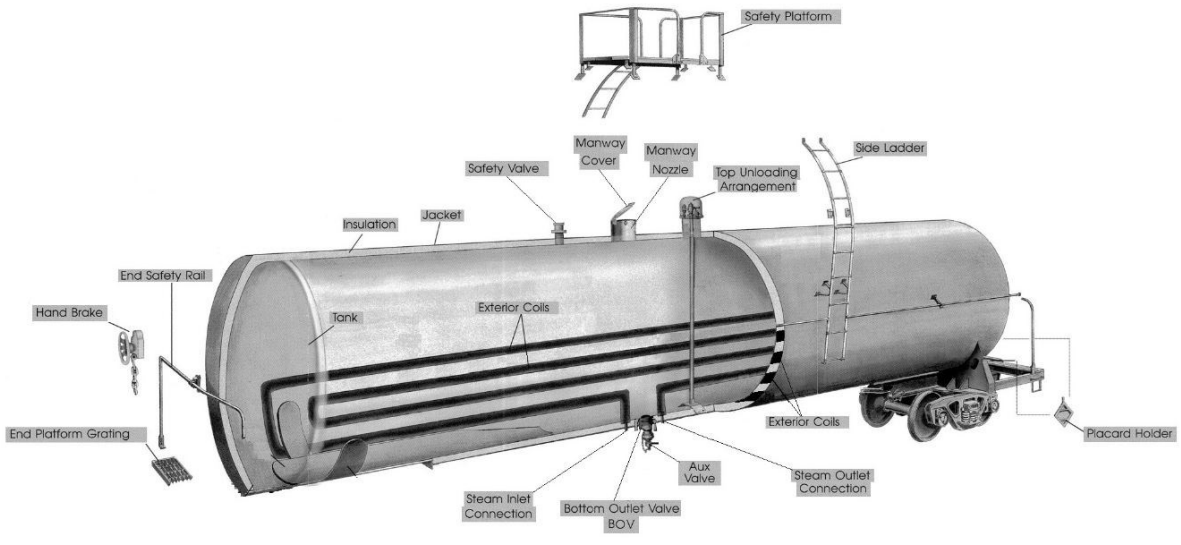
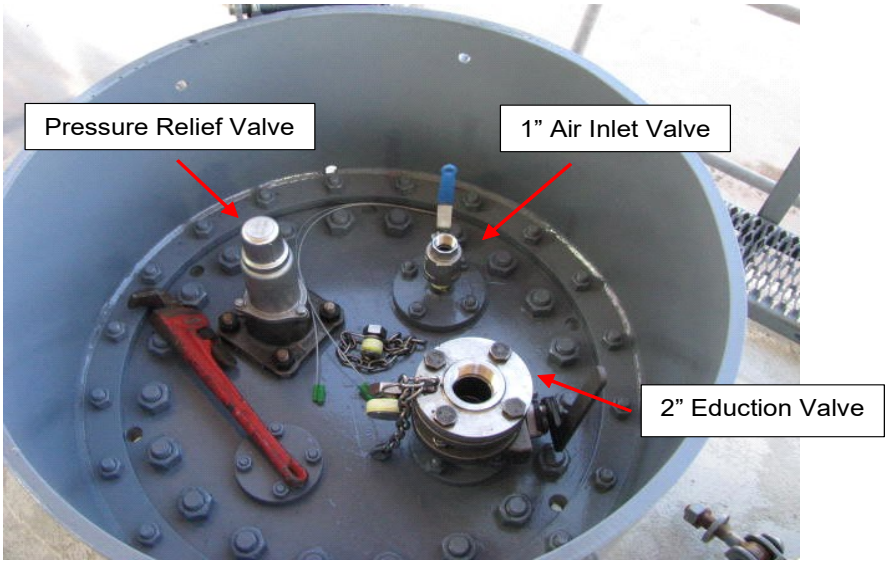


Figure 1 - Common Equipment on a Caustic Railcar

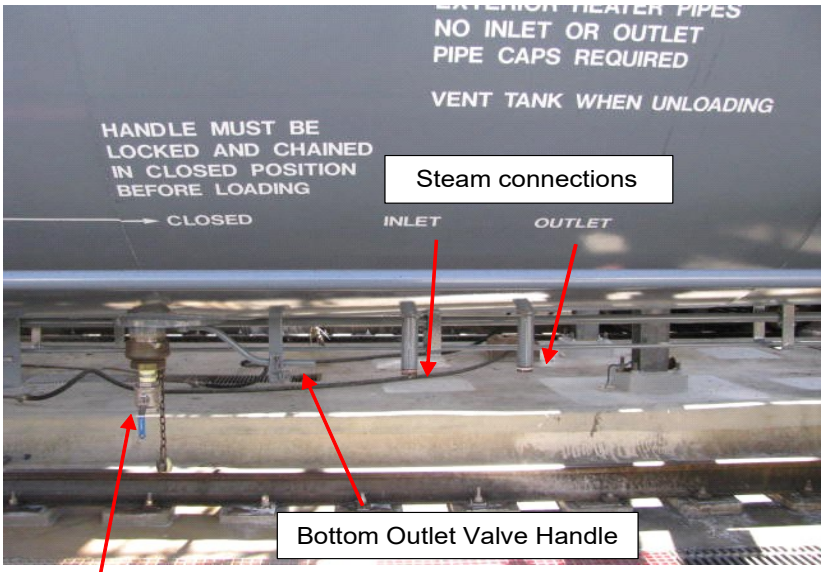
UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

In 2013, OxyChem began purchasing 286K size railcars. These railcars have an increased volume which permits transporting a larger quantity of product. Below are example pictures of the unloading equipment, and on the next page is a table which provides a comparison to the 263K series railcars.

A. Valve enclosure assembly



B. Bottom outlet valve handle and 2” auxiliary valve / Steam coil connections



UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

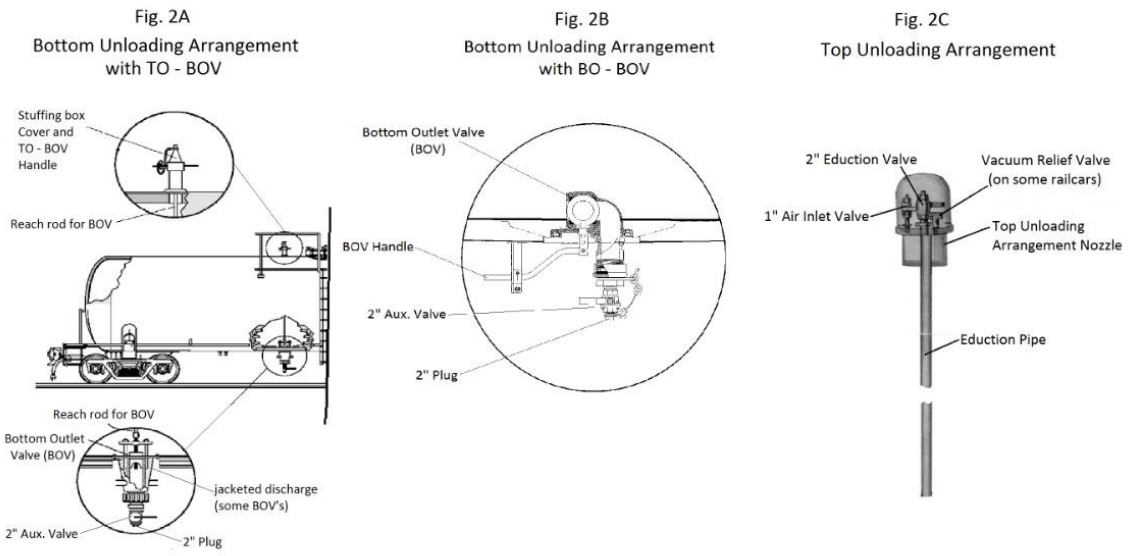
Comparison of OxyChem 286K vs. existing 263K railcars

	286K GP Railcar	263K GP Railcar
Max. Gross Weight (lbs.)	286,000	263,000
Lt. Wt. (empty - lbs.)	~67,000	~60,000
Max. Net Product Weight (lbs.)	~219,000	~203,000
Length of railcar (over coupler pulling faces)	~45 ft.	~42 ft.
PRD setting	165 psig	75 psig
Bottom Outlet Valve (BOV) operation [with 2" aux. valve]	Bottom Operated	Mostly Top Operated & some Bottom Operated
Top Unload Valve	2" flanged w/ 2" screw plug GATX: 3" flanged w/ 3" plug	2" screw plug
PRV location	Inside 'multi-housing' dome	Outside platform railing
Loading Manway cover	316L SS unlined	Lined carbon steel
Loading Nozzle	Lined CS with the top ~6" = SS	Lined carbon steel
Min. amount of product liquid needed to cover steam coils	~ 22" ~2300 gallons	

Dimensional Comparison of Equipment location on 286K (44' 7") vs. 263K (41' 11") railcars

Center line of:	Distance from "B" end coupler pulling face	
	286K	263K
Railcar	22' 3½" / 267.5"	20' 11½" / 251.5"
Filling Manway Nozzle	19' 7½" / 235.5"	18' 7" / 223"
Work platform ladder access opening	19' 7½" / 235.5"	18' 7" / 223"
Top 2" eduction valve	22' ¼" / 264.25"	22' 8" / 272"
Top 1" air valve	22' 7½" / 271.5"	23' 3" / 279"
Multi-accessory Fittings Nozzle	22' 7½ " / 271.5"	22' 11 ½" / 275.5"
Bottom Outlet Valve (BOV) outlet piping	22' / 264"	20' 11½" / 251.5"

Figure 2 - Unloading Arrangements on Caustic Railcars



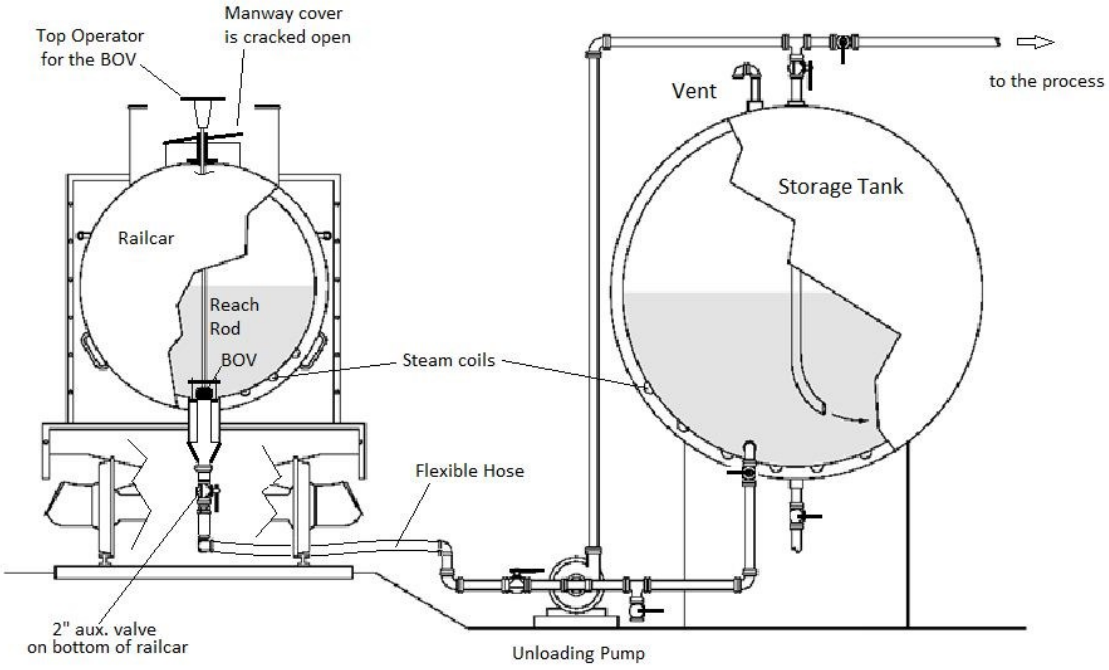


Figure 3 - Bottom Unloading to Storage

UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

UNLOADING RAILCARS

This section provides comments when unloading caustic soda from railcars in three ways: 1) via the bottom outlet valve (BOV) using gravity; 2) via the BOV using pad pressure; or 3) top unloaded through the well line using pad pressure. Refer to Figure 2 for the various unloading arrangements present on a caustic railcar.

BOTTOM UNLOADING - GRAVITY

1. Verify the contents are liquid and at the desired unloading temperature. If not, see “Handling in Cold Weather.”
2. Vent the railcar – OxyChem recommends opening the railcar manway cover.
3. **Refer to Figure 2A or 2B**. Ensure the internal BOV is closed tightly. If a top operated BOV, the valve rod which operates the bottom discharge valve has a handle on it which is located at the top of the railcar. The handle can be reversed and serves as a cap in transit.
4. Remove the plug from the auxiliary valve, then attach an appropriate fitting and unloading line. A flexible connection hose is recommended since a railcar will rise as it is unloading.
5. Check the downstream unloading line to see that all valves are in the proper position for unloading to storage.
6. Open the bottom auxiliary valve, then the internal BOV either by rotating the handle 90° if it is a bottom operated BOV, or by turning the top operator to allow contents to begin flowing by gravity to the pump or tank. If the BOV does not open upon application of light pressure, frozen caustic soda is probably present in the bottom of the car. Application of steam to the BOV area via a steam lance, or hookup to the heat coils may be necessary. See “Handling in Cold Weather.”
7. When the tank car is empty and the discharge pipe has completely drained, close the internal BOV and the auxiliary valve.
8. Disconnect the unloading fittings and hose and install the plug tool tight in the auxiliary valve.
9. Close the manway cover and secure all bolts tool tight. Close the vent valve if open and install the plug tool tight if removed.
10. Prepare the railcar for return.

Note: See **Figure 3** for an example setup for Bottom Unloading using gravity feed to an unloading pump and then to a storage tank.

UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

BOTTOM UNLOADING – PAD PRESSURE

Compressed air can be used to increase the flow rate of caustic soda to storage or to transfer product without the use of a pump. If compressed air is to be used, the prior section instructions for bottom unloading should be modified as follows:

1. Close and secure the manway cover tool tight.
2. Remove the plug from the vent valve and connect the air supply piping and flexible hose to it.
3. Open the vent valve, and apply air pressure slowly to the railcar until there is a normal flow of liquid to the storage tank. The pressure should be maintained until the railcar is completely empty. OxyChem recommends use of 20-25 psig max. A drop in air pressure or the sound of air rushing through the unloading line indicates the railcar is empty.
4. When the railcar is empty, shut off the air supply to the railcar and allow the residual air pad to vent from the railcar either through the unloading line, or through the vent valve on the air system piping - venting the pad from the railcar to a safe location.
5. Close the vent valve on the railcar.
6. Remove the air supply line and reinstall the plug tool tight.

TOP UNLOADING THROUGH THE EDUCTION (WELL) LINE – PAD PRESSURE

1. Verify the contents are liquid and at the desired unloading temperature. If not, see “Handling in Cold Weather.”
2. Refer to **Figure 2C.** Open the housing cover protecting the top unloading valves.
3. Remove the plug from the eduction valve, and using appropriate fittings, connect a flexible unloading hose. This is necessary since the railcar will rise while being unloaded.
4. Remove the plug from the vent valve, and connect the air supply piping and flexible hose to it.
5. Open the eduction valve and any other valves necessary to the storage tank.
6. Open the vent valve, and apply air pressure slowly to the railcar until there is a normal flow of liquid to the storage tank. The pressure should be maintained until the railcar is completely empty. OxyChem recommends use of 20-25 psig max. A drop in air pressure or the sound of air rushing through the unloading line indicates that the tank car is empty.
7. When the railcar is empty, shut off the air supply to the railcar and allow the residual air pad to vent from the railcar either through the unloading line, or through the vent valve on the air system piping - venting the pad from the railcar to a safe location.
8. When the railcar is at atmospheric pressure, close the eduction valve and disconnect the unloading line from the railcar.
9. Close the vent valve and disconnect the air supply from the railcar.
10. If desired, open the manway cover to verify the railcar is empty. Do not enter the car to make an inspection.
11. Replace both plugs in their respective valves tool tight, and secure the protective housing cover.
12. Prepare the railcar for return.

