Abstract

Caustic soda (sodium hydroxide, NaOH) and caustic potash (potassium hydroxide, KOH) are the chemicals of choice for pH control of water-based drilling fluids. Approximately 33,000 to 45,000 tons of these chemicals are used annually in the drilling fluids industry. Both are corrosive materials, handling of which causes reportable injuries in the drilling industry each year. Before being added to the drilling fluid, dry caustic is dissolved in water at the rig site. This process gives off a great deal of heat and results in a highly corrosive solution. Traditional methods of handling caustic at the rig site involve the risk of exposure to dry caustic and concentrated caustic solutions. This paper describes improved techniques and equipment that are available for rig-site mixing of caustic that significantly reduce the possibility of worker exposure.

Introduction

The use of caustic soda (sodium hydroxide, NaOH) to raise the pH of drilling fluids dates from the 1930s when commercial mud thinning agents became available. These thinning agents, such as quebracho and lignosulfonates, require a high mud pH in order to have their effect. High pH lime muds continued to be popular through the 1940s and 1950s and even today the pH of most water-based drilling fluids is maintained in the 10 to 12 range. To keep the pH in this range, caustic must be added frequently while drilling. Typical engineering recommendations call for 0.25 – 3.0-lb/bbl caustic in water-based drilling fluid. Caustic potash (potassium hydroxide, KOH) is used when the inhibiting effect of the potassium ion is desired. For the purposes of this paper, caustic soda and caustic potash are referred to collectively as "caustic."

Use of Caustic in Drilling Mud

Nearly 14 million tons of caustic soda is produced annually. The pulp and paper, detergent, and chemical industries are the largest users. Manufacturers typically supply caustic soda to industry as a 50% aqueous solution. Drilling fluids is one of the few industries where dry caustic soda is used.

Caustic used in drilling fluids is typically supplied to the rig in dry form (flakes or beads) in 40-lb or 50-lb sacks. While dry caustic is sometimes added directly to the drilling fluid system, more frequently it is dissolved in water at the rig site and added to the drilling fluid in liquid form to ensure that it is rapidly and evenly mixed throughout the entire drilling fluid system. In some cases liquid caustic has been supplied directly to the rig site, but this practice is widely viewed as impractical due to packaging, storage, logistics, and cost considerations.

Accurate data on annual caustic consumption in the drilling fluids industry is difficult to obtain. Table 1 gives estimates from two sources. This usage translates into rig workers handling approximately 1.5 million to 1.8 million 50-pound sacks annually.

A combination of lime and soda ash is sometimes used to raise the pH of drilling fluid by generating hydroxyl ions by the following reaction in solution:

\[ \text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2 \text{Na}^+ + 2 \text{OH}^- \]

This method of pH control has several disadvantages:

- The low solubility of lime and soda ash (Table 2) make this method of pH control inefficient for fluid systems which require pH greater than 10.
- The formation of insoluble CaCO₃ results in unwanted solids being added to the drilling fluid.
- In H₂S situations, the ability to raise the pH quickly is a safety consideration.

Hazardous Characteristics of Caustic

Two characteristics of caustic account for the dangers of handling it in drilling operations: its corrosive nature, and its high heat of solution.

Corrosivity

US OSHA criteria define dry caustic and caustic solutions as corrosive. A chemical is defined as corrosive if it causes visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact. Caustic soda solutions of 4% concentration are corrosive to skin, eyes and mucous membranes.
Airborne caustic dust or mist is irritating to the respiratory system. The American Conference of Governmental Industrial Hygienists (ACGIH) has set a Threshold Limit Value - Ceiling (TLV - C) of 2.0 mg/m³ for both caustic soda and caustic potash. This is the concentration in workplace air that should not be exceeded at any time.

**High Heat of Solution**

Caustic also has a very high heat of solution. The heat of solution ($\Delta H$) is the heat evolved or absorbed when a substance is dissolved in a solvent. A negative $\Delta H$ indicates heat is released (an exothermic reaction) and a positive $\Delta H$ indicates that heat is absorbed (an endothermic reaction). The $\Delta H$ of caustic soda and caustic potash are given in Table 3 with the data for sodium chloride and potassium chloride for comparison.

When caustic is dissolved in water the exothermic reaction results in a rapid increase in the temperature of the solution (Fig. 1). If dry caustic is added to water slowly with agitation, the caustic will dissolve rapidly and the resulting heat will be dissipated throughout the solution volume. However, if a large quantity of caustic is added rapidly to water without sufficient agitation, or if a large solid mass is added, the caustic mass will form a layer of hydrate, dissolve slowly, and result in local overheating, boiling and splattering of the solution. A similar condition will result if water is added to dry caustic.

