Prevention and Safe Management of Hydrates in Process Equipment

A Guideline

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SETTING THE STANDARD IN OIL AND GAS SAFETY

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This document is based on the Canadian Association of Petroleum Producers (CAPP) Prevention and Safety Handling of Hydrates Guide.

DISCLAIMER

This document is intended to be flexible in application and provide guidance to users rather than act as a prescriptive solution. Recognizing that one solution is not appropriate for all users and situations, it presents generally accepted guidelines that apply to industry situations, as well as recommended practices that may suit a company's particular needs. While we believe that the information contained herein is reliable under the conditions and subject to the limitations set out, Energy Safety Canada does not guarantee its accuracy. The use of this document or any information contained will be at the user's sole risk, regardless of any fault or negligence of Energy Safety Canada and the participating industry associations.

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Introduction

To safely move products in pipelines, it is critical to manage the relationship between temperature and pressure. Without proper management, changes in pressure can lower temperatures, creating ideal conditions for the formation of hydrates. Hydrates interrupt the flow of gas and liquids, which can damage equipment and/or release hazardous energy and cause injury to personnel.

This guideline was developed to provide operations staff with principles and advice to address hydrates. While it is intended for general oil and gas operations, it may not be applicable to all site conditions or operations, such as those associated with carbon dioxide (CO_2) systems.

Advice in this guideline uses the term “hydrates”, which is also commonly used for obstructions with ice. When there are differences in prevention or safe handling activities, the document will distinguish between hydrates and ice.

1.1 HYDRATES OVERVIEW

Hydrates are commonly thought of as “ice plugs” resulting from freezing water. While water plays a role in hydrate formation, hydrates are distinct from ice as they:

- Are saturated with gas, which can create flammability and worker exposure hazards.
- Can occur above freezing conditions any time of year.

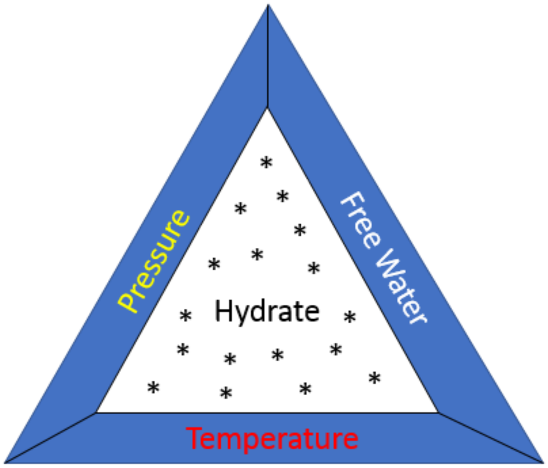
There are no regulations specific to hydrates. Provincial regulations require the identification of known safety hazards and management of hazardous energy. Additional industry guidance on hydrates can be found in the Drilling and Completions Committee (DACC) publication: Industry Recommended Practice (IRP) #4 Well Testing and Fluid Handling.

Figure 1. Hydrate in a Pipeline

2.0 How Hydrates are Formed

Hydrates are crystalline solids composed of “cages” of water molecules around natural gas molecules. These solid crystalline compounds are formed by hydrocarbon gases (methane, ethane, propane, etc.) and impurities (nitrogen, carbon dioxide, hydrogen sulphide) combined with water under reduced temperature and pressure. The extent to which a gas or impurity will occupy the space between water molecules depends on the solubility of the compound in water. All gases will dissolve in water to some degree at normal temperatures and atmospheric pressure conditions.

Figure 2: Hydrate Triangle



The hydrate triangle (Figure 2) depicts the relationship between water, gas, pressure and temperature. If any of the required elements symbolized in the hydrate triangle are missing or outside the required range, hydrate formation will not occur.

Generally, changes in pressure occur when flow restrictions or reductions are introduced. For pipelines, this could be a change in pipe diameter; a bend in the pipe; the addition of instrumentation or valves; or even the accumulation of fines and wax. When fluids and gas travel past a restriction, they are moving from high pressure to low pressure states. The pressure change expands the fluid causing a decrease in temperature, which is known in thermodynamics as the Joule-Thomson effect. As the hydrate forms and grows, it continues to contribute to the restriction until the flow is completely blocked.

Any segment of an operating system can be affected by hydrate formation, including:

- Downhole in wells.
- Gathering systems.
- Facility piping and equipment.
- Well drilling and servicing equipment.

