
CHAPTER 7 **U.S. Safety and Environmental Information**

This chapter is an introductory knowledge base regarding the safety and handling of CBFs in the U.S. and adjacent offshore waters and should be read carefully. It should in no way be considered exhaustive or the sole source of information. Reference should be made to the applicable regulations published by U.S. state and federal regulatory agencies that have the authority to oversee the health and safety of workers and environmental compliance during oil and gas development operations. Your primary contact should be your company's health, safety, and environmental personnel. In addition, TETRA fluids specialists are extensively trained and experienced in the proper methods of handling clear brine fluids and are a resource available to the completions engineer.



Before handling a specific CBF, read the appropriate Material Safety Data Sheet (MSDS) to understand all of the hazards involved when handling that particular fluid.

This chapter will cover:

1. CBF Chemical Constituents
2. Brine Handling and Personal Safety
3. Environmental Considerations: Brine Handling and Disposal
4. Agency Contact Information

CBF Chemical Constituents

Clear brine fluids are concentrated solutions of simple salts. As they are not highly reactive, their chemical behavior is secondary to their physical properties such as density and clarity. Chemical constituents of CBFs include the positively charged cations of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), calcium (Ca^{+2}), and zinc (Zn^{+2}). Of these, only zinc and ammonium are regulated environmentally. None of them are con-

sidered highly toxic. In fact, zinc is an essential micronutrient and has been shown to reduce the severity of common colds. The negatively charged anions are chloride (Cl^-) and bromide (Br^-), both of which are found in seawater, but at a much lower concentration than is found in a clear brine fluid.

Another family of CBFs is based on the formate ion. The formate ion (HCO_2^-) is also used in some CBF applications in conjunction with sodium, potassium, and cesium. Formate is a low molecular weight, organic anion and is biodegradable.

Despite the fact that none of the constituents are in and of themselves highly toxic, the concentrations at which these constituents exist in CBFs can create workplace hazards and cause damage to the environment. Since CBFs are chemically simple, it is easy to make light of their safety and environmental issues. However, these materials are hazardous and should be accorded all due respect.

Brine Handling and Personal Safety

Completion fluids containing compounds such as calcium chloride (CaCl_2), calcium bromide (CaBr_2), and zinc bromide (ZnBr_2) are made by dissolving these and other salts in water. The common CBF chemical salts are shown below in Table 45. The Chemical Abstracts Service registration number (CAS), given in the last column, is a universal reference number for each chemical compound.

TABLE 45. CBF Constituents and Chemical Abstracts Service Numbers

| Name | Formula | CAS |
|--------------------|-------------------------|------------|
| Ammonium Chloride | NH_4Cl | 12125-02-9 |
| Potassium Chloride | KCl | 7447-40-7 |
| Sodium Chloride | NaCl | 7647-14-5 |
| Sodium Bromide | NaBr | 7647-15-6 |
| Calcium Chloride | CaCl_2 | 10043-52-4 |
| Calcium Bromide | CaBr_2 | 7789-41-5 |
| Sodium Formate | NaO_2CH | 141-53-7 |
| Potassium Formate | KO_2CH | 590-29-4 |
| Cesium Formate | CsO_2CH | 3495-36-1 |
| Zinc Bromide | ZnBr_2 | 7699-45-8 |

Handling of Clear Brine Fluids

The high concentrations of dissolved salts in CBFs impart a strong affinity for water—to the point where they will readily absorb water from the air (hygroscopic). This strong tendency to absorb water is the basis for most of the safety precautions that should be observed when working with any clear brine fluid.

Contact While Handling

There are certain use and handling precautions that should be followed when rig personnel are working with these fluids. Fluid contact with the skin can cause slight irritation and redness upon a short, single exposure. Continued or prolonged exposure can cause superficial to severe burns of the skin. The fluids can also cause potential eye injury if contact occurs. Contact with the eyes can cause moderate to severe irritation to permanent corneal injury.



Eye protection is mandatory for all personnel working with clear brine fluids.

Heat of Solution

Another aspect of working with clear brine fluids which calls for respect, is that the addition of dry CaCl_2 or CaBr_2 salt can generate excessive heat of solution. If solid CaCl_2 is added too rapidly while preparing an 11.6 lb/gal brine, enough heat can be generated to raise the solution temperature to more than 200°F. Care must be taken to avoid being burned by the hot liquid or equipment.

For weight up applications, it is advisable to perform a pilot test first in order to check the kind of temperature rise that may be expected in the field.

Toxic Fumes

Two circumstances exist where toxic fumes can be released:

1. Brines are not flammable, but they can release chlorine and/or bromine gases in fires fueled by other sources, and
2. Oxidizers such as calcium hypochlorite, which is commonly used as a polymer breaker, can release chlorine and/or bromine gases under acidic conditions. Chlorine and bromine gases are both heavier than air and will settle into lower or confined spaces and displace all breathable air.