UNLOADING AND HANDLING CAUSTIC SODA IN RAILCARS

See **Figure 4** for an example setup for Top Unloading to a storage tank. Care should be taken not to spill caustic soda on the railcar, since it will cause damage to the paint and may endanger workers handling the empty railcar on its return. Wash off any spilled or dripped caustic.

PREPARING AN EMPTY RAILCAR FOR RETURN

1. Ensure both top valves are closed and plugs are installed tool tight. Secure the cover over the valves.
2. Close the manway cover taking care to ensure the gasket does not fall into the railcar, shift or fold. Ensure all manway cover bolts are tool tight.
3. Disconnect any steam lines used to heat the railcar. Do not place any caps or closures on the railcar steam pipes.
4. Make sure the bottom outlet valve (BOV) and auxiliary valve are closed, and the plug is installed tool tight. Return the empty railcar promptly in accordance with the shipper's instructions. The shipper's routing directions must be followed in all instances.

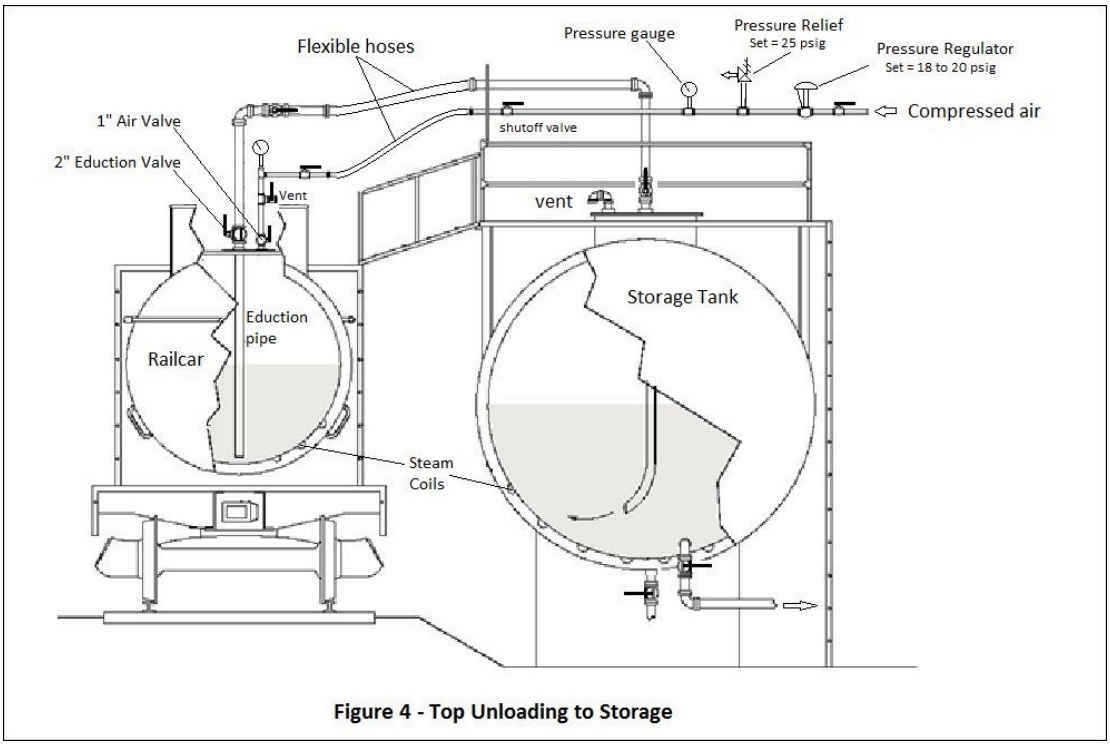


Figure 4 - Top Unloading to Storage

UNLOADING CAUSTIC SODA TANK TRUCKS

CARRIER RESPONSIBILITIES

OxyChem tank truck drivers have received instructions regarding equipment and delivery procedures. If an OxyChem arranged carrier, delivering caustic soda to your plant, fails to adhere to the following guidelines, please contact OxyChem so that corrective action can be taken.

Equipment

Equipment must meet Department of Transportation regulations, Code of Federal Regulations (CFR), Title 49.

Tank Truck Specification

Tank trucks should meet the established DOT requirements for hauling liquid caustic soda.

Four(4) DOT “CORROSIVE” placards must be affixed to the cargo tank. One on each side.

Unloading Equipment

If unloading is by gravity to storage or customer’s unloading pump, no special equipment is needed.

If unloading is by truck-mounted pump, use only an all iron or stainless steel unit. The pump can be driven by a tractor powered take-off or an auxiliary gasoline engine. Use at least a 2-inch pump line.

If unloading is by compressed air, the tank vessel must meet the DOT requirements of the CFR, Title 49. The line used to supply air to the tank truck is required to be equipped with a pressure reducing valve, a pressure relief valve, a pressure gauge and a block valve. The relief valve should be set at a maximum pressure of 20 PSIG and the pressure reducing valve should be set at 2 to 3 pounds lower. Whether this equipment is attached permanently to the tank or carried as an assembled unit to be attached at each unloading, it should be properly maintained and periodically tested.

A 40 foot length of air hose is required if the customer’s air supply is used. When compressed air is not available from the customer’s plant, trucks equipped with pumps or air compressors can be provided at the customer’s request.

Unloading Lines

Unloading hoses must be constructed of material resistant to caustic soda. Hoses should be at least 2 inches in diameter and 15 to 30 feet in length.

Whether the unloading hose is fitted with a union, pipe flange, or a quick type coupler, the truck driver should have available matching fittings and tools to facilitate a connection to a 2-inch or 3-inch threaded pipe.

UNLOADING CAUSTIC SODA TANK TRUCKS

TRUCK DRIVER RESPONSIBILITIES

Truck drivers must obtain permission to unload from the proper authorities and observe any special instructions from the customer.

Truck drivers must wear the protective equipment required by OxyChem as listed under Protective Equipment, (pg. 11) or by the customer, whichever is more inclusive, and at all times follow safe handling practices. Customers must not allow truck drivers who do not meet these requirements to unload.

The following unloading procedures are recommended:

Check the operation of the safety shower and eyewash fountain. Purge water through each to remove rust that may have accumulated.

Connect one end of the unloading hose to the customer's storage tank fill line.

During cold weather and if facilities are provided, use steam to preheat the fill line, the unloading hose, and, if needed, the truck outlet.

Check the unloading line to be sure that it is open.

Connect the unloading hose to the discharge outlet on the tank truck.

Start the pump or start pressurizing the tank, depending on the type of equipment used.

Open the valves on the truck discharge line.

Stand by until the truck cargo is completely unloaded.

If compressed air is used, allow the air to flush out the lines to the storage tank and then close and disconnect the air supply.

EQUIPMENT FOR HANDLING CAUSTIC SODA

GENERAL CONSIDERATIONS

Caustic soda is a corrosive chemical which is normally handled in either steel, nickel, nickel alloys or certain types of plastic equipment. The specific material will depend on the conditions under which the material is being used. Temperature, solution concentration, location and safety considerations are all important factors in equipment selection.

MATERIALS OF CONSTRUCTION

Carbon steel is the most commonly used material of construction for caustic soda at low to moderate temperatures. The ideal storage temperature for caustic soda in carbon steel is 80 to 100°F. Temperatures above 120°F will cause accelerated corrosion of the carbon steel and subsequent iron contamination of the caustic soda (above 120°F, cracking can occur if concentrated caustic is processed in steel equipment that has not been stress relieved). Where iron contamination or corrosion is unacceptable, epoxy lined carbon steel, 316L and 304L stainless steels are recommended. 316L and 304L stainless is acceptable to 200°F. At temperatures above 200°F, nickel is typically used but Monel®, Inconel®, or Hastelloy® can also be used. Consult with the supplier about the working temperature range of a particular lining.

Plastics, such as polyethylene, polypropylene, PVC, and CPVC, can be used. They do not contribute to iron contamination. They are chemically compatible with caustic soda so long as their maximum temperature limitation is not exceeded. When using PVC or CPVC as the material of construction, use a glue that does not contain silica as a filler. PVC and CPVC glues contain a filler (typically silica). Caustic soda will attack the silica filler causing leaks to develop at the glue joints. The manufacturer of the tank, drum, piping or equipment in question should be contacted to determine the exact limitations of the specific plastic.

DANGER: Aluminum, copper, zinc, lead and their alloys (e.g., brass and bronze) are NOT suitable for handling or storing caustic soda. Caustic soda readily attacks these materials.

STORAGE TANKS

Tanks can be either vertical or horizontal. They are usually fabricated from at least 1/4-inch steel plate. A 1/8-inch corrosion allowance should be included in the design. If iron contamination is a problem, tanks can be fabricated from 304L or 316L stainless steel. If the tanks are large, it's usually more economical to fabricate a steel tank and line it with an epoxy coating. Plastic tanks are usually fabricated from polypropylene or fiberglass reinforced plastics (FRP). Since caustic soda can attacks glass reinforcement fibers of improperly constructed FRP tanks, care must be taken to ensure the FRP tanks are built with the proper reinforcing materials, resins, catalysts, curing procedures and corrosion barriers.

The product discharge connection should be at least 4 inches above the bottom of the tank and the drain connection should be at the lowest point in the tank. This will facilitate drainage during periodic cleaning of the tank. Storage tanks should have a level indicating device for measuring liquid level.

Where heating is required, an external heat exchanger with a circulating pump or internal steam heating coils are most commonly employed. The preferred materials for the coils are nickel, Monel®, or Inconel®. Despite this, stainless steel is most commonly used because of cost considerations. At high temperatures, stainless steel may crack. If it is necessary to insulate the storage tank, a two-inch layer of polyurethane foam or cellular glass should be adequate.

Proper design of a storage system will include adequate containment in case of tank failure. State and local regulatory authorities should always be consulted during the design phase of construction.

EQUIPMENT FOR HANDLING CAUSTIC SODA

TANK CLEANING AND PASSIVATION

Tank cleaning is dependent on the previously stored product. A tank that previously contained caustic soda requires scale removal, wall thickness testing, rinsing, passivation, floor cleaning, and immediate filling. A tank previously containing another product requires cleaning with an appropriate solvent or soap, as well as the other steps mentioned above.

Scale removal is accomplished by blasting the walls with an abrasive such as sand or pecan shells. Abrasives containing high percentages of metals are not recommended.

The wall thickness of the tank should be measured to ensure the tank has structural integrity for the density of the product and the height of product in the tank.

Passivation requires permeation of the steel tank walls with caustic soda. This is usually accomplished by spraying the cleaned walls with a hot solution of caustic soda. A temperatures of 100-140°F and solution concentration of 5-20% are recommended. A standard recommendation would be spraying the walls for 2-4 hours with a 10% solution at 140°F. The larger the tank the longer it should be sprayed to complete the passivation. Utilizing a hotter and stronger solutions will require less time for passivation. One way to achieve the solution heat necessary is to dilute 50% caustic soda to 20%. The heat of dilution will cause the caustic soda temperature to rise. Additional heat may be necessary to achieve optimal solution temperatures. The coating of the tank walls is best accomplished with an elliptical sprayer.

After passivation, the tank bottom must be cleaned out as well as possible. The quality of the initial product stored in the tank will depend greatly upon the extent to which the tank bottom is cleaned of scale abrasive compound. After spraying, a squeegee will need to be used to clean the tank bottom.

After cleaning, the tank should be filled with caustic soda as soon as possible. This will prevent the tank walls from losing their passivation. If the tank cleaning is not completely successful, it may be necessary to filter the initial product from the tank to remove any remaining particulate matter. This would require a 5-10 micron filter media housed in a unit that would be compatible with the temperature, pressure, and chemical.

EQUIPMENT FOR HANDLING CAUSTIC SODA

PIPING AND VALVES

Pipelines are usually at least two inches in diameter and constructed of Schedule 40 black iron or mild steel with welded or flanged joints. Where disconnects are necessary, flanged joints are preferred to facilitate maintenance. A safety flange guard of wrap-around polypropylene is recommended for all flanged joints. This will protect against spraying in case a gasket leaks.

Proper pipeline design includes an adequate pitch to permit complete draining. Avoid any loops or pockets. Lines should also include water or air connections for purging after use.

Where slight iron contamination is unacceptable, CPVC, polypropylene, polypropylene-lined steel, and Teflon® lined steel pipe are suitable materials. Pay special attention to suitable operating temperatures and pressures with these materials.

Ductile iron, cast steel, stainless steel, Alloy 20, and Teflon®-lined quarter-turn plug or ball valves are recommended for caustic soda service. Various other types of valves can also be used; however, keep in mind that less elaborate fittings provide better reliability in this service.

PUMPS

Centrifugal pumps of stainless steel or Alloy 20 construction, with either double mechanical seals or a deep packing gland, is recommended. Packing material should be Teflon® impregnated, caustic resistant fibers, or equivalent. To avoid seals altogether, magnetically coupled pumps could be used.

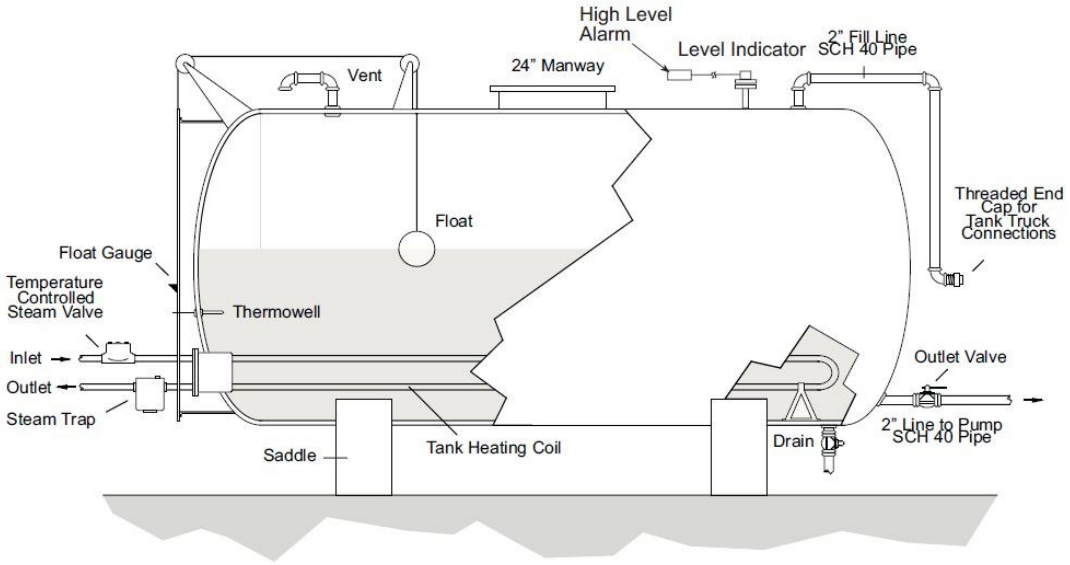
The pump location should receive careful consideration. For ease of operation, keep the suction lines as short as possible. A recirculating line will help prevent excess wear on the pump and, in many cases, can assist in controlling flow rates.

The pump seal area should have a liquid impervious shield installed.

METERS

Caustic soda solutions can be metered through standard rotameters having non-glass tubes and nickel or stainless steel floats. Magnetic, Coriolis or orifice-type meters are preferred for strong, hot solutions. They should be made of corrosion resistant materials such as stainless steel, alloy 20, Monel®, or nickel.

TYPICAL STORAGE TANK INSTALLATION



*NOTE: All tanks should be located within a diked area.

