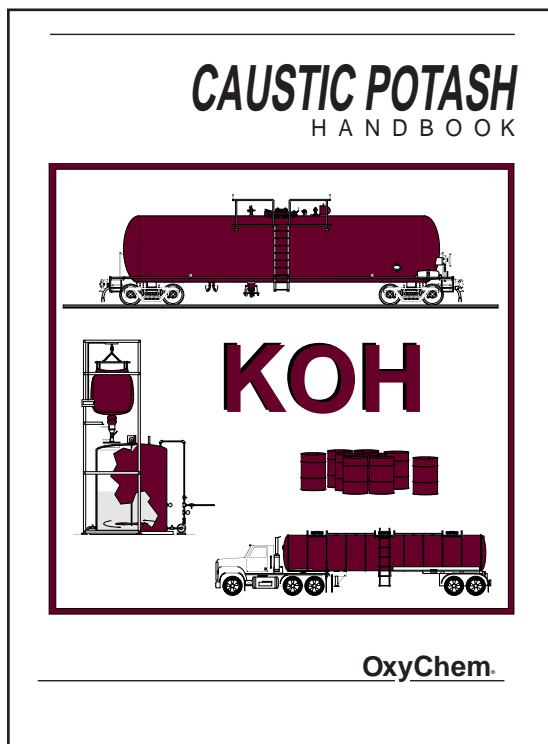


OxyChem Caustic Potash Handbook

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Forward

This handbook details methods for handling, storing, preparing and using caustic potash. It includes information on the manufacture, physical properties and analytical methods for testing caustic potash.

Additional information and contacts can be found on the internet at www.oxychem.com

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Introduction

Caustic potash is manufactured by the electrolysis of potassium chloride brine in either a mercury amalgam or membrane electrolytic cell. The co-products are chlorine and hydrogen.

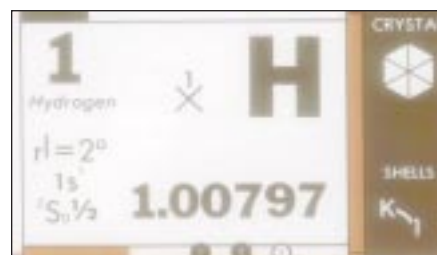
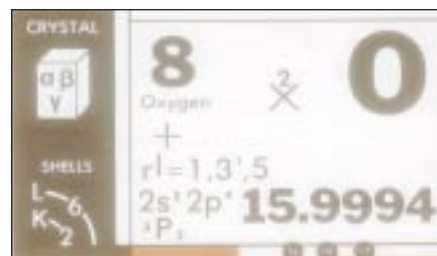
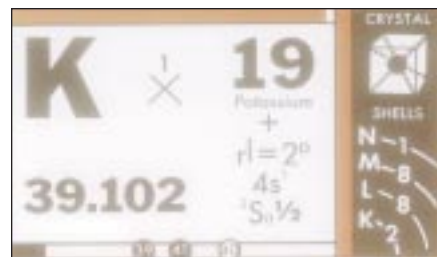
The largest users of caustic potash are the soap and detergent, fertilizer, and chemical industries. Minor uses for caustic potash are molten salts, dyes, pharmaceuticals, and photographic chemicals.

Occidental Chemical Corporation has played a leading role in providing caustic potash to meet the increasing demands of industry. OxyChem plants are located to conveniently and economically serve all

industries. Warehouse stocks of OxyChem caustic potash and other products are maintained in principal cities. . Distributor stocks are also available in these and many other cities that form a network of supply for the end users' convenience.

In 1994 Occidental Chemical Corporation became the first U.S. producer of membrane cell caustic potash at its Mobile, AL facility. This process demonstrates the latest in chlor-alkali technology.

*Acknowledgement is made of the courtesy of the Sargent-Welch Scientific Company, of Skokie, IL, in granting permission to reproduce in modified form the potassium, oxygen, and hydrogen portions of the 1979 revised edition of the "Periodic Chart of the Atoms."



Principal Uses and Consumption of Caustic Potash

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Caustic potash is one of the very few chemicals finding almost universal application. Some of the principal products or processes in which caustic potash is used, are:

- A dehydrating agent for drying gases
- A lubricant in the extrusion pressing of high melting alloys
- A scavenger in a gasoline treating process (dual layer) for removing mercaptans
- A methylating agent
- An alkaline builder in detergent formulations
- In refining petroleum fractions
- In removing insulating coatings from wire
- In purifying olefin feedstock containing hydrocarbons prior to polymerization
- In stabilizing synthetic lubricants
- In removing naphthenic acids from gas oils
- In fertilizers
- In descaling ferrous metals
- In sweetening sour petroleum fractions
- In a fused alkaline salt mixture used for metal cleaning
- In lye peeling
- In electrolytic stripping baths
- In chemical compounding
- In a molten bath for removing polyesters and polyurethanes from steel objects
- In an absorption cartridge for scavenging carbon dioxide
- As a chemical desiccant
- As a cleaner for eliminating scale from the surface of titanium alloy intermediates
- As an agent for lowering the sulfur content of coal
- In alkaline batteries

Manufacturing Process

Caustic potash is produced commercially by an electrolytic process as shown in the flow diagram on the following page. Brine, prepared from potassium chloride, is electrolyzed in either a mercury cell or a membrane cell. The co-products are chlorine and hydrogen.

In the mercury cell process, a potassium-mercury amalgam is formed in the cell. The amalgam is sent to the decomposer where it is

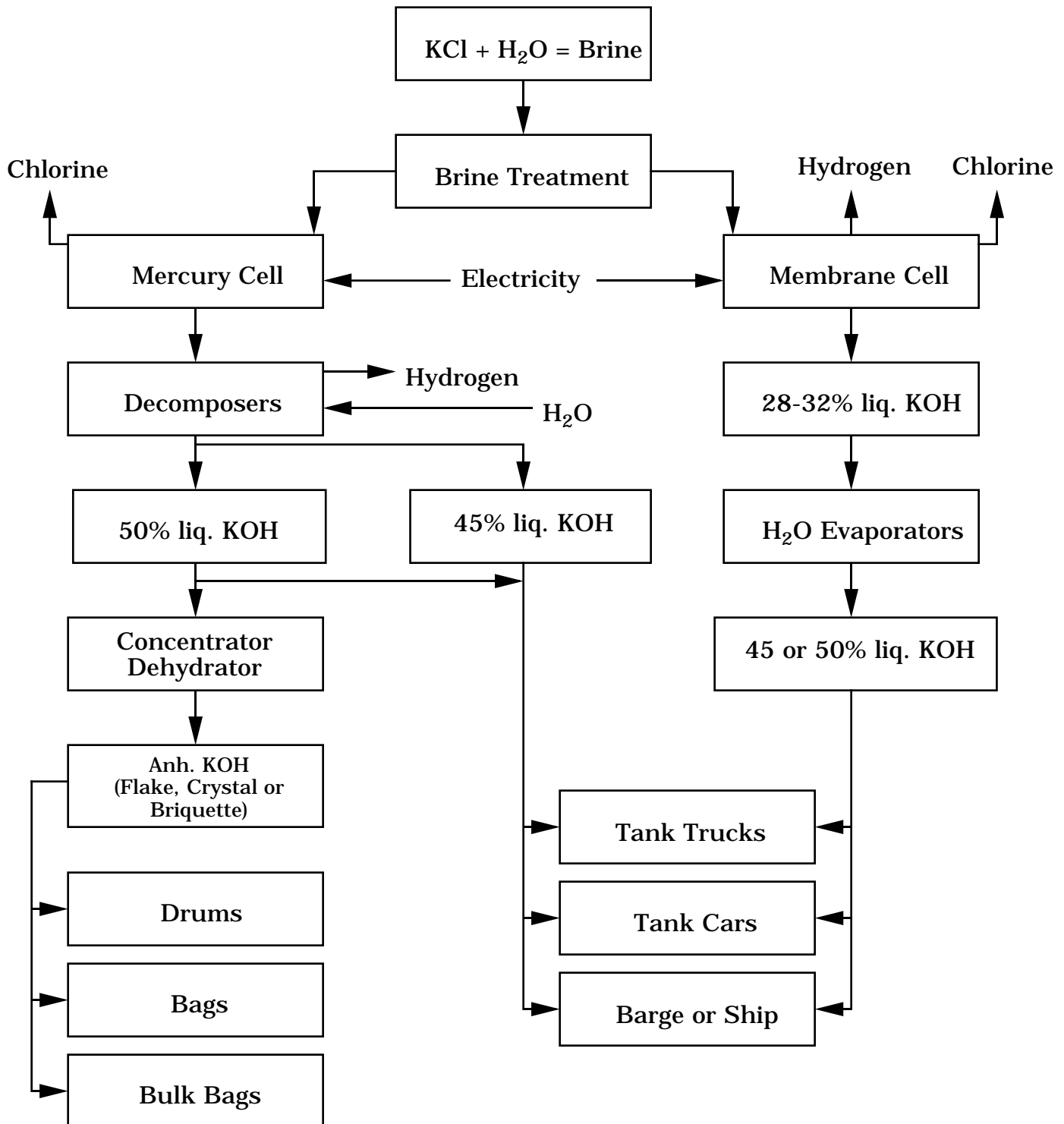
reacted with water to form liquid KOH, hydrogen and free mercury. The free mercury is returned to the electrolytic cell. The resulting caustic potash solution is either inventoried in storage tanks as 45% or 50% solutions or concentrated by evaporation to a 90% anhydrous form. The liquid is shipped in tank trucks, tank cars, barges or ships. The anhydrous forms are briquette,

flake and crystal. These forms are shipped in drums, bags or mini bulk bags

In the membrane process, a solution of approximately 30% in strength is formed. This solution is then sent to evaporators which concentrate it to a strength of 45% or 50% by removing the appropriate amount of water. The resulting caustic potash solution is inventoried in storage tanks prior to shipment.

Flow Diagram of Manufacturing

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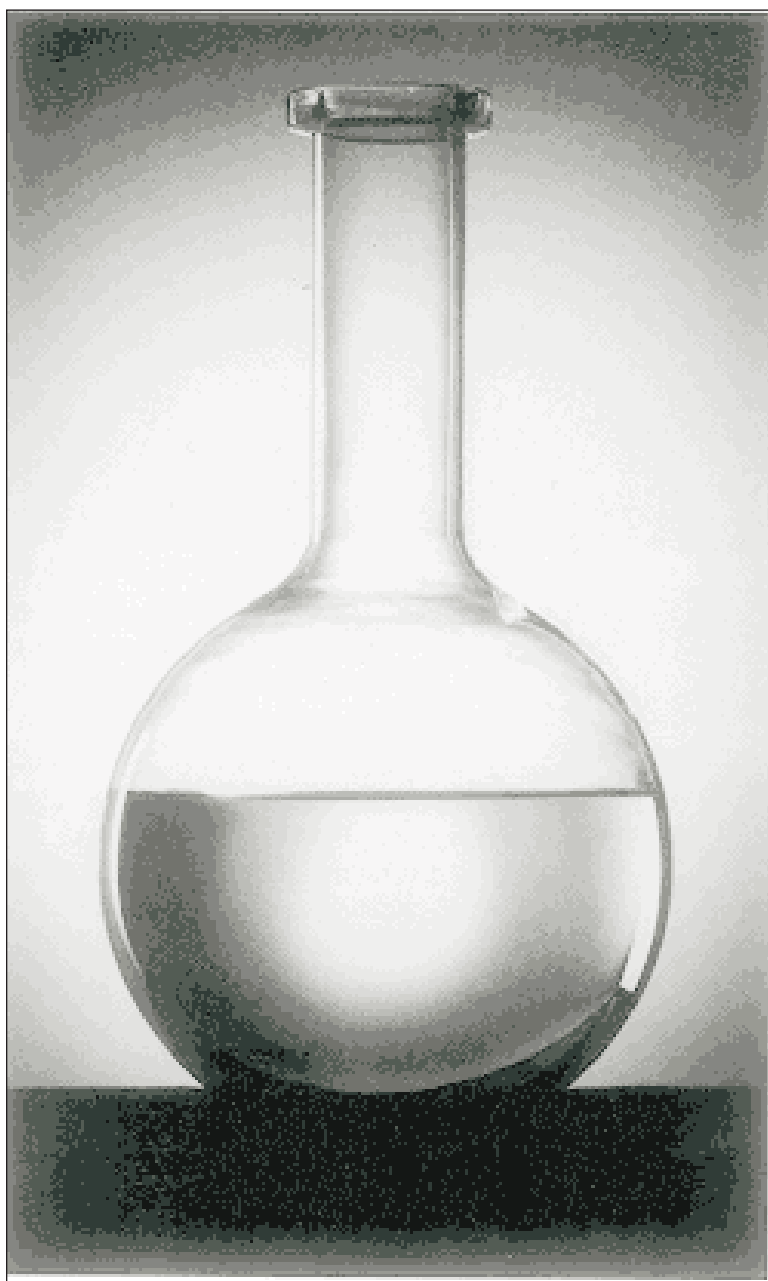
Forms of Caustic Potash

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Liquid caustic potash is available in two concentrations, 45% and 50% and in four grades, Commercial, Membrane, Industrial and Low Sodium.

Anhydrous caustic potash is marketed in three forms, briquette, flake and crystal. Drum packages include sizes of 100, 400 and 450 pounds. Each of the three forms is available

as a special order in 2000 pound bulk bags. Also, the flake form is available in 50 pound bags.

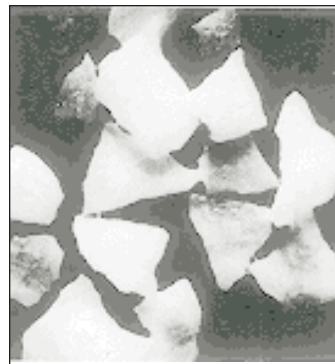


LIQUID

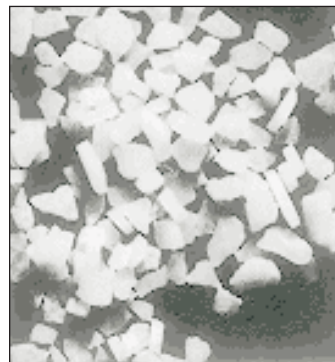
ANHYDROUS (DRY) FORM



BRIQUETTE



FLAKE



CRYSTAL

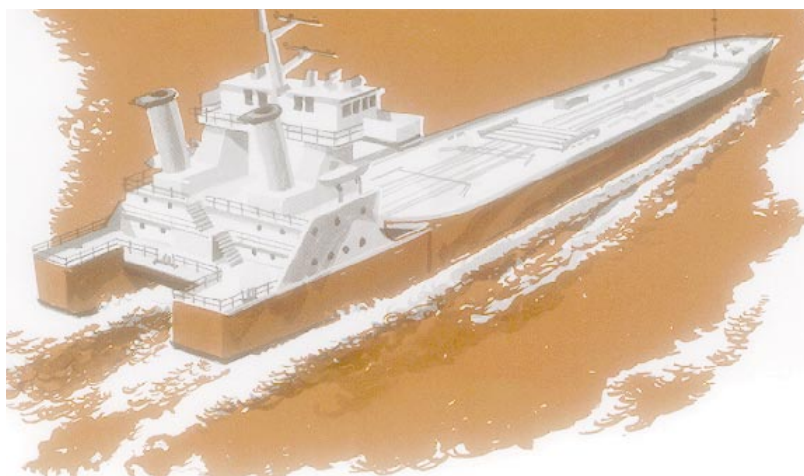
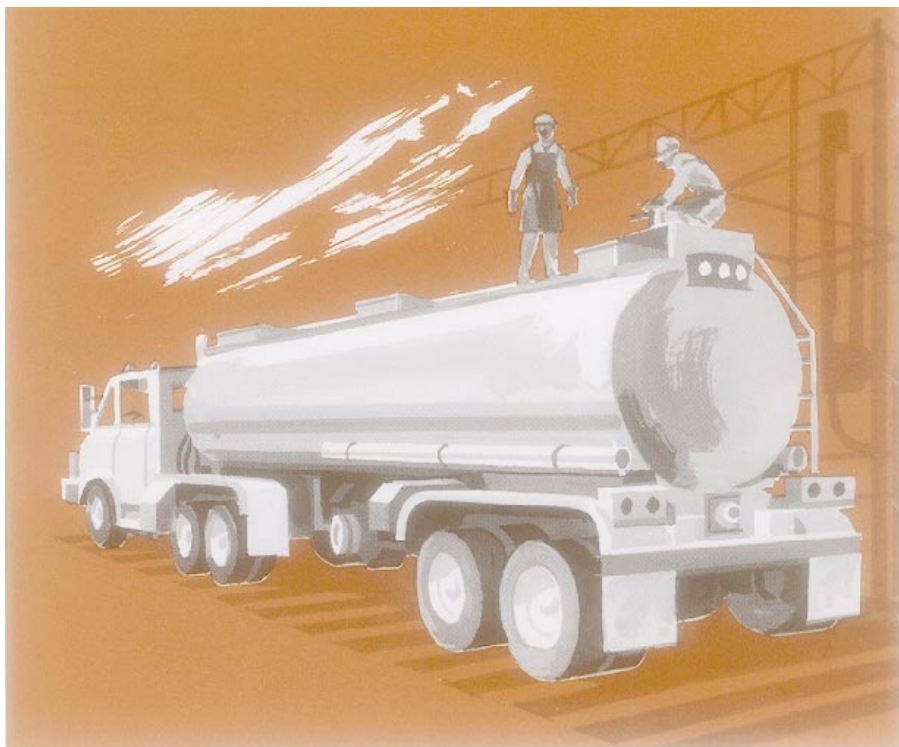
Methods of Shipping Liquid Caustic Potash

LIQUID

Liquid caustic potash is available from OxyChem's plants and terminals in tank truck, tank car, barge or ship quantities. Each form of transportation has advantages. The type of service selected will depend on such factors as size and location of storage, rate of consumption, plant location, freight rates, etc. OxyChem's Technical Service staff can survey your present facilities and recommend the most economical method of transportation for your requirements.

