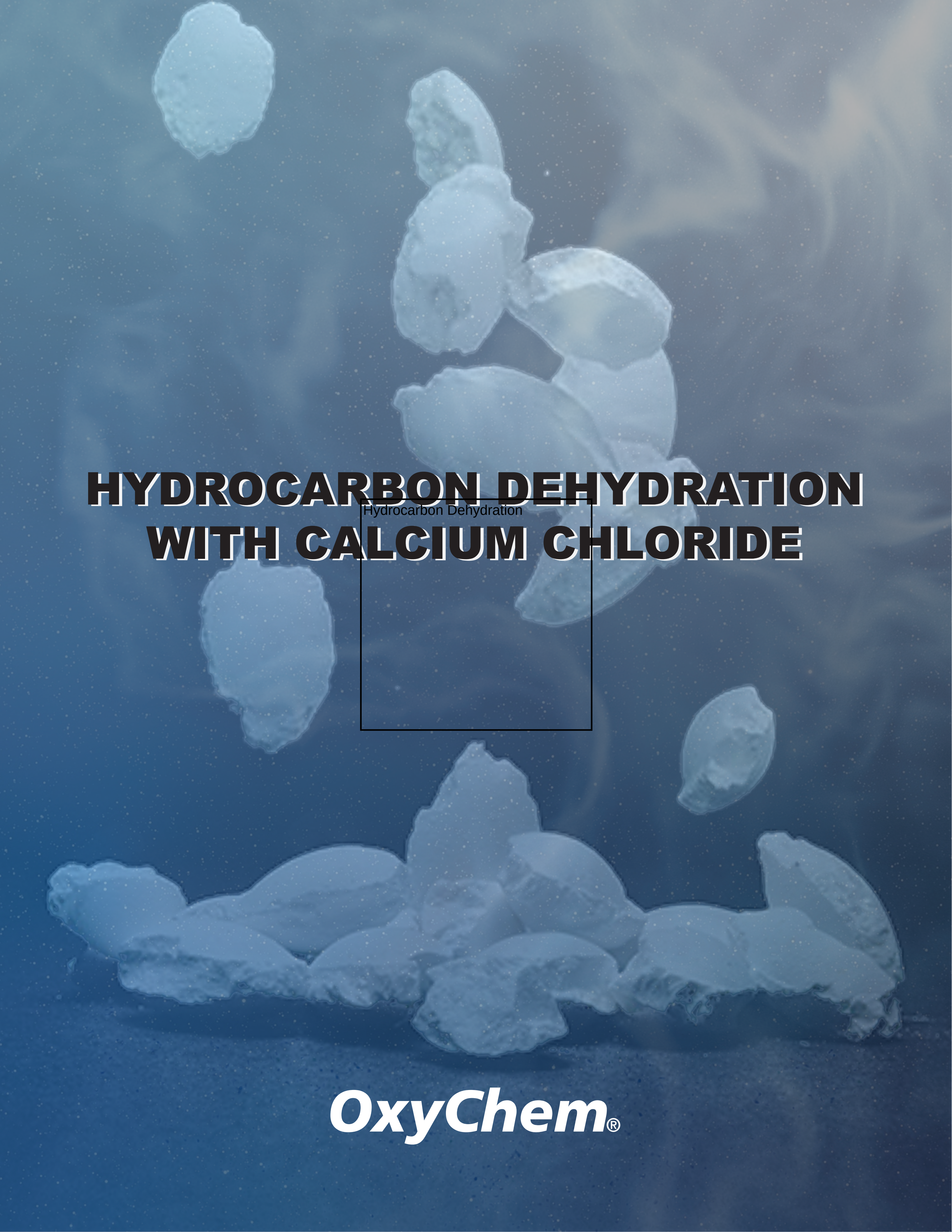


HYDROCARBON DEHYDRATION WITH CALCIUM CHLORIDE

Hydrocarbon Dehydration

OxyChem®

Hydrocarbon Dehydration with Calcium Chloride

Contents

SUMMARY

Water is one of the most common impurities in hydrocarbons. If not removed it can create several problems, such as corrosion, hydrate formation, or product haze. Fortunately, there are many ways to remove excess water from liquid hydrocarbons. However, choosing the most effective and economical method requires the consideration of many variables:

- Typical inlet water content
- Required outlet water content
- Amount of hydrocarbon to be dried
- Amount of water to be removed
- Solubility of water in the hydrocarbon
- Temperature of the hydrocarbon

This manual has been prepared to assist engineers reviewing the use of calcium chloride as a primary or supplemental dehydration agent when the above variables have been defined. OxyChem is not an equipment manufacturer, so people desiring detailed information about equipment should contact the appropriate supplier.