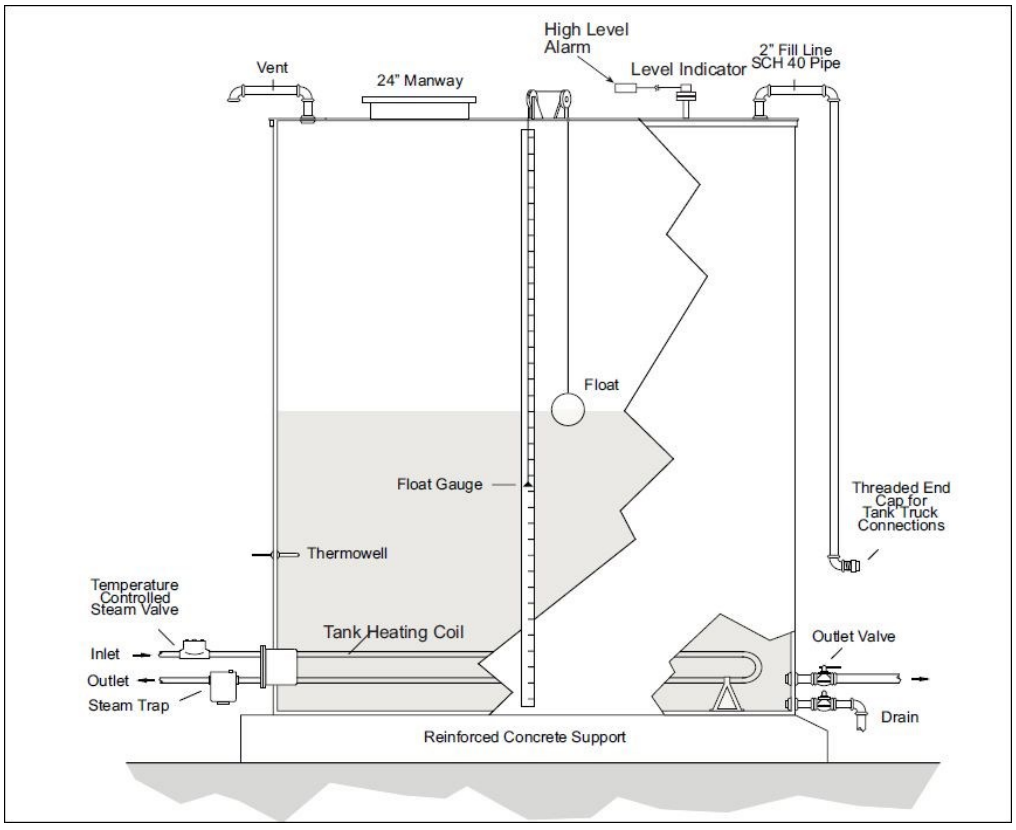


TABLE 1 DENSITY AND NAOH CONTENT OF MEMBRANE GRADE CAUSTIC SODA SOLUTIONS AT 60°F

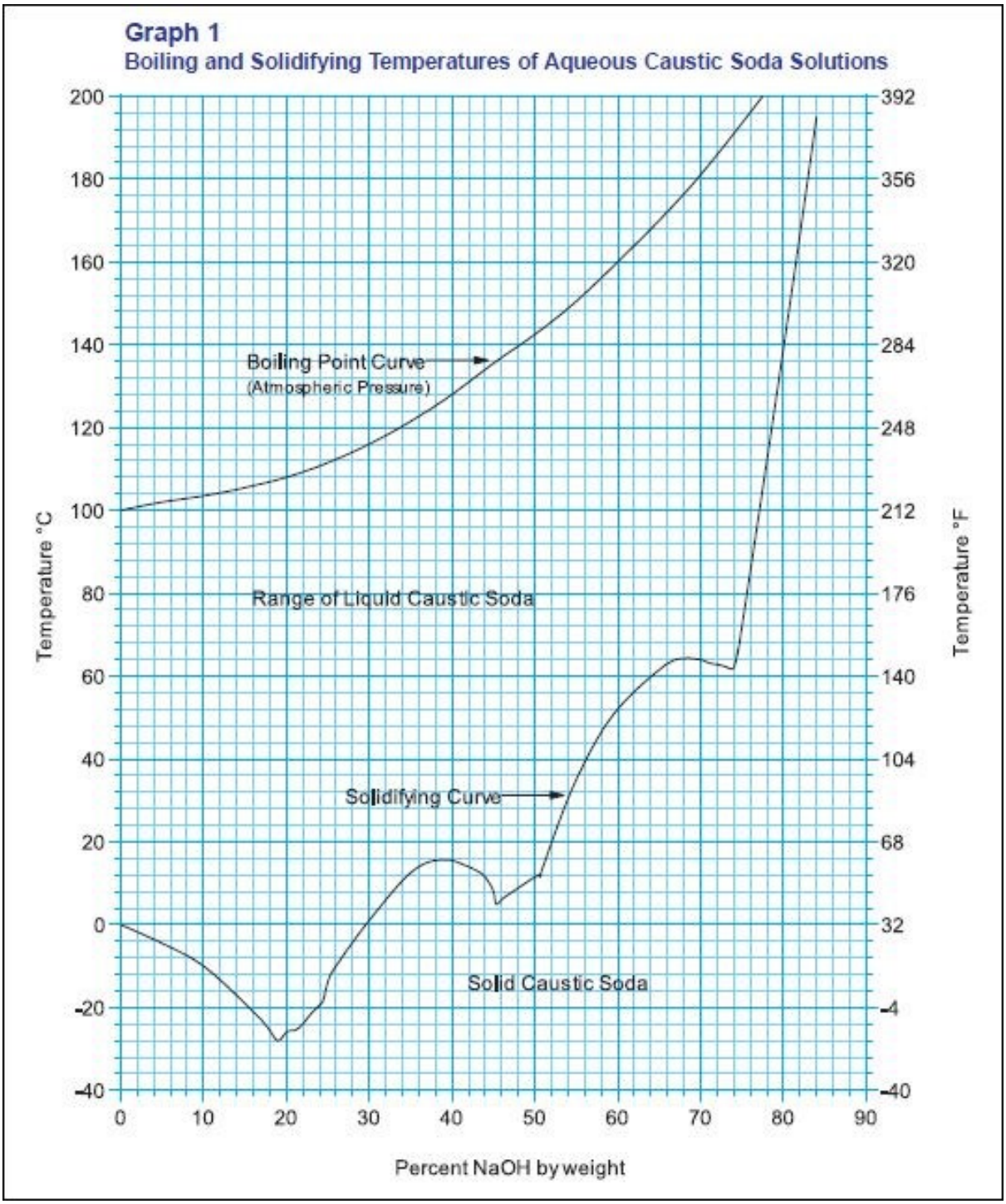
WT% NaOH	% Na2O	SPECIFIC GRAVITY	DEGREES BAUMÉ [AM STD]	NaOH G/L	NaOH LB/GAL	NaOH LB/CU FT	DENSITY LB/GAL	DENSITY LB/CU FT
1.0	0.775	1.0120	1.706	10.118	0.084	0.631	8.437	63.113
2.0	1.550	1.0230	3.259	20.457	0.171	1.277	8.529	63.804
3.0	2.325	1.0342	4.782	31.019	0.259	1.935	8.622	64.497
4.0	3.100	1.0453	6.274	41.803	0.349	2.608	8.715	65.191
5.0	3.874	1.0564	7.736	52.811	0.440	3.295	8.807	65.885
6.0	4.649	1.0676	9.170	64.042	0.534	3.995	8.900	66.581
7.0	5.424	1.0787	10.580	75.496	0.630	4.710	8.993	67.277
8.0	6.199	1.0899	11.960	87.174	0.727	5.438	9.087	67.973
9.0	6.974	1.1010	13.310	99.076	0.826	6.181	9.180	68.670
10.0	7.748	1.1122	14.630	111.210	0.927	6.937	9.273	69.367
11.0	8.523	1.1234	15.930	123.550	1.031	7.707	9.366	70.063
12.0	9.298	1.1345	17.200	136.130	1.136	8.492	9.459	70.759
13.0	10.080	1.1457	18.440	148.920	1.242	9.290	9.552	71.455
14.0	10.850	1.1569	19.660	161.930	1.351	10.110	9.645	72.150
15.0	11.630	1.1680	20.850	175.170	1.461	10.930	9.738	72.845
16.0	12.400	1.1791	22.030	188.630	1.573	11.770	9.830	73.539
17.0	13.180	1.1902	23.170	202.300	1.687	12.620	9.923	74.231
18.0	13.950	1.2013	24.300	216.200	1.803	13.490	10.020	74.922
19.0	14.730	1.2124	25.400	230.310	1.921	14.370	10.110	75.612
20.0	15.500	1.2234	26.480	244.640	2.040	15.260	10.200	76.300
21.0	16.280	1.2344	27.530	259.180	2.162	16.170	10.300	76.987
22.0	17.050	1.2454	28.570	273.940	2.285	17.090	10.390	77.672
23.0	17.830	1.2563	29.590	288.910	2.409	18.030	10.480	78.355
24.0	18.600	1.2672	30.580	304.090	2.536	18.970	10.570	79.035
25.0	19.370	1.2781	31.550	319.470	2.664	19.930	10.660	79.713
26.0	20.150	1.2889	32.510	335.070	2.794	20.910	10.750	80.389
27.0	20.920	1.2997	33.440	350.870	2.926	21.890	10.840	81.062
28.0	21.700	1.3105	34.350	366.870	3.060	22.890	10.930	81.731
29.0	22.470	1.3212	35.250	383.070	3.195	23.900	11.020	82.398
30.0	23.250	1.3317	36.120	399.450	3.331	24.920	11.110	83.057
31.0	24.020	1.3424	36.980	416.070	3.470	25.960	11.200	83.722
32.0	24.800	1.3529	37.830	432.860	3.610	27.010	11.280	84.379
33.0	25.570	1.3634	38.650	449.850	3.751	28.070	11.370	85.033
34.0	26.350	1.3738	39.450	467.010	3.895	29.140	11.460	85.681
35.0	27.120	1.3842	40.240	484.370	4.039	30.220	11.540	86.327
36.0	27.900	1.3944	41.020	501.910	4.186	31.310	11.630	86.968
37.0	28.670	1.4046	41.770	519.630	4.333	32.420	11.720	87.605
38.0	29.450	1.4148	42.510	537.520	4.482	33.530	11.800	88.237
39.0	30.220	1.4248	43.230	555.590	4,633	34.660	11.880	88.864
40.0	31.000	1.4348	43.940	573.830	4.785	35.800	11.970	89.487
41.0	31.770	1.4447	44.640	592.240	4.939	36.950	12.050	90.105
42.0	32.550	1.4545	45.310	610.810	5.094	38.110	12.130	90.717
43.0	33.320	1.4643	45.980	629.530	5.250	39.270	12.210	91.324
44.0	34.100	1.4739	46.630	648.420	5.407	40.450	12.290	91.926
45.0	34.870	1.4835	47.260	667.450	5.566	41.640	12.370	92.522
46.0	35.650	1.4930	47.880	686.640	5.726	42.840	12.450	93.113
47.0	36.420	1.5023	48.480	705.970	5.887	44.040	12.530	93.697
48.0	37.200	1.5116	49.080	725.440	6.049	45.260	12.610	94.275
49.0	37.970	1.5208	49.650	745.040	6.213	46.480	12.680	94.847
50.0	**38.740**	**1.5298**	**50.220**	**764.780**	**6.377**	**47.710**	**12.760**	**95.412**
51.0	39.520	1.5388	50.770	784.640	6.543	48.950	12.830	95.971
52.0	40.290	1.5476	51.310	804.630	6.710	50.200	12.910	96.523

TABLE 2 DENSITY AND NAOH CONTENT OF DIAPHRAGM GRADE CAUSTIC SODA SOLUTIONS AT 60°F

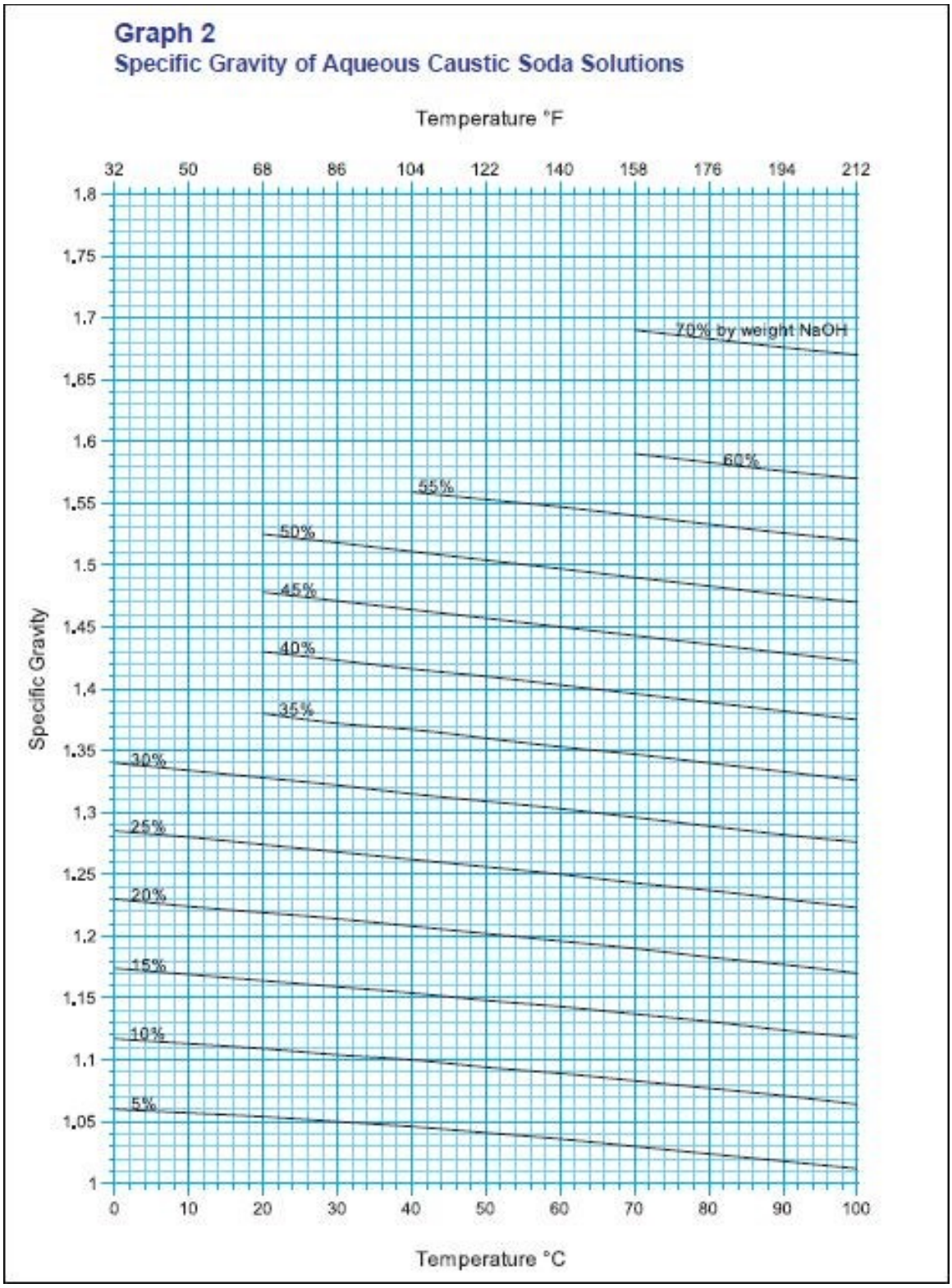
WT% NaOH	% Na2O	% NaCl	SPECIFIC GRAVITY	DEGREES BAUMÉ [AM STD]	NaOH G/L	NaOH LB/GAL	NaOH LB/CU FT	DENSITY LB/GAL	DENSITY LB/CU FT
1.0	0.775	0.020	1.0121	1.726	10.120	0.084	0.631	8.438	63.122
2.0	1.550	0.040	1.0233	3.300	20.463	0.171	1.277	8.532	63.823
3.0	2.325	0.060	1.0346	4.842	31.032	0.259	1.936	8.626	64.525
4.0	3.100	0.080	1.0459	6.351	41.827	0.349	2.610	8.719	65.227
5.0	3.874	0.100	1.0571	7.829	52.846	0.441	3.297	8.813	65.930
6.0	4.649	0.120	1.0684	9.282	64.095	0.535	3.999	8.908	66.636
7.0	5.424	0.140	1.0797	10.710	75.568	0.630	4.714	9.002	67.341
8.0	6.199	0.160	1.0911	12.100	87.269	0.728	5.444	9.096	68.047
9.0	6.974	0.180	1.1024	13.460	99.195	0.827	6.188	9.191	68.752
10.0	7.748	0.200	1.1137	14.800	111.350	0.928	6.946	9.285	69.458
11.0	8.523	0.220	1.1250	16.110	123.730	1.032	7.718	9.379	70.164
12.0	9.298	0.240	1.1363	17.390	136.340	1.137	8.505	9.474	70.870
13.0	10.080	0.260	1.1476	18.650	149.170	1.244	9.305	9.568	71.575
14.0	10.850	0.280	1.1589	19.880	162.220	1.353	10.120	9.662	72.279
15.0	11.630	0.300	1.1702	21.090	175.500	1.464	10.950	9.756	72.983
16.0	12.400	0.320	1.1815	22.270	189.000	1.576	11.790	9.850	73.685
17.0	13.180	0.340	1.1927	23.430	202.730	1.691	12.650	9.944	74.387
18.0	13.950	0.360	1.2040	24.560	216.680	1.807	13.520	10.040	75.088
19.0	14.730	0.380	1.2152	25.670	230.840	1.925	14.400	10.140	75.787
20.0	15.500	0.400	1.2263	26.760	245.230	2.045	15.300	10.230	76.485
21.0	16.280	0.420	1.2375	27.830	259.830	2.167	16.210	10.320	77.180
22.0	17.050	0.440	1.2486	28.870	274.650	2.291	17.140	10.410	77.874
23.0	17.830	0.460	1.2597	29.900	289.690	2.416	18.080	10.510	78.566
24.0	18.600	0.480	1.2708	30.900	304.930	2.543	19.030	10.600	79.255
25.0	19.370	0.500	1.2818	31.880	320.400	2.672	19.990	10.690	79.943
26.0	20.150	0.520	1.2928	32.840	336.070	2.803	20.970	10.780	80.628
27.0	20.920	0.540	1.3037	33.780	351.940	2.935	21.960	10.870	81.310
28.0	21.700	0.560	1.3146	34.700	368.020	3.069	22.960	10.960	81.988
29.0	22.470	0.580	1.3254	35.600	384.310	3.205	23.980	11.050	82.665
30.0	23.250	0.600	1.3362	36.490	400.800	3.342	25.010	11.140	83.338
31.0	24.020	0.620	1.3470	37.350	417.490	3.482	26.050	11.230	84.007
32.0	24.800	0.640	1.3576	38.200	434.370	3.622	27.100	11.320	84.673
33.0	25.570	0.660	1.3683	39.030	451.450	3.765	28.170	11.410	85.335
34.0	26.350	0.680	1.3788	39.840	468.720	3.909	29.240	11.500	85.994
35.0	27.120	0.700	1.3893	40.630	486.170	4.054	30.330	11.590	86.648
36.0	27.900	0.720	1.3997	41.410	503.820	4.201	31.430	11.670	87.299
37.0	28.670	0.740	1.4101	42.170	521.640	4.350	32.540	11.760	87.944
38.0	29.450	0.760	1.4204	42.920	539.650	4.500	33.670	11.850	88.586
39.0	30.220	0.780	1.4306	43.640	557.830	4.652	34.800	11.930	89.223
40.0	31.000	0.800	1.4407	44.360	576.190	4.805	35.950	12.020	89.854
41.0	31.770	0.820	1.4508	45.050	594.710	4.959	37.100	12.100	90.481
42.0	32.550	0.840	1.4607	45.740	613.400	5.115	38.270	12.180	91.103
43.0	33.320	0.860	1.4706	46.400	632.260	5.272	39.440	12.270	91.720
44.0	34.100	0.880	1.4804	47.060	651.270	5.431	40.630	12.350	92.330
45.0	34.870	0.900	1.4901	47.690	670.440	5.591	41.830	12.430	92.935
46.0	35.650	0.920	1.4997	48.320	689.760	5.752	43.030	12.510	93.535
47.0	36.420	0.940	1.5092	48.930	709.220	5.914	44.250	12.590	94.129
48.0	37.200	0.960	1.5187	49.520	728.830	6.078	45.470	12.670	94.716
49.0	37.970	0.980	1.5280	50.100	748.580	6.242	46.700	12.740	95.297
50.0	**38.740**	**1.000**	**1.5372**	**50.670**	**768.460**	**6.408**	**47.940**	**12.820**	**95.872**
51.0	39.520	1.000	1.5506	51.490	790.690	6.594	49.330	12.930	96.711
52.0	40.290	1.000	1.5604	52.070	811.250	6.765	50.610	13.010	97.317