Caustic potash, liquid and dry, is regulated by the U.S. Department of Transportation (DOT) and is classified as a Corrosive Material.

The DOT I.D. number is UN1814 for liquid and UN1813 for dry. Both liquid and anhydrous are Hazard Class 8 and Packing Group II.



Safety in Handling Caustic Potash

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Caustic potash in any form 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 act in case of contact. Accidental exposure to caustic potash 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.

- Read and understand the latest Material Safety Data Sheet.
- Provide eyewash fountains and safety showers in all areas where caustic potash is used or handled. Any caustic potash burn may be serious. DO NOT use any kind of neutralizing solution particularly in the eyes. Use only clean water.
- Move the patient to a hospital emergency room immediately after First-Aid measures are applied.

FIRST-AID MEASURES

EYES: If for any reason caustic potash contacts the eyes, flood the eyes immediately with plenty of clean water. Continue flushing for at least 15 minutes. While flushing, hold the eyelids apart to ensure flushing of the entire eye surface. **Do not use any kind of neutralizing solution in the eyes.**

GET MEDICAL ATTENTION IMMEDIATELY.

SKIN: If caustic potash comes in contact with skin or clothing, flush

with plenty of clean water for at least 15 minutes. Remove contaminated clothing and footwear. Wash affected clothing before reusing and discard footwear. **GET MEDICAL ATTENTION IMMEDIATELY.**

INHALATION: If discomfort is experienced from exposure to caustic potash dust, mist, or spray, use respiratory protection or leave the contaminated area until proper ventilation is restored.

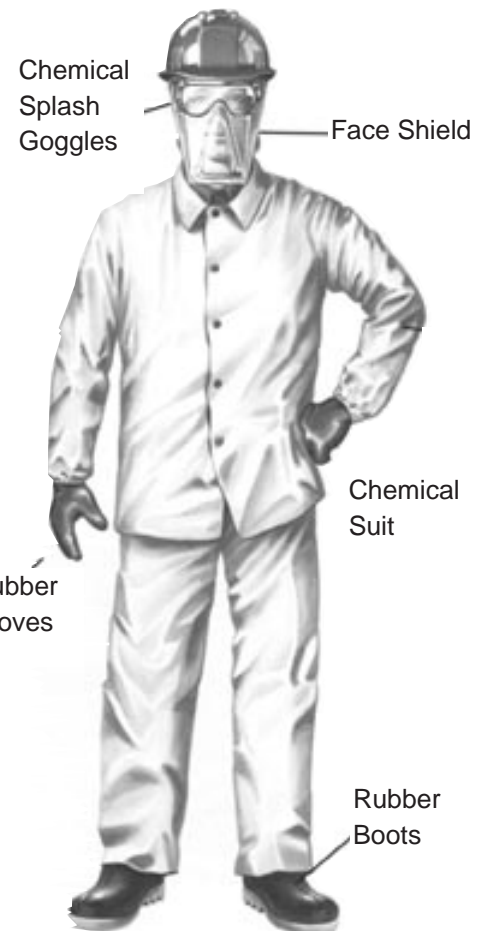
If a worker is overcome due to the inhalation of caustic potash, dust, mist, or spray, remove them from the contaminated area to fresh air. If breathing has stopped, start artificial respiration. Administer oxygen if readily available. **GET MEDICAL ATTENTION IMMEDIATELY.**

INGESTION: Although it is unlikely in an industrial situation that caustic potash would be ingested, it could be swallowed accidentally. If that occurs, DO NOT induce vomiting. Give large quantities of water. If available, give several glasses of milk. If vomiting occurs spontaneously, position individual's head to keep airway clear. **NEVER GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS PERSON. GET MEDICAL ATTENTION IMMEDIATELY.**

PROTECTIVE EQUIPMENT

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

- **Wear suitable goggles for eye protection during the handling of caustic potash in any form.** The goggles should be close-fitting and wrap-around style. Goggles which provide adequate ven-



tilation to prevent fogging, without allowing entry of liquids. The use of a face shield may be appropriate when splashing can occur.

- Wear rubber gloves or gloves coated with rubber, synthetic elastomers, PVC, or other plastics to protect the hands while handling caustic potash. Gloves should be long enough to come well above the wrist. Sleeves should be positioned over the glove wrists.
- Caustic potash causes leather to disintegrate quite rapidly. For this reason, wear rubber boots. Wear the bottoms of trouser legs outside the boots. Do **NOT** tuck in.
- Wear chemical resistant clothing for protection for the body.

Safety in Handling Caustic Potash

Impregnated vinyl or rubber suits are recommended.

- Wear hard hats for some protection for the head, face, and neck.
- Use NIOSH-approved air purifying respirators for protection from dusts and mists.

PROTECTIVE PRACTICES

- Avoid breathing dust, mist, or spray of caustic potash.
- Wear proper protective equipment.
- Keep equipment clean by washing off any accumulation of caustic potash.
- Weld pipelines where practical. Use flanged joints with gaskets made of caustic-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, verify that there is no internal pressure on the equipment and that the equipment has been drained and washed.
- Provide storage tanks with suitable overflow pipes.
- Shield the packing glands of pumps to prevent spraying of caustic solution in case the packing glands should leak.
- When releasing air pressure from a pressurized system, take every precaution to avoid spurts or sprays of caustic solution.
- Exercise extreme care when breaking solid caustic potash into smaller pieces.
- In case of a spill or leak, stop the leak. After containment, shovel up the spill then transfer it 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.

HANDLING ANHYDROUS CAUSTIC POTASH

Extreme care must be exercised when adding anhydrous caustic potash to water or to a solution. Its high heat of solution generates large amounts of heat which can cause local boiling or spurting. When making solutions, **always** add the caustic potash slowly to the water surface with constant stirring. **Never add the water to the caustic potash.** Always start with lukewarm water (80°-100°F). Never start with hot or cold water. Dangerous boiling and/or splattering can occur if caustic potash is added to rapidly, is not sufficiently agitated or added to hot or cold liquids. Care must be exercised to avoid these situations.

Anhydrous caustic potash will dissolve freely in a well agitated solution under proper conditions. Without agitation, the anhydrous caustic potash will fall to the bottom and form a layer of hydrate which dissolves quite slowly. Also, localized boiling can occur causing the solution to spatter.

To operate safely, slowly add the anhydrous caustic potash to the surface of a well-agitated water solution. The preferred equipment is a propeller-type agitator or a circulating pump with sufficient mixing capacity. Avoid agitation with air because air will cause excessive formation of potassium carbonate.

Accidental exposure to caustic potash may occur under several conditions. Potentially hazardous situations include handling and packaging operations, equipment cleaning and repairs, decontamination following spills and equipment failures. Employees who may be subject to such exposure must be

provided with proper personal protective equipment (including respirators) and trained in its use and care.

HANDLING LIQUID CAUSTIC POTASH

In handling caustic potash solutions, care must be taken to avoid solidification which will plug pipelines and equipment. For this reason it is desirable to know at what temperature a solution of known concentration will freeze. Chart 1, shows the freezing points for solutions of different concentrations. Chart 2, shows the boiling points for the various concentrations of aqueous caustic potash.

There are several methods for measuring the concentration of caustic potash solutions, but the most accurate method is by chemical analysis (see the Methods of Analysis section). The strength of the solution may also be determined by use of a hydrometer. Three scales for expressing density of caustic potash solutions are: specific gravity, degrees Baumé, and degrees Twaddell (Table 1). The density of the solution will vary with a change in temperature as shown on Chart 3.

Unloading Liquid Caustic Potash From Tank Cars

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It is imperative that tank-car quantities of liquid caustic potash be handled in a safe manner. This section includes many details; all are essential for safety.

Placement of the Car for Unloading

DOT requires setting the hand-brake and blocking the wheels after the car is properly spotted. Caution signs must be placed at both ends of the car being unloaded to warn switching crews and others approaching the car. DOT regulations also state that caution signs must be placed on the track or car to give warning to people approaching the car from the open end or ends of the siding. Caution signs must be left up until the car is unloaded and disconnected from the discharge connections. Signs must be made of metal or other suitable material, at least 12 X 15 inches in size, and bear the words, "STOP-TANK CAR CONNECTED," or, "STOP-MEN AT WORK." Place derail attachments at the open end or ends of the siding, approximately one car length (50 ft.) away.

- Entrust only responsible and well-supervised employees with the unloading of liquid caustic potash. Unloading operations must be monitored while the car is connected
- Provide workers with chemical splash goggles, rubber boots, hard hats, vinyl suits and rubber or rubber-covered gloves to protect against serious burns if Caustic potash contacts the skin. If rubber is not suitable for clothing, cotton offers some protection. A safety shower and eye-wash fountain must be located in the unloading area.
- Caution workers to exercise care
- Unload a car of caustic potash

only in the daytime or when adequate lighting is available.

- Before starting to unload, make certain that the tank car and the storage tank are vented and verify that the storage tank has sufficient capacity for the delivery.
- Do not allow entry into the car under any circumstances.
- If the tank car needs to be moved when partially unloaded, DOT regulations require disconnecting all unloading lines and replacing all car closures.
- If compressed air (20 psig max) is used in unloading operations, inspect all fittings for leaks or other defects before unloading. Dome fittings, particularly, must be inspected. If leaks are found, suspend unloading operations until they are fixed.

HANDLING IN COLD WEATHER

Since OxyChem tank cars are well insulated and the liquid caustic potash is at a temperature in excess of 100°F when loaded, it should arrive at its destination as a liquid. If for any reason the solution cools, it is possible that some crystallization may take place. (45% liquid solutions freezes at -28°F; 50% freezes at 41°F.) The most common source of trouble is not the temperature of the car but the leakage of solutions into the outlet leg where it can solidify. This can be liquefied by the application of steam. In case freezing occurs, follow these procedures: (refer to Figure 1.)

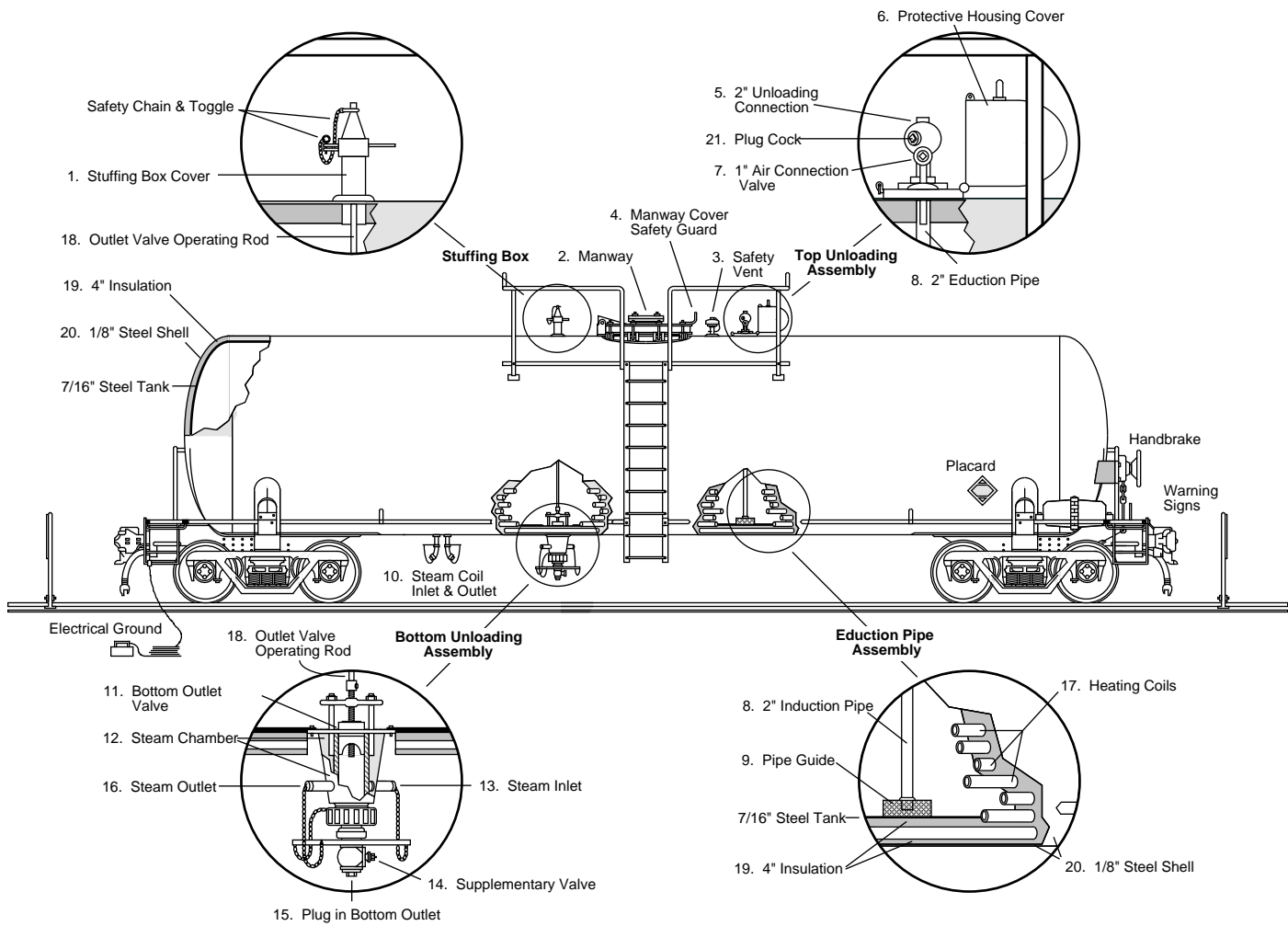
- Carefully open the tank car manway cover.
- If a layer of solid caustic potash has formed, break the crust before admitting steam to the jacket around the bottom outlet

valve. Puncturing the crust permits expansion of the liquid as it increases in temperature.

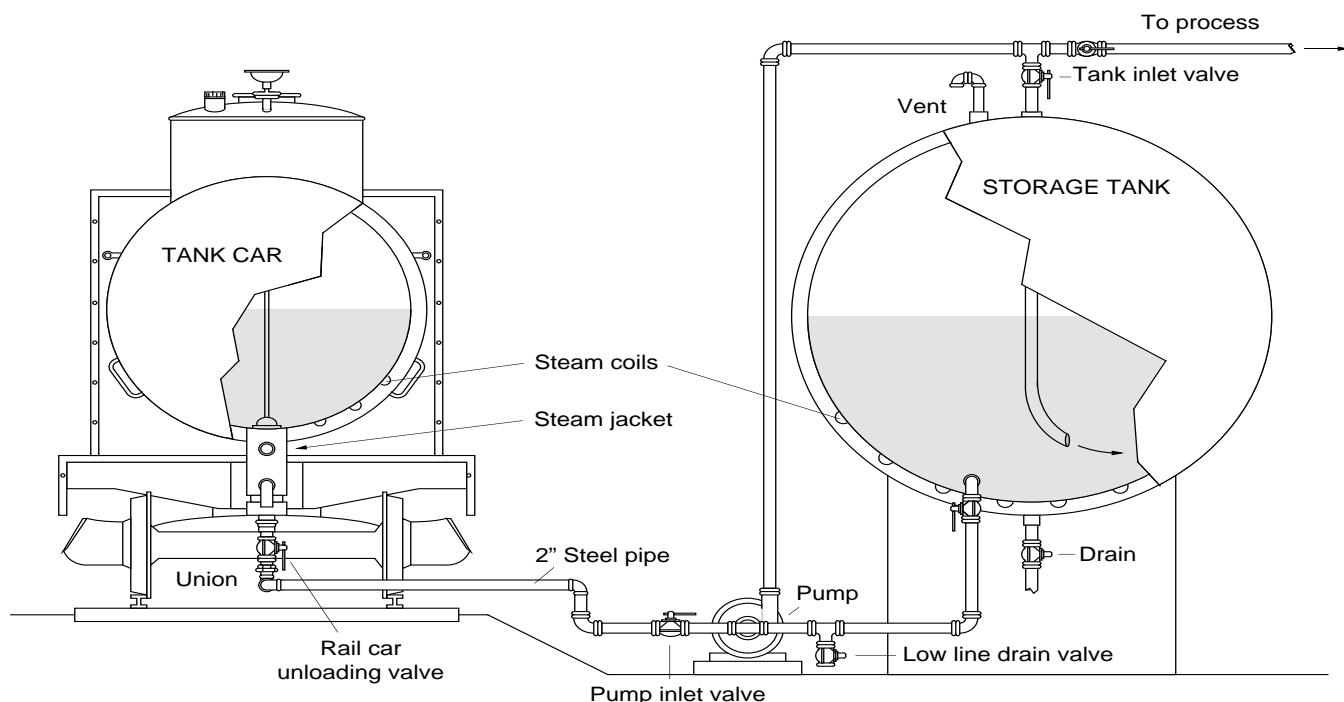
- If no crust is present, determine if crystals have formed on the bottom of the car by probing the bottom with a rubber-capped rod introduced through the manway opening. Use only a rubber-capped rod to avoid damaging the liner.
- If freezing has occurred, connect a steam line (10 PSIG or less) to a jacket around the bottom valve at opening (13). Connect a condensate return line at opening (16). OxyChem ships liquid caustic potash in specially-lined tank cars equipped with steam coils. The lining in these tank cars will withstand temperatures up to 225°F. To prevent damage to the liner, do not add water or steam **directly** into the tank car.
- If a condensate return line is not used, connect a valve at opening (16) and open it sufficiently to relieve condensate. Direct the condensate toward the ground or into a sewer. As contents liquefy, the valve can be closed further to conserve steam.
- When the contents have liquefied and operation of the valve rod (18) shows that the bottom outlet valve (11) is free, the solution is ready for unloading.
- If the above measures do not liquefy the contents on the car, contact your OxyChem representative.