Traditional caustic handling practices on drilling rigs have resulted in numerous serious accidents ranging from minor skin burns to fatalities. 1.2% of the lost time injuries in the worldwide drilling industry are caused by contact with chemicals.

**Traditional Practices**

From the initial utilization of caustic as a drilling fluid additive during the 1930’s to the present, the equipment and practices associated with adding caustic to drilling fluids has undergone only minimal evolution and development.

Early use of caustic in drilling fluids was most likely achieved by adding the product directly to the active fluid system. Methods of direct addition include dumping dry caustic into the suction pit or through a hopper system. Today, neither of these methods is considered to be an accepted industry practice, because of the inherent dangers of workers coming into contact with the caustic. From an operational perspective, the direct addition of dry caustic to the active drilling fluid system is less effective for pH control than if the dry caustic is first pre-solubilized in water prior to addition.

Over the years, it has been common practice among drilling contractors to allow each rig to fabricate caustic mixing equipment based on design criteria of their own discretion or past experiences. It has been only recently that significant advances have been made in the design of caustic mixing equipment.

The advent of the “chemical barrel” or “caustic barrel” resulted most likely from rig-site ingenuity in response to the need for pre-solubilizing caustic prior to addition into the drilling fluid. Initial caustic mixing barrels were of rudimentary design and usually built out of material available on site. The most common of such designs was in the re-use of a 55-gallon drum, as illustrated in Fig. 2. This design made use of the existing threaded drum bung for the attachment of a discharge valve. However, this also necessitated turning the drum on its side and cutting away a portion of the side to facilitate mixing operations. In the absence of restraining devices, this design is inherently unstable. In application, a caustic solution is created by adding dry caustic and water into the drum, then agitating the contents with a shovel. Once mixed, the discharge valve is opened allowing the solution to drain into the drilling fluid system. It should be noted that there are no design provisions directed at mitigating exposure of personnel to potential contact with the caustic solution.

Later improvements in the caustic mixing barrel are shown in Fig 3. This design incorporates some engineering controls designed to reduce worker exposure. A more stable, upright position for the 55-gallon drum is utilized and a paddle agitator is added to facilitate mixing. Later models were fabricated from heavier weight materials such as large casing or conductor pipe and were firmly affixed to the mud pit grating. Later still, hinged lids were added to minimize exposure during the agitation process. However, exposure due to splashing or “boil over” effects is still possible when the lid is opened for the addition of caustic and water. This type of mixing barrel is still widely used today.

**Improved Techniques**

Further evolution of caustic mixing equipment has come to include features such as an overflow vent, internal baffle, water inlet port and a worktable on which a sack of caustic may be placed to facilitate product addition into the mixing tank. These features are illustrated in Fig. 4. This design style, or some variation thereof, is becoming more common in today’s drilling industry. However, it must be noted that the design features still require the lid to remain open while the dry caustic is added to the mixing chamber that was previously filled with water. This process places personnel at risk of exposure to a caustic solution in the event a rapid “boil over” occurs during the addition of caustic to the mix tank. During a “boil over” event, escaping fluid will attempt to follow a path of least resistance once above the internal baffle; typically this will be through the top opening, as compared to the usually small inner diameter of most overflow vents.

Recent advances in the design of caustic mixing
equipment have begun to specifically address the hazards resulting from “boil over” and the potential for personnel to come into contact with a caustic solution during the mixing process. The need to completely isolate the worker from the mixing chamber has resulted in designs such as the one depicted in Fig. 5. This design allows for the addition of dry caustic to a hopper with subsequent transfer of the caustic to the mixing chamber via an auger.

Fig. 6 illustrates a mixing system that utilizes a fully enclosed mixing process. In this design, the system incorporates two separate chambers, each capable of being isolated or connected by either closing a valve or lid. In operation, dry caustic is placed into the upper chamber and sealed by closing the top lid. Then the middle flapper valve is opened, dumping caustic into the lower mixing chamber. Once the caustic is dumped, the middle flapper valve is closed. From a remote location, the addition of water and air (for agitation purposes) is applied to start the mixing process. In the event a “boil over” is initiated, the effects are directed through a system of overflow vents to a controlled area away from personnel. Field trials of the design have had favorable results and at least one major drilling contractor has retrofitted its rigs with this design.

All of the chemical barrel designs discussed so far have used gravity flow to transfer the caustic solution to the drilling fluid. An alternate method, shown in Fig. 7, utilizes suction from the mud hopper to transfer the caustic solution from the mixing chamber to the fluid system. The disadvantages of this system are the inability to use the mud hopper while caustic solution is being added to the drilling fluid and the possibility of caustic solution coming out through the hopper. A lock out tag out-type device must be used to prevent this.

Guidelines for Safe Handling of Caustic

Risk Assessments and Job Safety Analyses should be carried out on all operations where caustic is stored, transported, or handled. The guidelines below are general in nature and should be adapted to local circumstances and operating conditions.