TABLE 3 SPECIFIC HEATS OF CAUSTIC SODA IN BTU/lb·°F

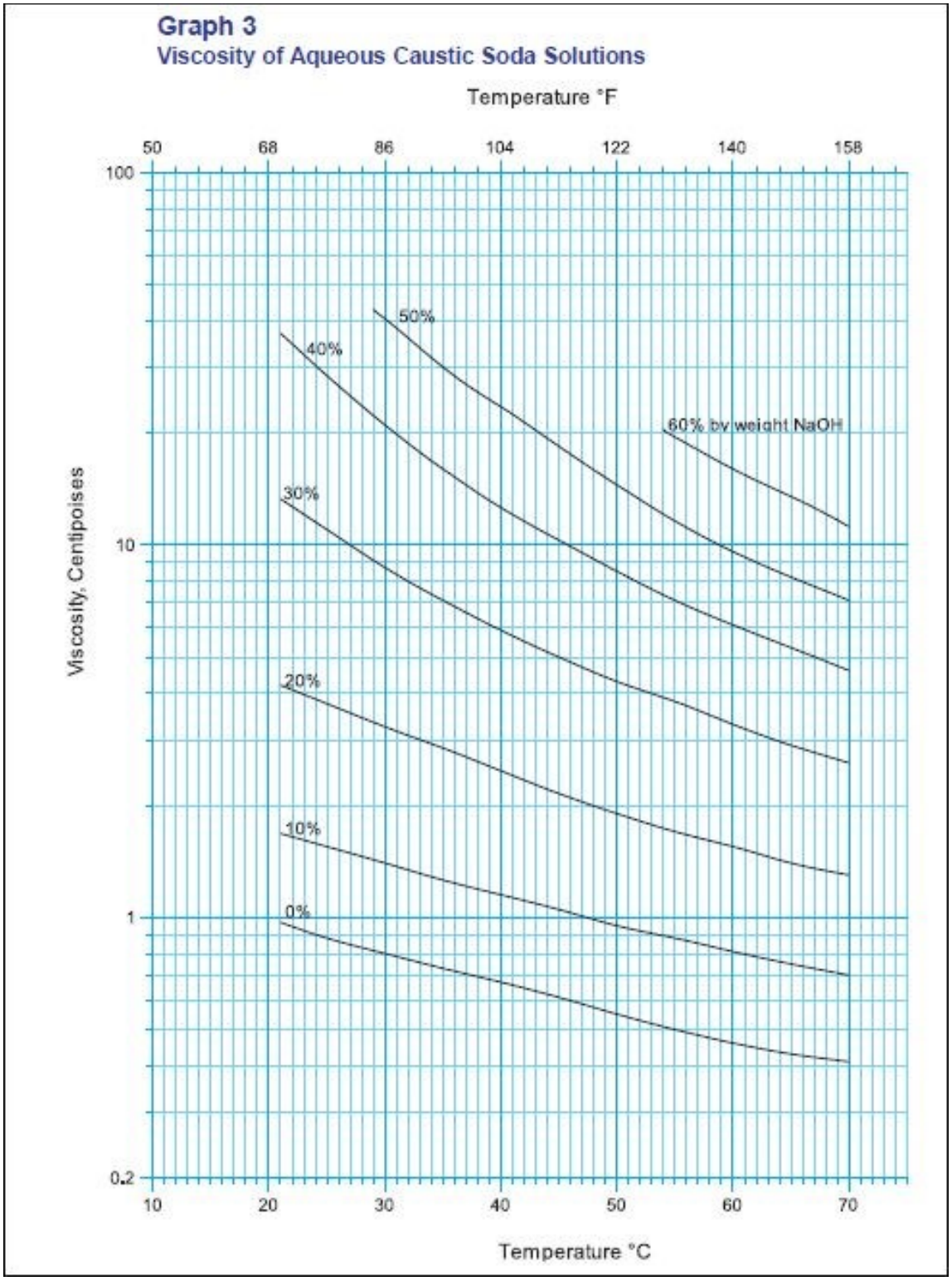
WT% NaOH	TEMPERATURE °F															
	32	40	50	60	80	100	120	140	160	180	200	220	240	260	280	300
0	1.004	1.003	1.001	0.999	0.998	0.997	0.998	0.999	1.000	1.002	1.004	-	-	-	-	-
2	0.965	0.967	0.968	0.969	0.972	0.974	0.977	0.978	0.980	0.983	0.986	-	-	-	-	-
4	0.936	0.940	0.943	0.946	0.951	0.954	0.957	0.960	0.962	0.965	0.966	-	-	-	-	-
6	0.914	0.920	0.924	0.928	0.933	0.938	0.941	0.944	0.946	0.948	0.950	-	-	-	-	-
8	0.897	0.902	0.907	0.911	0.918	0.923	0.927	0.930	0.932	0.934	0.936	-	-	-	-	-
10	0.882	0.888	0.893	0.897	0.905	0.911	0.916	0.918	0.920	0.922	0.923	-	-	-	-	-
12	0.870	0.877	0.883	0.887	0.894	0.901	0.906	0.909	0.911	0.912	0.913	-	-	-	-	-
14	0.861	0.868	0.874	0.879	0.886	0.892	0.897	0.901	0.903	0.903	0.904	-	-	-	-	-
16	0.853	0.860	0.866	0.871	0.880	0.886	0.891	0.894	0.896	0.897	0.897	-	-	-	-	-
18	0.847	0.854	0.860	0.865	0.873	0.880	0.885	0.888	0.890	0.891	0.891	-	-	-	-	-
20	0.842	0.848	0.854	0.859	0.868	0.875	0.880	0.884	0.886	0.886	0.887	-	-	-	-	-
22	0.837	0.844	0.849	0.854	0.863	0.870	0.876	0.880	0.882	0.882	0.883	-	-	-	-	-
24	-	0.839	0.844	0.849	0.858	0.866	0.873	0.877	0.879	0.879	0.880	-	-	-	-	-
26	-	0.835	0.840	0.845	0.854	0.863	0.869	0.874	0.875	0.876	0.876	-	-	-	-	-
28	-	0.830	0.836	0.841	0.850	0.859	0.866	0.870	0.872	0.872	0.873	-	-	-	-	-
30	-	0.826	0.832	0.837	0.846	0.855	0.862	0.866	0.868	0.869	0.869	-	-	-	-	-
32	-	0.822	0.828	0.833	0.842	0.850	0.857	0.862	0.863	0.864	0.864	-	-	-	-	-
34	-	-	0.823	0.828	0.837	0.845	0.852	0.856	0.857	0.858	0.858	-	-	-	-	-
36	-	-	0.819	0.824	0.832	0.840	0.845	0.849	0.850	0.851	0.851	-	-	-	-	-
38	-	-	0.816	0.820	0.827	0.833	0.837	0.841	0.842	0.842	0.843	-	-	-	-	-
40	-	-	0.812	0.815	0.821	0.826	0.829	0.831	0.832	0.832	0.832	-	-	-	-	-
42	-	-	0.807	0.809	0.813	0.816	0.819	0.819	0.820	0.820	0.820	-	-	-	-	-
44	-	-	-	0.802	0.804	0.806	0.807	0.807	0.807	0.806	0.804	-	-	-	-	-
46	-	-	-	0.793	0.794	0.795	0.794	0.794	0.793	0.791	0.789	-	-	-	-	-
48	-	-	-	-	0.783	0.782	0.781	0.780	0.779	0.777	0.776	-	-	-	-	-
50	-	-	-	-	0.771	0.769	0.768	0.767	0.765	0.765	0.764	0.763	0.762	0.762	0.761	0.761
52	-	-	-	-	0.759	0.757	0.756	0.754	0.753	0.752	0.751	0.749	0.748	0.747	0.746	0.745
54	-	-	-	-	0.746	0.744	0.741	0.739	0.739	0.738	0.737	0.735	0.733	0.731	0.730	0.728
56	-	-	-	-	0.733	0.730	0.728	0.726	0.724	0.723	0.722	0.721	0.719	0.717	0.715	0.713
58	-	-	-	-	-	0.719	0.717	0.715	0.713	0.711	0.709	0.707	0.705	0.703	0.702	0.700
60	-	-	-	-	-	0.706	0.705	0.703	0.701	0.699	0.697	0.696	0.693	0.691	0.690	0.688
62	-	-	-	-	-	-	0.694	0.692	0.690	0.688	0.687	0.685	0.683	0.681	0.679	0.677
64	-	-	-	-	-	-	0.684	0.682	0.681	0.679	0.677	0.675	0.673	0.671	0.670	0.668
66	-	-	-	-	-	-	0.675	0.673	0.671	0.669	0.668	0.666	0.664	0.662	0.660	0.658
68	-	-	-	-	-	-	-	0.663	0.662	0.660	0.658	0.656	0.655	0.653	0.651	0.649
70	-	-	-	-	-	-	-	0.655	0.653	0.651	0.649	0.647	0.646	0.644	0.642	0.640
72	-	-	-	-	-	-	-	-	0.645	0.643	0.641	0.639	0.637	0.635	0.634	0.632
73	-	-	-	-	-	-	-	-	-	0.639	0.637	0.635	0.633	0.631	0.630	0.628
74	-	-	-	-	-	-	-	-	-	0.635	0.633	0.631	0.629	0.628	0.626	0.624
74.5	-	-	-	-	-	-	-	-	-	0.633	0.631	0.629	0.627	0.626	0.624	0.622
76	-	-	-	-	-	-	-	-	-	0.628	0.627	0.625	0.623	0.621	0.619	0.617
78	-	-	-	-	-	-	-	-	-	-	0.620	0.618	0.616	0.615	0.613	0.611


Graph 1
Boiling and Solidifying Temperatures of Aqueous Caustic Soda Solutions
Boiling Point Curve
(Atmospheric Pressure)
Range of Liquid Caustic Soda
Solidifying Curve
Solid Caustic Soda
Temperature °C
Temperature °F
Percent NaOH by weight
200
180
160
140
120
100
80
60
40
20
0
-20
-40
392
356
320
284
248
212
176
140
104
68
32
-4
-40
0
10
20
30
40
50
60
70
80
90