Figure 1

Details of a Caustic Potash Tank Car



Unloading Caustic potash Through The Bottom Outlet



UNLOADING 45% AND 50% LIQUID CAUSTIC POTASH

45%-50% liquid caustic potash can be top or bottom unloaded. Both methods are described in this handbook.

Bottom Unloading

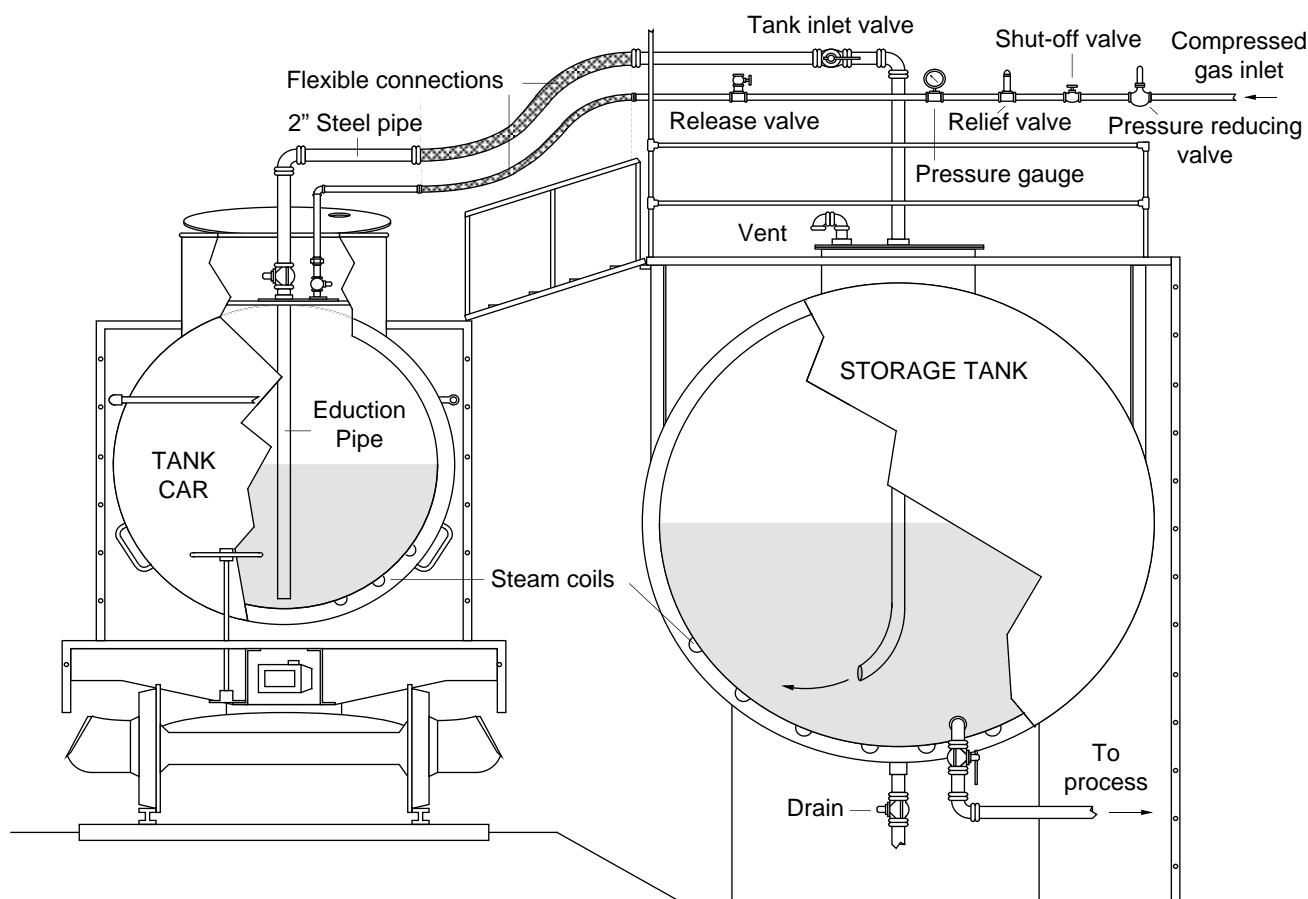
- Pipe the tank car to the storage tank as shown in the diagram above (Figure 2).
- Open the manway cover and see if the caustic potash in the car is liquid. If not, follow the instructions in "Handling in Cold Weather." Keep the dome cover at least partially open during the entire unloading operation to vent the tank car.
- Refer to the cutaway view of the tank car (Figure 1). See that the bottom outlet valve (11) is closed tightly. The valve rod (18) which operates the bottom outlet valve (11) has a handle on it which is located outside the dome of the car. The handle can be reversed and serves as a cap in transit (1).

- Remove the pipe and plug (15) and then carefully remove the supplementary valve (14) in order to drain out any liquid that may have seeped by the bottom outlet valve (11) during transit. If the supplementary valve (14) cannot be opened, apply steam from a steam lance on the valve to free it for opening.
- Check the unloading line to see that all valves are in the proper position for unloading. A flexible hose is recommended as the unloading line since the car may rise as much as two inches.
- Open the bottom outlet valve (11) by turning the valve rod (18) to allow the contents to flow by gravity to the pump or tank. If the valve (11) does not open upon application of light pressure, frozen caustic potash is probably present in the bottom of the car. Apply steam if necessary. Follow instructions in "Handling in Cold Weather."

- Compressed air can be used to increase the flow rate to storage or to transfer the liquid without the use of a pump. If compressed air is used, check the rupture disk in the dome to be sure it is intact. Close the dome cover securely. Remove the 1-inch air inlet plug (7) and connect a flexible air line. The air line should be equipped with a release valve, oil trap, pressure relief valve set at 20 psig, pressure-reducing valve set at 18 psig, and a shut-off valve. Apply air pressure slowly. Note that the pressure relief device (rupture disk and/or pressure relief valve) in the dome will relieve at a pressure between 65 or 165 psig, depending on the type of car. Refer to the stenciling on the side of the railcar
- When the car and unloading lines are empty, shut off the air supply and open the release valve.
- When the tank car is empty and

Figure 3

Unloading Caustic Potash Through The Top By Compressed Air



completely drained, disconnect the air line, if used, and detach the unloading line at the car. Prepare the car for return.

Top Unloading with Air Pressure

- Pipe the tank car to the storage tank as shown in the diagram above (Figure 3).
- Open the dome cover and see if the contents of the car are liquid. If not, follow instructions in "Handling in Cold Weather."
- Close the dome cover and fasten securely, making certain that it is air-tight. Check the rupture disk located in the dome to be sure it is intact.
- Check the storage tank to see that it is vented and has sufficient capacity.
- Refer to the cutaway view of the tank car (Figure 1). Connect the unloading line to the 2" unloading connection (5) on the eduction pipe (8), after removing the cover (6). A flexible steel hose connection for the unloading line is recommended since the car may rise as much as 2" during unloading.
- Connect the flexible air supply line to the 1" air inlet valve (7). This line should be equipped with a release valve, oil trap, pressure-relief valve set at 20 psig, pressure reducing valve set at 18 psig, and a shut-off valve. The car is equipped with a safety vent or rupture disc. The rating for the device is stenciled on the side of the car.
- Apply air pressure slowly until there is a normal flow of liquid to the storage tank. The pressure should be adjusted and maintained until the tank car is completely empty. A drop in air pressure or the sound of air rushing through the unloading line indicates that the tank car is empty.
- Shut off the air supply, open the

Unloading Caustic Potash

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release valve, and allow the education pipe to drain.

- When the education pipe has drained and the tank car is at atmospheric pressure, disconnect the air supply line at the car.
- Open the manway cover and determine if the car is empty. If empty, disconnect the unloading line at the car and tightly replace the manway cover (2) and the cover over the valves (6).
- Do not enter the car to make an inspection.
- Take care not to spill caustic potash on the car, since it will cause damage to the car and may endanger workers handling the empty car on its return.
- Prepare the car for return.

PREPARING EMPTY TANK CARS FOR RETURN

For Bottom Unloading

- Close the bottom outlet valve (11) and the supplementary valve (14).
- Disconnect the unloading line and replace the bottom outlet plug (15). Do not replace the closures on steam opening (13, 16).
- Close the manway cover (2) and fasten securely.

For Top Unloading

- Turn off air pressure to the car and close the air line valve (7).
- Disconnect the air supply hose.
- Open the air line valve to vent any remaining pressure.
- Disconnect the product unloading hose.
- Install the plug cock (21) and close the 1 inch air connection valve.

Completion of both top and bottom unloading

- Properly placard the car for return.
- Return the empty tank car promptly in accordance with the shipper's instructions. Follow the shippers routing directions in all instances.

UNLOADING LIQUID CAUSTIC POTASH IN TANK TRUCKS

Responsibility of the Carrier in Transporting Tank Truck Shipments of Liquid Caustic potash

The tank truck driver has received the following instructions regarding equipment and delivery procedures. If any carrier delivering caustic potash to your plant fails to follow these instructions, please contact Occidental Chemical Corporation so that corrective action can be taken.

Equipment

Equipment must meet DOT Regulations, Code of Federal Regulations, Title 49.

Tank Truck Specification

Tank trucks should meet all DOT regulations for carrying caustic potash.

Four DOT "CORROSIVE" placards must be permanently affixed to the cargo tank unless cleaned or loaded with nonregulated product.

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 nickel

unit. The pump can be driven by a tractor powered take-off or an auxiliary gasoline engine. Use at least a two inch pump line.

If unloading is by compressed air, the tank vessel must meet the requirements of the CFR, Title 49. The line used to supply air to the tank truck is required to be equipped with: pressure reducing valve, pressure release valve, pressure gauge. The relief valve should be set at a maximum pressure of 20 PSIG and the pressure reducing valve should be set at 2-3 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 request.

Unloading Lines

Unloading hoses must be constructed of material resistant to caustic potash. Hoses should be at least two (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 Potash

PERSONNEL

Truck drivers must be fully instructed in caustic potash handling prior to being dispatched with a shipment.

Truck drivers must follow any special instructions provided by the shipper for a special delivery.

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

Truck drivers must wear the protective equipment required by Occidental Chemical Company as listed under Protective Equipment, or follow the customer requirements, whichever are more inclusive and at all times follow safe handling practices.

The following unloading procedures are recommended:

- Check the operation of the safety shower and eye-wash fountain. Purge water through each to remove rust that may have accumulated.
- If a shower and eyewash are not available, a water hose connected to a source of water is required. If the valve on the line is not conveniently located near the unloading area, leave a stream of water flowing during unloading
- Connect one end of the unloading hose to the customer's storage tank fill line.
- During cold weather and if facilities are provided, preheat with steam, the fill line, the unloading hose and the truck outlet if needed.
- 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 cut off the air supply.
- When a pump is used, it is advisable to flush out the unloading line before disconnecting the hose. If water is available, a small quantity can be added into the truck while the pump is running to flush out the line. Air or water can be used to flush the line contents into the storage tank or back to the truck. If no water is available for flushing out lines, exercise great caution when lines are disconnected.
- Close the valve on the storage tank fill line.
- Close all valves on the tank truck.
- In some installations the customer's fill line is fitted with a drain to be used instead of flushing the line before the hose is disconnected.
- Disconnect the hose with caution and discharge any caustic potash remaining in the hose to a suitable container.
- Unload in an area with adequate safeguards for spill control. Clean up all spills and dispose in accordance with Federal, State and

Local Regulations.

Responsibilities of the Consignee when Receiving Tank Truck Shipments of Liquid Caustic Potash EQUIPMENT

Typical installations of storage vessels for receipt of truck shipments are shown in Figure 4.

A storage tank with a minimum capacity of 1.5 tank cars is recommended.

A fill line to the top of the storage is strongly recommended. If a bottom fill line is used, the truck driver must be informed.

A permanent fill line in a close proximity to the tank truck unloading area is required.

A 2-inch or larger fill line is recommended.

A 3/4-inch valve connection is recommended on the fill line for use in flushing out the line with air, water, or steam. It can also be used as a drain.

Cap or close the end of the fill line when not in use.

A source of running water for use during unloading operations is required. A safety shower and eyewash fountain are recommended.

PERSONNEL RESPONSIBILITIES

Inform truck drivers of any special instructions.

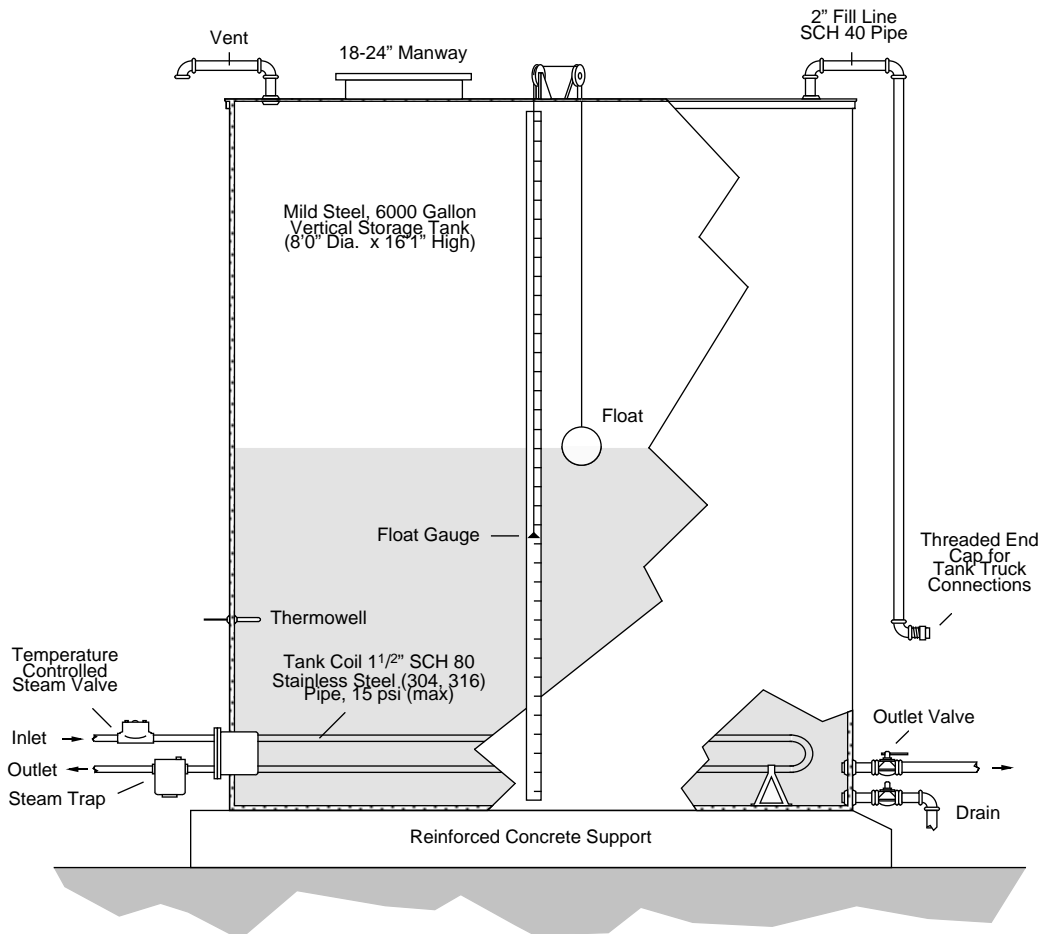
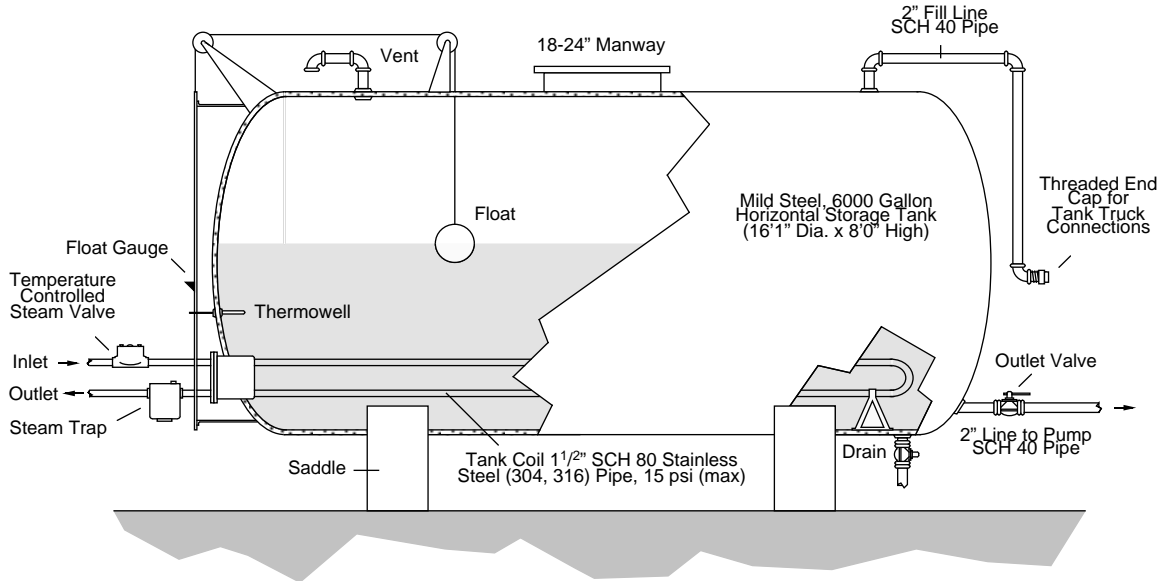
Truck unloading should not be unnecessarily delayed. Cooperation with the unloading operation is appreciated.