OxyChem®

PELADOW® DG CALCIUM CHLORIDE

PELADOW® DG, manufactured by OxyChem, is an almond shaped, briquetted calcium chloride product that is specially designed to be used for dehydration of gas and liquid hydrocarbons, such as natural gas, LPG, kerosene, and diesel fuel. The special design of PELADOW DG calcium chloride helps minimize the bridging and channeling in vessels that can occur with other deliquescent salts. PELADOW DG calcium chloride is available in 2100 pound flexible intermediate bulk containers (super sacks).

Table 1 presents some typical physical properties of PELADOW DG calcium chloride. These are considered the most important properties relative to the use of PELADOW DG in dehydration applications. Additional physical properties of PELADOW DG calcium chloride and solutions of calcium chloride can be found in OxyChem's Calcium Chloride Handbook.

Table 1: Typical Properties of PELADOW DG

Property	Typical Value[1]
Typical Assay	88 - 90% calcium chloride
Appearance	While almond shaped briquettes
Odor	None
Briquette Size	Approx. 0.7″ thick at thickest point 1.1″ length
Sieve Analysis	89% > ½ Inch 97-100% > ¼ Inch
Bulk Density	56 – 64 lbs/ft^3
Pressure Drop	0.01 to 0.1 psi/ft of bed height

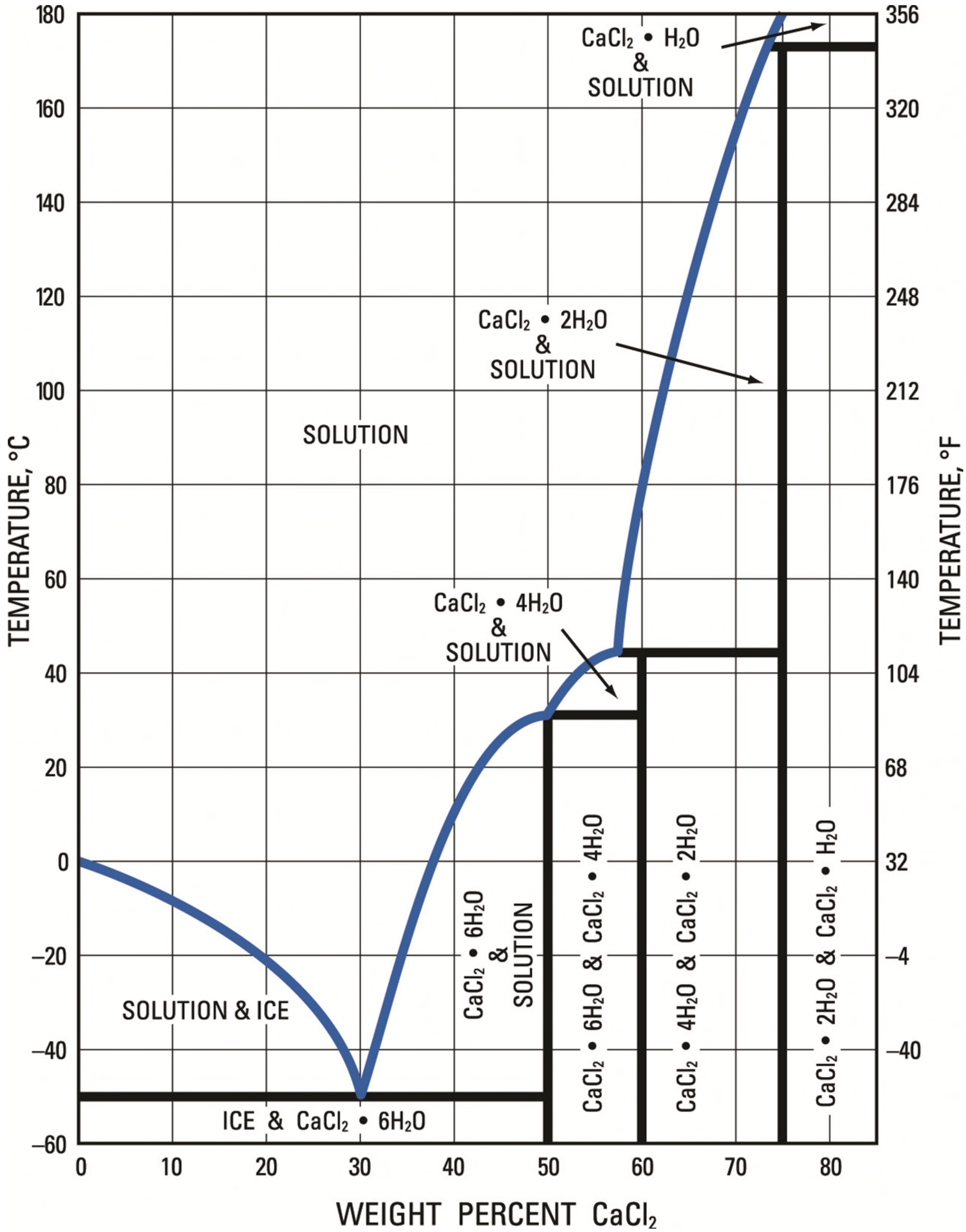
[1] These data are laboratory results typical of the product and should not be confused with or regarded as specifications. All percentages are by weight.

