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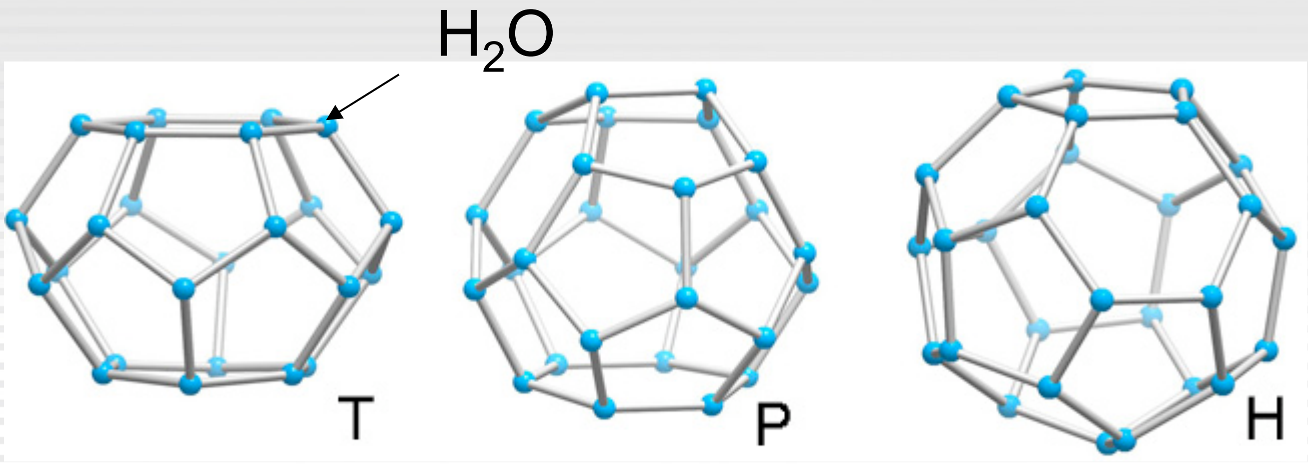
Hydrate and Hydrate Inhibition

by Sekar Darujati

- Definition of gas hydrate
- Hydrates in pipeline
- Hydrate prediction
- Hydrate prevention
- Hydrate inhibition
- Example problem

What is Gas Hydrate?

- Clathrate: HC molecules are entrapped in a cage structured composed of H_2O molecules
- The structure of hydrate depends on the type of HC molecules
- Hydrate can form at temperatures above water freezing temperature
- Favored conditions: low T, high P (water has to be present)
- Time dependent – rate depends on the gas composition, the presence of nucleation sites, flow turbulence, etc.



Hydrate former:

N_2
CO_2
H_2S
CH_4
C_2H_6
C_3H_8
$i\text{-}C_4H_{10}$
$n\text{-}C_4H_{10}$

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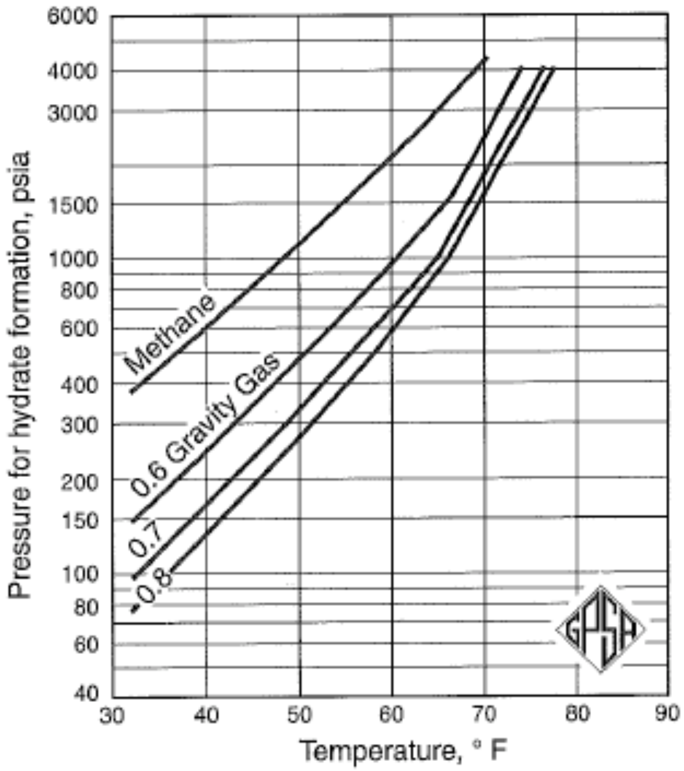
Hydrates in Pipelines