It is required that plant personnel handling liquid caustic Potash be fully informed of safe handling practices and in the methods of first aid in the event of an accident.

Figure 4

Installation of Tanks

* Steam System is not Required in the Storage of 45% KOH.



Materials of Construction

Corrosion of metals by caustic potash is very similar to that of caustic soda. In equal concentrations caustic potash has a lower viscosity and will penetrate cracks and pin holes more readily than caustic soda.

Aluminum, zinc, brass, bronze, and copper are all readily attacked by caustic potash solutions and are completely unsuitable as materials of construction.

Iron and steel are the two most common construction materials used for handling and storing caustic potash solution even though these metals are attacked by these solutions under high temperature conditions. However, 45% and 50% solutions may be safely handled in steel up to temperatures around 120°F.

Nickel resists attack by caustic potash solutions better than most metals. Nickel-lined equipment is often used when minimum contamination of the solution by metals is important.

Rubber has been used for lining steel caustic potash storage tanks. However, rubber does not withstand high temperatures. A number of epoxy type linings are preferred because of their long life and low cost. Under the right conditions, FRP, polyethylene or polypropylene can be used. Contact OxyChem Technical Service representatives for recommendations.

PIPELINES

Schedule 40 black iron or stainless steel are recommended for pipeline construction. Welded joints are preferred to minimize potential leakage. Flanged joints are preferred on lines which must be dis-

connected. With flanged joints, maintenance labor costs are kept to a minimum because of the comparative ease with which repairs and replacements can be made. A safety shield of wrap-around polypropylene is recommended for all flanged joints. This will protect against spraying in case a gasket leaks. Where screwed connections are necessary, use Teflon® tape on the threads. To allow lines to drain completely, install all piping with a slight slope. OPW Kamlok quick couplings or equivalent are safe and convenient where the coupling of hose to pipe is required. Normally, a two-inch male NPT (National Pipe Thread) fitting is all that is needed to accommodate tank truck deliveries. This pipe should be valved and capped at the unloading end and heat traced where exposed. There should also be a connection for steam, water, or air to clear the unloading line after delivery is complete.

In systems where a slight iron contamination is objectionable, PVC, Saran-lined steel, Kynar, or Fiberglass pipe can be used. Pay special attention to suitable operating temperatures and pressures with these materials.

METERS

Caustic potash solutions can be metered through standard rotameters having glass tubes and nickel or stainless steel floats. Magnetic or orifice-type meters are preferred for strong, hot solutions. They should have all iron or nickel construction.

PUMPS

If a pump is required, use either an open-impeller centrifugal, rotary,

positive-displacement, or piston-type pump. Include a by-pass or circulating line arrangement with the pump. This reduces wear on the pump and in many cases can be used as a means for controlling the rate of flow. Carefully consider pump location. For ease of operation the suction line must be as short as possible. Specify a pump with a deep packing gland. Specify caustic potash service when ordering.

Use graphite-braided asbestos or equivalent for the packing material.

VALVES

For general use, lubricated plug cocks of cast iron or steel construction are recommended for caustic potash service.

To control flow rates and for line shut-offs, Teflon® sleeve-lined quarter-turn plug valves are recommended.

STORAGE TANKS

Storage facilities must have adequate capacity to accommodate shipments. It is necessary to make provision for a reserve supply of caustic potash between shipments. In the case of 16,000 gallon tank car shipments, it is suggested that total storage space be at least double the tank car capacity (32,000 gallons). If tank trucks of 4,000 gallons are received, it is suggested that storage space of at least 6,000 gallons be available. Proper design of a storage system will include adequate containment in case of tank failure. Most tanks have a level transmitter for measuring liquid level.

Extra heavy metal is preferred in the construction of caustic potash storage tanks. Specifications for fabrication call for at least 3/8" wall thickness on the body of units larger than 10,000 gallon capacity and a 1/4" wall for smaller capacities. Design the pipe connection for withdrawing the liquid from storage a few inches above the bottom of the tank. Include a drain connection at the lowest point of the tank to facilitate flushing.

The ideal storage temperature for 50% caustic potash is 60°F to 80°F. Caustic potash solutions in the 23% to 45% concentration range are easily handled at ambient temperatures because their freezing points are below -20°F. Solutions outside this range may require heating and/or insulation. If higher temperatures are necessary or if iron contamination poses a problem, more resistant materials such as stainless steel, nickel, or nickel-based alloys, should be considered. Steel storage tanks are often lined with a protective epoxy coating. A small coil loop of 1 to 1.25 inch Schedule 80 stainless steel pipe connected to a source of low pressure steam (12 to 15 psi), is adequate to adjust temperatures. Avoid storage temperatures above 130°F for steel tanks. Insulation of tanks is desirable but not necessarily a requirement. The most economical thickness for common types of insulation is two inches. 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.

TANK CLEANING AND PASSIVATION

Tank cleaning, can be divided by the type of product stored in it previously. A tank that previously contained caustic potash would require scale removal, wall thickness testing, rinsing, passivation, squeegeeing, and immediate filling. A tank previously containing another product would require cleaning with an appropriate solvent or soap, as well as the other steps mentioned above.

Scale removal is accomplished by blasting the walls with abrasive such as sand or pecan shells. Abrasives containing high percentages of metals are not recommended in order to minimize contamination of the caustic potash.

The wall thickness of the tank should be measured and be approved for the density of the product and the height of product in the tank.

Passivation requires penetration of the steel tank walls with caustic potash. This is usually accomplished by spraying the cleaned walls with a hot solution of caustic potash. Temperatures of 100 - 140°F and solutions of 5 - 20% are recommended. While this is more of an art than a science, 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. The hotter and the stronger the solution, the less time should be needed. One way to achieve the solution heat necessary is to dilute 45% or 50% caustic potash to 20%.

The heat of dilution will cause the caustic potash 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. If this type of sprayer is not available, the spraying may be done manually with extreme caution taken to protect the operator.

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 and abrasive compound. If an elliptical sprayer is used for the cleaning, a squeegee will need to be used to clean the tank bottom. If manual spraying is used for cleaning, the sprayer can be used to push the scale and abrasive toward the sump followed up by use of a squeegee.

After cleaning, the tank should be filled with caustic potash 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 keep it free from particulate matter. This would require a 5-10 micron filter media housed in a unit that would be acceptable with the temperature, pressure, and chemical.

Technical Data

Table 1—Density and Solids Content of Caustic Potash Solution at 15.6°C (60°F)

% KOH	%K ₂ O	Specific Gravity 15.6°C/ 15.6°C	Degrees Baumé	Degrees Twaddell	Grams of KOH per Liter	Lbs. of KOH per Gal.	Solution Density Pounds per Gal.	Lbs. of KOH per Cu. Foot	Solution Density Lb. per Cu. Foot
0	0.00	1.000 (Water)	0.00	0.0	0.00	0.00	8.34	0.00	62.43
1	0.84	1.009	1.29	1.8	10.09	0.08	8.41	0.63	62.99
2	1.68	1.018	2.56	3.6	20.36	0.17	8.49	1.27	63.55
3	2.52	1.027	3.81	5.4	30.81	0.27	8.56	1.92	64.12
4	3.36	1.036	5.04	7.2	41.44	0.35	8.64	2.58	64.68
5	4.20	1.045	6.38	9.0	52.25	0.44	8.72	3.26	65.24
6	5.03	1.055	7.56	11.0	63.30	0.53	8.80	3.95	65.86
7	5.88	1.064	8.72	12.8	74.48	0.62	8.88	4.65	66.43
8	6.72	1.073	9.86	14.6	85.84	0.72	8.95	5.35	66.99
9	7.56	1.083	11.11	16.6	96.57	0.81	9.04	6.08	67.61
10	8.40	1.092	12.22	18.4	109.20	0.91	9.11	6.81	68.17
11	9.23	1.102	13.42	20.4	121.22	1.01	9.20	7.56	68.80
12	10.07	1.111	14.49	22.2	133.32	1.11	9.27	8.32	69.36
13	10.91	1.121	15.65	24.2	145.73	1.22	9.35	9.10	69.98
14	11.75	1.131	16.79	26.2	158.34	1.32	9.44	9.88	70.61
15	12.59	1.140	17.81	28.0	171.00	1.43	9.51	10.68	71.17
16	13.43	1.150	18.91	30.0	184.00	1.54	9.60	11.49	71.79
17	14.27	1.160	20.00	32.0	197.20	1.64	9.68	12.31	72.42
18	15.11	1.170	21.07	34.0	210.60	1.75	9.76	13.13	73.04
19	15.95	1.180	22.12	36.0	224.20	1.87	9.85	14.00	73.67
20	16.79	1.190	23.15	38.0	238.00	1.99	9.93	14.84	74.29
21	17.63	1.200	24.17	40.0	252.00	2.10	10.01	15.72	74.92
22	18.47	1.210	25.16	42.0	266.20	2.22	10.09	16.60	75.54
23	19.31	1.220	26.15	44.0	280.60	2.34	10.18	17.50	76.16
24	20.15	1.230	27.11	46.0	295.20	2.46	10.26	18.41	76.79
25	20.99	1.240	28.06	48.0	310.00	2.59	10.35	19.35	77.41
26	21.83	1.250	29.00	50.0	325.00	2.71	10.43	20.27	78.04
27	22.67	1.261	30.01	52.2	340.47	2.84	10.52	21.24	78.72
28	23.51	1.271	30.92	54.2	355.88	2.97	10.60	22.20	79.35
29	24.35	1.282	31.90	56.4	371.78	3.10	10.69	23.19	80.04
30	25.19	1.292	32.77	58.4	387.60	3.23	10.78	24.17	80.66
31	26.02	1.303	33.72	60.6	403.93	3.37	10.87	25.19	81.35
32	26.86	1.314	34.65	62.8	420.48	3.50	10.96	26.22	82.03
33	27.70	1.324	35.48	64.8	436.92	3.64	11.05	27.25	82.66
34	28.54	1.334	36.30	66.8	453.56	3.78	11.13	28.29	83.28
35	29.38	1.345	37.19	69.0	470.75	3.92	11.22	29.36	83.97
36	30.22	1.356	38.07	71.2	488.16	4.07	11.31	30.45	84.66
37	31.06	1.367	38.93	73.4	505.79	4.22	11.41	31.55	85.34
38	31.90	1.378	39.78	75.6	523.64	4.37	11.50	32.66	86.03
39	32.74	1.389	40.61	77.8	541.71	4.52	11.59	33.79	86.72
40	33.58	1.401	41.50	80.2	560.40	4.67	11.68	34.96	87.46
41	34.42	1.412	42.31	82.4	578.92	4.82	11.77	36.11	88.15
42	35.26	1.423	43.10	84.6	597.66	4.98	11.87	37.28	88.84
43	36.10	1.435	43.95	87.0	617.05	5.14	11.97	38.49	89.59
44	36.94	1.446	44.72	89.2	636.24	5.31	12.06	39.68	90.27
45	37.78	1.457	45.48	91.4	655.65	5.47	12.16	40.89	90.96
46	38.62	1.468	46.23	93.6	675.28	5.63	12.25	42.12	91.65
47	39.46	1.480	47.03	96.0	695.60	5.80	12.35	43.39	92.40
48	40.30	1.492	47.92	98.4	716.16	5.97	12.45	44.66	93.15
49	41.14	1.504	48.59	100.8	736.96	6.14	12.55	45.96	93.89
50	41.98	1.516	49.35	103.2	758.00	6.32	12.65	47.28	94.64

Technical Data

Table 2—Specific Conductivity (G) of Caustic Potash Solutions

C (Moles KOH/L)	G ₁₈	G _{19.1-23.4}	G ₂₅	G ₃₀	G _{50.5-52.4}	G _{80.1-80.2}
10.695	0.4212	—	—	—	—	—
9.292	0.4790	—	—	—	—	—
7.978	0.5221	—	—	—	—	—
6.744	0.5434	—	—	—	—	—
5.583	0.5403	—	—	—	—	—
4.491	0.5106	—	—	—	—	—
4.473	0.5199	—	—	—	—	—
3.806	—	0.5301 ⁴	—	—	0.7958 ⁵	1.0861 ⁹
3.467	0.4558	—	—	—	—	—
2.510	—	0.4044 ³	—	—	0.6202 ⁷	0.8291 ¹⁰
2.508	0.3763	—	—	—	—	—
2.013	0.3286	—	—	—	—	—
1.679	—	0.2968 ²	—	—	0.4563 ⁶	0.6089 ¹⁰
1.612	0.2723	—	—	—	—	—
1.005	0.1876	—	—	—	—	—
0.998	—	0.1870 ¹	—	—	0.3021 ⁸	0.3962 ⁹
0.961	—	—	—	0.2160	—	—
0.777	0.1464	—	—	—	—	—
0.500	0.1001	—	—	—	—	—
0.480	—	—	—	0.1165	—	—
0.2057	0.04334	—	—	—	—	—
0.1066	0.02309	—	—	—	—	—
0.05048	—	—	0.01284	—	—	—
0.01438	—	—	0.003689	—	—	—
0.009451	—	—	0.002434	—	—	—
0.007424	—	—	0.0019155	—	—	—
0.006455	—	—	0.0016723	—	—	—
0.005430	—	—	0.0014125	—	—	—
0.003481	—	—	0.0009144	—	—	—
0.002145	—	—	0.0005675	—	—	—
0.001175	—	—	0.0003124	—	—	—
0.0008087	—	—	0.00021495	—	—	—
0.0005917	—	—	0.00015654	—	—	—

Note: The exact temperatures for values with superscripts are as follows:

- | | |
|-----------|------------|
| 1. 19.1°C | 6. 50.6°C |
| 2. 20.7°C | 7. 51.3°C |
| 3. 21.6°C | 8. 52.4°C |
| 4. 23.4°C | 9. 80.1°C |
| 5. 50.5°C | 10. 80.2°C |

The specific conductivity “ G ” is expressed in reciprocal ohms (mhos) per cc.

Technical Data

Table 3 - Dielectric Constants (E) for Caustic Potash Solutions

C (Moles/L)	0	0.0000858	0.000171	0.000858	0.00171
E _{20.0°C}	80.50	80.28	80.08	78.71	—
E _{21.0°C}	80.15	—	—	78.30	76.37

Table 4 - Diffusion Coefficient (D) between Water and Caustic Potash Solutions

C (Moles/L)	0.01	0.02	0.05	0.10	0.20
D (cm ² /day)	1.903	1.889	1.872	1.854	1.843
C (Moles/L)	0.50	1.00	2.00		
D (cm ² /day)	1.841	1.855	1.892		

Table 5 - Dissociation Voltage (E) for Caustic Potash Solutions

C (Moles/L)	0.0125	0.125	1	4	10
E (Volts)	1.46	1.45	1.40	1.38	1.32

Note: A platinum cathode and an amalgamated zinc plated anode were used.

