

## Hydrates for Gypsum Stack Water Purification

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*Abstract:* Hydrate water processing is a method for assisting in the control of gypsum stack water inventories that is potentially competitive with chemical treatment. Formation of hydrates occurs with the rejection of salts and non-participatory materials, presenting a unique opportunity for processing saturated salt solutions. Lab results have shown that 90% of ionic, non-participatory materials are rejected in a single treatment stage. The low density of hydrates (~0.93 kg/l) allows for the separation from the residual salt slurry. Once separated from the residual brine, the hydrate is dissociated producing water that is substantially reduced in conductivity and non-clathrate forming compounds. This work aims to describe how hydrates can be used to purify water, the promise and limitations of deploying this technology, and science and engineering challenges that still remain.

**Keywords:** gas hydrates, clathrate, water purification, gypsum stack water

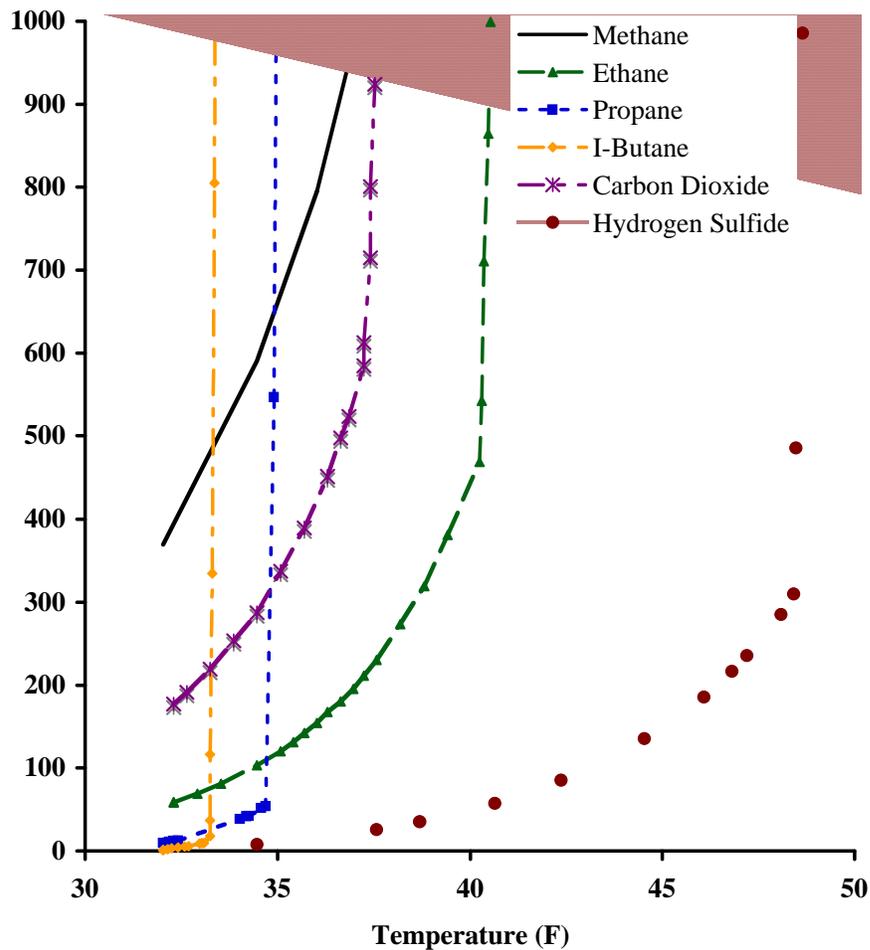
## Introduction

Gas hydrates are a family of solid crystalline materials composed of water and “guest” molecules. Most hydrates have the macroscopic appearance of water ice, but they differ from ice significantly in their composition, phase behavior, crystal structure, and growth dynamics. Hydrates are found naturally on Earth in Antarctic ice sheets,<sup>i</sup> arctic permafrost, in ocean sediment,<sup>ii</sup> and on the ocean floor,<sup>iii</sup> including the Gulf of Mexico.<sup>iv</sup> They also form in oil and gas pipelines, causing severe flow-assurance issues.<sup>v</sup>

