



# **Case Study on the Recovery of Salt from Produced Water Coming from Shale Gas Applications**

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## Overview

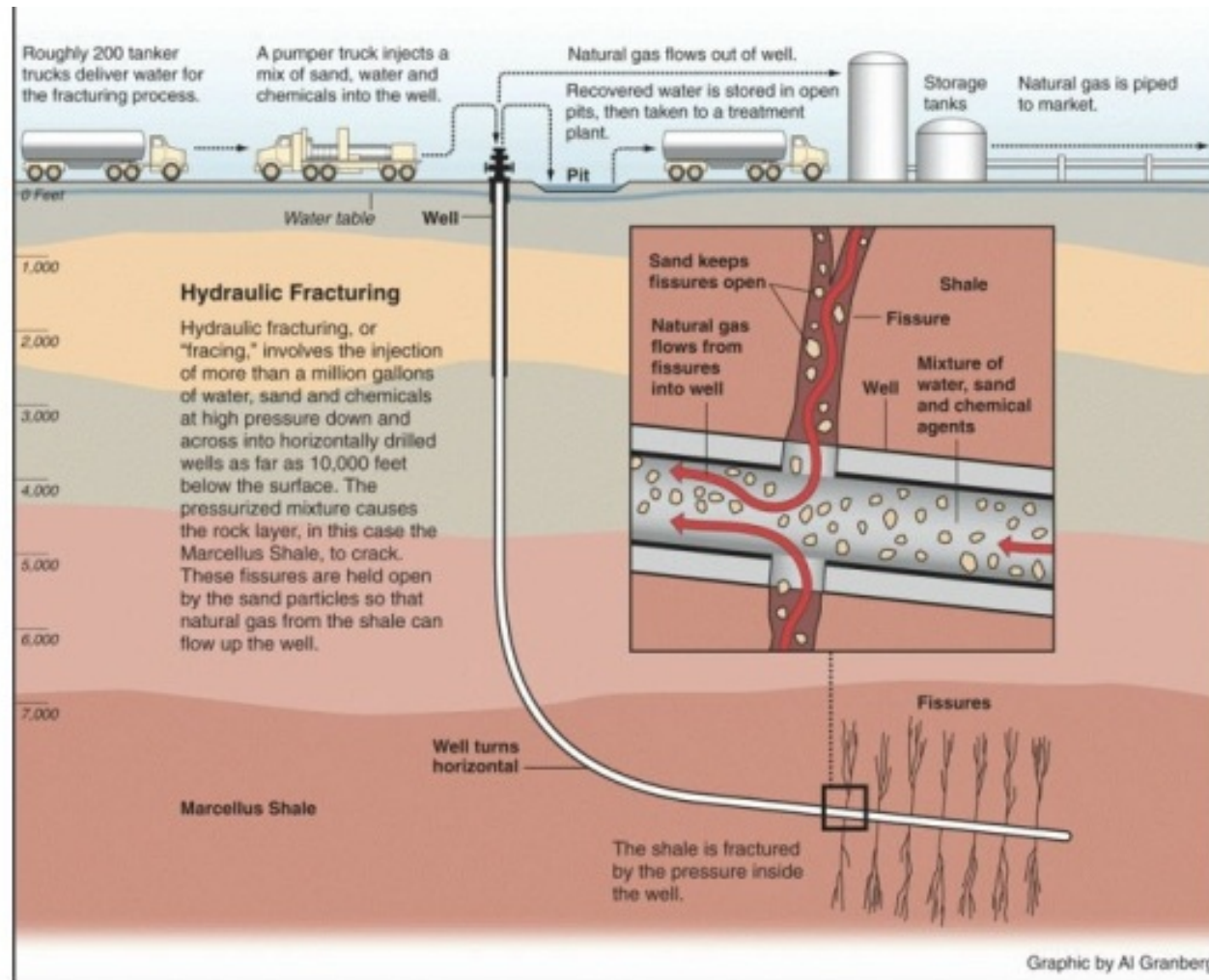
💧 Hydraulic Fracturing

💧 Waste Water Handling

💧 Case Study of Waste Water Crystallization



## Hydraulic Fracturing and Produced Water





## Water Coming out of the Wells

Chemical constituent or surrogate parameter	Unit of measure	Range reported in produced water from wells drilled in Marcellus Shale 5 days post hydraulic fracturing	Range reported in produced water from wells drilled in Marcellus Shale 14 days post hydraulic fracturing
Total Suspended Solids		10.8-3'22	
Turbidity		2.3-1'5	
Total Dissolved Solids		38'500	
Specific Conductance		79'500	
Total Organic Carbon		3.7-38	
Dissolved Organic Carbon		30.7-5	
Chemical Oxygen Demand		195-17	
Biochemical Oxygen Demand		37.1-1	
BOD/COD Ratio			
Alkalinity		48.8-3	
Acidity		<5-447	
Hardness (as CaCO <sub>3</sub> )	mg/L	5'100-55'000	650-95'000