Table 6 - Equivalent Conductance (Π) of Caustic Potash Solutions

°C	°F	Π _∞ (mho)
18°	64.4	238.7
18°	64.4	239
25°	77.0	274.9
25°	77.0	274.9
25°	77.0	238.92
25°	77.0	285.46
90°	194.0	599

Table 7 - Heat (ΔH) Evolved in Neutralizing One Mole of Alkali with One Mole of indicated Acid at 20°C

Acid	KOH ΔH (Calories/100 Moles H ₂ O)	NaOH ΔH (Calories/100 Moles H ₂ O)
HCl	14014	13895
HBr	13988	13843
HI	13915	13779
HNO ₃	14086	13836

Technical Data

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Table 8 - Heat of Solution of Caustic Potash

°C	°F	Moles H ₂ O/Mole KOH	Heat of Solution kcal/mole	BTU/lb
11.4	52.5	260	12.46	399.9
18	64.4	250	13.29	426.5
100	212.0	260	16.8	539.2

Table 9 - Index of Refraction (n) of Caustic Potash Solutions

At 17.5°C (64)		At 18°C (21)	
C (Moles/L)	n	C (Moles/L)	n
0.0321	1.33358	0.1066	1.33440
0.1658	1.33513	0.2057	1.33552
0.5116	1.33896	0.5000	1.33872
0.8770	1.34275	1.005	1.34398
1.264	1.34650	2.013	1.35366
1.656	1.35021	4.473	1.37306
2.055	1.35388	—	—
2.465	1.35750	—	—
2.891	1.36109	—	—
3.324	1.36464	—	—
3.592	1.36675	—	—

Table 10 - Molar Magnetic Rotation for Caustic Potash Solutions (14.78%) at 0°C

Wave Length (Å)	4360	5460	5780
[M]	2.88	2.75	2.87

Table 11 - Molar Magnetic Susceptibility of Caustic Potash Solutions

-21.2×10^{-6} cgs units/mole
 -22.0×10^{-6} cgs units/mole

Table 12 - Molar Refraction, R_{mole} (Lorentz-Lorentz), D-Line Sodium, for Caustic Potash Solutions at 18°C (64.4°F)

C (Moles/L)	0	0.2	0.5	1.0	2.0	4.0
R_{mole}	7.36	7.31	7.28	7.28	7.29	7.19

Technical Data

Chart 1

Freezing Points of Aqueous KOH Solutions

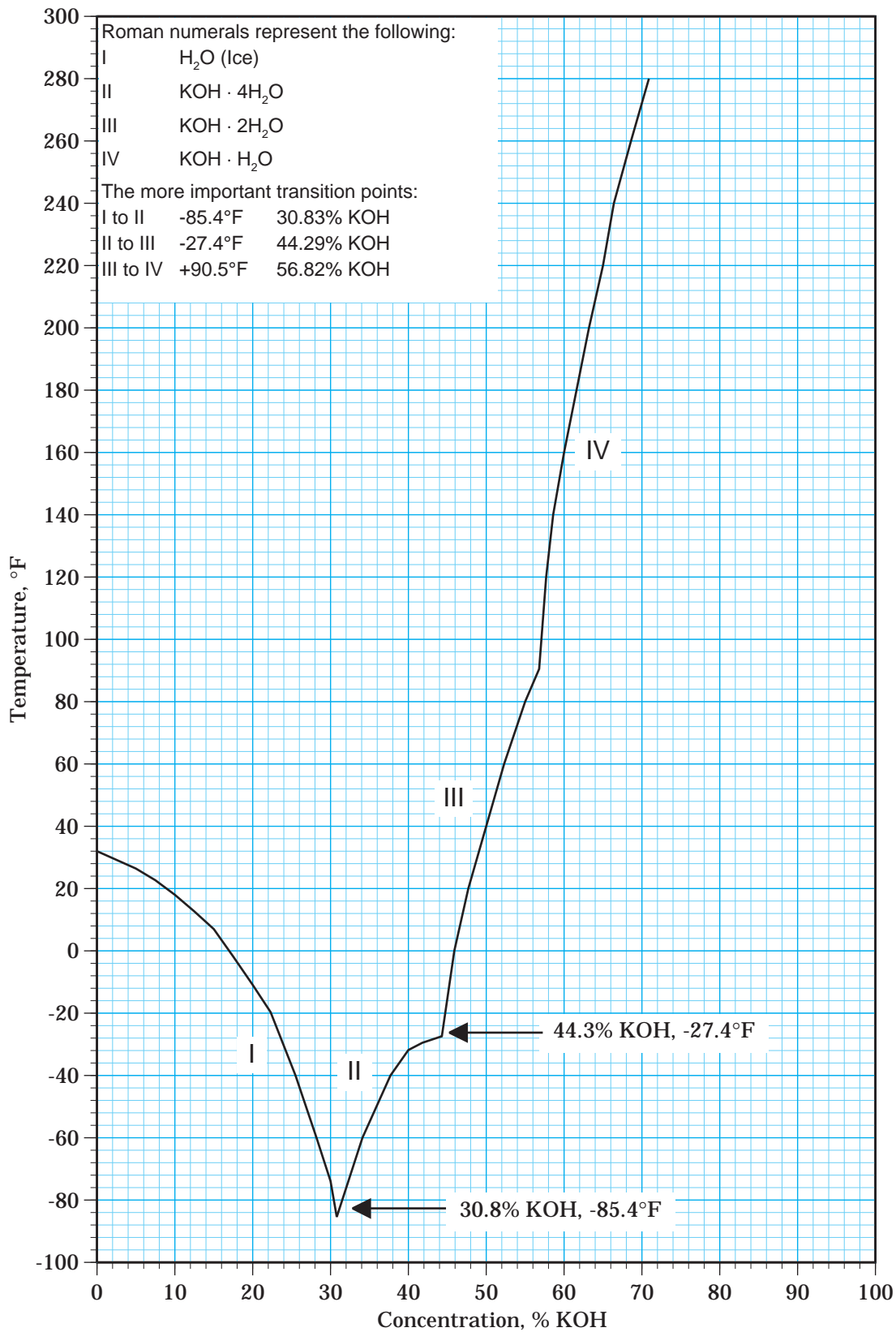
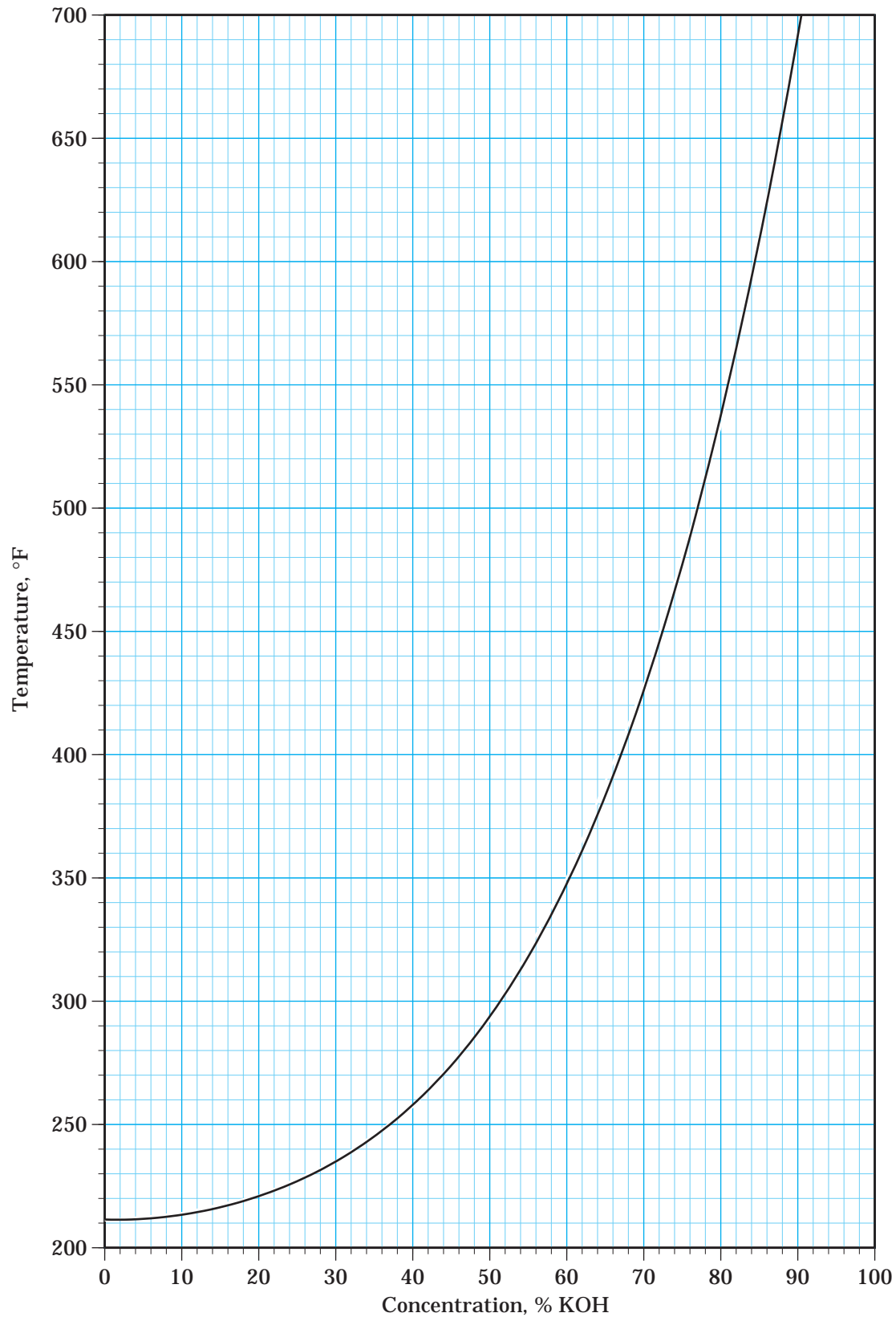


Chart 2

Boiling Points of Aqueous Solutions of KOH at Atmospheric Pressure



Technical Data

Chart 3

Density of KOH at Various Temperatures

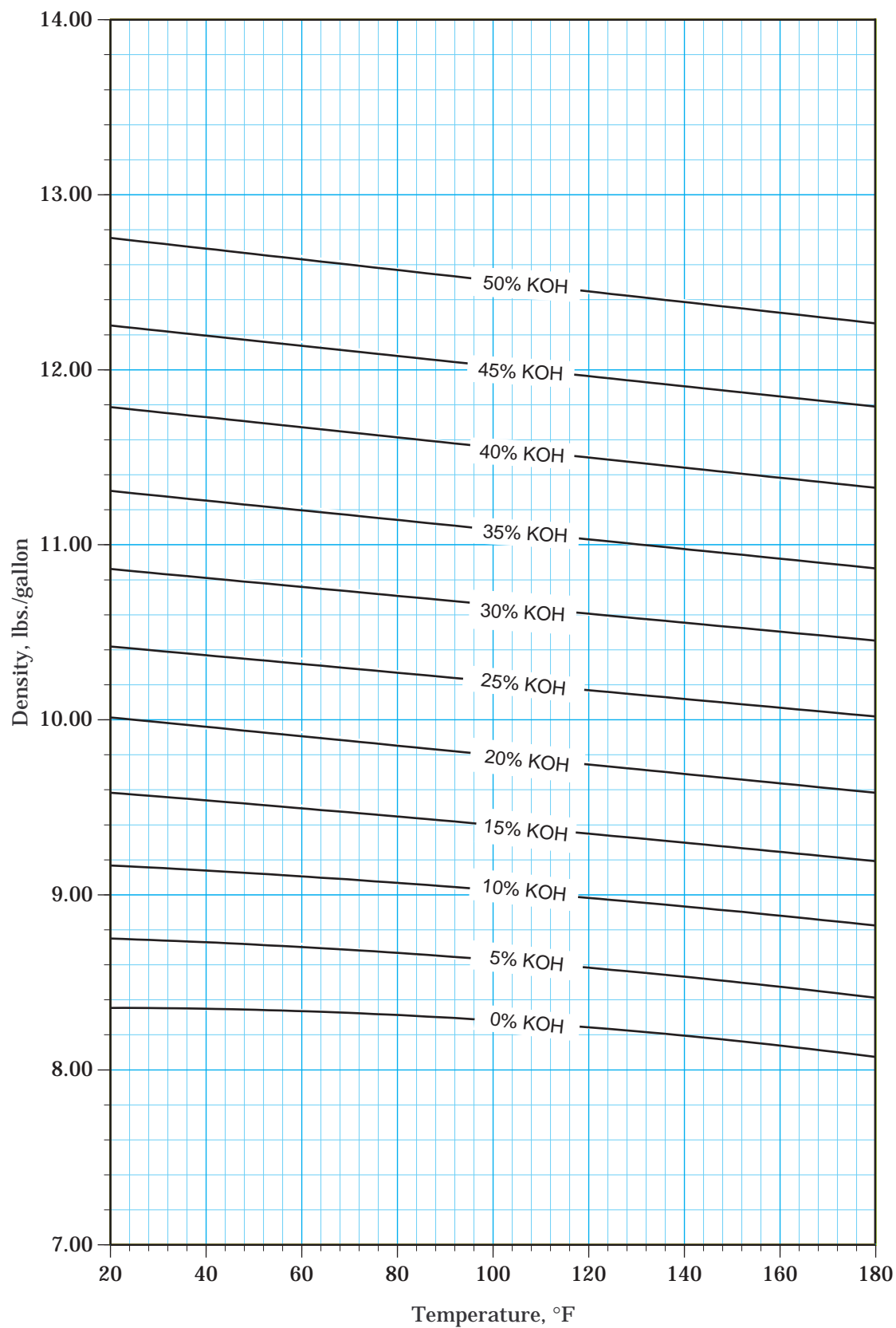
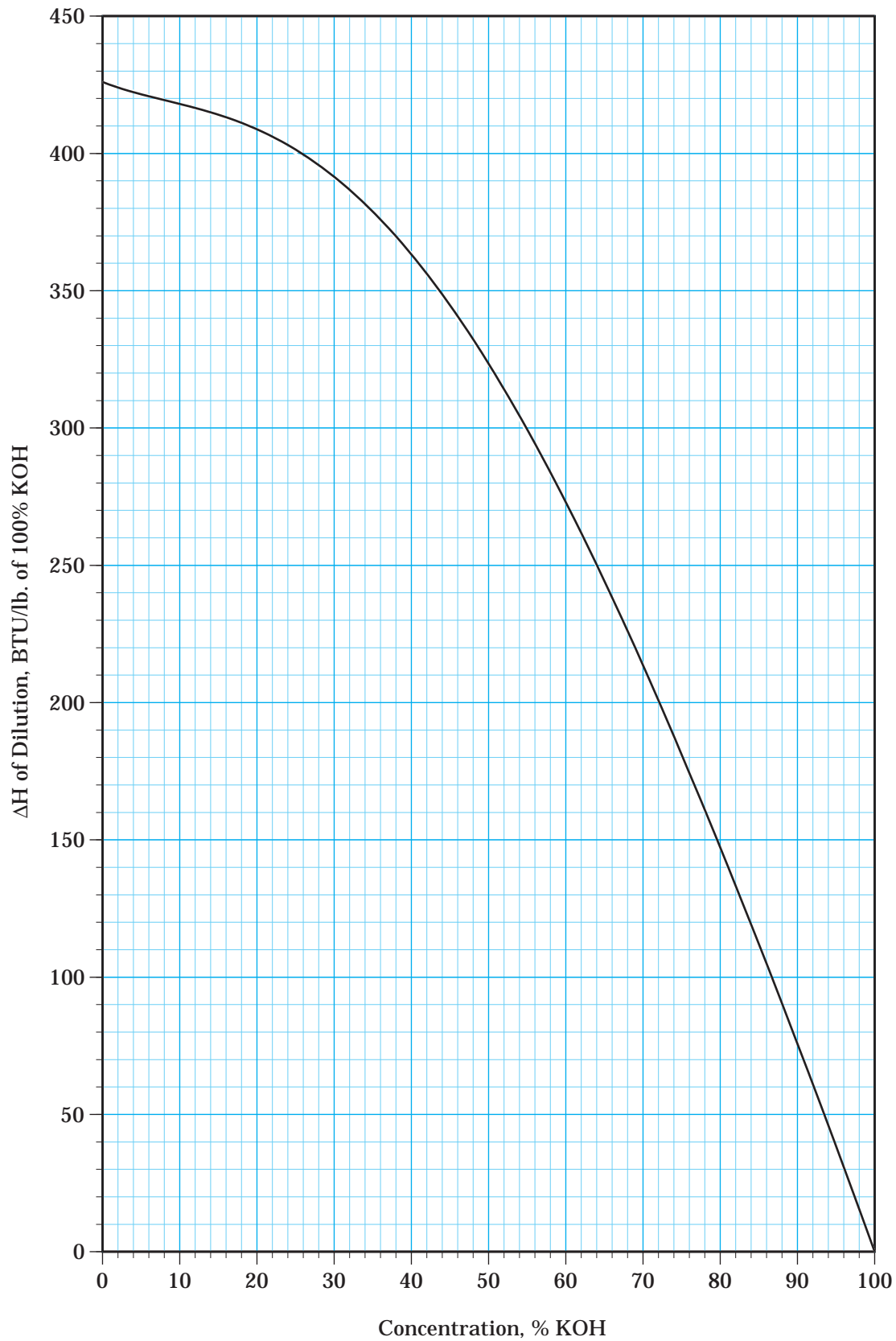