Figure 1 is a portion of the phase diagram for pure calcium chloride. It shows that the following chemical hydrates are possible:

- $CaCl_2$
- $CaCl_2 \cdot H_2O$
- $CaCl_2 \cdot 2H_2O$
- $CaCl_2 \cdot 4H_2O$
- $CaCl_2 \cdot 6H_2O$

Figure 1 also shows the temperature limits for stability of various hydrates at a pressure of one atmosphere.

Figure 1: Phase Diagram for $CaCl_2$-Water System



The physical properties of pure anhydrous calcium chloride and the hydrates of calcium chloride shown in Figure 1 are listed in Table 2.

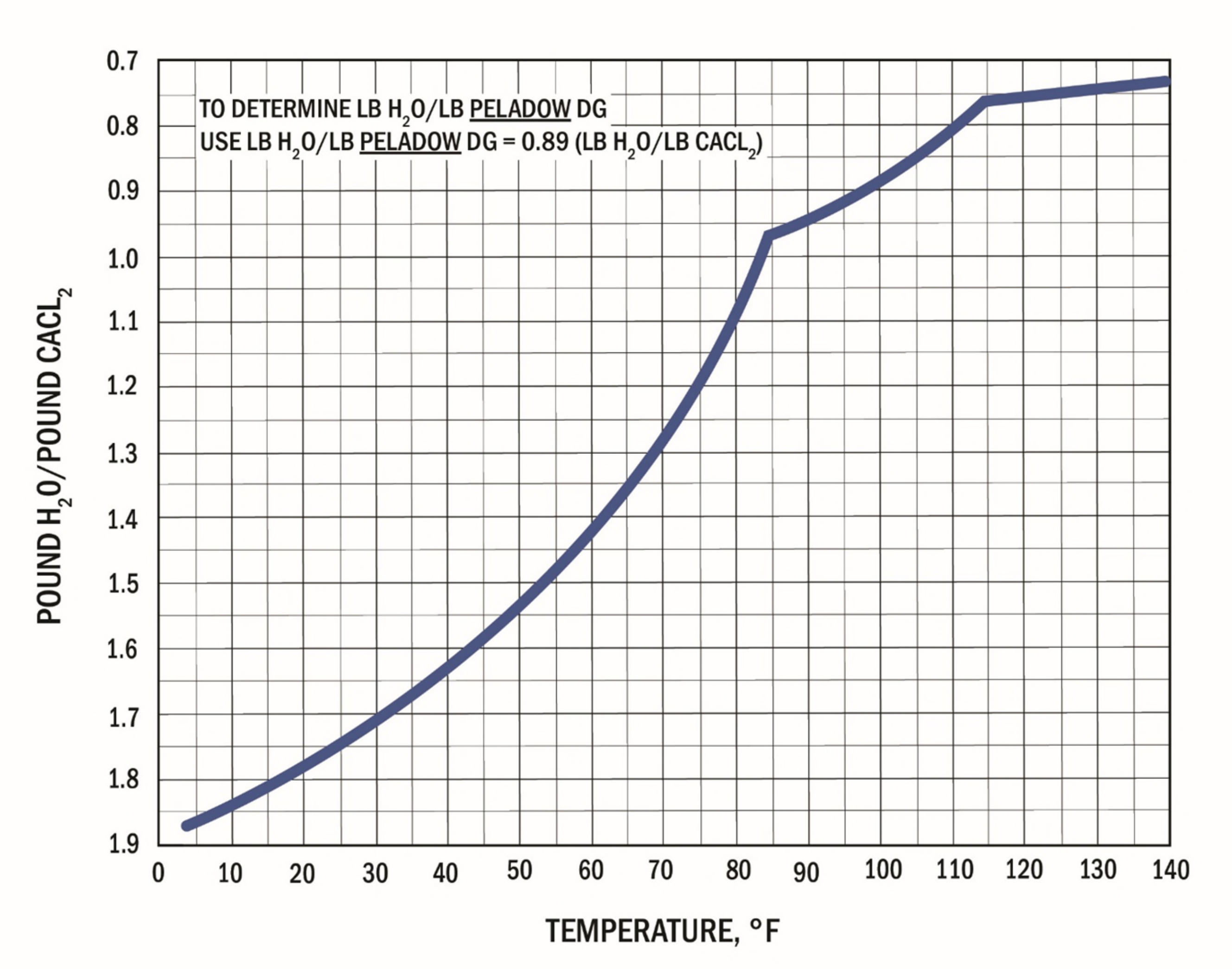
Table 2: Properties of $CaCl_2$ Hydrates