- When will it form? T drops below dew point AND hydrate formation T
- Typical locations:
  - Low points in the lines/pockets of water
  - Large pressure drop:
    - Orifices, sudden enlargement on pipeline, elbows, etc.
- Problems: block pipeline, cause pipe rupture around the pipe bend, pipe rupture due to high P generated by the plug momentum
- Removal is challenging and dangerous:
  - Large pressure differential across the plug
  - Large release of gas upon melting – especially sour gas
  - Refer to company guidelines for hydrate handling

Prediction of Hydrate Formation

- GPSA chart for quick approximations



CAUTION: Figures 20-19 through 20-21 should only be used for first approximations of hydrate formation conditions. For more accurate determination of hydrate conditions make calculations with $K_{v\text{-}s}$.

- Katz method using K_{vs} (reliable up to 1,000 psia)
- McLeod-Campbell method (for 5,000 – 6,000 psia)
- EOS → Hysys, ProMax, etc

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Hydrate Prevention

- Reducing the P below that of the hydrate formation (for a given T)
- Adding heat: keeping the operating T above the hydrate formation T
- Dehydration: reducing water content in the gas to keep the system above water dew point
- Inhibition: reducing the thermodynamic potential for hydrate formation or modify the rate formation
- Ensure proper design of the system

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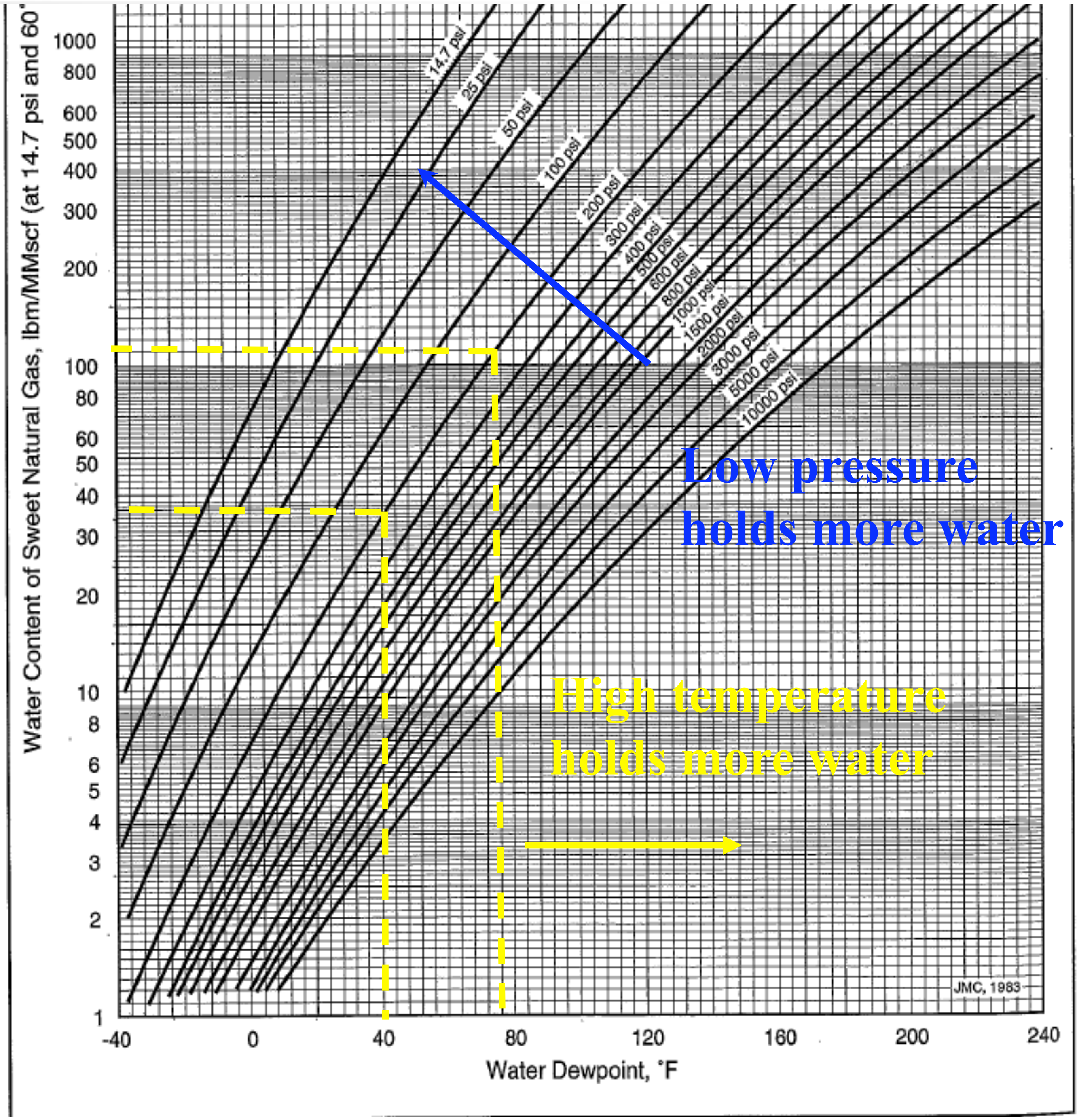
Water content of natural Gas