Chart 4

Heat of Dilution for Aqueous KOH Solutions at 64.4°F



Technical Data

Chart 5

Specific Heat of Aqueous KOH Solutions at 64.4°F

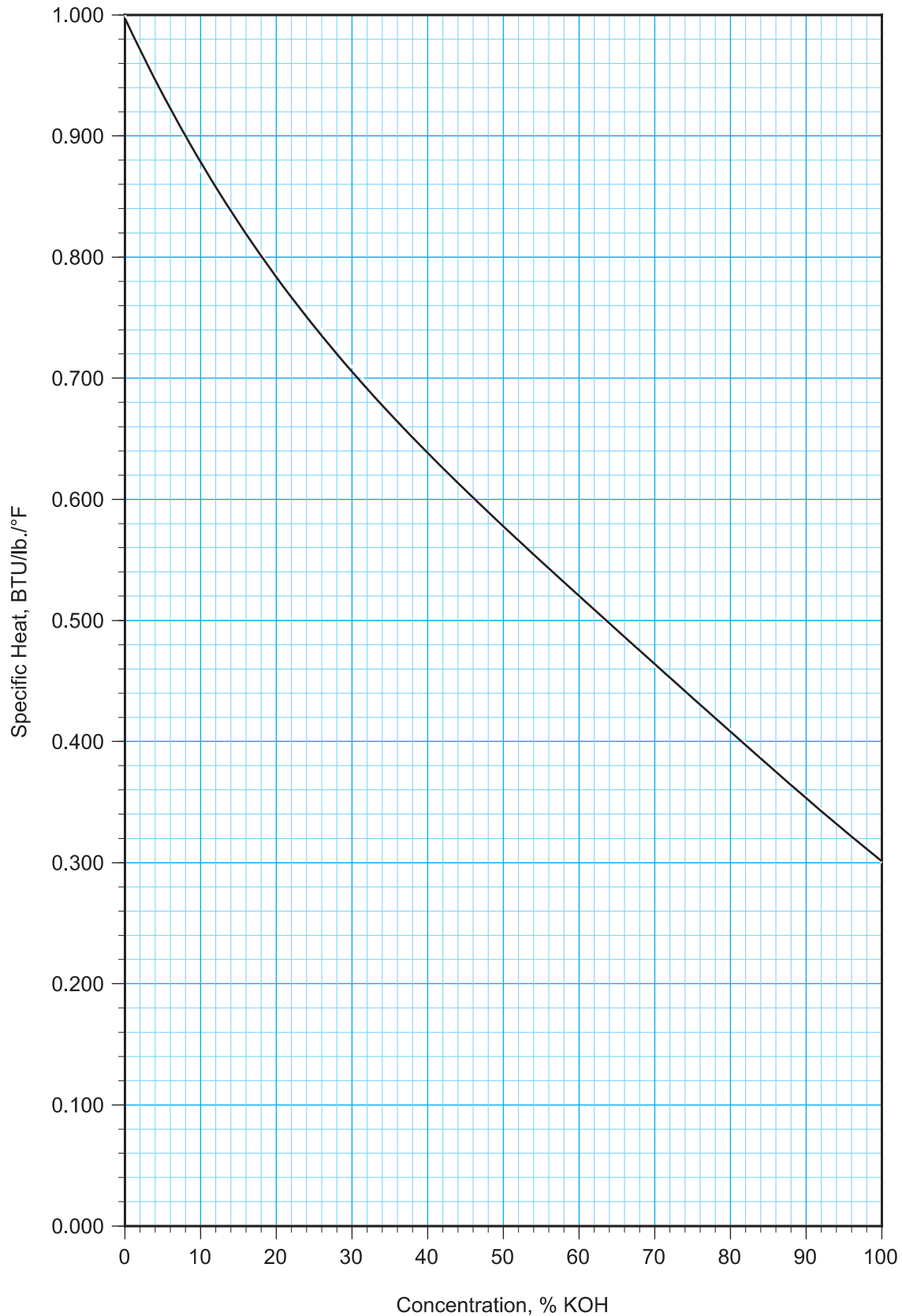
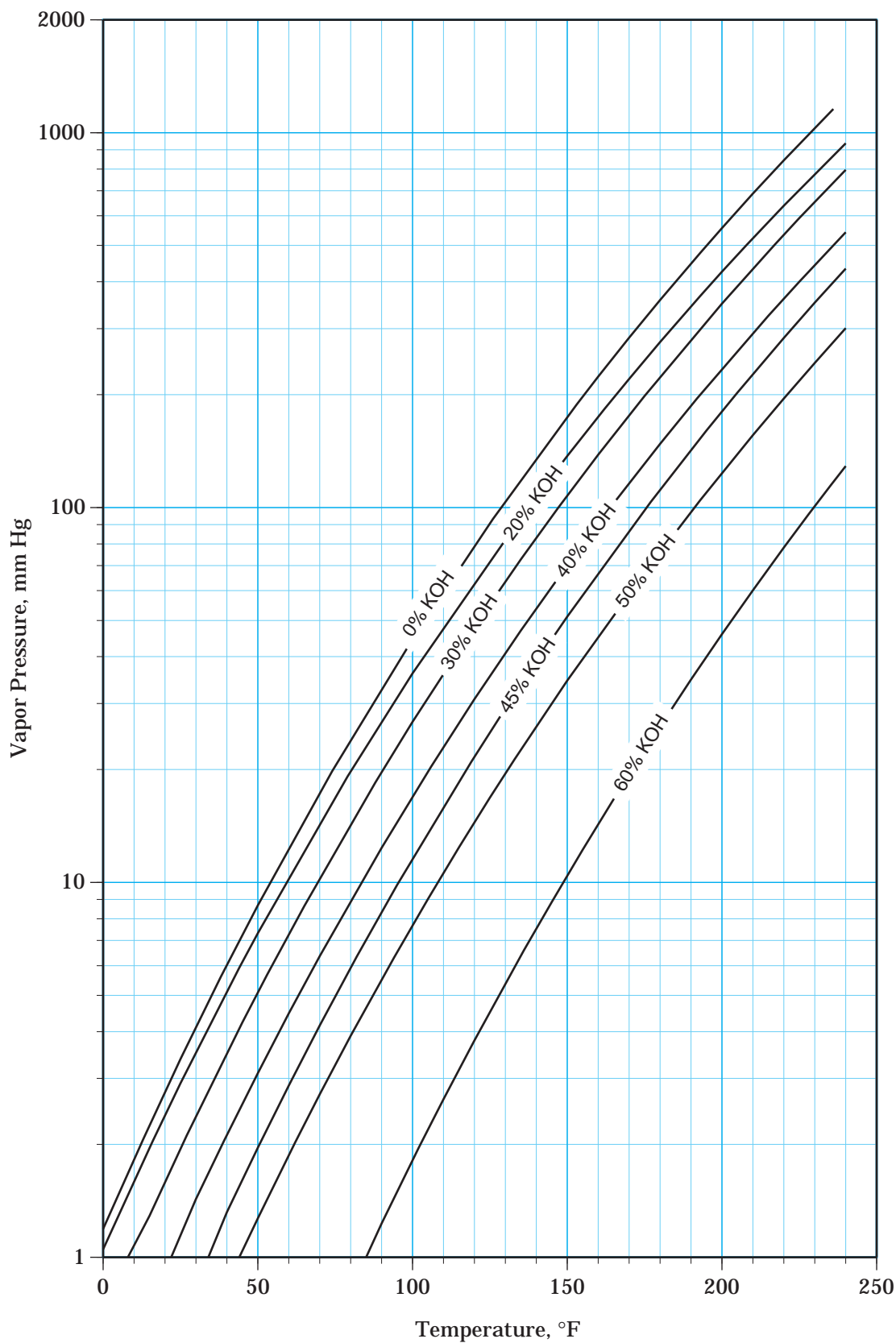


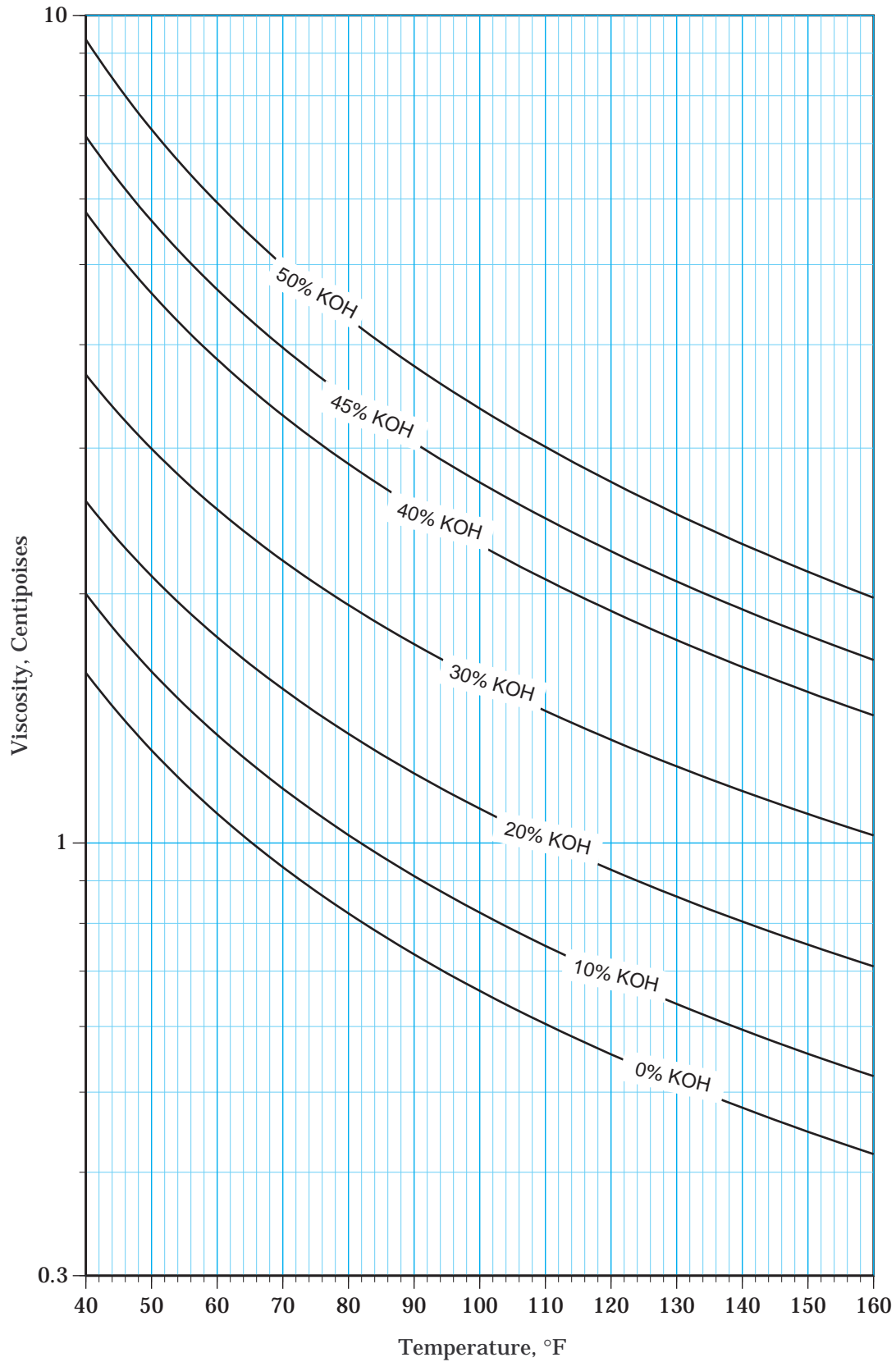
Chart 6



Technical Data

Chart 7

Viscosity of Aqueous KOH Solutions



HOW TO DILUTE/ STRENGTHEN CAUSTIC POTASH

Sometimes it is necessary to dilute or strengthen caustic potash solutions 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.

Refer to Table 1 for densities

DILUTING A SOLUTION

Problem:

To dilute 1,000 gallons of 45% KOH to a 20% solution. How much water is needed to accomplish this task?

Solution:

(The specific gravity of 45% KOH solution is 1.457 @ 60°F, taken from Table 1).

The dilution can be simplified by using the following formula:

$$D = V(A(B-C)/C)$$

Where:

A = Sp. Gr. of strong solution

B = Concentration of strong solution (% KOH)

C = Concentration of desired solution (% KOH)

D = Volume of water to be added

V = Volume of strong solution

And it Follows:

$$D = 1,000((1.457)(45-20)/20)$$

$$D = 1,000(1.82) = 1,820 \text{ gallons}$$

Result:

It will take 1,820 gallons of water to dilute 1,000 gallons of 45% KOH to a 20% solution.

VOLUME OF FINAL SOLUTION

Problem:

What is the final volume of the solution in the problem above?

In diluting caustic potash the volumes are not additive, so the diluted solution will not be the sum of the water and strong solution.

Solution:

The final volume is calculated by adding the weight of the original solution to the weight of the water added, then dividing by the density (in lbs./gal. from Table 1) of the desired solution:

$$\text{Density of Desired Solution (20\%)} = 9.93 \text{ lbs./gal.}$$

$$1,000 \text{ gallons of 45\% KOH weighs} = 12,160.0 \text{ lbs. [1,000}$$

$$\times 12.16 \text{ lbs./gal.}]$$

$$1820 \text{ gallons of H}_2\text{O weighs} =$$

$$15,178.8 \text{ lbs. [1,820} \times 8.34$$

$$\text{lbs./gal.}]$$

$$15,178.8 \text{ lbs. H}_2\text{O}$$

$$+ 12,160.0 \text{ lbs. 45\% KOH}$$

$$27,338.8 \text{ lbs.} \div 9.93 \text{ lbs./gal.} =$$

$$2,753 \text{ gallons of 20\% solution}$$

Result:

The actual volume is 2,753 gallons of 20% KOH solution, not the 2,820 gallons that might be expected by simply adding the volume of ingredients.

STRENGTHENING A SOLUTION

Problem:

How many gallons of 45% KOH must be added to 3,000 gallons of 20% solution to obtain a 30% solution?

Solution:

$$Y = X/S$$

$$X = ((C)(B)-A)/(D-C)$$

Where:

A = Weight of KOH in weak solution

B = Total Weight of weak solution

C = Percent of desired solution/100

D = Percent of strong solution/100

S = Density of strong solution

W = Density of the weak solution

Y = Gallons of strong solution necessary to produce desired solution

X = Weight of strong solution necessary to produce desired solution

For the example:

$$A = (9.93 \text{ lbs./gal.}) \times 3,000 \text{ gallons} \times 0.20$$

$$A = 5,958 \text{ lb. KOH}$$

$$B = (9.93 \text{ lbs./gal.}) \times 3,000 \text{ gallons}$$

$$B = 29,790 \text{ lb. of solution}$$

$$C = 30/100 = 0.3$$

$$D = 45/100 = 0.45$$

Substituting:

$$X = ((0.3)(29790) - 5,958) / (0.45 - 0.3)$$

$$X = 19,860 \text{ lb.}$$

$$Y = 19,860 / 12.16 \text{ lb./gal.}$$

$$Y = 1,633 \text{ gallons}$$

Result:

1,633 gallons of 45% KOH are needed to strengthen 3000 gallons of a 20% solution to 30%.

DISSOLVING ANHYDROUS (DRY) FORMS OF KOH

Problem:

What amount of anhydrous caustic potash and what amount of water must be added to obtain 1,000 gallons of a 20% solution?

Solution:

Using the equation above:

$$X = ((C)(B)-A)/(D-C)$$

Where:

A = 0, since there is no KOH in the water

$$B = (8.34)(Z)$$

$$C = 20/100 = 0.2$$

$$D = 90/100 = 0.9 \text{ (For all forms of anhydrous KOH the purity is 90\%)}$$

F = Density of desired solution

Z = Volume of water necessary to produce the 1,000 gal. of desired solution

Substituting:

$$X = ((0.2)[(8.34)(Z)] - 0)/(0.9 - 0.2)$$

$$X = 2.383(Z)$$

Since volumes are not additive for KOH solutions, the final volume of the desired solution is equal to the weight of the KOH added to the weight of the water, divided by the density of the desired solution.