2.1 TEMPERATURE AND PRESSURE

The amount of gas that dissolves in water to occupy spaces between water molecules depends on the temperature and pressure. When pressure is high, gas compresses and fills the spaces until they are saturated. This saturation from high pressure can occur at temperatures well above the freezing point of water, which explains why hydrates occur in “warm” gas streams. Once water is saturated with gas, chemical bonds change and crystal growth begins, leading to the eventual formation of a solid mass of water and gas.

Each component of natural gas has a different water solubility. As a result, hydrates form at different pressures and temperatures for different compounds. Heavier gases, like pentane, are too large to occupy the spaces between water molecules, whereas lighter gases, like methane and ethane, do so readily.

Figure 3. Pressure-Temperature Curves for Predicting Hydrate Formation
(Source: IRP #4 Well Testing and Fluid Handling)

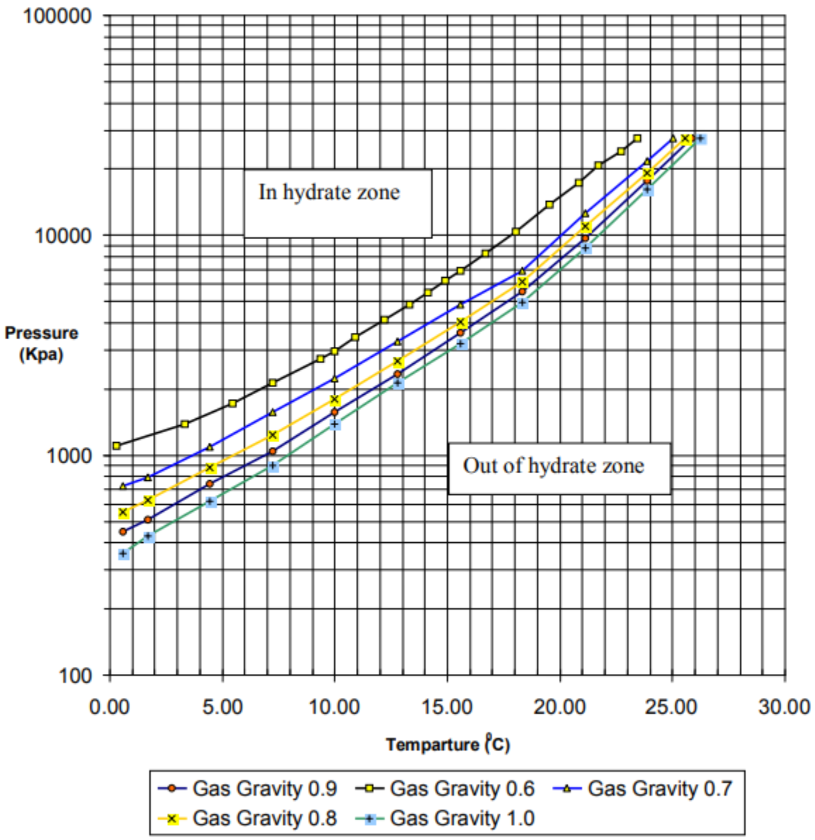


Figure 3 illustrates hydrate formation for different gas gravities. Higher gravities mean heavier gases. Heavier gases form hydrates at lower pressures than lighter gases. Also, hydrates from both light and heavy gases will form at higher pressures, even with flowing temperatures above 20 C.

A further complication arises if the hydrocarbon stream contains H_2S or CO_2. Then the temperature at which a hydrate could form will increase, since both gases are more soluble in water than other hydrocarbon-type gases.

2.2 HYDRATE MECHANISM

The mechanism for hydrate formation consists of:

- Presence of low temperature, high pressure, water and gas. At this point hydrate cages form and dissolve. The system is just entering the hydrate curve (see Figure 3).
- The system reaches balance and hydrate cages start forming around fines, wax, weld lines, chokes, etc. At this point the water cages start to trap gas inside, making them more stable.
- Full cages develop and start fast growth in a matter of minutes to an hour.
- Crystal cages reach a critical size where agglomeration is extremely fast. Expect plugging to occur quickly after this.

Remember: Hydrates take time to form and, therefore, there is time to detect them and take remedial action.