Low pressure holds more water

High temperature holds more water

McKetta & Wehe, 1958

Other Variables which Affect Water Content of Natural Gas

- Effect of CO_2 and H_2S:
  - Pure CO_2 and H_2S can hold more water than sweet natural gas especially at pressures above 700 psia
  - Corrections should be applied if the gas content CO_2 and/or H_2S above 5% at $P > 700$ psia

Hydrate Inhibition

- Thermodynamic inhibitors: methanol, glycol (most common)
- Kinetic inhibitors: polymer-based chemicals
- Hammerschmidt's equation is used to predict (thermodynamic) inhibitor concentration:

$$X_R = \frac{(d)(M)}{Ki + (d)(M)}(100)$$

d = depression of hydrate point

X_R = min. wt.% of inhibitor in the liquid phase (rich inhibitor concent.)

M = molecular weight of inhibitor; MeOH = 32

K_i = constant = 2,335 (FPS), 1,297 (SI)

- Inhibitor injection rate:

$$m_I = m_W \left(\frac{X_R}{X_L - X_R} \right)$$

m_I = mass flow of inhibitor solution [lb/d]

m_W = mass flow of liquid water [lb/d]

X_R = rich inhibitor concentration [wt.%]

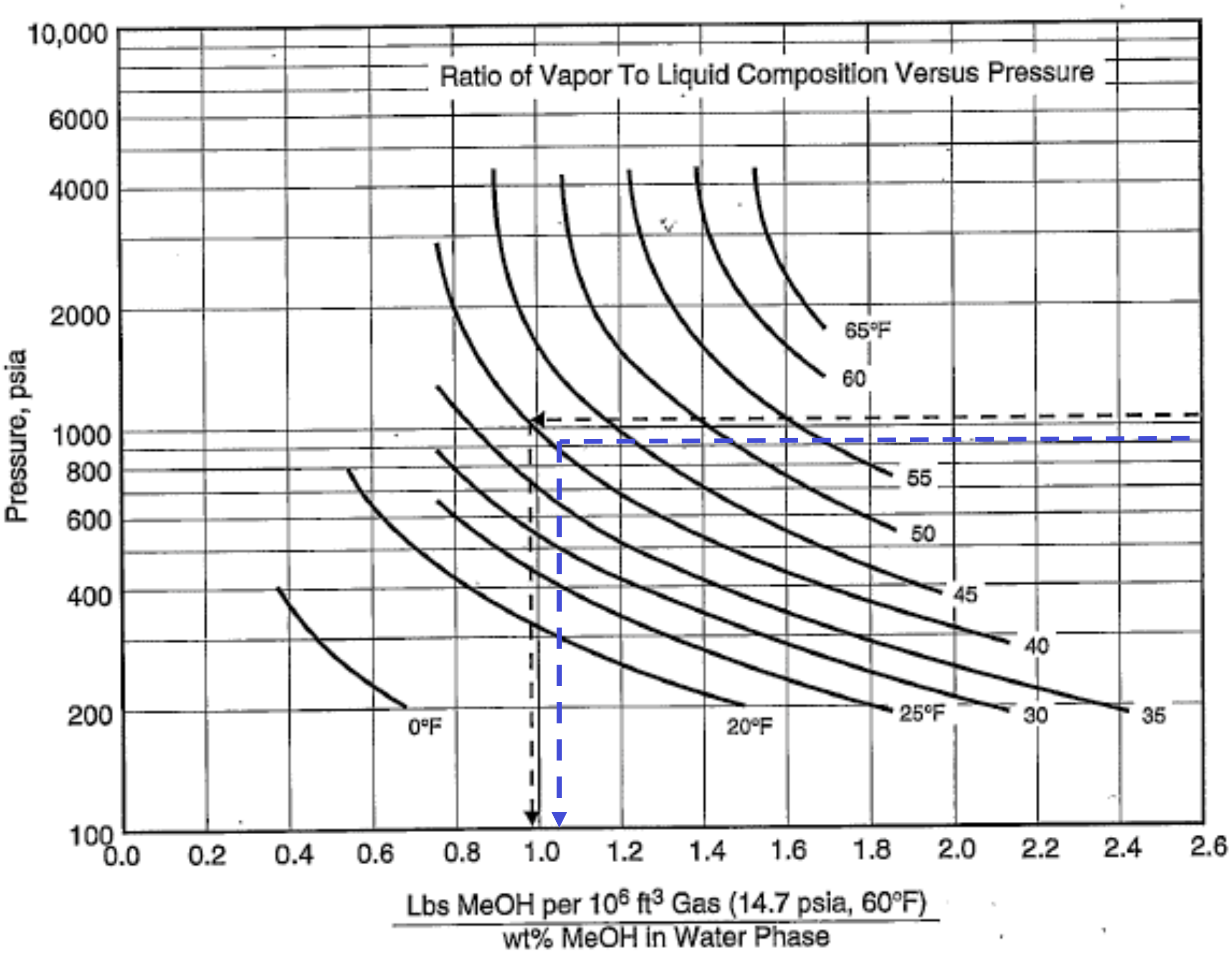
X_L = lean inhibitor concentration [wt.%]; 60 – 80% for glycol, ~ 95 - 100% for methanol

- Inhibitor losses to the hydrocarbon phase:

For glycol → small

For methanol → significant

- Methanol losses to HC vapor



- Methanol losses to HC liquid ~ 0.15 lb/bbl (JMC)