The hydrate structure is composed of a water network that creates geometric voids with dimensions of 0.3-0.9 nm ( $3-9 \times 10^{-4}$  micron).<sup>v</sup> The water structure is not stable unless non-water molecules, called guests, occupy the voids. Common guests include small hydrocarbons (up to the size of isobutane), carbon dioxide, and air. The guest-host relationship can be exploited to achieve separations, including purifying water,<sup>vi</sup> recovering solutes,<sup>vii</sup> and separating gases.<sup>viii</sup> Because of the importance of the guest, hydrates are named “guest hydrate”. For example, a hydrate with methane as the guest is methane hydrate. Hydrates made from mixtures are typically named for the mixture (air hydrate).

Gas hydrates formation is an exothermic process (54 kJ/mol (12.9 kcal/mol) for methane hydrate) and occurs at elevated pressures and up to 84 °F. The guest is of central importance to hydrates and plays a role in what cages are formed, the rate of formation,<sup>ix</sup> and the phase boundary (Fig. 1). The size of the guest determines what size and number of water cages are formed. The cage size, shape, and stoichiometry determine the structure. The most significant structure for industrial application is

called Structure-1. Structure-1 has the chemical formula  $\text{Guest}(\text{H}_2\text{O})_x$ <sup>1</sup> where x is 5.75 in the ideal case but is typically 6-6.2 because not all of the voids are filled with guest molecules.<sup>2</sup>



**Figure 1.** Gas hydrate phase boundaries labeled by guest. The hydrate is stable to the left of the line. To the right of the line is gas + water.

Gas hydrates grown from salt solutions are known to reject most common salts<sup>x</sup> and non-guest molecules. Salts that are not rejected participate in the formation of

<sup>1</sup> The empirical structure is  $(\text{Guest})_8(\text{H}_2\text{O})_{46}$ .

<sup>2</sup> Excellent illustrations of the hydrate structures can be easily found using an internet search.

semi-clathrate structures, a closely related chemical family. These salts include  $\text{PF}_6^-$  and  $(\text{C}_4\text{H}_4)_4\text{N}^+$ .<sup>xi</sup> Gas hydrates are superior to ice in rejection of salts. The hydrate crystal structure is very dynamic resulting in rapid curing and ripening processes. Where ice can take 1-2 years to expel trapped brines, hydrate takes only hours or days.<sup>x</sup> The purification of water with hydrates takes place in three steps:

**Step 1** Hydrate formation: Solution + Gas  $\rightarrow$  Hydrate + Concentrated Solution

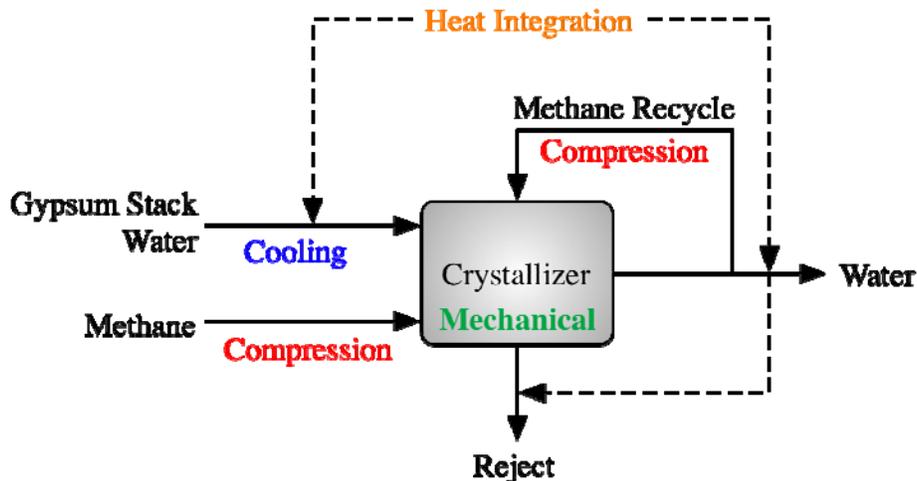
**Step 2** Hydrate is physically separated from the concentrated solution