Hydrate formation and disintegration are not well understood. Hydrates grow like crystals, resembling wet snow in appearance. The crystallizing process is complex. Factors that contribute to the initiation of hydrate formation include:

- Degree of sub-cooling – hydrates may not begin to form immediately upon reaching the hydrate point; as much as 5°C to 10°C of sub-cooling is needed to form the first seed crystals of hydrates.
- Presence of artificial nucleation sites – rust, scale, sand, etc.
- Degree of mixing – system geometry and flow regime.

Because hydrates absorb the heat as they dissociate, the system temperature can fall below the normal freezing point of water. This accounts for the confusion between hydrates and ice. Often, ice remains after hydrates have been removed.

Abnormal operating conditions or situations could also lead to crystal formation in the pipeline. Examples include mixing, salinity or corrosion, which add a physical site for crystal formation.

2.3 HYDRATES IN PIPING

Hydrate formation is a major hazard in pipelines that carry wet gas. Pockets of water form in low points of the line and hydrates can form downstream of that water, particularly if the pipe passes through a temperature change. Apart from the pipe temperature change, the gas temperature itself decreases while traveling through the pocket of water, resulting in a pressure drop. The saturated gas then contacts the free water at reduced temperature. For pipelines that carry wet gas and traverse changing elevations, hydrates can form at any elevation change where pockets of water lie.

Hydrates also form where there is a sharp reduction in pressure, such as at:

- Orifice plates.
- Partially open control valves.
- Basket strainers.
- Sudden enlargement on pipelines.
- Short radius elbows.

The reduction in pressure causes the temperature to drop and, consequently, free water to condense.

2.4 RESERVOIR DEPLETION EFFECT ON HYDRATES

Maturing reservoirs frequently experience decreased flow, increased H_2S concentrations, increased water production and, in some segments of the system, reduced pressures. These factors can change the hydrate temperature of the system. In addition to the hydrate point, other changes from reduced volumes include reduced line velocities, increased liquid holdup, reduced heat input from the source of flow and, perhaps, line heaters in the wrong location of a heated line.

It is good practice to identify the hydrate point for each stream, so each component of the system can be operated above the temperature.

3.0 Locating Hydrates

3.1 HYDRATE DETECTION

Like any obstruction in a line, hydrates can be detected by the consequences they create. Obstructions reduce flow, increase back pressure on a system and increase the differential pressure across the obstruction. Compounding the issue, instrumentation taps can be blocked by hydrates, leading to false readings.

Remember: It is important to first identify these potential downstream locations as the likely points of failure if an impact occurs.

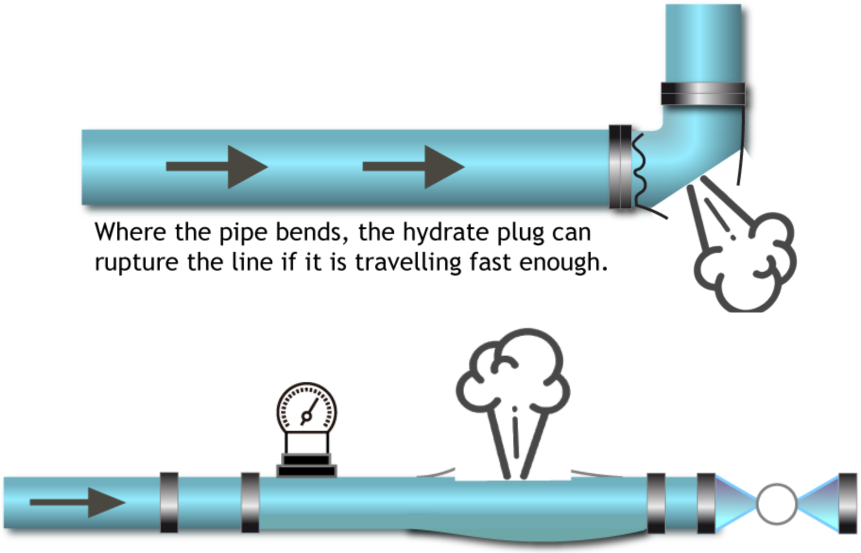
The exact location of the hydrate or ice plug can be determined several ways: based on past experience, system geometry (low spots in piping), volumetric methods (flow provers, positive displacement meters) and sonic detection methods.

Companies should develop situation-specific maximum differential pressures considering elements such as piping configuration, distance to first point of impact and public proximity. This applies to all restrictions including hydrate plugs, wax plugs and asphaltenes.