$CaCl_2$ Concentration	$CaCl_2 \cdot 6H_2O$	$CaCl_2 \cdot 4H_2O$	$CaCl_2 \cdot 2H_2O$	$CaCl_2 \cdot H_2O$	$CaCl_2$
Composition (% $CaCl_2$)	50.66	60.63	75.49	86.03	100
Molecular Weight	219.09	183.05	147.02	129	110.99
Melting Point[1] (°C)	29.9	45.3	176	187	773
(°F)	85.8	113.5	349	369	1424
Boiling Point[2] (°C)	-	-	174	183	1935
(°F)	-	-	345	361	3515
Density at 25°C (77°F), g/cm^3	1.71	1.83	1.85	2.24	2.16
Heat of Fusion (cal/g)	50	39	21	32	61.5
(BTU/lb)	90	70	38	58	110.6
Heat of Solution[3] in H_2O (cal/g)	17.2	-14.2	-72.8	-96.8	-176.2
(to infinite dilution) (BTU/lb)	31.0	-25.6	-131.1	-174.3	-317.2
Heat of Formation[3] at 25°C (77°F), kcal/mol	-623.3	-480.3	-335.58	-265.49	-190.10
Heat Capacity at 25°C (77°F), cal/g°C or BTU/lb°F	0.34	0.32	0.28	0.20	0.16

1) Incongruent melting points for hydrates
2) Temperature when dissociation pressure reaches one atmosphere for hydrates
3) Negative sign means that heat is evolved (process is exothermic)