Final volume of solution: = 1,000 gallons = (X + B)/F

Substituting:

$$1,000 = (X + B)/9.93$$

$$X = 9,930 - B$$

$$\text{Since } B = 8.34(Z)$$

$$X = 9,930 - 8.34(Z), \text{ from above we also know } X = 2.383(Z)$$

$$\text{Solving for Z: } 2.383Z = 9,930 - 8.34(Z) \quad Z = 926 \text{ gallons}$$

Solving for X:

$$X = 9,930 - 8.34(926)$$

$$X = 2,207 \text{ lbs of KOH}$$

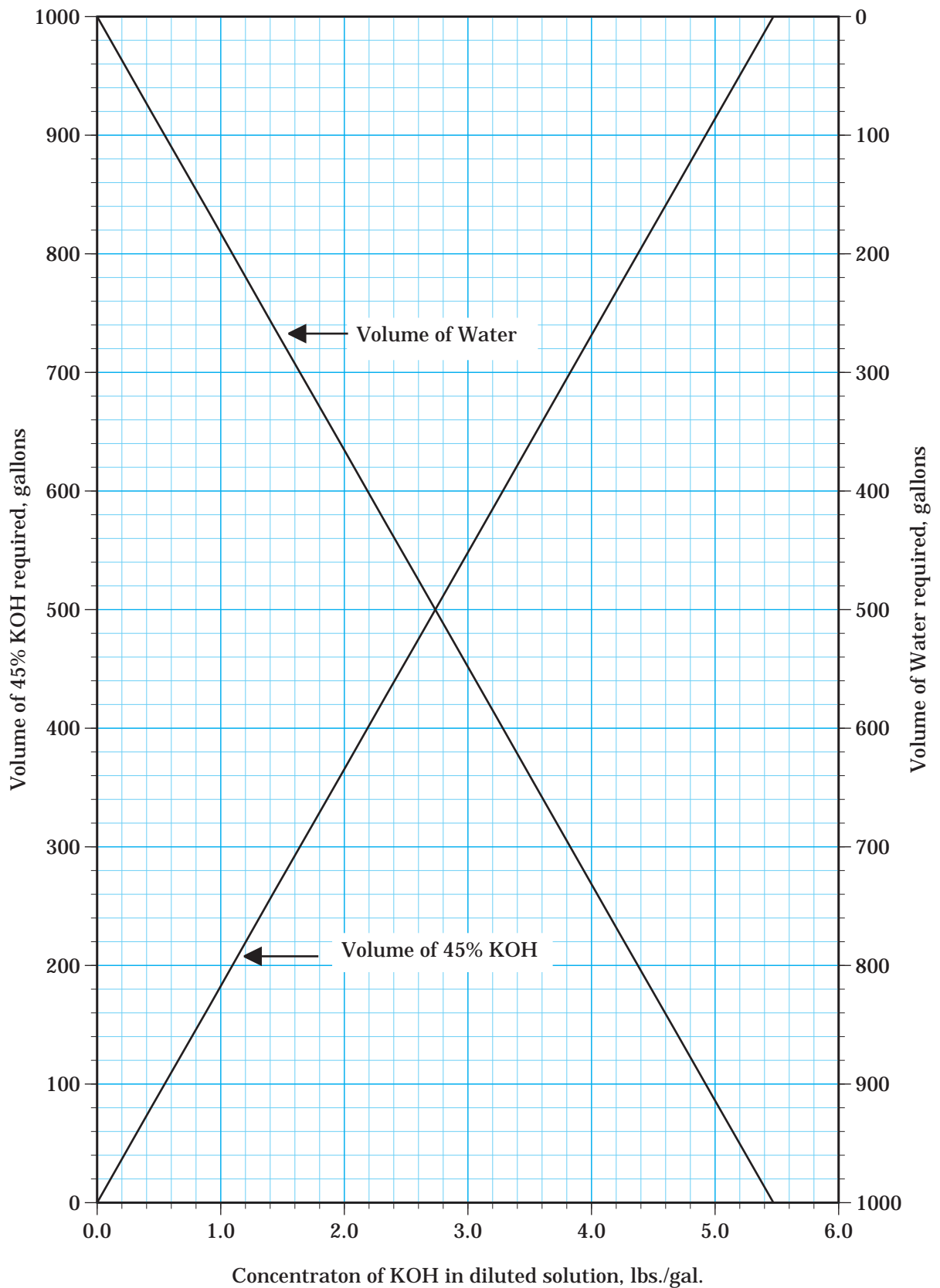
Result:

Add 2,207 lbs. of KOH to 926 gallons of water to produce 1,000 gallons of a 20% solution.

Technical Data

Chart 8

Dilution of 45% KOH



DETERMINATION OF THE TOTAL ALKALINITY OF CAUSTIC POTASH

PURPOSE AND THEORY

The accurate determination of the total alkalinity value for caustic potash is necessary for calculating the correct billing concentrations of this product.

Total alkalinity in caustic potash 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.

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#: 14-493-120MR 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 $\pm 0.0001N$ 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 cyanol FF (Fisher Cat#: BP125-50) in deion-

ized 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.

SAFETY

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

Caustic potash 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.

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 magenta 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 $Na_2CO_3 = 0.053$

$N = W/V \times 0.053$

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

B. ANALYSIS

1. To a clean, dry Erlenmeyer flask, accurately weigh to the nearest 0.001 grams an amount of sample as determined in the table below. Weighing should be performed as rapidly as possible. The sample sizes are:
45% KOH.....8 - 9 g
50% KOH..... 7 - 8 g
Anhydrous KOH..... 3 - 4 g
2. Immediately add 50 ml of deion-

ized 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 KOH = 0.05611

$$\% \text{ KOH} = \frac{(V)(N)(0.05611)(100)}{W}$$

$$\% \text{ K}_2\text{O} = 0.8394 (\% \text{ KOH})$$

EXAMPLE

8.470 grams of caustic potash required the addition of 68.62 ml of 1.0011N HCl to reach the modified methyl orange endpoint.

$$\% \text{ KOH} = \frac{(V)(N)(0.05611)(100)}{W}$$

$$\% \text{ KOH} = \frac{(68.62)(1.0011)(5.611)}{8.470}$$

$$\% \text{ KOH} = 45.51\%$$

$$\% \text{ K}_2\text{O} = (0.8394) (45.51)$$

$$\% \text{ K}_2\text{O} = 38.20\%$$

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.

Methods of Analysis

DETERMINATION OF POTASSIUM HYDROXIDE IN CAUSTIC POTASH

PURPOSE AND THEORY

The potassium hydroxide content of caustic potash 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 per cent KOH on a sample-weight basis.

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#: 14-493-120MR 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 phenolphthalein (Aldrich Cat#: 10,594-5 or equivalent) in 100 ml of methanol.

10% Barium Chloride; Dissolve 120 g of reagent grade $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Fisher Cat#: Bi34-500) 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.

SAFETY

Refer to the MSDS for the proper handling procedures for each of the chemicals listed in this procedure. caustic potash 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 protec-

tion and other protective clothing when handling these chemicals. Barium chloride is highly toxic. Avoid inhaling barium chloride dust.

A. STANDARDIZATION OF 1N HYDROCHLORIC ACID

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

B. ANALYSIS

- To a clean, dry Erlenmeyer flask, accurately weigh to the nearest 0.001 grams an amount of sample described in the table below. Weighing should be performed as rapidly as possible. The sample sizes are:
45% KOH..... 8 - 9 g
50% KOH..... 7 - 8 g
Anhydrous KOH..... 3 - 4 g
- Immediately add 100 ml of barium chloride solution, making sure the sides of the beaker are washed down.
- Add 3 to 4 drops of phenolphthalein indicator and carefully add the magnetic stirring bar.
- 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 dioxide from the air.
- 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 % KOH.

Let:

W = Weight (g) of sample titrated

N = Normality of HCl

V = Volume (ml) of HCl required

Milliequivalent wt. of KOH =

0.05611

$$\% \text{ KOH} = \frac{(V) (N) (0.05611) (100)}{W}$$

EXAMPLE

8.470 grams of caustic potash required the addition of 68.52 ml of 1.0011N HCl to reach the phenolphthalein endpoint.

$$\% \text{ KOH} = \frac{(V) (N) (0.05611) (100)}{W}$$

$$\% \text{ KOH} = \frac{(68.52) (1.0011) 5.611}{8.470}$$

$$\% \text{ KOH} = 45.44\%$$

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 POTASSIUM CARBONATE IN CAUSTIC POTASH (Gravimetric)

PURPOSE AND THEORY

The potassium carbonate content of a sample of caustic potash is determined by a direct gravimetric method. The method involves acidification of the caustic potash sample with dilute sulfuric acid, boiling, and weighing the carbon dioxide evolved. Accurate results can be obtained when the potassium carbonate content is 0.01% or greater. This method should be used to analyze samples of 45% or 50% caustic potash containing 0.01% to 0.25% K_2CO_3 .

APPARATUS

See the CO_2 train sketch below.

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 mois-

ture 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°F to 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 perchlorate 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. FeSO₄·7H₂O per liter.

Sulfuric Acid, concentrated.

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

Magnesium perchlorate, anhy-

drous.

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 potash 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 (pgs. 7 - 8).

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 potash samples or acids solutions.

PROCEDURE

1. Sample Preparation

The 50% liquid caustic potash will solidify at 40°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.

No special preparation is required for anhydrous samples. 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 min-

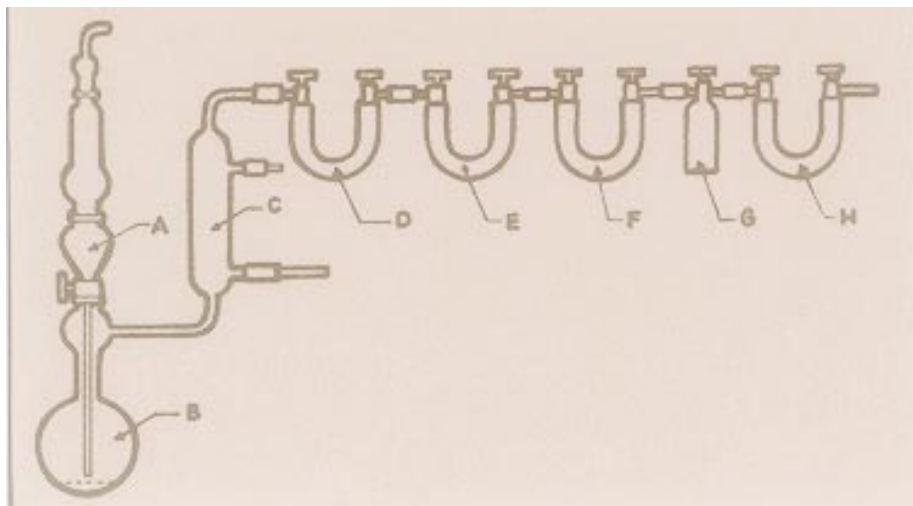
imize carbon dioxide pickup from the atmosphere.

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 20 g. (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 to 5 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



Methods of Analysis

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 procedure 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 CO₂ found in the first sample. Tower G1 is then ready for Run No. 3.

CALCULATIONS

Report results as per cent K₂CO₃ calculated to the nearest 0.01. Let:

W(CO₂) = Weight of CO₂ evolved
 W(S) = Weight of sample

$$\% K_2CO_3 = \frac{W(CO_2)(3.140)(100)}{W(S)}$$

EXAMPLE

If a 25 gram sample was used and the weight of CO₂ absorbed in tower "G" = 0.0125 grams, then:

$$\% K_2CO_3 = \frac{(0.0125)(3.140)(100)}{25}$$

$\% K_2CO_3 = 0.12\%$

DETERMINATION OF POTASSIUM CHLORIDE IN CAUSTIC POTASH

PURPOSE AND THEORY

Chloride is a contaminant in all grades of caustic potash. Potassium chloride is present at < 60 ppm in 45% caustic potash. Higher concentrations of this compound can have undesirable effects in many applications of the product. Conse-

quently, accurate determination of this impurity is most important.

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 potash 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:

$$AgNO_3 + KCl \Rightarrow AgCl + KNO_3$$

$$Excess AgNO_3 + NH_4SCN \Rightarrow AgSCN + NH_4NO_3$$

$$6NH_4SCN + Fe_2(SO_4)_3 \Rightarrow 2Fe(SCN)_3 + 3(NH_4)_2SO_4$$
 (reddish brown color)

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#:14-493-120MR 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.

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 photodecomposed 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 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 $\pm 0.0001N$ prior to use.

Ferric Indicator; prepare a saturated aqueous solution of ferric ammonium sulfate [FeNH₄(SO₄)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 MSDS for the proper handling procedures for each of the chemicals listed in this method.

Caustic potash 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.

METHOD

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; E200-86, 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 AgNO_3 with the NH_4SCN solution until the first permanent reddish-brown color appears and persists after vigorous shaking for 15 seconds. Record the volume of NH_4SCN 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:

$$N_1 = (N_2)(V_2)/(V_1)$$
 where:
 N_1 = Normality of NH_4SCN
 N_2 = Normality of AgNO_3
 V_1 = Volume of NH_4SCN required
 V_2 = Volume of AgNO_3 added
3. Determine the normality by averaging the results of at least three titrations.

C. PROCEDURE

1. To a clean dry Erlenmeyer flask, accurately weigh, to the nearest 0.01 g, 80 g of 45% liquid caustic potash or 40 to 80 g of dry caustic potash. Weighing should be performed as rapidly as possible.
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 (see Note 1).
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 (see Note 2). Record the volume of NH_4SCN required to reach the color change.
8. Titrate the sample solution with 0.1N ammonium thiocyanate until the same color change is reached and record the volume of NH_4SCN (see Notes 3 and 4).

D. CALCULATIONS

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

Let:

W = Weight of sample titrated

N = Normality of NH_4SCN

V_1 = Volume of NH_4SCN required to titrate blank

V_2 = Volume of NH_4SCN required to titrate sample

Milliequivalent wt. of $\text{Cl} = 0.03545$

$$\% \text{Cl} = \frac{(V_1 - V_2)(N)(0.03545)(100)}{W}$$

Calculate the percentage of potassium chloride as follows:
 $\% \text{KCl} = (\% \text{Cl})(2.1029)$

EXAMPLE

79.28 grams of 45% KOH required the addition of 19.54 ml of

0.1005 N NH_4SCN to reach the titration endpoint while the reagent blank required 19.95 ml of NH_4SCN to reach the same endpoint.

$$\% \text{Cl} = \frac{(V_1 - V_2)(N)(0.03545)(100)}{W}$$

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

$$\% \text{Cl} = 0.00180$$

$$\% \text{KCl} = (\% \text{Cl})(2.1029)$$

$$\% \text{KCl} = (0.00180)(2.1029)$$

$$\% \text{KCl} = 0.00378 \text{ or } 37.8 \text{ ppm}$$

NOTES

1. 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.
2. 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 end point 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.
3. 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.

Methods of Analysis

- 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 .

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 POTASH

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.

Ferric ion in an acidic medium reacts with thiocyanate ions to produce a red color complex. 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 potash can be determined.

APPARATUS

Visible Spectrophotometer; able to perform absorbance or % transmittance measurements at a wavelength of 480 nanometers.

Analytical Balance; capable of weighing to 0.01 grams.

100 ml Volumetric Flasks; Fischer Scientific Cat# 10-210-8C or equivalent.

Pipets, Class A Volumetric;
0.50 ml, Fischer Cat#: 13-650A or equivalent.
1.00 ml, Fischer Cat#: 13-650B or equivalent.
2.00 ml, Fischer Cat#: 13-650C or equivalent.
5.00 ml, Fischer Cat#: 13-650F or equivalent.
10.00 ml, Fischer Cat#: 13-650L or equivalent.
20.00 ml, Fischer Cat#: 13-50N or equivalent.

Spectrophotometer Cells, standard silica windows, 1 cm path-length; Fischer Cat#: 14-385-910C or equivalent.

REAGENTS

Deionized Water.

Hydrochloric Acid; ACS Reagent grade concentrated acid, Fisher Cat# A144 or equivalent.

1.5N Potassium Thiocyanate; add 145.77 grams of ACS Reagent grade KSCN (Fischer Cat#: P317-500 or equivalent) to a one liter volumetric flask, dilute to volume with deionized water and mix thoroughly.

Potassium Chloride, 240 g/L; add 240.0 grams of ACS Reagent grade KCl (Fisher Cat# P217-500 or equivalent) to a one liter volumetric flask, dilute to volume with deionized water and mix thoroughly.

Hydrogen Peroxide, 30%; Fischer Cat#: H325-500 or equivalent.

Iron Reference Standard Solution, 1000 ppm; Fischer Cat#: SI124-500 or equivalent.

pH Test Ribbons; Fischer Cat#: A979 or equivalent.

SAFETY

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

Caustic potash is a strong base. Hydrochloric acid is a strong acid. Hydrogen Peroxide is a strong oxidizing agent. 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 protec-

tion and other protective clothing when handling these materials.

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

METHOD

A. CALIBRATION OF THE SPECTROPHOTOMETER

- Prepare a stock iron standard by diluting 1.00 ml of the 1000 ppm iron reference solution to 100.0 ml with deionized water. This standard will have an iron concentration of 10 µg/ml.
- From the stock standard, transfer 0.50, 1.00, 2.00, 5.00, 10.0 and 20.0 ml aliquots to 100 ml volumetrics containing 50 ml of 240 g/L KCl. To the volumetrics, add 2.5 ml of conc. HCl and one drop of 30% hydrogen peroxide and allow to set for approximately one minute. After the minute, add 10.0 ml of 1.5N KSCN, fill the flasks to the 100 ml mark with deionized water and mix thoroughly. These calibration standards will contain 5.0, 10.0, 20.0, 50.0, 100, and 200 µg/100 ml of iron, respectively (see Notes 1,2 and 3).
- A reagent blank is prepared in the same manner although no iron solution is added to the blank.
- Refer to the instruction manual supplied with the spectrophotometer for specific instructions on the proper use of the instrument.
- Set the wavelength on the spectrophotometer to 480 nanometers.
- Fill two matched 1 cm spectrophotometer cells with the reagent blank. Place one cell in the reference compartment and one cell in the sample compartment if the instrument is a double beam type or place the reagent blank in just the sample compartment if it is a single beam unit. Adjust the absorbance reading obtained by the spectrophotometer to zero.

7. Proceed by taking absorbance readings for each of the calibration solutions, leaving the reagent blank in the reference cell of the spectrophotometer (double beam instrument). Absorbance readings must be taken within 15 minutes of adding the KSCN to the solutions since the color complex that is formed has limited stability.
8. Insert the concentrations of the iron standards ($\mu\text{g}/100\text{ ml}$) and their absorbance readings into a linear regression formula (available on many hand held calculators). Determine the best fit straight line for this data and the correlation coefficient (r^2) for the line. The correlation coefficient indicates how well the data conforms to the best fit line that has been calculated. It should be greater than 0.99. As an alternative to using a linear regression formula, the concentrations and absorbance readings of the calibration standards can be plotted on quadrilinear graph paper and the best straight line drawn through the data points.