Differential pressure can quickly accelerate a moving hydrate plug to velocities approaching the speed of sound, creating excessive forces. Moving hydrates can cause serious mechanical damage at downstream locations where restrictions (control valve), obstructions (closed valve) or sharp change of direction (elbow, tee) exist.

The failure can be either an impact or overpressure (shock wave). Keep all workers away from the potential point of impact. Impact failures occur due to the mass and momentum of the hydrate hitting and fracturing the pipe or fittings (see Figure 4).

Figure 4. Impact and Overpressure Failures



Where the pipe bends, the hydrate plug can rupture the line if it is travelling fast enough.

If the hydrate plug velocity is high enough, the momentum of the plug can generate pressures high enough to rupture the flowline.

Factors that increase the danger of pipe failure due to moving hydrates include:

- High differential pressure across the plug.
- Long lengths of trapped upstream pressure causing more stored energy.
- Low downstream pressures with differentials less than 300 KPA (i.e., less cushion for hydrate to impact).
- Restrictions or sharp bends downstream of the plug.
- Short travel distances between the hydrate and a restriction.

If a line is bled down to zero on both ends and no pressure has built up for some time, it may be an indication of multiple plugs. This would likely require additional planning mitigations such as a coiled tubing flush.

No analytical methods can accurately predict whether hydrate formation will result in single or multiple plugs in any given situation. The formation of multiple hydrate plugs causes pressure to be trapped between the plugs. High differential pressures can be created if multiple hydrates are treated as a single plug. That is, high pressure can be trapped between the plugs even though the ends of the piping have been de-pressured.

LINE OF FIRE

Energy Safety Canada has information and resources relating to Line of Fire hazards, one of the Life Saving Rules.

3.2 FORMATION MODELING

Hydrate formation modeling is an effective way to identify the system's susceptibility to forming hydrates. At a minimum, the following information is required:

- Highest pipeline operating pressure.
- Lowest pipeline operating pressure.
- Gas composition including CO_2 and H_2S mole fraction.
- Production flow rates.
- Concentration of chlorides, sulfates and bicarbonates.
- Physical sites with a sudden expansion such as orifices, regulators and chokes.

Hydrate formation modeling should provide hydrate equilibrium curves and determine injection locations, subcooling, type of hydrate inhibitor and a method of hydrate breaking. Without sophisticated software, the hydrate formation curves presented in Figure 3 can be used to approximate the susceptibility of hydrate formation in gas systems provided the mole fractions of CO_2 and H_2S are known.

4.0 Hydrate Prevention

Hydrates can be prevented and should not be accepted as routine or a normal part of operations. A hydrate prevention program is more effective than remedial measures.

Hydrate formation can be prevented in the following ways:

- Prevent free water in the gas stream by:
    - Dehydrating the gas, or
    - Elevating the temperature to vaporize more water.
- Increase the gas temperature above the level needed for hydrate formation at the operating pressure.
- Decrease the pressure below the point needed for hydrate formation at the operating temperature.
- Introduce chemical inhibitors (methanol and/or glycol).
- Heat well heads and fittings by wrapping.
- Redesign piping system (e.g., low points, restrictions).

4.1 PREVENTION EQUIPMENT

Equipment and methods used for hydrate prevention include line heaters, dehydration equipment and methanol/glycol injection systems.

- Line heaters and insulated/heat traced lines keep the temperature of flowing gas above the hydrate formation temperature within a specific range of gas flow rates. This is a very effective method for hydrate prevention in steady flow conditions.
- Dehydration equipment typically involves glycol dehydrators, but may also involve molecular sieve, silica gel and calcium chloride towers. Glycol dehydrators remove water vapour from the gas stream. It is important to ensure the dehydrator is working properly within its design limits.
- Methanol/glycol injection systems tie up free water and water vapour to prevent hydrate formation.
    - **Methanol** is cheaper on a volume basis but is costly to recover and regenerate as it readily distributes itself into both gas and liquid phases. In gas-condensate and oil streams, methanol injected is “lost” into the produced water and, to a lesser extent, in hydrocarbon liquids compared to glycol. The result is a very high injection rate compared to glycol.
    - **Glycol** is more expensive but can be recovered and regenerated for reuse similarly to methanol. Also, glycol is comparatively more “attracted” to the water phase of the gas stream, so the injection rates are lower than methanol.

The use of methanol and glycol can impact the performance of inhibitors designed to coat the inside of pipes, thereby mitigating internal corrosion risk. As a result, the use of glycol and methanol to manage hydrates should be conducted in concert with the corrosion protection program to ensure that hydrate risk is managed while maintaining corrosion risk management.