Before working with caustic, it is important to be aware of its properties, know what safety precautions to follow, and know how to react in case of contact. Also, read, understand, and follow the recommendations on the latest Material Safety Data Sheet (MSDS).

Accidental exposure to caustic may occur under several conditions. Potentially hazardous situations include all transporting or handling operations, mixing and diluting operations, equipment cleaning and repair, and decontamination following spills, and equipment failures.

Employees who may be subject to such exposure must be provided with the proper Personal Protective Equipment (PPE) and trained in proper procedures, precautions and emergency response.

Personal Protective Equipment (PPE)

When handling caustic, the following PPE is required:

- Wear chemical splash goggles for eye protection during the handling of caustic in any form. The goggles should be close fitting and provide adequate ventilation to prevent fogging, without allowing entry of liquids.

- The use of a full-face shield may be appropriate when splashing can occur.

- Wear chemical-resistant gloves made of natural or synthetic rubber, PVC, or other plastics to protect the hands while handling caustic. Gloves should be long enough to come well above the wrist. Sleeves should be positioned over the glove wrists so that caustic can not get into the gloves.

- Wear protective, steel-toe boots. Wear trouser legs on the outside of the boots; if tucked inside, caustic can get into the boots.

- Wear chemical resistant clothing for protection of the body. Impregnated vinyl or rubber suits or aprons are recommended. Ensure full coverage of arms, legs, and torso.

- Because of its irritating nature, even at low exposure levels, caustic should be mixed only in a well-ventilated area. It is advisable to wear a respirator at all times when handling caustic. Use a NIOSH-approved N95 air purifying respirator.

Mixing Equipment

Equipment for mixing caustic varies greatly from rig to rig. The special precautions outlined below for safe mixing of caustic will apply to most caustic mixing systems; however, they may not apply to certain specialized equipment. Always follow any specific instructions that apply to a specific system.

Special Precautions for Mixing Caustic

A great deal of heat is given off when dry caustic is dissolved in water; however, if caustic is added to water slowly and allowed to dissolve with agitation, boiling of the solution will not occur. A violent reaction occurs with boiling, spurtting, and splattering of the solution when dry caustic is added to water so rapidly that the heat can not be dissipated.

Follow the precautions below whenever mixing caustic solutions:

1. Make sure that emergency eyewash and shower equipment are available. A functioning and easily accessible emergency eyewash and shower should be located wherever caustic is stored or handled. All workers should know the location of the eyewash and shower and be trained in its proper use. Emergency eyewash and shower equipment should meet the requirements of ANSI Z358.1-1990.

2. Wear all PPE described above. Do not allow
caustic to come into contact with the body. Do not breathe caustic dust, mist, or spray.
3. Add the caustic to the water. When making solutions with dry caustic, always add the caustic to the water. Never add the water to the caustic.
4. Agitate the water while adding the caustic. Dry caustic will dissolve rapidly in a well-agitated solution. Without agitation, the dry caustic will fall to the bottom and form a layer of hydrate that will dissolve quite slowly and can lead to overheating and splattering.
5. Add slowly. Dry caustic may absorb moisture from the air and partially solidify in the container into large blocks or lumps. If these large pieces are dropped into a caustic solution during preparation, they may cause dangerous splashing or a violent reaction with boiling. Carefully break up large pieces of caustic before adding them to the solution. Be certain that most of the caustic has dissolved before adding more.
6. Do not use very hot or very cold water. Always start with lukewarm water (80 – 100 °F, 26 – 37 °C). Never add dry caustic to hot or cold water.
7. Never add caustic through a mixing hopper. Many dry drilling fluid products are mixed into the system through a mixing hopper attached to a circulating line. Because of the danger of caustic particles or dust blowing back onto the operator, caustic should never be mixed through this type of hopper.
8. Handle empty containers with caution. Empty caustic containers (bags or drums), shrink wrap material and pallets will be contaminated with caustic residue. Use caution in handling these wastes.
   Remember that a violent reaction with boiling and splattering can occur if caustic is added to water too rapidly, if the solution is not sufficiently agitated, or if the caustic is added to hot or cold water. Care must be taken to avoid these situations.

Other Protective Practices
- Keep equipment clean by washing off any accumulation of caustic.
- Caustic mixing equipment should have welded piping where practical. Use flanged joints with gaskets made of caustic resistant material such as rubber, PTFE, Viton® B or EPDM rubber. If a screwed fitting is used, apply Teflon® tape to the threads.
- When disconnecting or disassembling equipment for repairs, first verify that there is no internal pressure on the equipment and that the equipment has been drained and washed.
- Provide mixing equipment with adequate overflow pipes. Overflow pipes should be directed into the mud pits.
- If pumps are used, shield the packing glands to prevent the spraying of caustic solutions in the event of a leak.
- In case of a spill or leak, wear all PPE and stop the leak as soon as possible. After containment, collect the spilled material and recycle, reuse, or transfer to a chemical waste area. Neutralize residue with dilute acid (preferably acetic). Flush spill area with water and follow with a liberal covering of sodium bicarbonate or other acceptable drying agent.