Total Kjeldahl Nitrogen (TKN)	mg/L as N	38-204	5.6-261
Ammonia Nitrogen	mg/L as N	29.4-199	3.7-359
Nitrate – N	mg/L as N	<0.1-1.2	0.1-0.92
Chloride		26'400-1	
Bromide		185-1'	
Sodium		10'700	
Sulfate		2.4-10	
Oil and Grease		4.6-65	
BTEX (benzene, toluene, ethylbenzene, xylene)			
VOC (volatile organic compounds)			
Naturally occurring radioactive materials (NORM)		Non-detect	
Barium		21.4-13	
Strontium	mg/L	345-4'830	100-6'000
Lead	mg/L	Non-detect-0.606	Non-detect-0.349
Iron	mg/L	21.4-180	13.8-242
Manganese	mg/L	0.881-7.04	1.76-18.6

High Salinity

Industrial Chemicals

Hydrocarbons

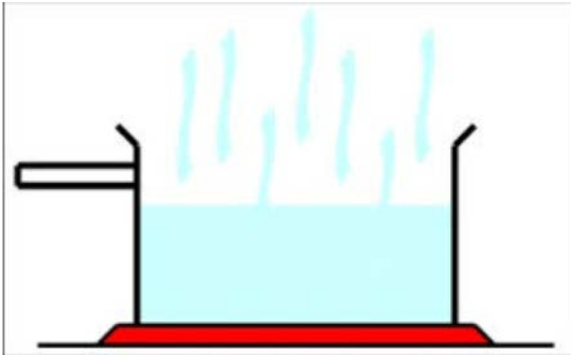
NORM (naturally occurring radioactive materials)

# Water Waste Water Management Possibilities

- 💧 Reduction of Waste Water Being Generated
- 💧 Recycling of Waste Water in the Fracking Process
- 💧 Disposal of the Waste Water
- 💧 Beneficial Reuse of the Waste Water
- 💧 Treatment of Waste Water for Further Processing or Disposal