Graph 2
Specific Gravity of Aqueous Caustic Soda Solutions

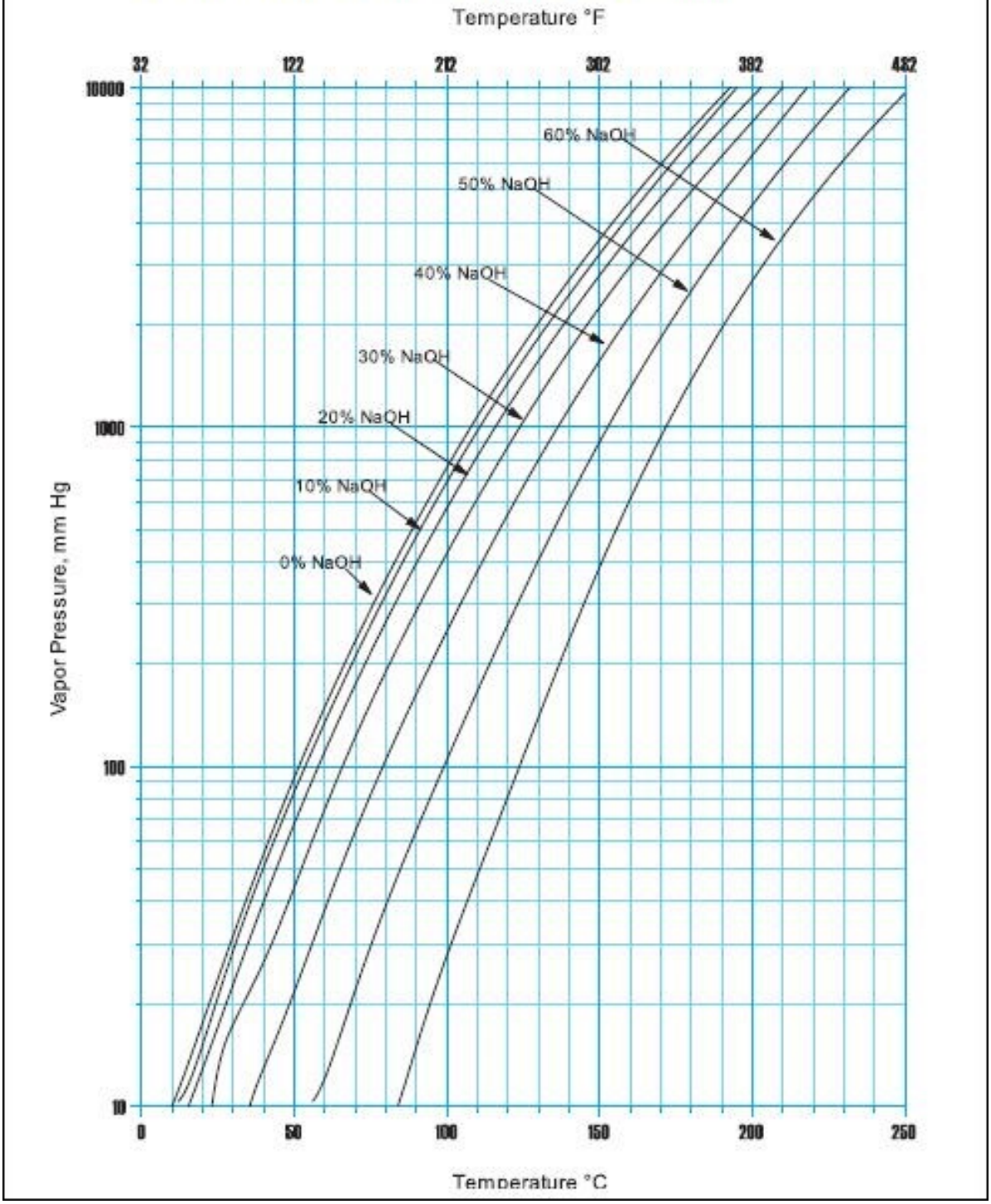


Graph 3
Viscosity of Aqueous Caustic Soda Solutions



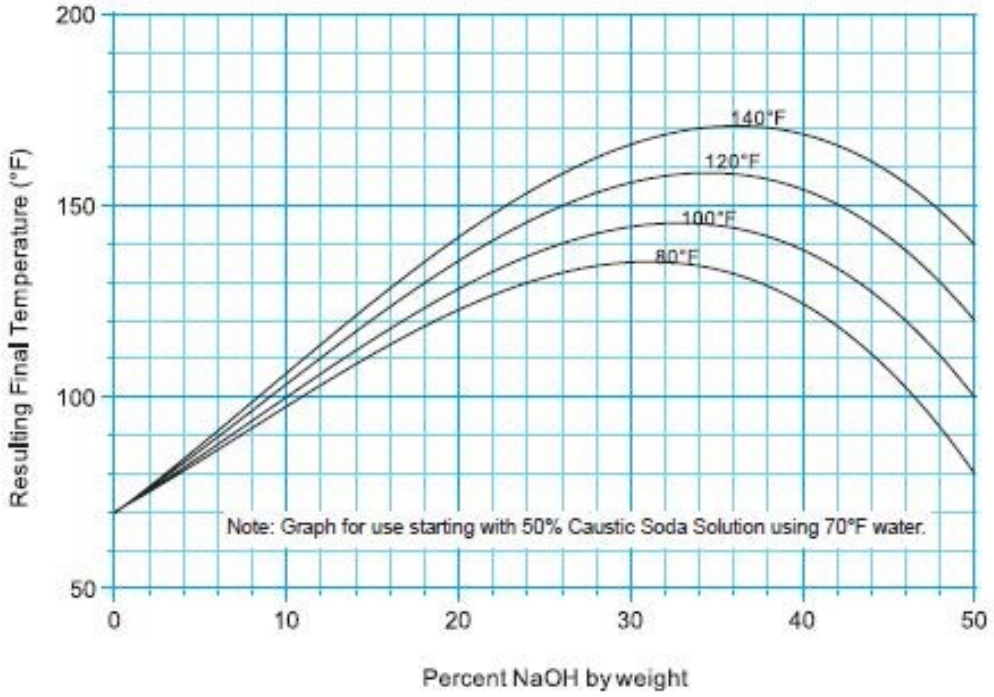
Graph 4

Vapor Pressures of Aqueous Caustic Soda Solutions



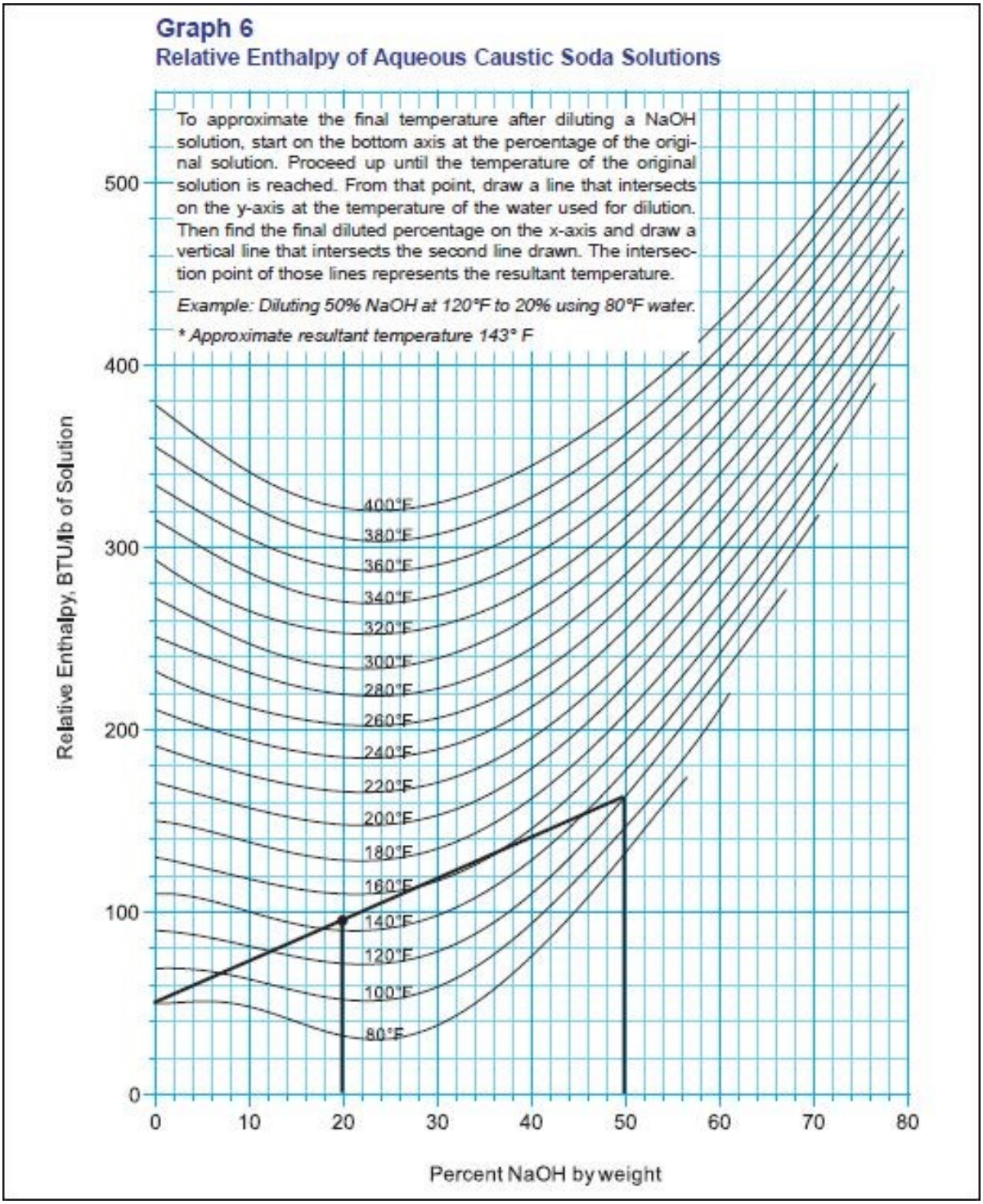
Graph 5

Approximate Resultant Temperature When Diluting Caustic Soda



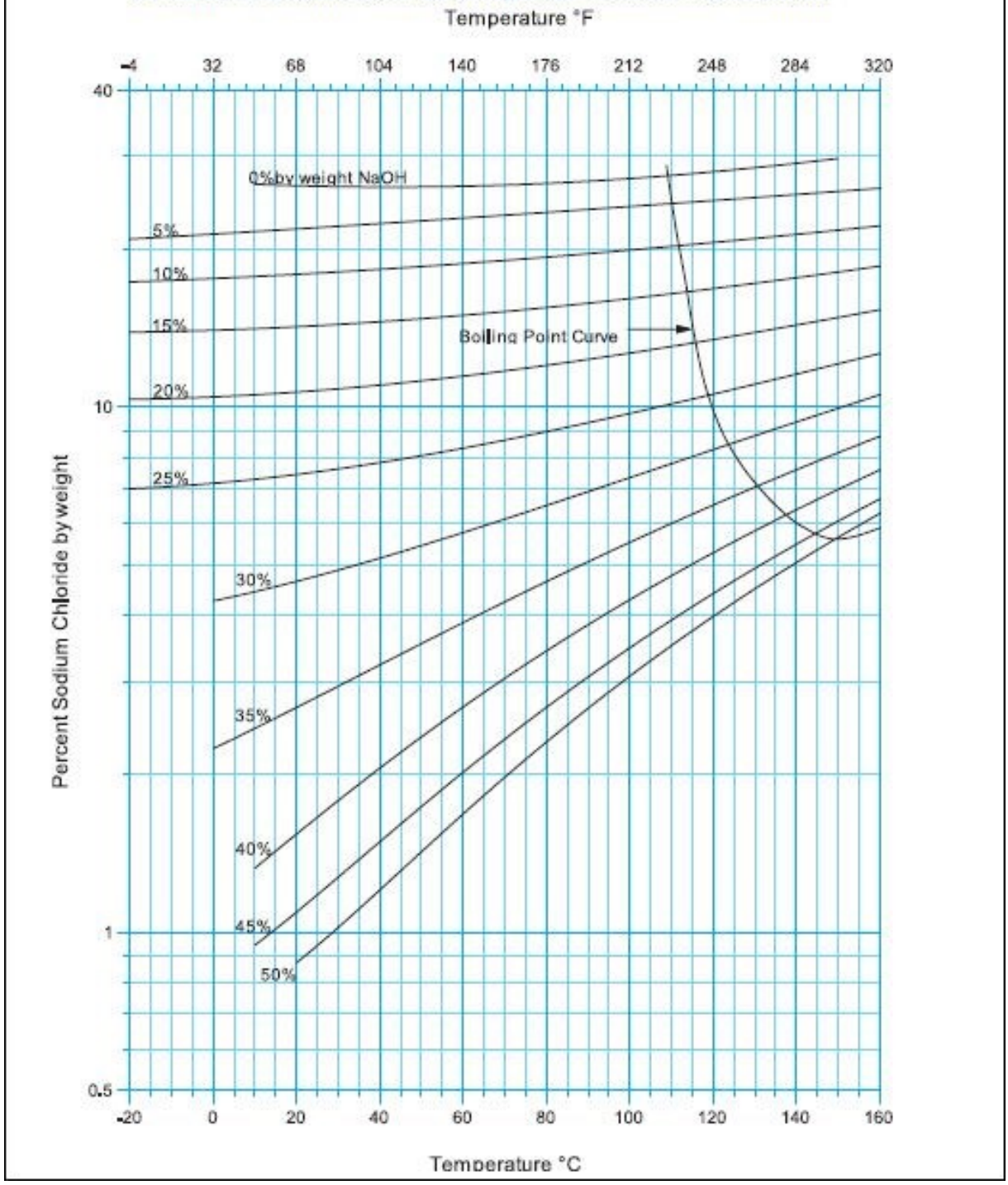
Graph 6

Relative Enthalpy of Aqueous Caustic Soda Solutions

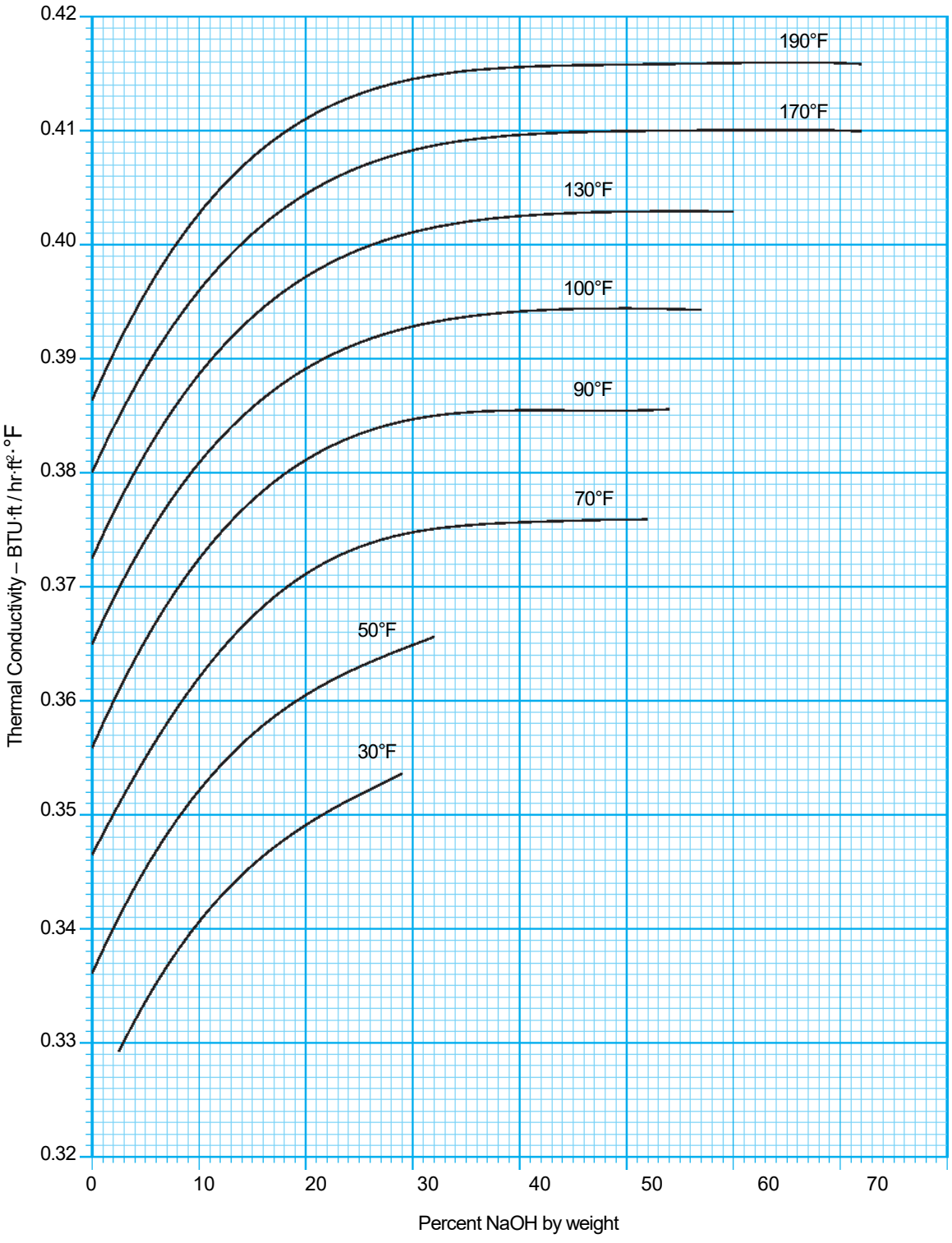


Graph 7

Solubility of Sodium Chloride in Aqueous Caustic Soda Solutions

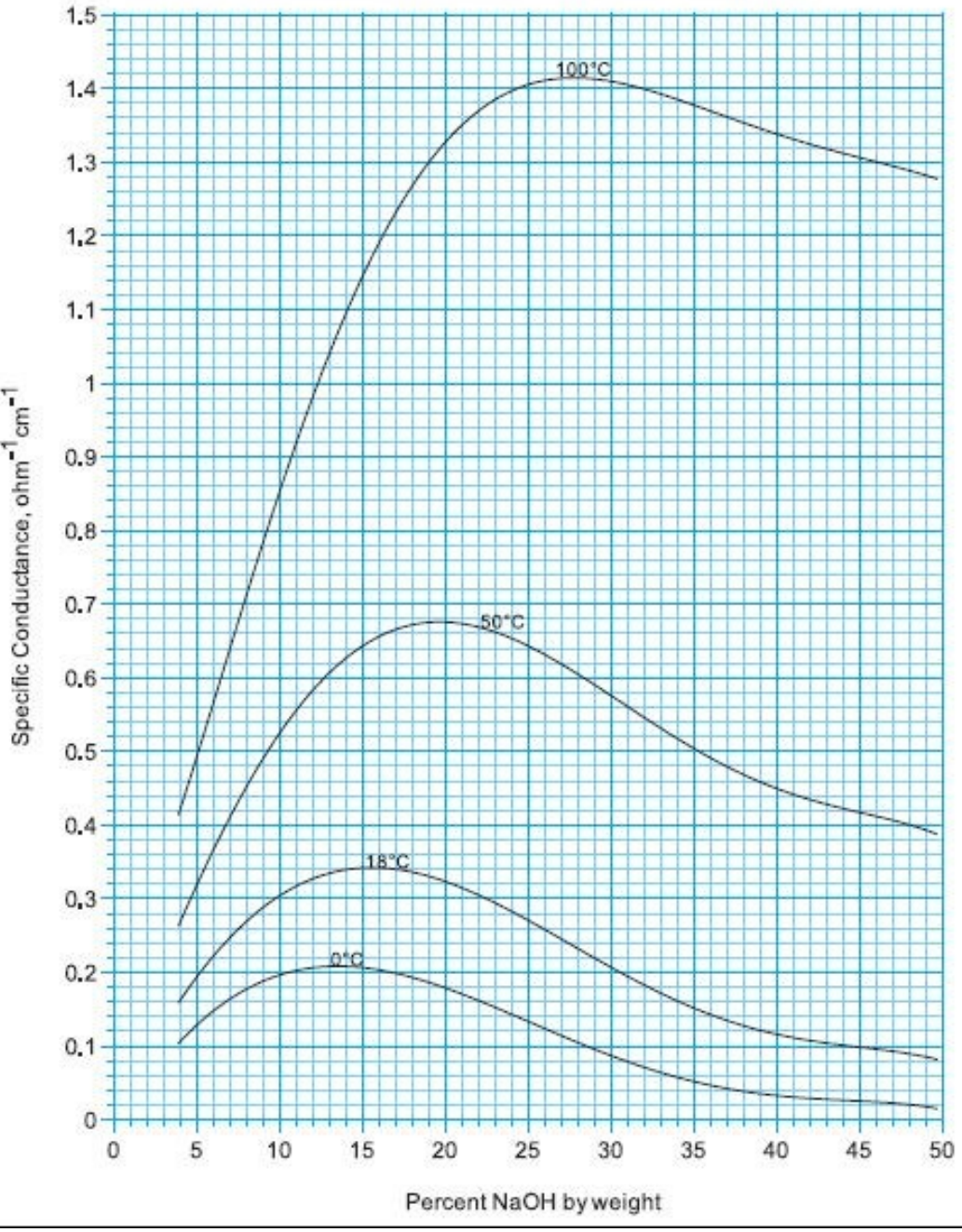


GRAPH 8
Thermal Conductivity of Aqueous Caustic Soda Solutions



Graph 9

Specific Conductance of Aqueous Caustic Soda Solutions



DILUTION CALCULATIONS

HOW TO DILUTE CAUSTIC SODA SOLUTIONS

Sometimes it is necessary to dilute caustic soda before it is used, or when the potential for freezing exists. A procedure for calculating the amount of concentrated caustic and water required is given below.

DILUTING A SOLUTION

Example: To dilute 3,000 gallons of 50% NaOH to a 20% solution. How much water is necessary to accomplish this task?

Solution: The dilution can be simplified by using the following formula:

D = V [A (B - C) / C] *where:*

A = Specific gravity of strong solution

B = Concentration of strong solution (%NaOH)

C = Concentration of desired solution(%NaOH)

D = Volume of water to be added

V = Volume of strong solution

(The specific gravity of 50% Diaphragm NaOH is 1.5372 taken from Table 2)

Therefore:

D = 3,000 [(1.5372 (50 - 20) / 20)]

D = 6,917 gallons

Result: It will take 6,917 gallons of water to dilute 3,000 gallons of 50% NaOH to a 20% solution.

VOLUME OF FINAL SOLUTION

It should be noted that when diluting caustic soda, volumes are not additive. Therefore, in the previous example, the final volume of the solution would not be 6,917 gallons of water + 3,000 gallons of 50% NaOH = 9,917 total gallons. The actual volume will be slightly less. To calculate the final volume, the water and caustic soda must be converted to a weight basis, and then divided by the density of the resulting solution.

DILUTION CALCULATIONS

DILUTION GRAPH

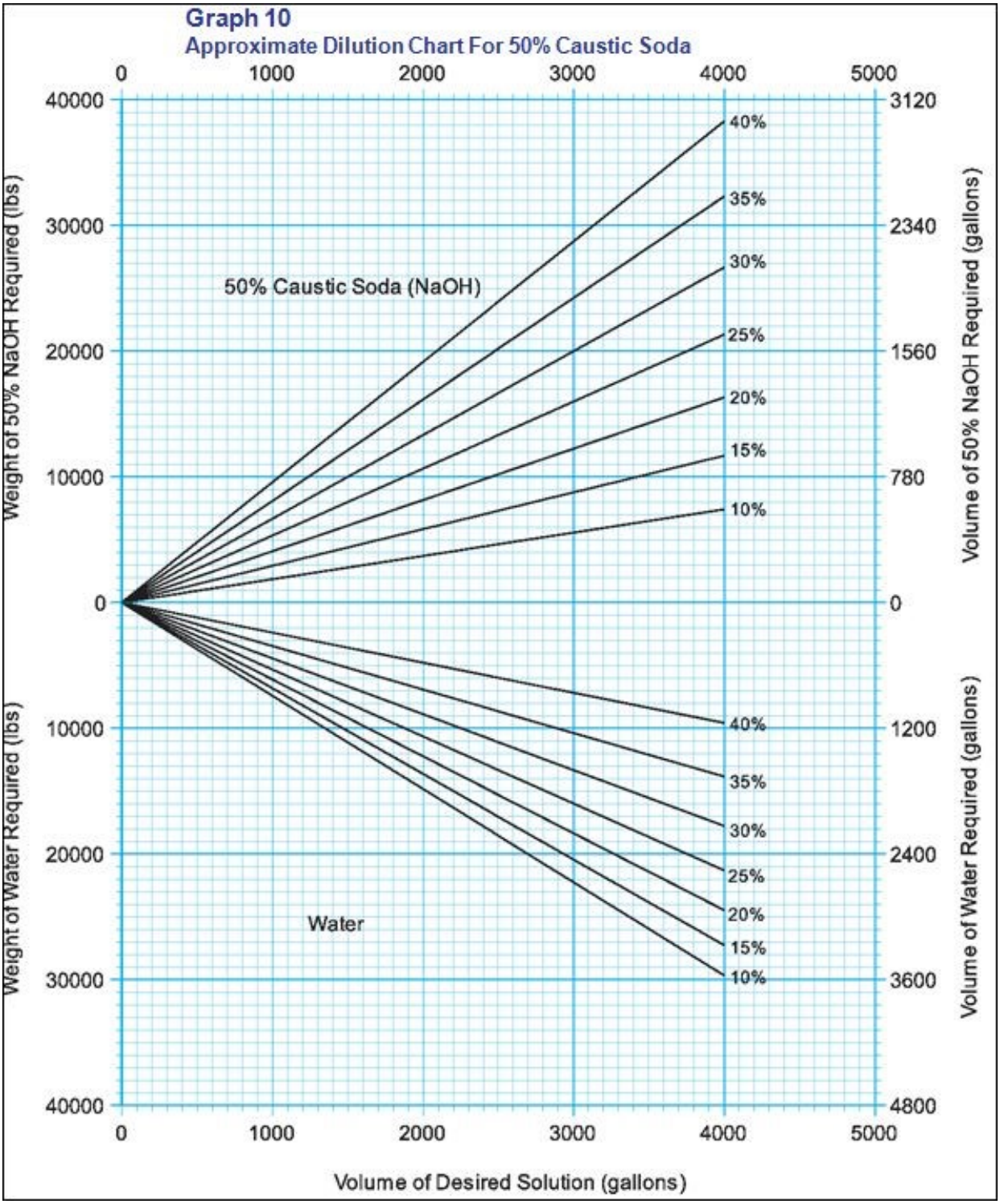
Graph 10 on the next page can also be used to determine approximate volumes of 50% NaOH and water necessary to achieve a particular dilution. For example, you want to produce 3,000 gallons of a 25% NaOH solution and want to know how much water and 50% NaOH are needed to accomplish this goal.

Using the chart, start on the bottom axis at the 3,000 gallon line. Proceed upward until you intersect the first 25% line on the bottom half of the graph. From the intersection point go to the right and left axes to determine the volume and weight of water needed. In this case the volume is read at 1,920 gallons and the weight at 16,000 pounds.

Then continue upward until you intersect the 25% line at the top of the graph. Again from the intersection point go to the left and right axes to determine the volume and weight of 50% NaOH needed. In this case the volume is read at 1,248 gallons and the weight at 16,000 pounds.

Therefore, it would take 1,248 gallons of 50% NaOH to be added to 1,920 gallons of water to produce 3,000 gallons of a 25% solution.

DILUTION CALCULATIONS



DETERMINATION OF THE TOTAL ALKALINITY OF CAUSTIC SODA

PURPOSE AND THEORY

The accurate determination of the total alkalinity value for caustic soda is important. It is used to calculate the weight of product shipped and ultimately the amount of money billed for the shipment.

Total alkalinity in caustic soda products is determined by titration of a sample with a standardized solution of 1N hydrochloric acid. Modified methyl orange indicator is used to determine the titration endpoint.

This procedure is based on ASTM E291-09, Standard Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash, sections 8 through 14.

APPARATUS

100 ml Buret; Class A Volumetric, Fisher Scientific Cat #: 03-775 or equivalent.

Analytical Balance; capable of weighing to 0.001 grams.

250 ml Erlenmeyer Flasks; wide mouth, Fisher Cat#: 10-090B or equivalent.

Magnetic Stirrer; Fisher Cat#: 14-493-120S or equivalent.

Magnetic stirring bars; 1 1/2” x 5/16” dia. Fisher Cat#: 14-511-64 or equivalent.

REAGENTS

1N Hydrochloric Acid; measure 83.0 ml of ACS Reagent grade concentrated hydrochloric acid into a graduated cylinder and transfer it to a one liter volumetric flask containing approximately 500 ml of deionized water. Dilute to volume with additional water, mix well and store in a tightly closed container. A prepared solution of 1N HCl can also be purchased (Fisher Scientific Cat# SA48-20 or equivalent). Hydrochloric Acid must be standardized to ±0.0001N before use.

Sodium Carbonate; anhydrous, volumetric grade (EM Science Cat#: 6394-2 or equivalent.) Dry at 250° C in a platinum or porcelain crucible for 4 hours. Store in a desiccator.

Modified methyl orange indicator; dissolve 0.14 grams of methyl orange (Fisher Cat#: M216- 25) and 0.12 grams of Xylene Cyanole FF (Fisher Cat#: BP565- 10) in deionized water and dilute to 100 ml.