Safety Equipment

The type and amount of safety apparel recommended will vary with the specific task being performed. However, hard hats, goggles or safety glasses with side shields, rubber gloves, and rubber boots should be the minimum safety apparel worn when working with, or in the vicinity of, clear brine fluids. Safety packages that contain this necessary equipment are available from all of TETRA's stock points.

Safety Equipment Overview:

- Goggles or safety glasses with side shields will provide eye protection.
- Face shields may be used in conjunction with goggles or safety glasses, but should not be used alone as they are primarily used to protect the face and throat from frontal splashing.
- Safety showers and eyewash stations should be easily accessible to each area of high activity. Portable eyewash units are highly recommended for remote locations.
- Rubber gloves prevent direct contact of any brine fluid with the hands and arms. A popular alternative to these gloves is thin latex gloves that are worn under cotton knobbies.
- Rubber boots should always be worn around brines. The hygroscopic nature of the brines can dehydrate and cause severe shrinkage in leather boots.
- When splashing is likely, such as when tripping pipe, slicker suits are recommended. Extra time should be allowed for completing projects to prevent personnel from overheating. Slickers should be worn properly and should be periodically cleaned.
- Dust masks should be available when mixing dry additives.
- Moisturizing creams can help prevent the loss of moisture to brines when used beforehand and can help replace the oils and moisture that may already have been lost.

Several precautions may be taken at the well site in order to create a safer environment:

- Pipe wipers not only reduce fluid loss when pulling pipe, they also minimize the danger of fluid dripping onto the floor and rig crew.
- Bristle type floor mats should be used wherever the floor may become wet with clear brine fluid.
- All spills should be cleaned with soap and fresh water in order to remove any slippery residue.

Recommendations for Immediate Treatment

The following are recommendations to follow in the event that rig personnel come in contact with a completion fluid:

- If eye contact occurs, irrigate the eyes with flowing water immediately and continuously for at least 15 minutes. Consult with medical personnel as soon as possible.
- In case of contact with the skin, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Consult with medical personnel as soon as possible.
- Wash clothing thoroughly before reuse. Destroy contaminated shoes.
- As fluids can cause slipping hazards on surfaces, sand or other absorbent material should be applied to any fluid spills to reduce the possibility of falls. Once the spill has been absorbed, the material should be placed in containers for disposal.
- Everyone directly involved with a project should be instructed in the possible hazards of working with clear brine fluids. TETRA's fluids specialists conduct precompletion safety meetings to review the Job Safety Analysis and inform all personnel of the safety and handling precautions to be taken with these fluids and the need for proper use of safety equipment.

Environmental Considerations: Brine Handling and Disposal

Certain environmental regulations apply to completion/workover fluids as well as to some of the additive products used when working with these fluids. A listing of TETRA's brine fluids and additive products with established EPA reportable quantities (RQs) are found in Table 48 and Table 49.

A few definitions are provided to help you understand the applicable rules and regulations.

Hazardous Substances

Hazardous substances are:

1. Any elements, compounds, mixtures, solutions, or substances specially designated by the EPA under Section 311 of the Clean Water Act (CWA) (40CFR 116.4) or under Section 102 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (40CFR 302.4);
2. Any toxic pollutants listed under Section 307(a) of the CWA;

3. Any hazardous substances regulated under Section 311(b)(2)(A) of the CWA;
4. Any listed or characteristic Resource Conservation and Recovery Act (RCRA) hazardous wastes;
5. Any hazardous air pollutants listed under Section 112 of the Clean Air Act (CAA); or
6. Any imminently hazardous chemical substances or mixtures regulated under Section 7 of the Toxic Substances Control Act (TSCA).

Discharges

A discharge is any flow of surface water in a stream or canal or the outflow of ground water from a flowing artesian well, ditch, or spring. It can also apply to the discharge of liquid effluent from a facility or to chemical emissions into the air through designated venting mechanisms.



For a glossary of environmental terms, visit the EPA Web site at: www.epa.gov/OCEPaterms.

Permitted Discharges

Completion Fluids. Under the regulations of the National Pollutant Discharge Elimination System (NPDES), a discharge of clear brine fluid may be permitted as long as it does not have an RQ designation and passes certain tests. Permit effluent limitations pertinent to completion, well treatment, and workover fluids are listed in Table 46.