**Step 3** Hydrate dissociation: Hydrate  $\rightarrow$  water + gas

The remainder of this work will focus on the potential application of hydrate water treatment to the treatment of gypsum stack water. Prior lab-scale results and process analysis on a system developed to treat water contaminated with boron using carbon dioxide as the hydrate guest will be presented. This will be followed by a description of our current effort to develop a demonstration system for treating gypsum stack water, including our initial tests with synthetic stack water.

### **Process Cost Model**

The operating cost of the model (Table 1) under operating conditions has been estimated using the flow paths in Figure 2. The inputs to the process are gypsum stack water and methane (natural gas). The outputs are water for discharge and a reject stream that contains brine and solids. Methane is recycled during the process.



**Figure 2.** Wire diagram of general process flows for hydrate water treatment.

The methane input is delivered at atmospheric pressure. The recycled methane is recovered at 385 psig. Both are pressurized adiabatically to 535 psig. The delivered gas is make-up and is due to a small amount of methane in the discharge that cannot be recycled. The cost of the make-up methane<sup>3</sup> is estimated to be \$0.02 per 1000 gallons with a compression cost of 0.1¢/kgal.<sup>4</sup> Cost to recompress the recycle methane is \$0.73/kgal.

The gypsum stack water must be cooled to operating conditions (37 °F). This is performed in a separate chamber that is capable of handling the solids that may be produced, and is the largest single cost element. The heat of crystallization due to precipitation of materials during this cooling process has not been considered. Cooling the gypsum stack water has been modeled as requiring a refrigeration unit that has a coefficient of performance (COP) of 1. Heat integration of 50% with the output streams is included.

<sup>3</sup> \$10.00/Mscf is used as the price of natural gas.

<sup>4</sup> \$0.10/kWh is used as the price of electricity.

The crystallization process produces a large amount of heat and the hydrate dissociation process requires an equally large amount of heat. These two processes must be closely heat integrated. Because dissociation of the hydrate takes place at a slightly lower temperature than formation (the pressure is lowered) a device is required to increase the rate of heat transfer over the spontaneous rate. A heat pump is used as a model device. A “COP” of 4 and an internal heat integration of 96% are used. It is further estimated that the crystallizer will require 1-10 kWh/kgal of mechanical work to be performed. We have used 5 kWh/kgal in our cost estimate.

The overall cost of operating the process is estimated to be \$6-7/kgal, non-inclusive of the cost of ownership.

**Table 1.** Cost element breakdown.

Process	kWh/kgal	\$/kgal <sup>1</sup>	Note
Compression	7.6	\$0.76	
Make-up Gas	—	\$0.05	\$4.50/Mscf natural gas
Mixing/Pumping	5	\$0.50	
Crystallizer	5.2	\$0.52	96% heat integration, COP = 4
Cooling	48.2	\$4.82	50% heat integration, COP = 1
<b>Total</b>	<b>66</b>	<b>\$6.65</b>	

1. \$0.10/kWh is used to value power requirements

## Experimental

*Boron Water Treatment:* Carbon dioxide hydrate was induced to form on a refrigerated surface using natural seawater and seawater with adjusted boron concentration. To obtain seawater with higher than natural boron levels, boric acid ( $\text{H}_3\text{BO}_3$ , MW 61.83g/mol, [10043-35-3], Alfa Aesar, 99.6% purity, density 1.435 g/ml) and sodium borate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , MW 381.37g/mol, [1303-96-4], MP Biomedicals, LLC, density 2.367 g/ml, ACS grade) were added.