Water, Deionized & Carbon Dioxide free; boil and cool the deionized water or purge it with nitrogen for two hours.

METHODS OF ANALYSIS

SAFETY

Refer to the SDS for the proper handling procedures for each of the chemicals listed in this procedure.

Caustic soda is a strong base. Hydrochloric acid is a strong acid. These chemicals are corrosive to body tissue and can cause immediate and severe burns to eyes. Wear proper gloves, proper eye protection and other protective clothing when handling these chemicals.

PROCEDURE

A. STANDARDIZATION OF 1N HYDROCHLORIC ACID

1. Weigh 4.2 grams of sodium carbonate to the nearest 0.0001 gram into a weighing dish. Carefully transfer to an Erlenmeyer flask. Add 75 ml of deionized water and swirl to dissolve. Add three drops of the modified methyl orange indicator and titrate with the HCl solution to a steel gray color change.
2. The following formula is used to calculate the normality of the HCl.

   Let:

   N = Normality of HCl
   W = Weight (g) of Na_2CO_3 used
   V = Volume (ml) of HCl required to endpoint. Milliequivalent weight of Na_2CO_3 = 0.053

   $N = W / V \times 0.053$

   Determine the normality by averaging the result of at least three titrations.

B. ANALYSIS

1. In a clean, dry Erlenmeyer flask, accurately weigh, to the nearest 0.001 grams, 6 to 7 grams of 50% NaOH. Weighing should be performed as rapidly as possible.
2. Immediately add 50 ml of deionized water, making sure the sides of the beaker are washed down.
3. Add 3 to 4 drops of modified methyl orange indicator and carefully add the magnetic stirring bar.
4. Titrate the sample to a steel gray color with 1N HCl. Samples should be titrated as soon as possible to avoid pick up of carbon dioxide from the air.
5. Record the volume of acid required to reach this color. Estimate the buret reading to the nearest 0.02 ml.

C. CALCULATIONS

The following are formulas used to calculate total alkalinity.

Let:

W = Weight (g) of sample titrated N = Normality of HCl
V = Volume (ml) of HCl required Milliequivalent wt. of Na_2O = 0.03099

$$\%Na_2O = \frac{(V)\ (N)\ (0.03099)(100)}{W}$$

%NaOH = 1.2907 (%Na2O)

EXAMPLE

6.530 grams of caustic soda required the addition of 81.77 ml of 1.0011N HCl to reach the modified methyl orange endpoint.

$$\%Na_2O = \frac{(V)\ (N)\ (0.03099)(100)}{W}$$

$$\%Na_2O = \frac{(81.77)\ (1.0011)\ (3.099)}{6.530}$$

$\%Na_2O$ = 38.85%

%NaOH = (1.2907) (38.85)

%NaOH = 50.14%

QUALITY ASSURANCE

With each batch of samples being analyzed, at least one of the samples should be analyzed in duplicate. On a regular basis, samples that have been previously analyzed for total alkalinity should be reanalyzed and the results compared.

Alkalinity values obtained for each sample should be compared with OxyChem specifications for that product. Hydrochloric acid should be restandardized at least monthly.

DETERMINATION OF SODIUM HYDROXIDE IN CAUSTIC SODA

PURPOSE AND THEORY

The sodium hydroxide content of caustic soda is determined by adding barium chloride to a prepared sample and titrating with 1 N HCl to the phenolphthalein end point. The results are reported as percent NaOH on a sample weight basis.

Even with the utmost care, the separate determination of total alkalinity (previous method) and hydroxide alkalinity often provides significant differences. This difference is then typically attributed to the presence of carbonate. It has been found that separate titrations for total alkalinity and hydroxide alkalinity, or dual end-point titrations that attempt to quantify total and hydroxide alkalinity in a single procedure, often provide results for carbonate that are many times higher than the actual carbonate content of the material.

Although the method for hydroxide alkalinity is included here, because the usual carbonate content of caustic soda is very low, we suggest the use of the method for total alkalinity alone. The carbonate content is typically as low as or lower than the measurement error inherent in the analytical methods. As an alternative, we suggest the use of the method for total alkalinity, the method for sodium carbonate determination (next method in this handbook), and a calculation for hydroxide alkalinity as shown in ASTM E291-09, Standard Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash, section 12.

APPARATUS

100 ml Buret*;* Class A Volumetric, Fisher Scientific Cat #: 03-775 or equivalent.

Analytical Balance; capable of weighing to 0.001 grams.

250 ml Erlenmeyer Flasks; wide mouth, Fisher Cat#:10-090B or equivalent.

Magnetic Stirrer; Fisher Cat#: 14- 493-120S or equivalent.

Magnetic stirring bars; 1-1/2” x 5/16” dia. Fisher Cat#: 14-511-64 or equivalent.

REAGENTS

1N Hydrochloric Acid; the preparation of this reagent is described in the method for: “Determination of Total Alkalinity”.

1% Phenolphthalein Indicator; dissolve one gram of phenolph-thalein (Aldrich Cat#: 10,594-5 or equivalent) in 100 ml of methanol.

10% Barium Chloride; Dissolve 120 g of reagent grade BaCl2.2H2O (Fisher Cat#: B34-500) in 880 ml of deionized water.

Water, Deionized & Carbon Dioxide free; boil and cool the deionized water or purge it with nitrogen for two hours.