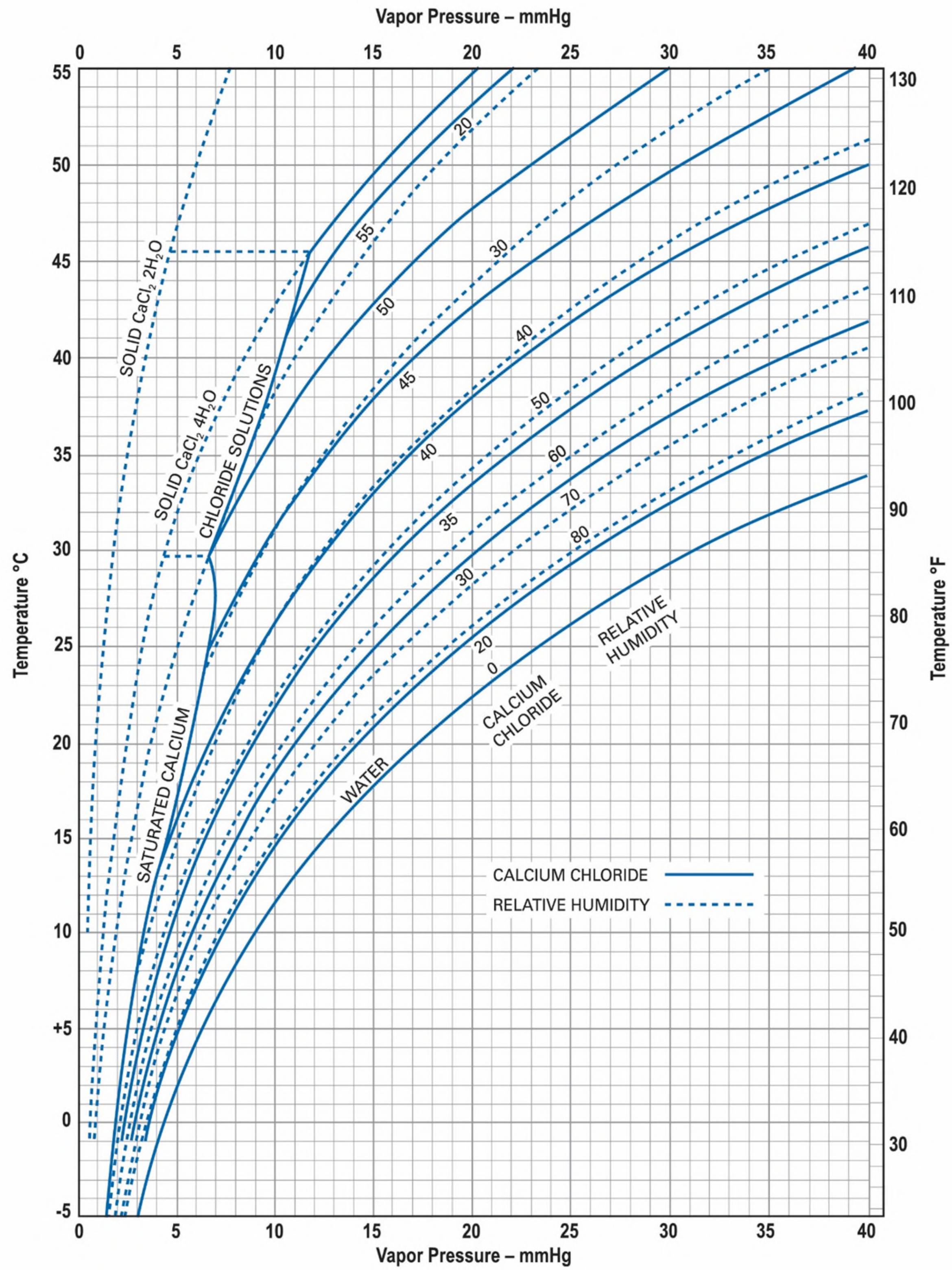
The relationship between crystallization temperature and the $H_2O/CaCl_2$ ratio for solutions of pure calcium chloride are shown in Figure 2. These results can be used with little error when reviewing PELADOW DG.

Figure 2: Crystallization Temperatures of $CaCl_2$ – Water System



The vapor pressure exhibited by each of the calcium chloride hydrates and solutions as a function of temperature is given in Figure 3.

Figure 3: Vapor Pressure of $CaCl_2$



CHEMISTRY OF THE DRYING PROCESS

When a hydrocarbon containing moisture contacts calcium chloride or its hydrates, the calcium chloride will extract moisture from the hydrocarbon so long as the water vapor pressure above the hydrocarbon is greater than vapor pressure exhibited by the calcium chloride hydrate. In result, the driest liquid should be nearly in equilibrium with the lowest hydrate present in the bed.