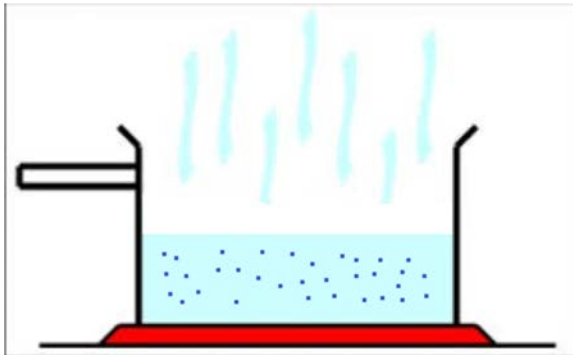
## Thermal Treatment of Waste Water



💧 Evaporation of Water Vapour

💧 Vapour Condensate is Clean

💧 Energy Intensive Process

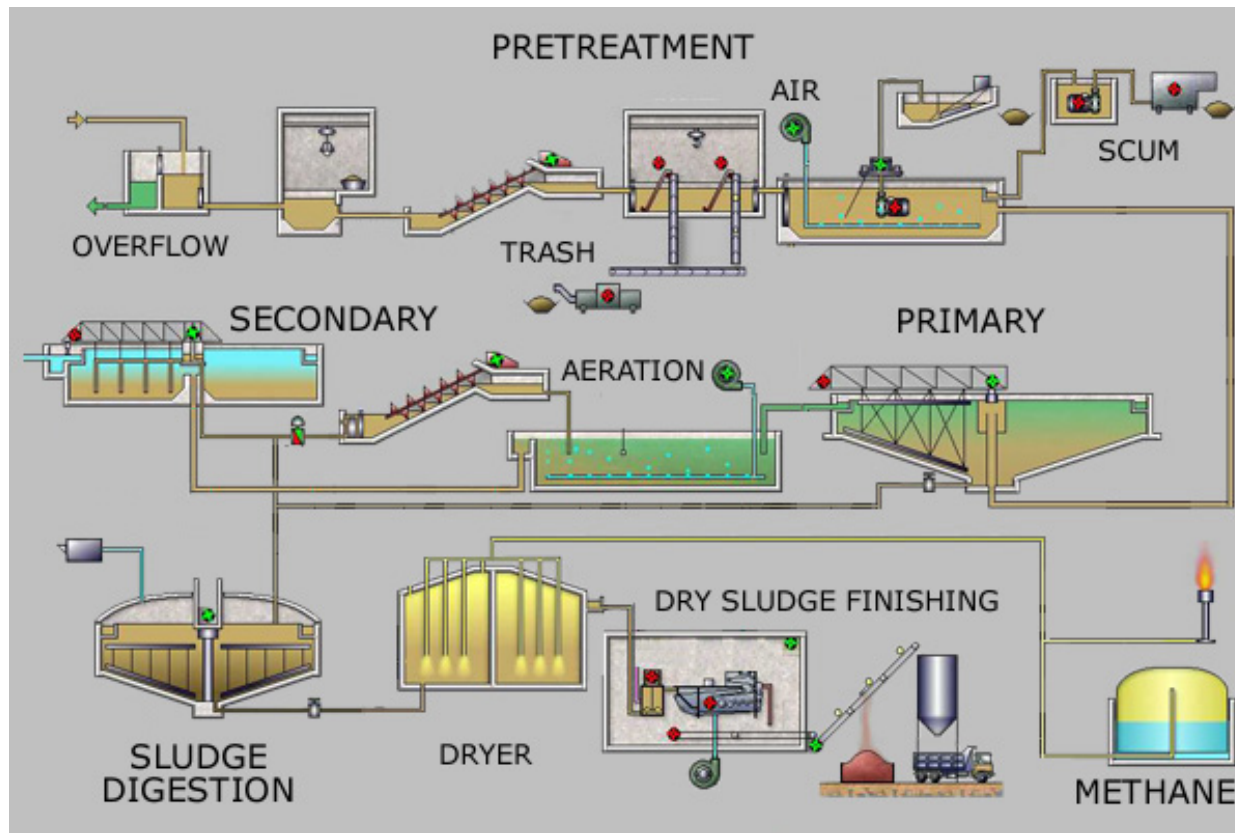