METHODS OF ANALYSIS

SAFETY

Refer to the SDS for the proper handling procedures for each of the chemicals listed in this procedure. Caustic soda is a strong base. Hydrochloric acid is a strong acid. These chemicals are corrosive to body tissue and can cause immediate and severe burns to eyes. Wear proper gloves, proper eye protection and other protective clothing when handling these chemicals. Barium chloride is highly toxic. Avoid inhaling barium chloride dust.

PROCEDURE

STANDARDIZATION OF 1N HYDROCHLORIC ACID

Standardization procedure is described in the method for: “Determination of Total Alkalinity”.

ANALYSIS

1. In a clean, dry Erlenmeyer flask, accurately weigh, to the nearest 0.001 grams, 6 to 7 grams of 50 NaOH. Weighing should be performed as rapidly as possible.
2. Immediately add 100 ml of barium chloride solution, making sure the sides of the beaker are washed down.
3. Add 3 to 4 drops of phenolphthalein indicator and carefully add the magnetic stirring bar.
4. Titrate the sample with 1N HCl until the pink color changes to water white. The sample should be titrated as soon as possible to avoid pick up of carbon diox-ide from the air.
5. Record the volume of acid required to reach this color, estimating the buret reading to the nearest 0.02 ml.

CALCULATIONS

The following are formulas used to calculate %NaOH.

Let:

W = Weight (g) of sample titrated
N = Normality of HCl
V = Volume (ml) of HCl required Milliequivalent wt. of NaOH = 0.04000

$$\%NaOH = \frac{(V)\,(N)\,(0.04000)\,(100)}{W}$$

EXAMPLE

6.467 grams of caustic soda required the addition of 80.85 ml of 1.0020N HCl to reach the phenolphthalein endpoint.

$$\%NaOH = \frac{(V)\,(N)\,(0.04000)\,(100)}{W}$$

$$\%NaOH = \frac{(80.85)\,(1.0020)\,(4.000)}{6.467}$$

%NaOH = 50.11%

METHODS OF ANALYSIS

QUALITY ASSURANCE

For each batch of samples being analyzed, at least one of the samples should be analyzed in duplicate. On a regular basis, samples that have been previously analyzed for total alkalinity should be reanalyzed and the results compared. Alkalinity values obtained for each sample should be compared with OxyChem specifications.

Hydrochloric acid should be restandardized at least monthly.

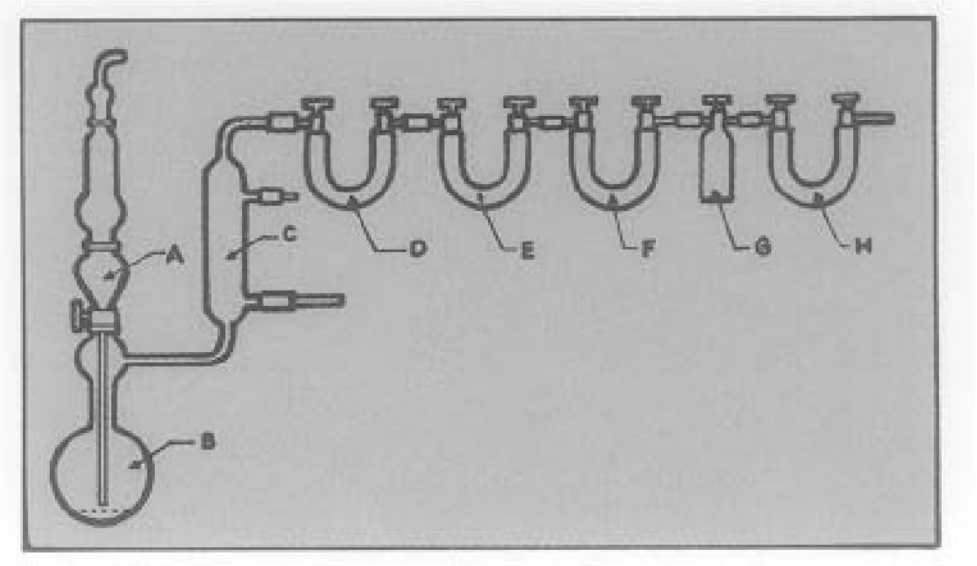
DETERMINATION OF SODIUM CARBONATE IN CAUSTIC SODA (Gravimetric)

PURPOSE AND THEORY

The sodium carbonate content of a sample of caustic soda is determined by a direct gravimetric method. The method involves acidification of the caustic soda sample with dilute sulfuric acid, boiling, and weighing the carbon dioxide evolved. Accurate results can be obtained when the sodium carbonate content is 0.01% or greater. This method should be used to analyze samples of liquid caustic soda containing 0.01% to 0.25% Na_2CO_3.

This procedure is based on ASTM E291-09, Standard Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash, sections 25 through 33. Although it is included as a reference for anyone who may wish to perform the analysis, it should be noted that the procedure is rather lengthy, may show poor precision and is susceptible to error because of air intrusion into the apparatus.

OxyChem typically utilizes a carbon analyzer in inorganic mode for the rapid and precise determination of carbonate content of caustic soda. For further information regarding the carbon analyzer method, please contact Technical Service.



METHODS OF ANALYSIS

APPARATUS

See the CO_2 train sketch on the previous page. Air for sweep is drawn in through "A." This air must be scrubbed free of CO_2. The ground-glass jointed tube fitted into the top of "A" should be packed with 8-20 mesh ascarite with a layer of anhydrous granular copper sulfate on top.

U-tube "D"
Add a few glass beads and 5 to 10 ml of concentrated H_2SO_4. The acid takes up the bulk of the moisture passing through condenser "C" and should be changed often depending on frequency of use.

U-tube "E"
Pack with dehydrated copper sulfate pumice. This packing material is prepared by soaking pulverized pumice having the grain size of wheat in saturated copper sulfate solution drying at 150-180°F. The product must be kept in a well stoppered bottle.

U-tube "F"
Pack with anhydrous magnesium perchlorate. This removes all final traces of moisture carried through the system.

Ascarite - Absorbing Tower "G"
Pack inside tube with 8-20 mesh ascarite. Over the top layer add about 0.25 inch of magnesium pechlorate and cover with absorbent cotton. The cotton will prevent loss of weight due to carry-over of dust particles. After tower is packed, it should be hooked into the system and swept with CO2-free air for a period of 15 to 20 minutes.

U-Tube "H"
Pack with 8-20 mesh ascarite.

REAGENTS

Sulfuric Acid; 12 N with 27.8 g. $FeSO_4.7H_2O$ per liter.

Sulfuric Acid, concentrated.

Ascarite II; 8-20 mesh (sodium hydroxide coated silica.)

Magnesium Perchlorate, anhydrous.

Copper (II) Sulfate, anhydrous. Water, Deionized & Carbon Dioxide free; boil and cool the deionized water or purge it with nitrogen for two hours.

SAFETY

Caustic soda as dust or mist is intensely irritating to the respiratory system, skin, and eyes. Become familiar with the first aid measures recommended in this handbook.

When preparing 12 N sulfuric acid, the concentrated acid must be poured slowly into water with constant stirring.

Wear safety glasses with side shields when handling caustic soda samples or acid solutions.

METHODS OF ANALYSIS

PROCEDURE

1. Sample Preparation

50% liquid caustic soda will solidify at 54°F. If the sample is solidified at the time of analysis, it may be thawed out by placing the container in hot water until no solids are present. The lip of the bottle may be wiped before the sample is poured into a weighing bottle.

Carbonate and moisture pickup should be avoided by rapid sample handling.

In all cases, samples for carbonate analysis should be the first taken from the sample bottle to minimize carbon dioxide pickup from the atmosphere.

2. Analysis

The train must be conditioned daily before any samples are run. This is done by making a regular determination using a sample that contains carbonate. Following this, a blank should be run on the train to make sure that the train is leak free. This is done by making a regular determination but omitting the sample. If the ascarite weighing tower gains more than 0.2 mg in weight during the blank run, the train probably has a leak.

After the train has been conditioned and found to be leak free, the samples are run as follows:

1. Two absorbing towers (G) must be conditioned and weighed prior to analysis. These will be called G1 and G2 in the procedure. The use of two towers will enable the analyst to conserve time when performing more than one analysis.
2. Weigh a sample of at least 20g. (50% basis) or large enough to contain 5 mg of CO2 into a flask “B” using an analytical balance. Add 4 or 5 glass beads and 80 ml of CO2-free deionized water and immediately place the flask into its proper position in the train.
3. Add 50 ml of 12 N sulfuric acid to funnel “A.”
4. Place tared tower G1 between U-tubes “F” and “H.”
5. Open the system starting at U-tube “H” and working back to “D.”
6. Open cock on funnel “A” and allow acid to run into flask “B” and immediately hook vacuum line to tube “H.” Adjust the flow of air to 4 bubbles per second through the tip of the stem of funnel “A.”
7. Apply heat to flask “B” and bring to a boil. Hold “B” contents to boiling point for 3 minutes and remove heat.
8. Sweep the system for 20 minutes. While this is being done, the next sample can be weighed into another flask (B), and the beads and distilled water added. This flask is then stoppered and set aside until needed.
9. At the end of 20 minutes, the vacuum line is removed tower G1 is shut off and removed and tower G2 placed into position. The cock on funnel “A” is closed and 50 ml of 12 N sulfuric acid is again added to funnel “A”.
10. Flask “B” is removed, the stem of funnel “A” is washed down with deionized water and the new sample is placed into position.
11. Tower G2 is opened and the pro-cedure is repeated beginning at Step 6.
12. When G1 is removed from the train, a period of 20 minutes will condition the sample for weighing. During this 20 minute sweep time, another sample is prepared and tower G1 is reweighed in order to determine the weight of CO_2 found in the first sample. Tower G1 is then ready for Run No. 3.

CALCULATIONS

Report results as percent Na_2CO_3 calculated to the nearest 0.01.

Let:

$W(CO_2)$ = Weight of CO_2 evolved

W(S) = Weight of Sample

$$\%Na_2CO_3 = \frac{W(CO_2)\ (2.409)\ (100)}{W(S)}$$

Note: Molecular weight of Na_2CO_3 / Molecular weight of CO_2 = 106 / 44 = 2.409

EXAMPLE

If a 25 gram sample was used and 0.0125 gram of CO_2 was absorbed in tower "G", then:

$$\%Na_2CO_3 = \frac{(0.0125)\ (2.409)\ (100)}{25}$$

$\%Na_2CO_3 = 0.12\%$

DETERMINATION OF SODIUM CHLORIDE IN CAUSTIC SODA

PURPOSE AND THEORY

Chloride is a contaminant in all grades of caustic soda. Sodium chloride is present at <100 ppm in 50% membrane caustic soda and at approximately 1% in 50% diaphragm caustic soda. Higher concentrations of this compound can have undesirable effects in many applications of the product. Consequently, accurate determination of this impurity is most impor-tant.

When acid solutions of silver ion and an alkali thiocyanate are mixed in the presence of a ferric salt, the thiocyanate has a selective action toward silver, resulting in the formation of silver thiocyanate. Any excess of thiocyanate not required by the silver reacts with ferric salt to form reddish-brown ferric thiocyanate. This color indicates the completion of the reaction.

An excess of silver nitrate and the ferric indicator is added to a sample of caustic soda that has been acidified with nitric acid. Any chloride that is contained in the sample will react with the silver nitrate to form a silver chloride precipitate. The silver nitrate that is remaining in the sample solution after this reaction is titrated with a standardized solution of ammonium thiocyanate. The equations involved are:

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

Excess $AgNO_3 + NH_4CNS \rightarrow AgCNS + NH_4NO_3$

$6NH_4CNS + Fe_2(SO_4)_3 \rightarrow 2Fe(CNS)_3 + 3(NH4)_2SO_4$ (reddish brown color)

This procedure is based on ASTM E291-09, Standard Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash, sections 34 through 40.

OxyChem typically utilizes turbidimetric determination, potentiometric titration (similar to ASTM E291-09, sections 41 through 47, with modifications to account for the low chloride content of membrane grade caustic soda) or ion chromatography. For further information regarding any of these methodologies, please contact Technical Service.

APPARATUS

25ml Buret; Class A Volumetric, Fisher Scientific Cat#:03-724-10A or equivalent.

20ml Pipet; Class A Volumetric, Fisher Cat#: 13-650-2N

500ml Erlenmeyer flasks; wide mouth, Fisher Cat#: 10-090C or equivalent.

Magnetic stirrer; Fisher Cat#:14- 493-120S or equivalent.

Magnetic stirring bars; 1 1/2” x 5/16” dia, Fisher Cat#: 14-511-64 or equivalent.

Analytical Balance; capable of weighing to 0.001 grams

METHODS OF ANALYSIS

REAGENTS

Water, Deionized.

0.1N Silver Nitrate; accurately weigh 16.99 grams of ACS

Reagent grade silver nitrate (dried at 110°C for 1 hr) and transfer to a 1L volumetric flask. Dilute to volume with deionized water, mix well and store in a tightly closed amber container. Silver nitrate and its aqueous solutions are photo-decomposed by light and should be stored in a dark place.

0.1N Ammonium Thiocyanate; accurately weigh 7.612 grams of ACS Reagent grade ammonium thiocyanate and transfer to a one liter volumetric flask. Dilute to volume with deionized water, mix well and store in a tightly stoppered glass bottle. The thiocyanate solution must be standardized to within ±0.0001N prior to use.

Ferric Indicator; prepare a saturated aqueous solution of ferric ammonium sulfate [$FeNH_4(SO_4)2$], Aldrich Cat# 22,126-0 or equivalent.

1% Phenolphthalein Indicator; dissolve one gram of phenolphthalein (Aldrich Cat#: 10,594-5 or equivalent) in 100 ml of methanol.

Nitric Acid, 1:1 (v/v); slowly pour 500 ml of ACS Reagent grade nitric acid in 500 ml of deionized water as it is stirring. Allow the solution to cool.

SAFETY

Refer to the SDS for the proper handling procedures for each of the chemicals listed in this method.

Caustic soda is a strong base and nitric acid is a strong acid. These chemicals are corrosive to body tissue and can cause immediate and severe burns to eyes. Wear proper gloves, proper eye protection and other protective clothing when handling these chemicals.

Silver Nitrate is a strong oxidizing agent. Wear rubber gloves when handling. Contact with skin causes a black discoloration. Keep away from heat, sparks and open flames.

PROCEDURE

A. STANDARDIZATION OF 0.1N SILVER NITRATE

Since this procedure determines the chloride content of a sample by comparing the amount of unreacted silver nitrate remaining in a sample with the amount that is remaining in a reagent blank, the exact normality of the silver nitrate need not be known. If a reagent blank is not used, silver nitrate standardization is essential. A manual titration method is described in “ASTM Standard Practice for Preparation, Standardization and Storage of Standard Solutions for Chemical Analysis”, Vol 15.05; E200-91, 44- 48.

B. STANDARDIZATION OF 0.1N AMMONIUM THIOCYANATE

1. Use a volumetric pipet to transfer 20.00 ml of freshly standardized 0.1 N silver nitrate into a 250 ml Erlenmeyer flask containing 50 ml deionized water, 5 ml of 1:1 nitric acid and 1 ml of ferric indicator. Titrate the AgNO3 with the NH4SCN solution until the first permanent reddish-brown color appears and persists after vigorous shaking for 15 seconds. Record the volume of NH4SCN required. Repeat the above procedure on at least three more solutions of silver nitrate.

2. Use the following formula to calculate the normality of the ammonium thiocyanate solution:

   N1 = (N2) (V2) / (V1)

   where:

   N1 = Normality of NH_4SCN
   N2 = Normality of $AgNO_3$
   V1 = Volume of NH_4SCN required
   V2 = Volume of $AgNO_3$ added

3. Determine the normality by averaging the results of at least three titrations.

C. PROCEDURE

1. In a clean dry Erlenmeyer flask, accurately weigh, to the nearest 0.001 g for smaller samples and 0.01 g for larger samples, an amount of product as determined in the following table. Weighing should be performed as rapidly as possible.