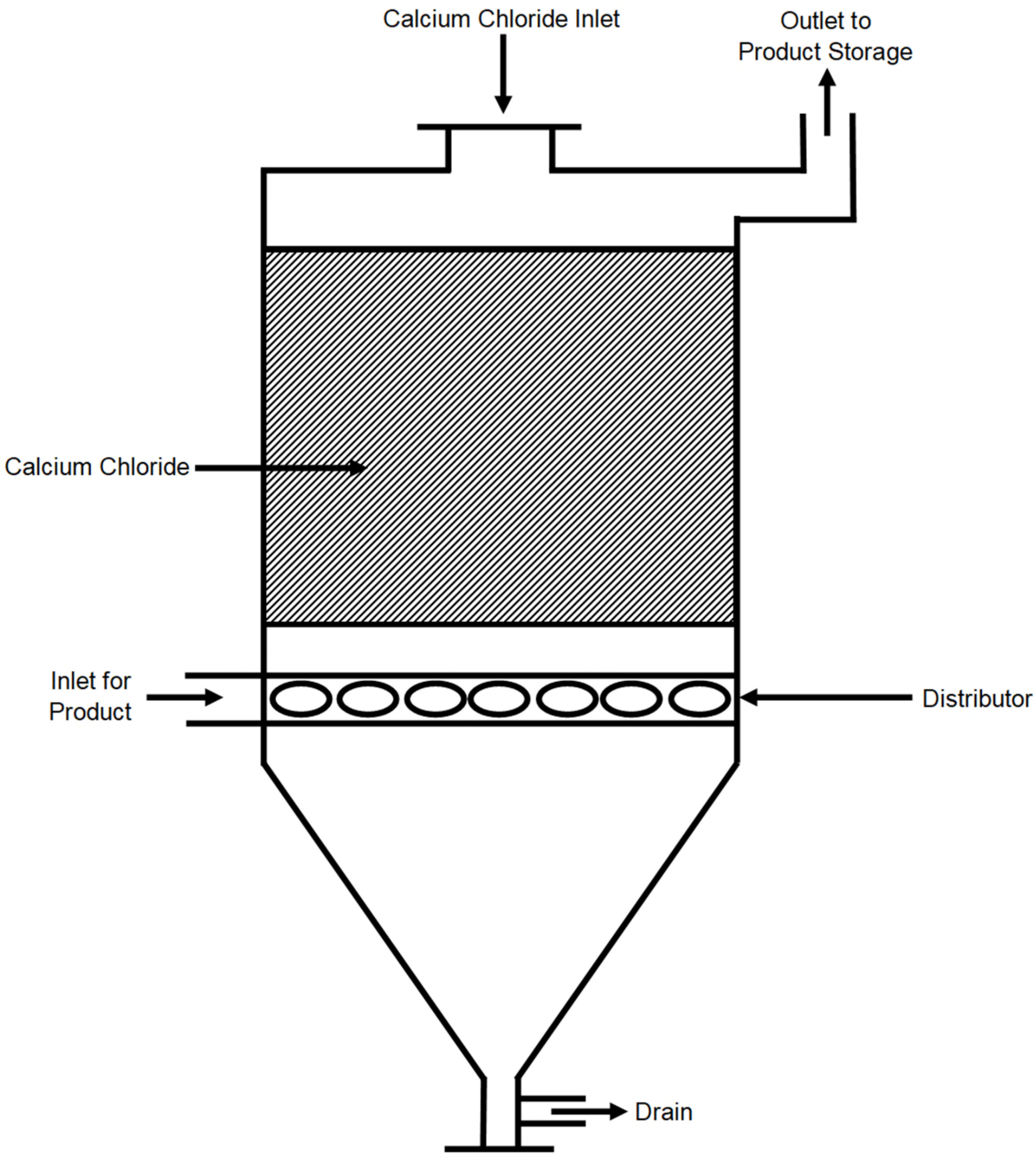
The water-saturated hydrocarbon enters the calcium chloride bed where it contacts the calcium chloride in the tower. As water is absorbed, calcium chloride converts through successive states of hydration, ultimately converting to a brine which, depending on the relative density of the product being dried, will either sink or rise in the tower.

As PELADOW DG is consumed it begins to shrink in size. As this occurs, the weight of the material from above causes the bed to settle so that the bed level gradually diminishes as time progresses. Typically, the operation can continue until approximately 80% of the bed is depleted and breakthrough starts to occur. At this time the bed section must be recharged by adding fresh calcium chloride material to the top of the remaining bed.

EQUIPMENT DESIGN

An example of a typical calcium chloride dehydration unit is shown in Figure 4. In this example, the hydrocarbon is passed upward through the bed, since the hydrocarbon's specific gravity is less than the specific gravity of the brine. However, if the feed stream has a specific gravity greater than calcium chloride brine, the stream must flow downward through the bed.