The pressure vessel included an internal aluminum plate that was piped with coolant. The vessel is equipped with four sight glasses for visible inspection of the chilled surface, and instrumented with pressure transducers, temperature sensors, and a conductivity meter. The surface was refrigerated but mixing and temperature was controlled so that the conditions for in the bulk solution and other portions of the vessel were unfavorable for hydrate formation. Further growth of the hydrate into the water space was maintained through continued refrigeration that removed heat produced during the process of crystallization. Masses of carbon dioxide hydrate 4 to 5 inches thick were formed, which upon dissociation, produced water with very low salinity, boron levels and other contaminants.

The pressure vessel consists of an aluminum tube with titanium endcaps held in a compression fitting using four tie rods tightened to 50 ft-lbs torque. O-rings provided a seal. The outside of the vessel was insulated using one-inch thick expanded neoprene. 500psig of  $\text{CO}_2$  was added followed by the addition of the pre-cooled ( $36^\circ\text{C}$ ) test solution. The solution was added via a sprayer tip through a  $\text{CO}_2$  atmosphere to pre-saturate the solution. A high-pressure back-pressure regulator was set to maintain the pressure inside the vessel at 500 psig as solution was added.

The hydrate forms in less than 1 hour and is then ripened for 1-2 hours. After the ripening process, the residual brine was drained from the system and the hydrate was dissociated. The product water was collected and measured for salinity. Water samples were bottled and sent to Southern Analytical Laboratories (SAL) in Oldsmar, FL for characterization. SAL is nationally accredited under the National Environmental Laboratory Accreditation Conference (NELAC) program for both drinking water and environmental analyses.

*Synthetic Stack Water:* synthetic stack water was produced dissolving calcium sulfate dihydrate (Aldrich) in tap water. Due to material compatibility concerns, the reactor vessel was constructed from 316l stainless steel endcaps and an acrylic tube. The acrylic is incompatible with carbon dioxide (pressurizing and depressurizing leads to crazing and structure failure). Methane, ethane, and natural gas are used as the hydrate forming materials. The vessel is equipped with a 3hp mixer with a 5" and 2.5" blade. A 316l stainless steel coil provides cooling and a surface to collect the hydrate.

## **Results and Discussion**

*Boron Water Treatment:* CO<sub>2</sub>-hydrate has been used to reject boron, calcium, and magnesium from seawater. The boron species tested were both non-ionic (boric acid) and ionic (sodium borate) under the conditions of the test. The results for the rejection of these materials are presented in Tables 2 and 3.

**Table 2.** Rejection of boron from seawater by hydrate water purification.

<b>Source Water</b>	<b>Initial Boron</b>	<b>Product Water</b>	<b>Boron</b>
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	(mg/l)	Boron (mg/l)	Rejected (%)
Seawater only	4.1	0.15	96%
Boric acid	5.4	1.2	78%
Boric acid	15	1.3	91%
Boric acid	27	2.0	93%
Sodium borate	7.6	0.85	89%
Sodium borate	13	1.7	87%
Sodium borate	21	1.6	92%
		Median	91%
		Average	89 ± 7%

**Table 3.** Rejection of calcium and magnesium using hydrate water purification.

Trial	Sample	Concentration of Ca <sup>2+</sup> in mg/l & (% rejected)	Concentration of Mg <sup>2+</sup> in mg/l & (% rejected)
1	Before	380	1200
	After	21 (94%)	61 (95%)
2	Before	380	1200
	After	41 (89%)	130 (89%)
3	Before	400	1300
	After	26 (93%)	80 (94%)
4	Before	390	1200
	After	33 (91%)	100 (92%)
5	Before	340	1100
	After	17 (95%)	51 (95%)
Rejection	<b>Median</b>	93%	94%
	<b>Average</b>	92 ± 2%	93 ± 3%

CO<sub>2</sub>-hydrate water treatment rejects approximately 90% of non-participating (non-guest) ionic and non-ionic compounds. Known participatory ions have not been tested. Of this family of materials, only PF<sub>6</sub><sup>-</sup> seems to be remotely likely to be found in associated with stack water.