   SAMPLE SIZE FOR CHLORIDE ANALYSIS

Product	Sample size
50% Diaphragm grade	6g
50% Membrane grade	80g

2. Immediately add 100 ml of deionized water, making sure the sides of the beaker are washed down.

3. Add 2 drops of 1% phenolphthalein indicator and carefully neutralize the sample with 1:1 nitric acid.

   Caution: The sample solutions generate considerable heat when being neutralized with acid. The flask should be continuously cooled in an ice bath while the acid is slowly added. After the phenolphthalein endpoint has been reached (color changes from pink to colorless), add an additional 5.0 ml of acid.

4. Allow the solution to cool to room temperature and add a stirring bar to the flask.

5. Using a volumetric pipet add 20.00 ml of 0.1N silver nitrate, also add approximately 1 ml of the ferric indicator solution.

   Note: Sample solutions should be titrated within several minutes of adding the silver nitrate. The silver chloride has a tendency to decompose with exposure to light giving the solution a purplish color. This color can interfere with an accurate determination of the endpoint color change.

6. Prepare a reagent blank by adding two drops of phenolphthalein, 5ml nitric acid, 20.00 ml silver nitrate solution and 1ml of ferric indicator to a flask containing 100 ml of deionized water and a stirring bar.

7. Place the flask containing the reagent blank on a magnetic stirrer and titrate the solution with 0.1N ammonium thiocyanate until a reddish-brown color persists for at least 15 seconds. Record the volume of NH4SCN required to reach the color change.

   Note: From the outset of the back-titration with ammonium thiocyanate, an appreciable quantity of silver ions are absorbed on the surface of the precipitates. Because of this, there is a tendency for a premature appearance of the endpoint color. Vigorous stirring or shaking of the solution is essential to bring about desorption of silver ions from the precipitates so they can react with the thiocyanate.

8. Titrate the sample solution with 0.1N ammonium thiocyanate until the same color change is reached and record the volume of NH_4SCN.

   Note: As the endpoint is approached, increasing amounts of silver thiocyanate precipitating out of solution will actually increase the solubility of silver chloride. Silver chloride that has precipitated will redissolve, allowing additional silver ions to react with the thiocyanate. This causes a fading endpoint and results in low chloride values. For samples containing concentrations of chloride greater than 0.01%, it is advisable to filter the sample solution through semi-quantitative paper after the addition of silver nitrate but prior to titration with thiocyanate. Removing most of this precipitate will greatly decrease the amount of silver that can be redissolved during the titration.

   Note: The white precipitate of silver thiocyanate interferes with observation of the color change at the titration endpoint. It is sometimes helpful to stop the stirring or shaking of the sample and allow the precipitate to settle, in order to observe the color of the sample solution. If it is determined during this observation that the endpoint has not yet been reached, resume vigorous stirring before addition of more NH_4SCN.

D. CALCULATIONS

The following is the formula is used to calculate the percent chloride in the sample.

Let:

W = Weight of sample titrated
N = Normality of NH_4SCN
V1 = Volume of NH_4SCN required to titrate blank
V2 = Volume of NH_4SCN required to titrate sample
Milliequivalent wt. of Cl = 0.03545

$$\%Cl = \frac{(V1-V2)\,(N)\,(0.03545)\,(100)}{W}$$

Calculate the percentage of sodium chloride as follows:

%NaCl = (%Cl) (1.6485)

EXAMPLE

79.28 grams of 50% Membrane grade caustic soda required the addition of 19.54 ml of 0.1005 N NH_4SCN to reach the titration end-point while the reagent blank required 19.95 ml of NH4SCN to reach the same endpoint.

$$\%Cl = \frac{(V1-V2)\,(N)\,(0.03545)\,(100)}{W}$$

$$\%Cl = \frac{(19.95-19.54)\,(0.1005)\,(3.545)}{79.28}$$

%Cl = 0.00180

%NaCl = (%Cl)(1.6485)

%NaCl = (0.00180) (1.6485)

%NaCl = 0.0030% or 30 ppm

QUALITY ASSURANCE

Because of difficulties in determining the exact endpoint when using this method, only skilled laboratory personnel should attempt to perform these titrations.

On a regular basis, samples that have been previously analyzed for chloride content should be reanalyzed and the results compared.

Chloride values should be checked against OxyChem specifications.

DETERMINATION OF IRON IN CAUSTIC SODA

PURPOSE AND THEORY

Iron can result from contamination during storage or transport of the product. Since iron is often detrimental to the end use of the product, accurate quantitation of this element is essential.

Caustic soda is neutralized with hydrochloric acid and the resulting solution buffered with sodium acetate. Hydroxylamine hydrochloride reduces any iron present in the ferric state to the ferrous state. o-Phenanthroline (1,10-Phenanthroline Monohydrate) forms an orange-red complex with ferrous iron. The intensity of the color is proportional to the amount of iron present. By measuring the color intensity with a spectrophotometer, the concentration of iron in a sample of caustic soda can be determined.

This procedure is based on ASTM E291-09, Standard Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash, Sections 56 through 64.

APPARATUS

Visible Spectrophotometer: able to measure absorbance or percent transmittance at 510 nanometers.

Analytical Balance: capable of reading to 0.01 grams.

Volumetric Flask, 1 L, class A: Fisher catalog # 10-210-8G or equivalent

Volumetric Flask, 100 ml, class A: Fisher catalog # 10-210-8C or equivalent

Pipets, Volumetric, Class B:

1 ml - Fisher catalog # 13-650B or equivalent
2 ml - Fisher catalog # 13-650C or equivalent
5 ml - Fisher catalog # 13-650F or equivalent
10 ml - Fisher catalog # 13-650L or equivalent
15 ml - Fisher catalog # 13-650M or equivalent

Indicator Paper, Hydrion, pH 3.0 to 5.5: Fisher catalog # 14-853-70 or equivalent)

Disposable plastic pipets ("Dispo-pipet")

Cuvettes, quartz: appropriate to the spectrophotometer in use, 25 mm diameter is typical but other path lengths providing detection limits suitable for the user are acceptable.

METHODS OF ANALYSIS

REAGENTS

Deionized Water

Hydrochloric Acid, concentrated: reagent grade, Fisher catalog # A144 or equivalent

Sodium Acetate, 164 grams per liter: weigh 164.0 (+/- 0.1) grams of sodium acetate, Fisher catalog # S210-500 or equivalent, dissolve and dilute to 1 liter with deionized water in a 1 liter volumetric flask

Hydroxylamine Hydrochloride, 100 grams per liter: weigh 100.0 (+/- 0.1) grams of hydroxylamine hydrochloride, Fisher catalog # H330-500 or equivalent, dissolve and dilute to 1 liter with deionized water in a 1 liter volumetric flask.

o-Phenanthroline, 0.25 %: weigh 2.50 (+/- 0.05) grams of 1,10-Phenanthroline Monohydrate, Fisher catalog # P70-10 or equivalent, dissolve and dilute to 1 liter with deionized water in a 1 liter volumetric flask

1000 µg/ml Iron Standard, suit-able for ICP/AA, Spex standard available from Fisher as catalog # PLFE2-2Y or equivalent

SAFETY

Refer to the SDS for the proper handling procedures for each of the chemicals listed in this procedure.

Caustic soda is a strong base. Hydrochloric acid is a strong acid. The Iron Reference Solution is acidified with HCl. All of these chemicals are corrosive to body tissue and can cause immediate and severe burns to eyes. Wear proper gloves, proper eye protection and other protective clothing when handling these materials.

Refer to instrument manual for the proper use of equipment described in this method.

PROCEDURE

A. SAMPLE ANALYSIS

1. Weigh the appropriate sample, based on the table below, into a clean 100 ml volumetric flask. Record the sample weight.

   SAMPLE SIZE

Product	Sample size
50% diaphragm grade	5-10g
50% membrane grade	15-20g

2. Add deionized water to the flask, such that the flask is slightly less than half-full, and swirl to mix the solution.

3. SLOWLY and CAREFULLY, add concentrated hydrochloric acid to the flask while constantly swirling the flask. Continue to add until the solution is just acidic. Check the pH by dipping a clean glass rod into the flask and touching the rod to the pH indicator paper. If acidic, the paper will turn red. If it is still basic, the paper will be blue. (If another type of indicator paper is used, verify the appropriate colors for the paper you are using.)

   CAUTION: This is a reaction involving a strong base and a strong acid. Be sure to add the acid slowly and to maintain swirling so that spattering does not occur. The solution and flask will become quite

4. If additional samples are to be analyzed, repeat steps 1 to 3 above for each sample.
5. Prepare a blank by adding about 40 ml of deionized water and about 2 ml of concentrated hydrochloric acid to a separate, clean 100 ml volumetric flask.
6. Using a dispo-pipet, add sufficient sodium acetate solution to the flasks (the samples and the blank) to buffer the solution to pH 3.5 +/- 0.5 pH units. Check the pH by dipping a clean glass rod into the flask and touching the rod to the pH indicator paper. At the proper pH, the paper will have a light green color. (If another type of indicator paper is used, verify the appropriate color for the paper you are using.)
7. Pipet 5 ml of hydroxylamine hydrochloride solution to each flask.
8. Pipet 5 ml of o-Phenanthroline solution to each flask.
9. Fill the flasks to volume with deionized water and shake well to mix. Allow a minimum of 15 minutes for color development but complete the reading of the samples within 30 minutes.
10. Rinse a clean cuvette twice with small portions of the blank solution. Then fill the cuvette with the blank solution. Assure that there are no bubbles present and wipe off the outside of the cuvette with a soft, lint-free tissue. Place the cuvette into the spectrophotometer and zero the instrument at 0 (zero) absorbance (A) or 100% transmittance (T). Operate the spectrophotometer as directed in your instrument manual. Remove the cuvette from the instrument.
11. Fill a cuvette with the sample solution and load it into the spectrophotometer in the same fashion as described in step 9 above. Record the instrument reading as either A or T, depending upon how your calibration curve was constructed. (See section C below.)

B. QUALITY CONTROL

1. Perform a duplicate analysis with each batch of samples. Simply repeat the Sample Analysis in section A above using an additional aliquot of a sample. If large numbers of samples are tested, it is suggested that a duplicate analysis is performed on one of every ten samples.
2. Perform a sample spike analysis with each batch of samples. To do so, prepare a second aliquot of a sample as directed in steps 1 and 2 of the Sample Analysis in section A above. Then pipet 2 ml of the 10 pg/ml iron stock standard (see step 1 in section C below) into the flask. Complete the sample preparation as described in the remaining steps of section A. This procedure provides about a 1 (one) pg/g (1 ppm) spike for membrane caustic soda or about a 2 to 4 pg/g (2 to 4 ppm) spike for diaphragm caustic soda. Different spike levels may be obtained by adding more or less of the iron stock standard or using different iron concentration solutions.
3. The relative percent difference between duplicates should be no more than 20%.
4. The spike recovery should be in the 80% to 120% range.

METHODS OF ANALYSIS

C. SPECTROPHOTOMETER CALIBRATION

1. Prepare a stock 10 pg/ml iron standard by pipetting 1 ml of the 1000 pg/ml iron standard to a 100 ml volumetric flask and diluting to volume with deionized water.
2. Obtain six 100 ml volumetric flasks and label them as 'Blank', '10 pg', '20 pg', '50 pg', '100 pg' and '150 pg'. To each of these, add about 25 ml of deionized water and 2 ml of concentrated hydrochloric acid.
3. Pipet 1 ml of the 10 pg/ml iron stock standard (prepared in step 1 above) to the flask labeled '10 pg'. Similarly, pipet 2 ml of the iron stock to the flask labeled '20 pg', 5 ml to the flask labeled '50 pg', 10 ml to the flask labeled '100 pg', and 15 ml to the flask labeled '150 pg'.
4. Complete the preparation and reading of the standards by following steps 6 through 11 in section A above.
5. Many spectrophotometers will allow storing the calibration curve directly on the instrument. If this is not the case, you may wish to use a least squares regression analysis to store the calibration on a calculator or PC program. Finally, calibration curves may be drawn manually using normal graph paper if plotting concentration vs. absorbance (A) or semi-log paper if plotting concentration (linear axis) vs. transmittance (T - log axis).

CALCULATION

Calculate the ppm iron by dividing the micrograms of iron found from the calibration curve (C) by the sample weight (W):

$$ppm\ Fe = C / W$$

DETERMINATION OF OTHER ELEMENTS IN CAUSTIC SODA

OxyChem typically utilizes inductively Coupled Argon Plasma-Atomic Emission Spectroscopy (ICAP-AES) for the analysis of metals or elements in caustic soda.

Hydride Generation Atomic Absorption (HG-AA) is used for the determination of antimony, arsenic and bismuth in order to obtain lower detection limits than are achievable via ICAP-AES.

For the determination of mercury, an automated cold vapor atomic absorption (CVAA) method, based on EPA Method 245.1 and ASTM E538, is utilized.

Note: OxyChem is a mercury-free producer of caustic soda and caustic potash. OxyChem last used mercury cells in 2008, becoming the first mercury-free producer of caustic potash in North America. OxyChem was already a mercury-free producer of caustic soda before 2008.

Since the operation of these instruments varies from manufacturer to manufacturer, a specific method is not included here. Follow your instrument manufacturer's instructions and recommendations for performing analysis of this type.

IMPORTANT!!!

Regardless of the brand of instrument, it is necessary to keep in mind that calibration standards must be similar to the sample being analyzed if results are to be considered accurate.

Caustic soda will form a significant amount of salt when neutralized; for example, sodium chloride if neutralized with hydrochloric acid or sodium nitrate if neutralized with nitric acid. Since the sample contains a high amount of dissolved solids, calibration standards must be prepared in a similar matrix or sample results will be in error.

One means of addressing this is to prepare standards containing the same amount of dissolved salt that a sample would contain. This requires obtaining high purity salts, which can be quite costly. Another more economical means of accomplishing the "matrix match" is to use calibration by standard addition.

In general, analytical results obtained for elements in caustic soda will be significantly higher than the actual values if the samples are analyzed using a calibration based on "clean" aqueous standards as might be used for water analysis.

BILLING FOR LIQUID CAUSTIC SODA

Caustic soda solutions are billed on a basis that is standard to the industry. They are billed by the dry ton based on NaOH being 76% Na_2O.

Example: A customer orders a truck of 50% NaOH. The net weight was 45,160 pounds. The total alkalinity as Na_2O from the COA is 38.53%. Also referred to as the test factor on the invoice. The Billing Price is $551.77/DT.

1. Billing Weight in Dry Ton (DT):

$$\frac{45{,}160 \text{ lb}}{2{,}000 \text{ lb/ton}} \times \frac{38.53\% \ Na_2O}{76\% \ Na_2O} = 11.447 \text{ DT NaOH}$$

2. Invoice Amount:

11.447 DT NaOH × $551.77/DT = $6,316.11

HISTORY OF THE 76% Na_2O BASIS FOR BILLING CAUSTIC SODA

Lye was first produced by reacting soda ash with lime.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

Soda Ash	Lime	Lye	Calcium Carbonate

The soda ash industry used alkalinity reported as Na_2O to express concentration. Alkalinity is a measure of the amount of acid a solution can neutralize. The lye industry adopted using alkalinity reported as Na_2O to express concentration, so it could be directly compared to soda ash.

$$Na_2CO_3 \rightarrow Na_2O + CO_2$$

$$2NaOH \rightarrow Na_2O + H_2O \text{ (eq.1)}$$

Lye was sold dry and at best was 98% pure, which equated to an alkalinity of 76% (77.48 × 98% ≈ 76). So instead of caustic soda being 77.48% Na_2O, 76% Na_2O became the basis.

Note: Per eq.1 above it take two moles of NaOH to make one mole Na_2O, therefore 80 pounds of NaOH (2 × 40.00 = 80.00) will make 61.98 pounds of Na_2O or NaOH is 77.48% Na_2O (61.98 / 80.00 × 100 = 77.48%).

The molecular weight of NaOH and Na_2O is 40.00 and 61.98 lb/mole, respectively.

NOTES

® Teflon is a registered trademark of DuPont de Nemours.

® Hastelloy is a registered trademark of Haynes International.

® Inconel is a registered trademark of Inco Limited.

® Monel is a registered trademark of Inco Limited.

BIBLIOGRAPHY

Cell diagrams (page 7 & 9) courtesy of www.eurochlor.org

Other pictures courtesy of www.oxychem.com

OXYCHEM

14555 Dallas Parkway
Suite 400
Dallas, Texas 75254

Technical Service
1-800-733-1165 option 2