Figure 4: Typical Calcium Chloride Dehydrator



Outlet Moisture Content

The outlet moisture content will vary with time. Initially, low humidity will be obtained. Over a period of several hours, the outlet moisture content will rise to a nearly steady-state value which is maintained until approximately 80% of the bed has been consumed. Then breakthrough will occur, and the unit must be charged with a new supply of PELADOW DG calcium chloride.

The outlet moisture content after steady-state has been reached may be determined by assuming that the fluid is in equilibrium with calcium chloride tetrahydrate ($CaCl_2 \cdot 4H_2O$). This is a conservative rule-of-thumb that has been determined by lab experiments and also field experience.

Figure 3 can be used to find the vapor pressure exerted by the $CaCl_2 \cdot 4H_2O$ at the system's operating temperature. The partial pressure of the water in the exiting hydrocarbon stream will be approximately in equilibrium with the vapor pressure of the hydrate. Modeling software may then be used to determine the outlet moisture content based on this water partial pressure.

Equipment Considerations

Maximum Velocity

The maximum velocity through the bed section is limited by entrainment considerations, and should not exceed 5 feet/minute. If the velocity is too high, entrainment may be excessive, and in extreme cases brine that is formed may be carried overhead with the fluid.

Brine Removal

Provisions must be made to drain or remove the brine periodically from the unit to present brine entrainment in the hydrocarbon stream and bridging of the calcium chloride bed.

Feed Considerations

To minimize channeling in the packed bed, it is necessary to provide even distribution of the feed stream entering the bed. A perforated pipe type distributor will provide a very uniform flow through the packed bed if sized correctly.

Vessel Operating Life

Once the dehydrator is loaded with calcium chloride and placed in service, it will continue to remove water until approximately 80% of the bed has been used. If flow through the bed needs to be interrupted for any length of time, the dehydrator should be shut-in full of the feed stream rather than be drained. This will prevent any tendency toward bridging and subsequent channeling when the unit is put back online.

Multi-Vessel Operation

Depending on the drying requirements, it may be advantageous to use two driers in series. This 2-bed system will maximize the utilization of calcium chloride while allowing continuous dehydration. In two bed operations the first dryer can be operated until it is spent. Then it can be bypassed and refilled. After refilling, this dryer is placed online in the "polishing" position with the second bed now in the lead position. Hence the hydrocarbon stream will always flow from the most hydrated bed to the freshest (driest) calcium chloride bed which will provide maximum drying efficiency.

When it is time to refill the dryer with fresh desiccant the inside of the dryer should be checked before new desiccant is added. If the spent desiccant is agglomerated into lumps or built up on the sides of the dryer, it should be washed from the dryer before recharging. If this is not done it could cause channeling and premature breakthrough.

Once the dryer is recharged with fresh desiccant, it is advantageous to fill the dryer with the product feed stream and leave the dryer shut for 4 – 8 hours. This will allow the small fines to dissolve and the larger fines to settle within the unit. This prevents calcium chloride carryover and contamination of the product stream.

PROCESS CONSIDERATIONS

Pressure Drop

For a calcium chloride unit operating normally, a pressure drop should not exceed 0.1 psi per foot of bed height (excluding any pressure drop across the distributor). Upon start up, the calcium chloride dryer should exhibit a very low pressure drop (0.1 psi/ft of bed height excluding the distributor). As the bed ages, the size of the calcium chloride briquettes will decrease, and the bed will consolidate. A small rise in pressure drop up to 0.1 psi per square foot of bed height is considered normal.

Heat Effects

Under normal temperatures (50-120°F) and pressures (300-3,000 psia) encountered, heat effects due to the heat evolved upon absorption of water vapor by calcium chloride are negligible. The dissolved water removed by the calcium chloride from hydrocarbons is so small in relation to the mass of fluid treated that no measurable temperature change should be produced from the latent heat solution of the calcium chloride.

Temperature

The normal operating temperature range for a calcium chloride dryer is from 25°F up to 120°F. The lowest operating temperature is determined by the crystallization temperature of the brine leaving the dehydrator. If the temperature of the bed is allowed to drop below this crystallization temperature, bridging and channeling could occur.