*Synthetic Stack Water:* Because of materials of construction limitations, stack water from an active or closed plant cannot be used in the same apparatus developed to purify boron-containing water. Stack water is not compatible with the largely aluminum construction of the apparatus. We currently only possess two types of pressure reactors: aluminum and acrylic. The acrylic vessels are not compatible with CO<sub>2</sub> gas – they craze and suffer unacceptable levels of mechanical degradation.

The reactor to test synthetic stack water was constructed from acrylic and 316L stainless steel. Carbon dioxide could not be used as the hydrate forming gas because of rapid, irreversible damage to the acrylic. Instead hydrocarbon gases, which may be the more ideal candidate since they are more widely available, were used. The change in vessel design and configuration has led to a significant change in observed performance (Table 4).

We have, at the time this manuscript was prepared, had what can be characterized only as minor success with these hydrate formers in the new reactor. We can grow these hydrates in the synthetic stack water but we cannot grow them using the same procedure that was successfully developed for the boron water purification.

**Table 4.** Differences between Boron and Stack Water Tests

Variable/Observation	Boron Test	Stack Water Test
Guest	Carbon Dioxide	Methane, Ethane, or Natural Gas
Pressure Vessel Construction	Aluminum tube, aluminum cooling surface, and titanium endcaps.	Acrylic tube with 316l stainless steel cooling surface and endcaps.
Hydrate Sticks to Cold Surface	Yes	No
Observed Hydrate Morphology	Inch-scale Plates	Dendrites
Purified Water Produced	Yes	No

The difference in performance between the two reactors is not surprising given the large-scale changes in configuration and chemistry. Our current efforts are focused on modifying our procedures to produce higher quality crystals. The first step we have taken is to modify the process to avoid or reform the dendrites produced using fines destruction methods and forcing the Ostwald series. The Ostwald series is the progression of polymorphs produced by a crystallization process that move from the least stable (the first to be produced) to the most stable. Generally, the crystal quality and morphology improve dramatically with each step down the series. The Ostwald series is known to improve hydrate crystal quality.<sup>xii</sup>

The growth of high quality crystals of significant size (1/32-1/8") may reduce all the other problems because such crystals do not need to be attached to a surface for processing. These large, high quality crystals can be separated in relatively simple

fashion by gravity or hydrocyclone and then delivered to the dissociator where purified water is produced.

Our second effort is focused on improving the mechanical functioning of the system. In particular we are working on modifying the heat exchanger surface to improve hydrocarbon sticking – we are not counting on the production of large crystals.

One interesting possibility of working with real stack water is the relationship between surfactants and hydrate formation.<sup>xiii</sup> It is known that many surfactants and amphiphilic compounds catalyze hydrate formation and dissociation, some of which may be present in the stack water solution. Once a suitable procedure has been developed to overcome the chemical and mechanical issues associated with the change in guest and reactor and real water is processed, it may be found that hydrate formation from actual stack water samples occurs at a faster pace than predicted. The addition and recycling of hydrate catalysts is an additional possibility that can be explored.

## **Conclusions**

Gas hydrates can be used to purify water solutions. Results from saline systems have show that hydrates reject about 90% of non-participatory materials. This level of rejection has been hypothesized to be extendable to gypsum stack water processing. The current status of our experimental program to test that hypothesis has been described. Methane, ethane, and natural gas hydrates have been grown in synthetic stack water. However, issues with the construction of the experimental

apparatus due to the corrosive nature of pond water have taken center stage. The original experimental procedure was significantly modified which resulted in a change in the chemistry and mechanical process and a temporary loss of purified water production. The steps being taken to overcome these changes have been outlined. A  $\pm$  30% operating cost estimate of \$6-7/kgal has been developed and presented.

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