TABLE 46. NPDES Permit Effluent Limitations for Completion Fluids

| Constituent | Test | Limit | Frequency |
|-----------------------------------|-------------------------|-------------------------------------|---------------------------|
| Free Oil | Static Sheen Test | No free oil | Daily, when discharging |
| Oil and Grease¹ | Oil and Grease Analysis | <29 mg/l mo avg <42 mg/l day max | Monthly, when discharging |
| Priority Pollutant (Zinc) | | No discharge | Prohibited |

¹The analytical method for Oil and Grease determination should be specified as EPA Method 1664, Revision A, N-Hexane Extractable Material (HEM: Oil and Grease), a liquid/liquid extraction gravimetric procedure.

Drilling Fluids. A different set of requirements applies to reservoir drilling fluids. TETRA recommends that, in the case of drilling fluids, the standards regarding Free Oil should be based on the Static Sheen Test and the standards for Oil and Grease should be based on the HEM method as noted above. In addition, a toxicity test should be run to determine the LC₅₀ rating.

TABLE 47. NPDES Permit Effluent Limitations for Drilling Fluids

| Limitation | Test | Limit | Frequency |
|---|--|----------------------------------|----------------|
| Oil Based Fluids | | No Discharge | |
| Oil Contaminated Drilling Fluids¹ | | No Discharge | |
| Free Oil | Static Sheen 58 12506 | Number of days sheen observed | Once per day |
| Toxicity | Grab 96 hr LC ₅₀ using Mycidopsis Bahia | 30,000 ppm daily minimum | Once per month |
| Maximum Discharge Rate | Estimate | 1000 bbl/hr | Once per hour |

¹EPA Method 1664 Revision A: N-Hexane Extractable Material (HEM: Oil and Grease)

Releases

A release is any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of a hazardous or toxic chemical or extremely hazardous substance into the environment.

Reportable Quantities (RQs)

A reportable quantity (RQ) is the amount of a hazardous substance which, when released to the environment, must be reported to the National Response Center (NRC). Reportable quantities are action levels that may trigger an appropriate response to a release under provisions of the CWA, the CERCLA, or the Emergency Planning & Community-Right-To-Know Act (EPCRA).

CBF RQs

The following table outlines the RQ information for ammonium chloride (NH₄Cl) and zinc bromide (ZnBr₂), which are the only brine salts that have established EPA reportable quantities.

TABLE 48. CBF RQ Information

| Compound | Formula | RQ lb (Kg) ¹ |
|-------------------|--------------------|-------------------------|
| Ammonium Chloride | NH ₄ Cl | 5,000 (2,268) |
| Zinc Bromide | ZnBr ₂ | 1,000 (454) |

¹RQ based on 49 CFR 172.101 Appendix A



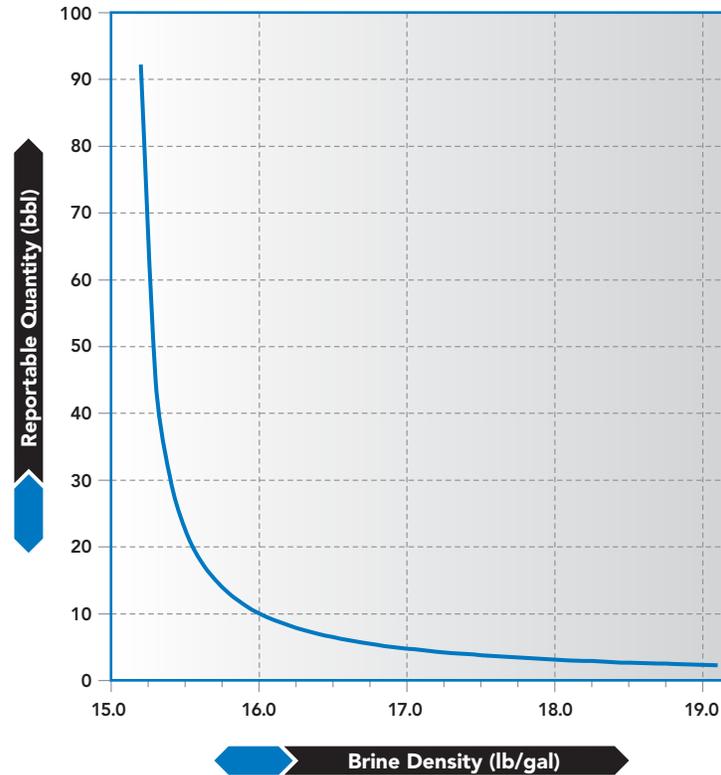
Consult with your company's environmental professionals regarding use of any regulated chemical.

Figure 17 shows how the reportable quantity in barrels of a three salt brine containing zinc bromide (ZnBr₂) varies as the density goes up. As

can be seen in Figure 17, a release of as little as 10 bbl constitutes a reportable release for all zinc containing brines with densities greater than 16.0 lb/gal. This quantity decreases to approximately two bbl at a density of 19.2 lb/gal.