The upper temperature limit is determined by the vapor pressure increase of the calcium chloride hydrates and the increase in solubility of water in the product stream. The upper temperature should not generally exceed 120°F to maintain efficient calcium chloride drying capacity.

Deactivation

Any chemical reaction of the product stream constituents with calcium chloride will result in a loss of capacity. For example, calcium chloride will react with alcohols to form alcoholates and caustic to form calcium hydroxide. The only indication may be a sudden decrease in drying efficiency. Additionally, calcium chloride brine cannot be soluble in the product stream. The product stream must be free of constituents that could physically coat the calcium chloride pellets to the extent they can no longer form a hydrate.

Corrosion

A calcium chloride dehydrator should only encounter minimal corrosion if air is excluded from the system.

Bridging and Channeling

Bridging

The fusion or joining together of adjacent calcium chloride briquettes is known as bridging. Under normal operation, as the chemical is consumed the bed settles to a lower level. However, when bridging occurs, the bed may adhere to the sides of the column and the chemical will be consumed from the bottom up. This condition causes an erroneous bed level to be indicated and can cause some difficulty in determining when a unit needs recharging.

When bridging is observed, the bed can be dropped by pouring water around the outer edge at the side of the vessel when the dehydrator is being recharged. Sometimes manual assistance may be required in dislodging the bed.

Bridging can be caused by a variety of reasons. In general, any condition that tends to dry the bed after it has been in a wetted condition can cause some degree of bridging. This section covers some of the most common reasons for bridging.

Decrease in Bed Temperature

A decrease in bed temperature can cause freezing of the concentrated brine that is in contact with the calcium chloride briquettes. Recrystallization occurs when the ambient temperature drops below the crystallization temperature of the salt brine being formed in the lower portion of the bed.

Generally, recrystallization begins at the outer rim of the desiccant bed in contact with the metal walls of the tower, and the attendant bridging action works its way inwards. Heat loss to ambient is the main mechanism in this process. Insulating the tower or, in some extreme cases, heating the tower should reduce this problem. It has also been reported that a plastic type liner or epoxy coating inside the tower reduces briquettes bridging onto the tower walls and promotes slippage of briquettes down the sides of the tower.

Cycle Operation of the Dehydrator

Removing the dehydrator from service, leaving it idle, then placing it back in service can cause bridging if there is a large decrease in bed temperature while the bed is idle. Also, because water tends to diffuse from the saturated brine on the briquette surfaces into the briquettes, the brine tends to crystallize and bridge the adjacent pellets together.

For liquid hydrocarbon dehydrators, if the dehydrator is to be taken offline for any extended period it should be shut-in full of the product stream. This will minimize the tendency toward bridging when the dehydrator is placed back in service.

Free Water in the Bed

Large amounts of free water in the product stream (in excess of the solubility of water in the hydrocarbon), slugs of water, or dilute brine entering the bed section can contribute to bridging problems.

A coalescer may be put in place to remove free water. If this is not practical, a separate dehydrating tower of rock salt (NaCl) or a layer of rock salt 1-2 feet thick underneath the calcium chloride in the same tower can be used to remove the entrained water from the stream before it reaches the calcium chloride.

In addition, care should be taken to drain brine from the dehydrator periodically. This will prevent flooding of the bed with dilute brine which will be conducive to bridging.

Calcium Chloride Fines

Calcium chloride fines can hasten bridging problems in addition to plugging valves or carrying over into the product stream. When a bed of calcium chloride is to be replenished, this problem can be eliminated by filling the unit with the product to be dried and allowing the larger fines to settle and the smaller fines to dissolve before starting the unit (4-8 hours). If this is not possible, a filter in the product line out of the tower will catch any fines dislodged in processing.

Channeling

Channeling usually takes place after bridging has occurred. In this case, the fluid seeks the path of least resistance through the bed. Eventually a hole is developed through the bed due to the dissolution of the calcium chloride in its path.

Channeling can also be caused by maldistribution of the fluid into the bed. Using a distributor that will evenly disperse the hydrocarbon will reduce the tendency toward channeling.

When channeling occurs, breakthrough (poor dew point depression) starts prematurely, and this is good evidence that channeling has taken place.

When channeling has occurred, the dehydrator must be opened and the bed section redistributed.