💧 Stopped before Crystallization occurs

💧 Liquid Distillate left as Waste Material

## Pretreatment in POTW's

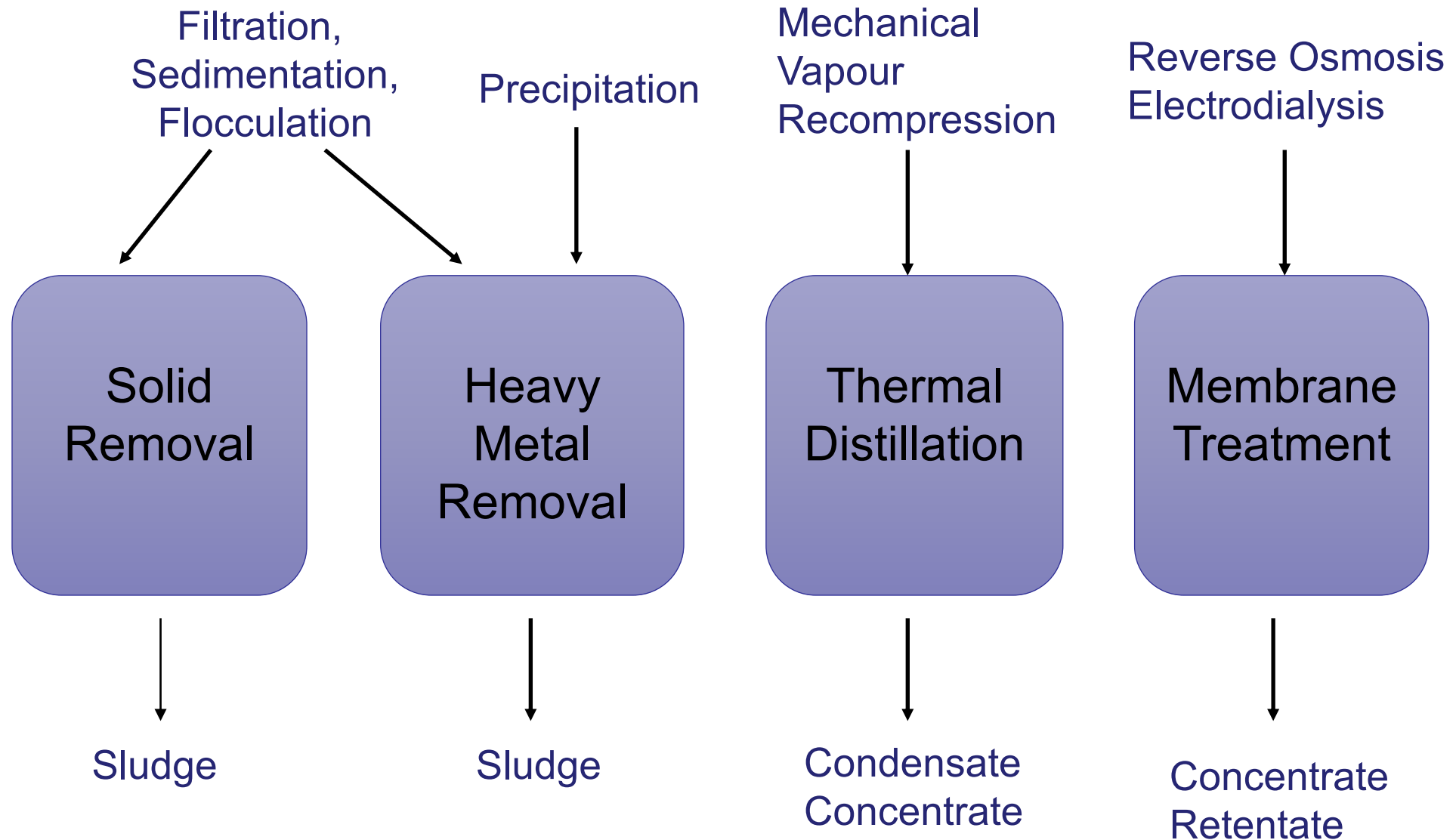
Publicly Owned Treatment Works for Municipal Waste Water:



- 💧 Salt
- 💧 Formaldehyd
- 💧 Capacity Limits

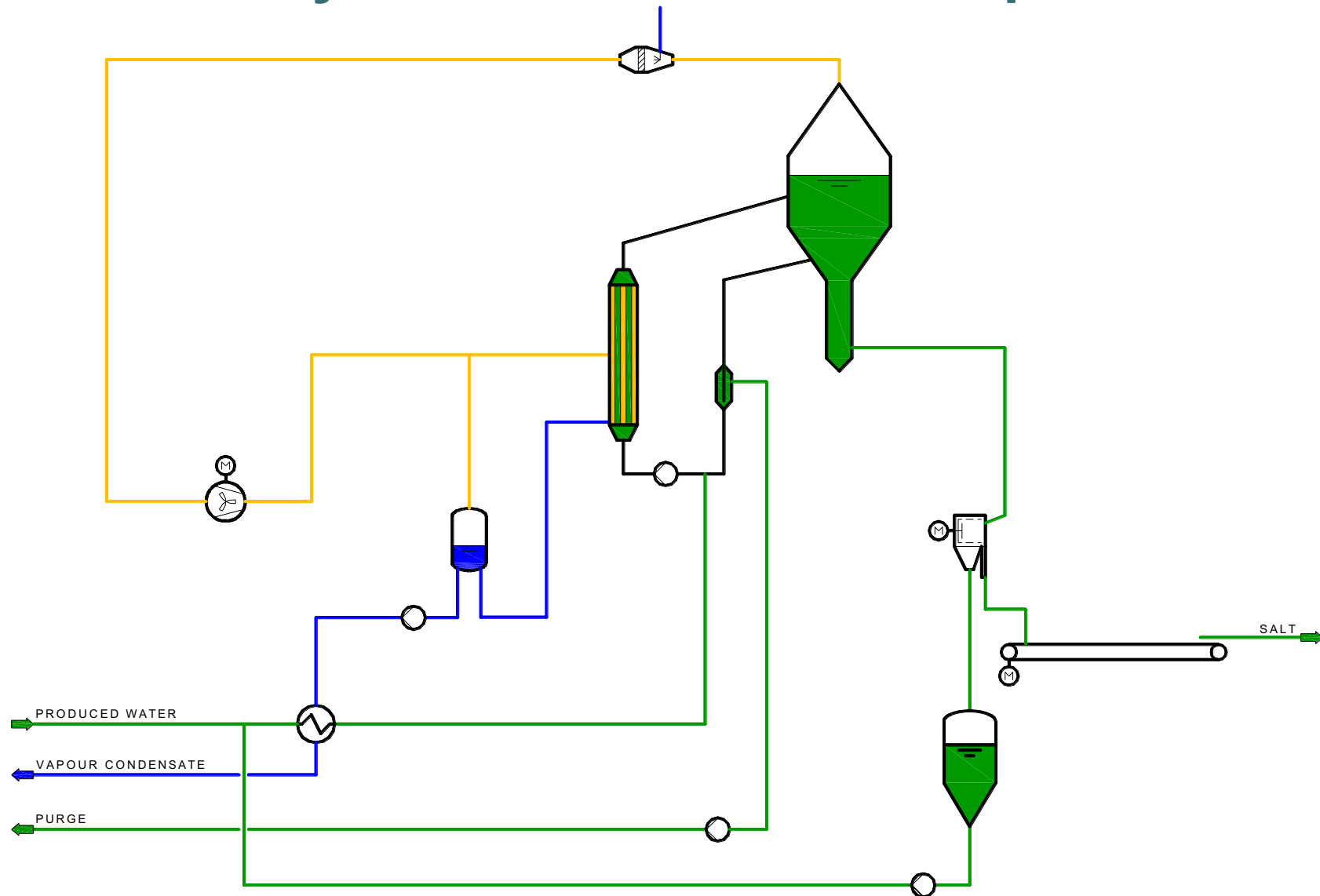


## Pretreatment in CTW's





## Crystallization Plant Concept



## Chemical and Physical Challenges

- 💧 Solids are Hard to Remove in the Pretreatment Plant Upstream of the Crystallizer
- 💧 Reactions can take Place in the Crystallizer and lead to Precipitation or Incrustation
- 💧 Chemical Agents can Cause Foaming
- 💧 Volatile Chemicals at high Temperatures can Cause Corrosion
- 💧 Changing Feed Compositions can lead to Crystallisation of Impurities

## Chemical and Physical Requirements

### Chemical:

- 💧 Pretreated Produced Water as Feed
- 💧 pH Higher than 6 - 7
- 💧 No Corrosive Volatiles in the Feed Solution
- 💧 No Solids in the Feed Solution

### Physical:

- 💧 Stable Conditions of Utilities
- 💧 Steam of 2-3 bar
- 💧 Electrical Power @ 480 V
- 💧 Compressed Air
- 💧 Make-up Water