Determine safe shut-in periods for lines to avoid pressure build-up. In shut-in conditions, even insulated lines will not prevent the gas stream from cooling down to the hydrate range within hours. A safe shut-in time can be determined from temperature data gathered during short shut-in periods.

Pre-determining likely hydrate points and installing injection points or reducing hydrate possibilities by design is an effective way to engineer out potential hydrate problems. The threat of hydrates should be included in design risk assessment processes such as a hazard and operability study (HAZOP) as defined by the Center for Chemical Process Safety (CCPS). In addition, supplemental glycol/methanol injection is recommended for start-ups, scheduled shutdowns and low flow conditions.

4.2 CHEMICAL INHIBITORS

Chemical inhibition may be required when it is not practical or feasible to remove water from a system.

- Thermodynamic inhibitors such as glycol or methanol lower the temperature of hydrate formation.
- Low dosage hydrate inhibitors (LDHIs), such as kinetic hydrate inhibitors (KHI), lower the rate of hydrate formation, while antiagglomerants (AA) allow crystals to develop but restrict their size.

4.3 SOLUBILITY IMPLICATIONS

Glycol and methanol are water soluble and, therefore, can impact the available space between molecules to hold other compounds such as dissolved salts. As such, the use of methanol and glycol has the potential to change the solubility of these other dissolved compounds and can result in increased scale formation in equipment. Select the injection rates of methanol and glycol that work in concert with scale prevention and mitigation programs.

4.4 CHEMICAL EXPOSURE HAZARDS

Hydrate prevention and handling may involve potential exposure to health and safety hazards associated with either process stream chemicals, such as gases and liquids (methane, H_2S, crude oil, benzene and other hydrocarbons, etc.) or chemicals used for hydrate prevention, such as methanol and glycol.

For more information on controlling chemical hazards, refer to the Controlling Chemical Hazards Guideline. Additionally, the Fire and Explosion Hazard Management Guideline may be relevant.

5.0 Handling and Removing Hydrates

Once formed, hydrates pose a threat to people and equipment if not handled properly. The real hazard from hydrates comes from trying to remove them. Proper procedures can prevent pipe and vessel ruptures and personal injury.

Do not attempt to remove hydrates by force through increased or decreased pressure on either side of the plug. Attempting to move hydrate plugs may rupture pipes, vessel and other equipment. The best-case scenario is to disintegrate the hydrate(s) without allowing them to move.

Hydrates have the potential to create a line of fire hazard where workers can be in the path of potential moving objects, such as the hydrate or pressure releases. As a result, worker body positioning and other administrative controls are integral to preventing serious injuries. Additionally, equipment must be designed with line of fire hazards related hydrate management in mind. This is particularly true for managing trapped pressure (stored energy) that may be located between two hydrates.

Examples of hazards associated with hydrate removal include:

- A hydrate plug can be several meters in length, and if it is freed by high pressure at one end with the line depressurized and open to flare at the other end, it will travel at such a high velocity that it could rupture the pipe at a sharp bend. If it impacts a valve or tee in the line, it can tear even heavy-walled piping span. Damage could also occur to equipment that is mechanically tied to the pipeline.
- Depressurizing both ends of a pipeline containing a hydrate plug is dangerous. There may be more than one plug in the line with high-pressure gas trapped between them, and one plug could be freed (and potentially be followed by a second plug), resulting in ruptured pipe and damaged equipment.
- Piping or fittings ruptured because of the hydrate moving may release sour gas in large volumes, catching personnel unprepared.
- Over-pressuring of pipe and fittings can also result from using a high-pressure pumper truck to pump a chemical inhibitor, such as methanol, into a line.
- The use of chemical inhibitors such as methanol requires additional precautions. One example is to consider all ignition sources, including static electricity, because methanol in the form of mist from a ruptured fitting is highly flammable.
- If applying steam to a line suspected of containing hydrates, the rapid vaporization should be monitored to avoid pressure buildup. Open flames must never be used for hydrate removal.
- If bleeding a line, it must be securely anchored to prevent movement.

Partially hydrated systems, in which a plug is forming but has not yet completely blocked the line, can be treated with methanol or glycol once the condition that caused the hydrate is removed. If this cannot be done, shut-in and depressure the line below the hydrate formation zone as indicated in Figure 3.