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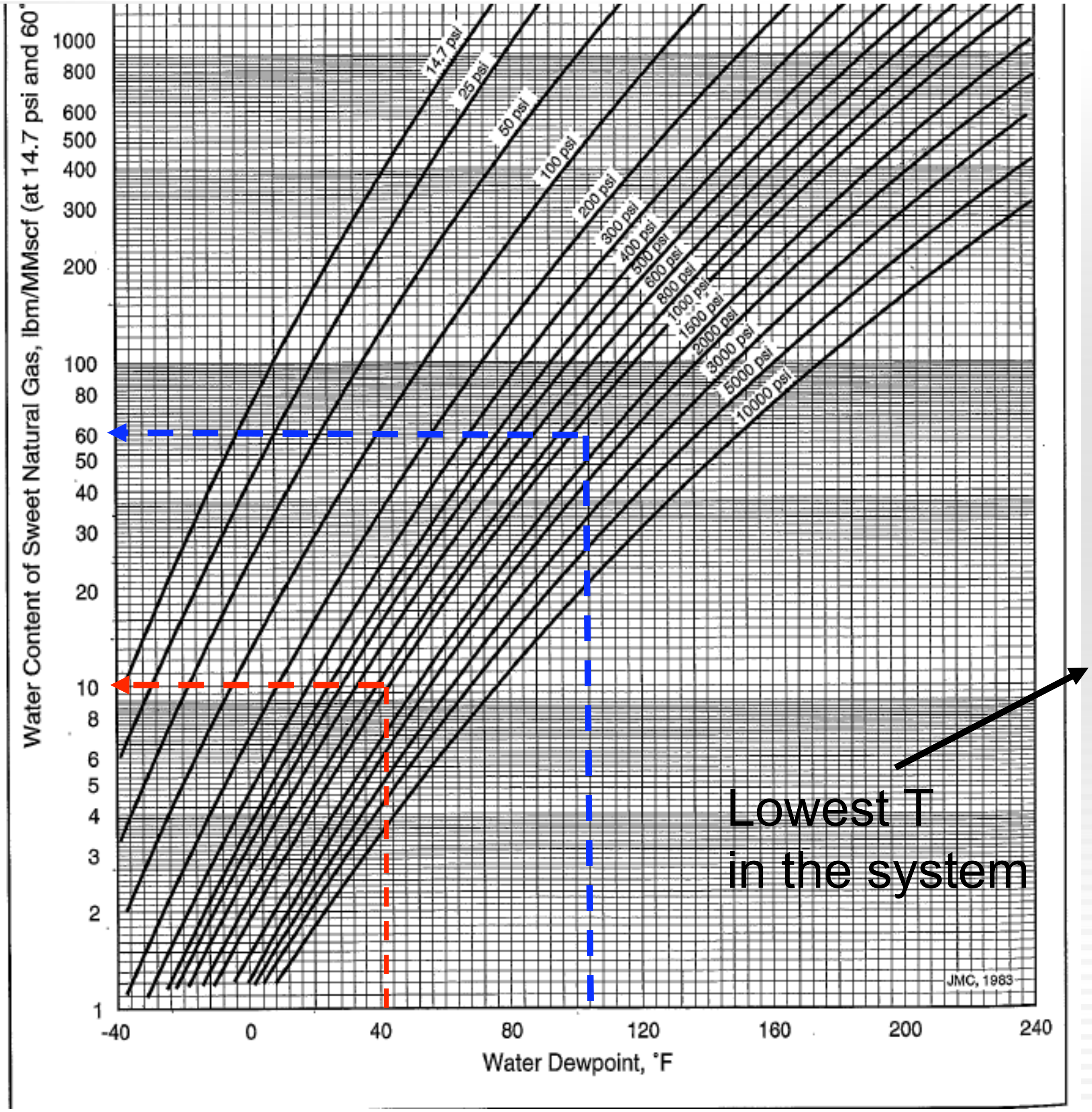

Lowest T
in the system

Example:

10 MMSCFD (283 e^{3}m^3/d) Sweet gas, entering pipeline:

P = 1,160 psia
(8,000 kPa)
T = 104°F (40°C)

Gas arrives at the gas plant:

P = 900 psia
(6,205 kPa)
T = 41°F (5°C)

Hydrate T = 63°F

Methanol required to prevent hydrate formation?

- Calculate water content of the gas at the inlet of pipeline (at 1,000 psia, 67°F)
  = 60 lb/MMSCF (1,000 kg/10^6 std m^3)

- Calculate water content at the inlet of gas plant (at 900 psia, 41°F)
  = 10 lb/MMSCF (170 kg/10^6 std m^3)

- Calculate water condensed
  = (60 - 10)lb/MMSCF x 10 MMSCF
  = 500 lb/d (235 kg/d) → m_W

- Calculate d (depression of hydrate point)
  = 63 – 41 = 22°F (12°C)

- Calculate X_R (rich methanol concent.)
  = (22)(32)/{(2,335)+(22)(32)}x100
  = 23%

- Calculate methanol injection rate, m_I
  = (500) x [(23%)/(95% - 23%)]
  = 160 lb/d (75 kg/d)

- Calculate methanol losses to vapor
  = 1.1 lb/MMSCF/wt.%MeOH (from chart)
  = (1.1)x(10)x(23)
  = 253 lb/d (114 kg/d)

- Total injection rate = 160 + 253 = 413 lb/d (189 kg/d)
  Volumetric rate = (413)/(49.7)x(7.48)/1440 = 0.04 USGPM (0.16 L/min)

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Questions/Comments?

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