B. ANALYSIS OF SAMPLES

1. Weigh to the nearest 0.1 gram, 10 grams of anhydrous or 20 grams of liquid caustic potash into a 100 ml volumetric.
2. Add 20 ml of deionized water and a 0.25 inch piece of pH test ribbon.
3. Slowly add conc. HCl until the test ribbon turns red, then add an additional 2.5ml of acid.
4. Cool the solution in a water bath until it has reached room temperature.
5. Add one drop of 30% hydrogen peroxide and mix. The purpose of the peroxide is to oxidize any ferrous ion that may be present in the sample to its ferric state since the KSCN only reacts with ferric ion.
6. Add 10 ml of 1.5N KSCN. Dilute to volume with deionized water and mix thoroughly.
7. Carefully transfer a portion of the sample solution to a 1 cm cell and measure the

absorbance on the spectrophotometer at a wavelength of 480 nm. Use the reagent blank in the reference cell of the spectrophotometer (double beam instrument only). Absorbance reading should be taken within 15 minutes after the KSCN has been added to the sample.

8. Insert the absorbance reading for the sample into the linear regression program established with the calibration standards and obtain the concentration of Fe in $\mu\text{g}/100\text{ ml}$ of the solution.

CALCULATIONS

Report results as ppm Fe, based on the weight of the sample. Let:
 C = concentration of Fe in $\mu\text{g}/100\text{ ml}$ solution
 W = weight of sample in grams

$$\text{ppm Fe} = C/W$$

NOTES

1. If a 20 gram sample of liquid product is used, the calibration standards will correspond to concentrations of 0.25 - 20.0 ppm of iron in the sample. If more or less iron is expected to be found in the products, the amount of iron in the standards should be adjusted accordingly.
2. If concentrations of less than 0.25 ppm iron are expected, the sensitivity of this method can be increased. The instrument can be calibrated with more dilute iron standards while using spectrophotometer cells with a 5 cm rather than 1 cm path-length. Increasing the path-length will proportionally increase the absorbance readings.
3. When caustic potash samples are neutralized with HCl, the resulting solutions contain KCl. Calibration standards and reagent blanks should therefore contain this compound. Adding 50 ml of 240 g/L KCl to the standards and blanks approximates the amount of KCl formed in neutralized samples if a 20 gram sample of liquid product is used. If a sample size other than 20 grams is used, the amount of KCl added should be adjusted accordingly.

QUALITY ASSURANCE

With each batch of samples, analyze at least one of the samples in duplicate. On a regular basis, reanalyze samples that have been previously tested and compare results.

Concentrations of iron found in the analyzed samples should be compared with OxyChem specifications.

Perform duplicate and sample spike analyses on a minimum of 10% of all samples analyzed. Duplicate analyses should be reproducible within 15%. Samples should be spiked with iron at approximately 1 to 2 times the concentration that is expected to be in the sample.

DETERMINATION OF SODIUM IN CAUSTIC POTASH

ATOMIC ABSORPTION METHOD

PURPOSE AND THEORY

Sodium may be present in caustic potash products. If sodium is detrimental to the end use of the product, the concentration should be determined.

APPARATUS

Atomic Absorption Spectrophotometer.

100-ml Volumetric Flasks; Polypropylene, CMS Cat.# 253-260 or equivalent.

10-ml Volumetric Pipets; Fisher Cat.# 13-650-2L or equivalent.

Adjustable Pipetter; with disposable plastic tips, Eppendorf Model 4810 (100 to 1000 μl), CMS Cat.# 382-283 or equivalent.

Analytical Balance; accurate to 0.001 grams.

REAGENTS

Sodium Reference Standard Solution, 1000 ppm; transfer 2.542 grams of NaCl (dried at 110 °C for two hours) to a one liter volumetric flask. Dilute to volume with deionized water and mix. Transfer to a plastic bottle. Standards are commercially available (CMS Cat.# 737-631).

Sodium Working Standard Solution, 100 $\mu\text{g}/\text{ml}$; transfer 10.00 ml of the reference standard to a

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100 ml volumetric. Dilute to volume with deionized water and mix. Prepare a fresh standard daily.

SAFETY

Refer to the MSDS for the proper handling procedures for each chemical.

Caustic potash and hydrochloric acid are corrosive solutions. These chemicals are corrosive to body tissue and may cause severe and immediate burns. Wear proper gloves, eye protection and other protective clothing.

Improper operation of the AA can cause a flashback or explosion. Refer to the instrument manual for proper use procedures.

ANALYSIS

1. Weigh 1.25 grams of caustic potash to 0.001 grams into a 100-ml volumetric flask. Dilute to volume and mix. This will be the stock sample solution from which dilutions are made and analyzed.
2. Pipet 10 ml of the diluted caustic potash sample (if low sodium grade) or 1 ml (if commercial grade) into each of three 100-ml volumetric flasks.
3. Dilute the contents of one flask to volume and mix.
4. To the second and third flask, add aliquots of the working sodium standard solution so that the amounts of Na added to the flasks will be approximately 100% and 200%, respectively, of the anticipated sodium concentration. Typically, aliquots of 0.20 ml and 0.40 ml will be appropriate. (See notes 2 and 3.)
5. Dilute the contents of flasks 2 and 3 to volume.
6. Optimize the AA for sodium analysis. The 589.0 nm wavelength is the most sensitive and stable wavelength for sodium. Refer to the instrument manual for specific instructions.
7. Aspirate the unspiked sample solution into the AA flame and record the absorbance.
8. Aspirate the standard addition samples from flasks two and three into the flame and record the absorbances.

9. Calculate the micrograms of Na in the working sample solution using the standard addition method. Consult the instrument manual for details.
10. Taking into account the dilution factor, calculate the μg of Na in the stock sample solution. To determine ppm Na in the product, let:
 C = concentration of Na in the stock solution
 W = weight of sample
 $\text{ppm Na} = C/W$

EXAMPLE

45% caustic potash is to be analyzed for sodium by flame AA. It is expected to contain approximately 200 ppm.

If 1.25 g of the sample is diluted to 100 ml and a 10 ml aliquot of the solution is diluted to 100 ml, the final dilution will contain:
 $= (200\text{ppm})(1.25\text{g}/100\text{ ml}) \times 10 = 25\text{ }\mu\text{g Na}/100\text{ ml}$

Standard addition samples should then be prepared to give an additional 25 μg and 50 μg of sodium in 100 ml samples.

These spikes can be prepared by adding 0.25 and 0.50 ml aliquots of a 100 $\mu\text{g Na}/\text{ml}$ working standard to the second and third flasks, respectively.

NOTES

1. Sodium is extremely sensitive to atomic absorption. There may be enough sodium in the sample to cause an extremely high readout. If this should occur, rotate the burner head. This has the same effect as diluting the sample.
2. Store all reagents in plastic bottles to avoid either sodium pickup from the glass or absorption on the glass container walls.
3. Once the samples have been prepared, they should be run as soon as possible to avoid sodium contamination from the air or the surroundings.
 - a. Several rinses with hot tap water.
 - b. Several rinses with sodium-free distilled water.
 Initial glassware cleaning may be done with acid chromate

cleaning solution.

4. The amount of diluted standard prepared is for a limited number of samples. If many samples are to be analyzed, a larger volume of diluted standard may be prepared.
5. The diluted standard should be prepared fresh daily. This is necessary to avoid either sodium pickup from the glassware, the surroundings, or sodium absorption on the walls of the glassware.
6. Use distilled water from the same supply for any one analysis.

DETERMINATION OF NICKEL IN CAUSTIC POTASH

PURPOSE AND THEORY

Nickel may be present at varying concentrations in caustic potash products. Nickel can be detrimental to the end use of the product. When it is present at concentrations of less than 1 ppm in liquid caustic potash, the heptoxime method can be used for accurately determining levels of at least 0.1 ppm. By reducing the sample size, higher concentrations of nickel can be measured, making this method applicable for all grades of caustic potash products. This procedure has been found to be faster than methods which require the nickel to be extracted by an ion exchange resin or an organic solvent.

Nickel in caustic matrices can be quantified by using a visible spectrometer (at 445 nm) to measure the intensity of the orange color formed by the addition of heptoxime (cycloheptanedionedioxime). Nickel/heptoxime complexes are similar to those formed with dimethylglyoxime, however, the heptoxime complex is reported to be more stable (Ref. 1). Divalent nickel forms a pink color complex with heptoxime which is less intense than the orange colored complex at higher oxidation states. To insure nickel is oxidized to a higher valence state, bromine is added as an oxidizing agent prior to addition of the hep-

toxime. Citric acid is also added to the sample solution to complex any iron which would interfere with the analysis.

APPARATUS

Visible Spectrophotometer; capable of measuring absorbance or % transmittance at a wavelength of 445 nanometers.

Spectrophotometer Cells; standard silica windows, 5 cm path-length; Fisher Cat#: 14-385932E or equivalent.

Analytical Balance; capable of weighing 100 +/- .01 grams.

100 ml Volumetric Flasks; Class A Volumetric, Fisher Scientific Cat# 10-210-8C or equivalent.

Pipets, Class A Volumetric; 2.00 ml, Fisher Cat#: 13-650-2C or equivalent.

4.00 ml, Fisher Cat#: 13-650-2E or equivalent.

6.00 ml, Fisher Cat#: 13-650-2G or equivalent.

10.00 ml, Fisher Cat#: 13-650-2L or equivalent.

20.00 ml, Fisher Cat#: 13-650-2N or equivalent.

REAGENTS

Water, Deionized.

Hydrochloric Acid, Concentrated; Trace Metal grade, Fisher Cat#: A508.

Citric Acid, 10%; dissolve 10 g citric acid (Aldrich Cat#: 24,062-1 or equivalent) into water and dilute to 100 ml.

Hepoxime (1,2-Cycloheptanedionedioxime), 0.1%; dissolve 0.1g of cycloheptanedionedioxime (CAS# 530-97-2) (Pfaltz & Bauer. Cat#: C29880 or ICN Cat#: 204213) into 100 ml of ethanol.

Ammonium Hydroxide, Concentrated; Trace Metal grade, Fisher Cat#: A144.

Nickel Reference Standard Solution, 1000 ppm; Atomic Absorption standard, Fisher Cat#: SN70-100 or equivalent.

Bromine water, saturated; add approximately 4-5 ml. of ACS Reagent Grade bromine. (Aldrich Cat#: 27,757-6) to 100 ml of deionized water and mix.

pH Test Paper; pH range 1-12, Fisher Cat#: 14-850-11B or equivalent.

SAFETY

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

Caustic potash and ammonium hydroxide are strong bases and 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 materials.

Bromine is highly toxic, very corrosive and a strong oxidizing agent. Use only in a well ventilated fume hood. Wear proper gloves, proper eye protection and other protective clothing when handling this material.

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

CALIBRATION OF THE SPECTROPHOTOMETER

1. Transfer 1.00 ml of the 1000 ppm nickel reference standard solution to a 1 L volumetric flask and dilute to volume with deionized water. This stock standard will have nickel concentration of 1.00 µg/ml.
2. Transfer 2.00, 4.00, 6.00, 10.00, and 20.00 ml aliquots of the 1.00 µg/l nickel stock standard to 100 ml volumetrics containing approximately 50 ml of deionized water. Add one drop hydrochloric acid and mix. Add 5 ml of the citric acid solution and mix. Add 2 ml. of saturated bromine water and mix. Add 3 ml of conc. ammonium hydroxide and mix. Add 2 ml. of hepoxime solution, mix and dilute the flask to volume.

Note: These standard concentrations will be equivalent to 0.1, 0.2, 0.3, 0.5 and 1.0 ppm of nickel if a 20 gram sample of caustic potash is used.

3. A reagent blank is prepared in the same manner although no nickel solution is added to the blank.
4. The solutions should set for 20 minutes from the time the hepoxime is added to allow for full color development.

5. Set the spectrophotometer wavelength to 445 nm. Refer to the instruction manual supplied with the spectrophotometer for specific instructions on the proper use of the instrument.
6. Transfer portions of the reagent blank solution to matched spectrophotometer cells and place them in both the reference and sample cell holders of the spectrophotometer if it is a double beam instrument or just the sample cell holder if it is a single beam instrument. Zero the absorbance reading of the instrument.
7. With the blank solution remaining in the reference compartment (double beam instrument only), record the absorbance readings for each calibration standard. Plot absorbance vs. nickel amount (µg) using a linear regression program to generate a calibration curve.

ANALYSIS OF SAMPLES

1. Into a 100 ml volumetric flask, weigh to the nearest 0.01 grams, the amount of caustic potash product needed to accurately determine its nickel concentration. After addition of the product, add 20 ml of deionized water. Use the table below as a guideline for the correct sample size.

Expected Ni Sample Concentration	Size
0.0-0.1 ppm.....	20 g
0.1-0.2 ppm.....	10g
0.2-0.4 ppm.....	5 g
0.4-0.8 ppm.....	2.5g

2. Place the flask in an ice bath to cool the contents. Slowly neutralize the sample with concentrated hydrochloric acid. Check the pH of the solution with pH test paper. The paper can be touched to the flask's stopper after HCl addition and some mixing. Do not add a piece of pH paper to the flask itself. The paper can dissolve and the resulting turbidity can affect the final colorimetric reading. For

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every gram of 45% caustic potash, 0.66 ml of conc. HCl will be required. When the neutralization point is near, the solution can be adjusted to neutral by the addition of more dilute HCl. After the sample is pH neutral, add one additional drop of concentrated hydrochloric acid.

CAUTION: Neutralization of these products with concentrated acid will generate a considerable amount of heat. Add the acid in small increments and cool in between additions to prevent splashing and excessive heating.

3. After the solution has reached room temperature, add 5 ml of the citric acid solution and mix well. The purpose of the citric acid is to complex any iron that might be present so that it does not compete with the nickel for consumption of the complexing reagent. If concentration of iron in these samples is known to be low, it may not be necessary to add this reagent.
4. Add 2 ml of saturated bromine water and mix thoroughly.
5. Add 3 ml of conc. NH_4OH and mix.
6. Add 2 ml of heptoxime solution and mix.
7. Dilute the flask to volume with deionized H_2O and mix thoroughly.
8. Allow the flasks to set for 20 minutes from the time the heptoxime was added for full color development.
9. Carefully transfer a portion of the sample solution to a 5 cm cell, stopper the cell and place in the sample compartment of the spectrophotometer. (For double beam instruments, the reagent blank should be placed in the reference compartment.) Read the absorbance of the sample solution at a wavelength of 445 nm.
10. Use the absorbance reading to obtain the amount (μg) of nickel in the sample solution from the calibration curve.
11. Calculate the concentration of nickel in the original product and report as ppm.

CALCULATIONS

Let:

C = concentration of Ni in $\mu\text{g}/100 \text{ ml}$ of solution

W = weight of sample in grams

$$\text{ppm Ni} = C/W$$

EXAMPLE

20.11 g of caustic potash was analyzed by the above procedure for nickel. An absorbance reading of 0.1000 was obtained on the sample solution. Standards containing 2 μg to 20 μg Ni were prepared and a calibration curve generated using Procedure A.

Standard Concentration	Absorbance Reading
2.00 μg . Ni.....	0.0258
4.00 μg . Ni.....	0.0510
6.00 μg . Ni.....	0.0775
10.00 μg . Ni.....	0.1287
20.00 μg . Ni.....	0.2610

A calibration curve was generated by performing a linear regression analysis on these readings. In this example the coefficient of correlation is 1.000. Coefficients of correlation greater than 0.99 are acceptable.

From the linear regression equation, the absorbance reading obtained for the sample is 0.1000 which is equivalent to 7.72 μg Ni.
 $\text{ppm Ni} = 7.72 \mu\text{g Ni}/20.11 \text{ g ppm Ni} = 0.38 \text{ ppm Ni}$

QUALITY ASSURANCE

Perform duplicate and sample spike analyses on a minimum of 10% of all samples analyzed. Duplicate analyses should be reproducible within 15%. Spike samples with nickel at approximately 1 to 2 times the concentration that is expected.

Compare concentrations of nickel found in the analyzed samples to OxyChem specifications.

REFERENCES

1. APHA, AWWA, WPCF; Standard Methods for the Examination of Water and Wastewater; 17th ed.; pp 3-121-123.
2. Vogel, Arthur I., A Text-book of Quantitative Inorganic Analysis, 3rd edition, 1961.
3. Kolthoff, Sandell, Meehan & Bruckenstein; Quantitative Chemical Analysis; 4th ed.; Macmillan Co.

DETERMINATION OF MERCURY IN CAUSTIC POTASH

PURPOSE AND THEORY

Mercury is a toxic material and must be monitored as a pollutant. It can cause adverse effects if present in caustic potash used in certain manufacturing processes.

Mercury is converted to mercuric ion by oxidation with potassium permanganate, then reduced to metallic mercury which is aerated from the solution and determined by flameless (cold vapor) atomic absorption spectroscopy.

PROCEDURE

ASTM E 538: "Standard Test Method for Mercury in caustic Soda (Sodium Hydroxide)" is the procedure used for analyzing mercury in caustic potash products and is published in the Annual Book of ASTM Standards, Vol. 15.05. For a copy of this test procedure, contact: ASTM, 1916 Race St., Philadelphia, PA 19103 or OxyChem's Technical Service Dept.