For pipelines, there may be more than one plug with full pressure trapped between them. In this situation, depressure the space between the two plugs if possible.

5.1 REMOVAL OPTIONS

Several options to remove the hydrate are presented below. These options should be considered with respect to three guiding principles:

Principle 1: Minimize the pressure differential and use hydraulics to cushion the effects of a moving hydrate. Stopping or reducing the flow will stop or limit movement of the plug.

Principle 2: Ensure the maximum allowable working pressure (MAWP) of the system is never exceeded. Best practice is to stay below 80 per cent of the MAWP.

Principle 3: Develop an emergency response plan (ERP) to handle a situation in which a pipe ruptures and results in gas release, fire or injury. Non-essential personnel should be evacuated from the area and all workers should remain out of the line of fire. Preliminary job safety procedures should be reviewed with all personnel.

The following are options for removing a hydrate plug that has completely blocked a line:

- Disintegrate the hydrate by depressurizing equally on both sides below the hydrate point, but not to zero. Use a pressure indicator on each end of the isolation section of the line to ensure there is no significant difference in pressure (less than 10 per cent). The pressure difference gives the plug the energy to move. Once pressure has been reduced below the point at which hydrates form, the plug will begin to disintegrate. Allow time for the hydrate to dissolve, and test for completion.

  Test for disintegration of the plug and return the line to service using the following steps:

  - Close the valve nearest the downstream side of the plug. The hydraulic effect of trying to move against a closed valve will have a cushioning effect.
  - Slowly pressurize the line. Both gauges should always read the same if the plug has disintegrated. If the downstream gauge does not respond at the same rate as the upstream, the plug has only partially dissolved. Depressure and allow more time.
  - Once the plug has disintegrated, ensure the condition that created the hydrate is no longer present. Slowly re-establish flow through the process. Low initial flow rates will help ensure there is not enough energy for portions of any remaining plug to cause a problem.

- For longer pipelines with more than one plug, isolate a section of the line, preferably at a change in elevation as this is the most likely location for a hydrate. Install a pressure indicator at each end. Slowly depressure one end of the isolation section by about 10 per cent. If both pressure indicators read the same and decrease at the same rate, the plug is not in that section. Continue to move along the pipeline and isolate the shortest possible sections, until the section containing the plug is located. Be aware that there may be more than one plug. Doing this test in the shortest possible sections reduces the distance a plug could travel once it becomes dislodged.

  - Once located, inject methanol at one end of the line while slowly depressuring the other end. Ensure pressure does not exceed the MAWP.
  - Do not fully depressure one side but reduce the pressure below the point of hydrate formation, close the depressuring valve and allow time for the hydrate to disintegrate. If the plug disintegrates enough to start moving, gases will start compressing against a closed valve that will slow the hydrate and minimize damage.

- At the injection end of the line, methanol will vaporize and move through the line by diffusion in the same way that gasoline antifreeze works in a car's gas tank.
- Monitor pressure indicators at each end of the line. A change in either gauge indicates a plug is moving. Stop or dramatically reduce the flow at the depressure point. Control the movement of the plug(s) by controlling the rate of depressuring. The rate of pressure decrease through the vent line will help determine the distance the hydrate is from the vent location.

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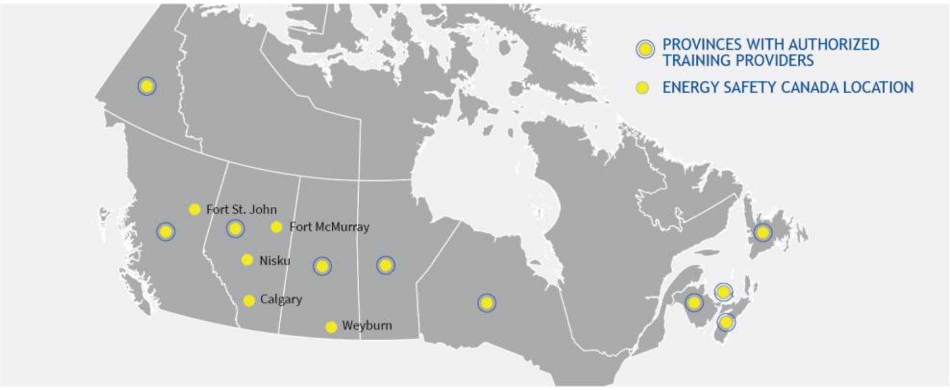

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