First Aid
- For Eyes: If caustic contacts the eyes, flood them immediately with plenty of clean water. Continue flushing for at least 15 minutes. While flushing, forcibly hold the eyelids apart to ensure rinsing of the entire eye surface. Seek professional medical attention immediately after following emergency first aid procedures. Do not use any kind of neutralizing solution in the eyes.
- For Skin: If caustic comes in contact with skin or clothing, flush with plenty of clean water for at least 15 minutes. If eyes have not been exposed, do not remove goggles until the face and hair have been thoroughly rinsed. Remove contaminated clothing and footwear. Thoroughly wash affected clothing and chemical-resistant footwear before reuse. Discard contaminated leather footwear. Seek professional medical attention immediately following first aid.
- For Inhalation: In the event of inhalation of caustic dust, mist, or spray, remove the victim from the contaminated area to fresh air. If breathing has stopped, start artificial respiration. Administer oxygen if available. Seek professional medical attention immediately after emergency first aid.
- For Ingestion: Although it is unlikely in an industrial situation that caustic would be ingested, it could be swallowed accidentally. If that occurs, DO NOT induce vomiting. Give the victim large quantities of water and, if available, several glasses of milk. If vomiting occurs spontaneously, position the victim’s head to keep airway clear. NEVER give anything by mouth to an unconscious person. Seek professional medical attention immediately following emergency first aid.

Conclusions
1. Large quantities of corrosive caustic (NaOH and KOH) are handled by drilling rig workers every year.
2. Traditional methods of handling caustic at the rig site involve the risk of exposure to dry caustic and concentrated caustic solutions.
3. Improved techniques and equipment are available for rig site mixing of caustic that significantly reduce the possibility of worker exposure.

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technical assistance.

References
2. Occidental Chemical Corp.: *Caustic Soda Handbook*.
3. Estimate based on data from M-I L.L.C.
7. International Association of Drilling Contractors (IADC) data.

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<table>
<thead>
<tr>
<th>Table 1</th>
<th>Annual Use of Caustic in Drilling Fluids</th>
<th>Short Tons (Metric Tons)</th>
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<tbody>
<tr>
<td></td>
<td><strong>1978</strong></td>
<td><strong>2001</strong></td>
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<tr>
<td>NaOH</td>
<td>45,000 (40,823)</td>
<td>33,000 (29,937)</td>
</tr>
<tr>
<td>KOH</td>
<td>700 (635)</td>
<td>4,100 (3,720)</td>
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<th>Table 2</th>
<th>Solubility @ 25°C ***</th>
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<tr>
<td>Substance</td>
<td>Solubility (%)</td>
</tr>
<tr>
<td>NaOH</td>
<td>50.0</td>
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<tr>
<td>KOH</td>
<td>54.7</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>23.5</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>Slight</td>
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* Mass % of solute

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<th>Table 3</th>
<th>Heat of Solution *</th>
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<tr>
<td>Substance</td>
<td>ΔH (kJ/mole)</td>
</tr>
<tr>
<td>NaOH</td>
<td>– 44.51</td>
</tr>
<tr>
<td>KOH</td>
<td>– 57.61</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.88</td>
</tr>
<tr>
<td>KCl</td>
<td>17.22</td>
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Fig. 1 - Dilution temperatures of dry caustic soda
(Data from PPG Industries, Inc.).
Figure 2
Traditional Chemical Barrel Early Design
Figure 3
Traditional Chemical Barrel
Upright Design with Agitator and Lid
Figure 4
Improved Chemical Barrel
Internal Baffle Design
Figure 5
Improved Chemical Barrel
Auger Transfer Design

Sealed Lid for Hopper Tank
Work Table for Caustic Sack
Feed Hopper
Screen / Strainer
Auger Feed System
Mechanical Hand Crank
For Auger / Agitator Systems
Chain / Sprocket Drive
Bevel Gear Drive
Water Fill Inlet
Mixing Chamber
Mix Agitator
Discharge Outlet
Overflow / Vent Line
Figure 6
Improved Chemical Barrel
Valve Isolation Design

Sack Slide
Flapper Valve
Hopper
Overflow
Water Line
Caustic Bed
Air Line
Vent Line
Thermometer
Discharge
Figure 7
Improved Chemical Barrel
Hopper Suction Design

Mud Hopper
Hopper Valve
Mud Line to pits
Shut off ball valve

Caustic Barrel
Blade mixer