FIGURE 17. Estimated RQs for Zinc Fluids

(in barrels for three salt fluids containing zinc at different densities)



Additive RQs

The following table provides a list of TETRA additive products containing at least one ingredient with an established EPA reportable quantity. Keep in mind that TETRA is continually developing new additives aimed at solving corrosion, fluid loss, and production impairment issues. While Table 49 provides a complete list of TETRA additives containing at least one ingredient with an established EPA reportable quantity as of this guide's publication, the list may become outdated as new products are introduced to the marketplace. Consult your TETRA representative regarding reportable quantity information for the particular additive package you select for your well.

TABLE 49. TETRA Additive RQ Information

| Additive Product Name | TETRA Packaging | RQ for Product ¹ | |
|--------------------------------------|-----------------|-----------------------------|--------|
| | Unit | lb | gal |
| Acetic Acid | 55 gal | | 570 |
| Ammonium Chloride Dry Salt | 50 lb | 5,000 | |
| Caustic Soda (Sodium Hydroxide) | 50 lb | 1,000 | |
| Caustic Potash (Potassium Hydroxide) | 50 lb | 1,000 | |
| CORSAF SF | 5 gal, 55 gal | | 11,000 |
| Hydrochloric Acid | 55 gal | | 510 |
| OxBan | 5 gal | | 790 |
| TETRAHib | 5 gal, 55 gal | | 940 |
| TETRAHib Plus | 5 gal, 55 gal | | 250 |
| TETRAVis Breaker | 5 gal, 55 gal | | 75 |

¹RQ for products are approximate and are based on 49 CFR 172.101 Appendix A

Releases to the Environment and Notification Requirements

Releases are spills or unplanned discharges. They are regulated by the Clean Water Act (CWA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Notification of a release in excess of the Reportable Quantity is required. Notification requirements (for releases) 40CFR 302.6 reads as follows:

Any person in charge of a vessel or an offshore or onshore facility shall, as soon as he has knowledge of any release (other than a permitted release) of a hazardous substance from the facility in a quantity equal to or exceeding the reportable quantity (RQ) in any 24 hour period, notify the National Response Center at 800.424.8802.

Other agencies to be notified:

U.S. Federal Agencies

- U.S. Coast Guard
- U.S. Department of Interior Minerals Management Service (MMS)

Louisiana Agencies

- Department of Environmental Quality–Water Resources Control Division
- Department of Public Safety

Texas Agencies

- The Railroad Commission of Texas (operations and waste)

- Texas Commission on Environmental Quality
- Texas General Land Office (Oil Spill Response)

Addresses and phone numbers for some, but not all, regulatory agencies are included in the following section.

Due to the number of involved agencies, many of which have overlapping boundaries or authorities, as well as differing interpretations of regulations, most companies working in oil and gas development have departments established specifically to deal with environmental compliance issues.

Agency Contact Information

Various regulatory agencies administer environmental programs that, in one way or another, guide the activities of operators of oil and gas production facilities. While not exhaustive, the following list should be of some help when additional information is required. Information is current as of February 1, 2006.

United States Federal Agencies

National Response Center

800.424.8802

U.S. EPA Region 6 Dallas

Regional Coverage: Arkansas, Louisiana, New Mexico, Oklahoma, Texas

1445 Ross Ave., Suite 1200

Dallas, Texas 75202-2733

<http://epa.gov/region6>

866.EPASPILL (866.372.7745)

Minerals Management Service (MMS)

U.S. Department of the Interior

Public Information Office

1201 Elmwood Park Blvd.

New Orleans, Louisiana 70123-2394

<http://www.gomr.mms.gov>

504.736.2504 (New Orleans District)

U.S. Coast Guard**Coast Guard District Eight**

Marine Safety Division
Hale Boggs Federal Bldg.
500 Poydras Street
New Orleans, Louisiana 70130
<http://www.uscg.mil/d8>
504.589.6271

State of Louisiana**Louisiana Department of Environmental Quality**

Office of Environmental Compliance
P.O. Box 4312
Baton Rouge, Louisiana 70821-4312
<http://www.deq.state.la.us>
225.342.1234 (24 Hour Notification Hotline)

State of Texas**Railroad Commission of Texas**

P.O. Box 12967
Austin, Texas 78711-2967
www.rrc.state.tx.us
512.463.6788 (24 Hour Emergency Number)

Texas Commission on Environmental Quality

P.O. Box 13087
Austin, Texas 78711-3087
<http://www.tceq.state.tx.us>
800.832.8224 (Spill Reporting Hotline)

Texas General Land Office

1700 North Congress Ave., Suite 840
Austin, Texas 78701-1495
<http://www.glo.state.tx.us>
800.832.8224 (CHEMTEL)

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