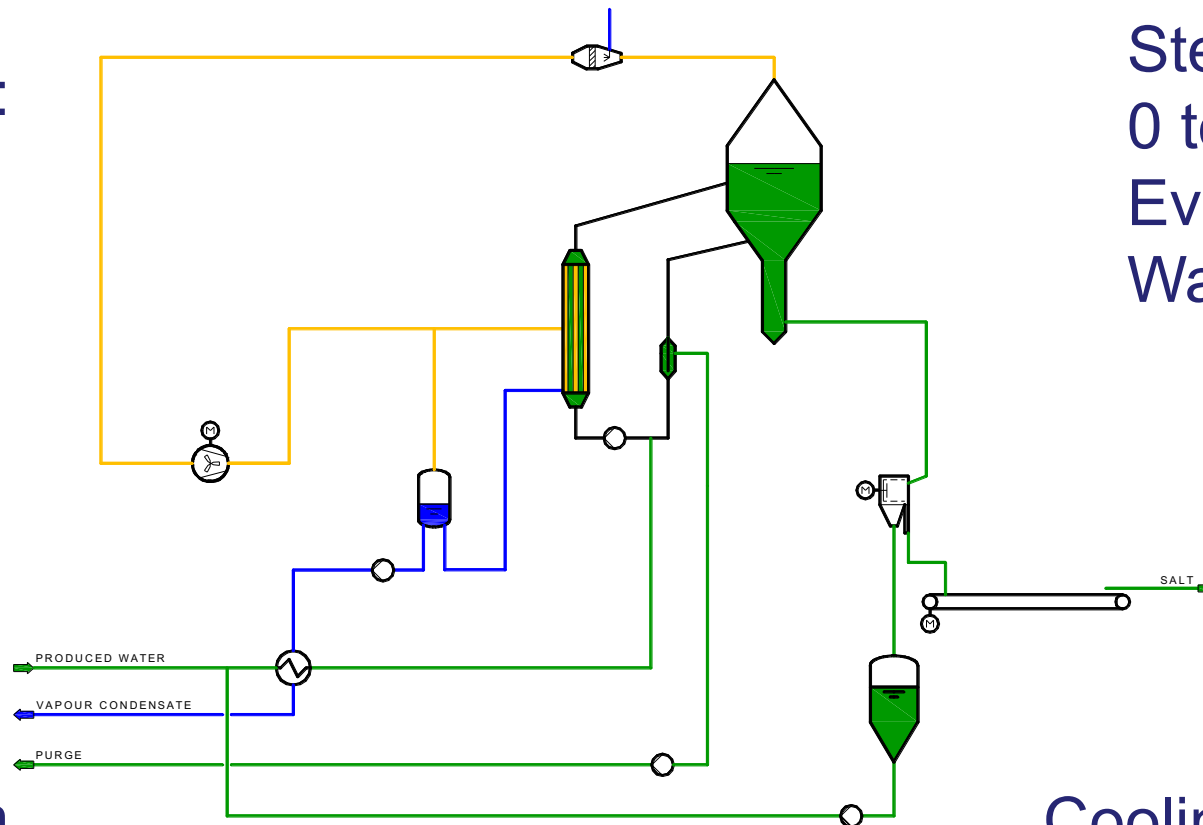


## Frame Data – Consumption Figures

Electrical  
Consumption:  
70 kWh/ t  
Evaporated  
Water

Steam:  
0 tons / ton  
Evaporated  
Water

Concentrate:  
Depending on  
Feed  
Composition



Cooling Water:  
< 1m<sup>3</sup>/h

Feed Capacity: 5000bbl/d



## Standing Stone Plant



## Salt Production



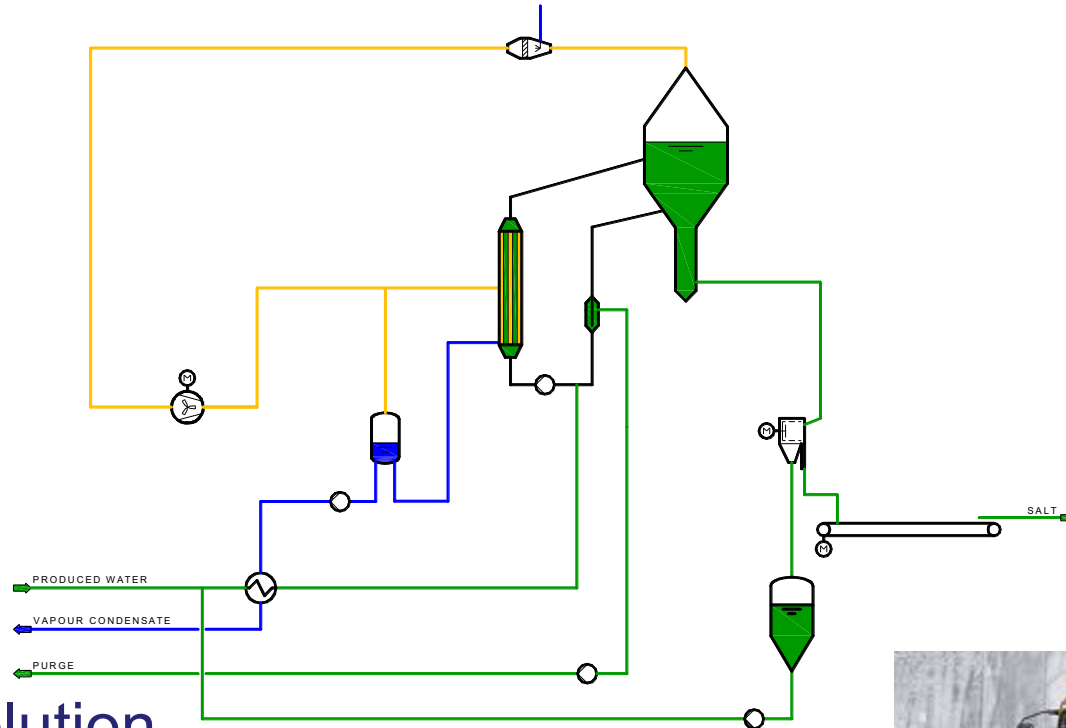


## Salt Production



## Products

Clean Water



Salt:  
NaCl 99.6%  
Guaranteed

Concentrated Solution  
Rich in  $\text{CaCl}_2$



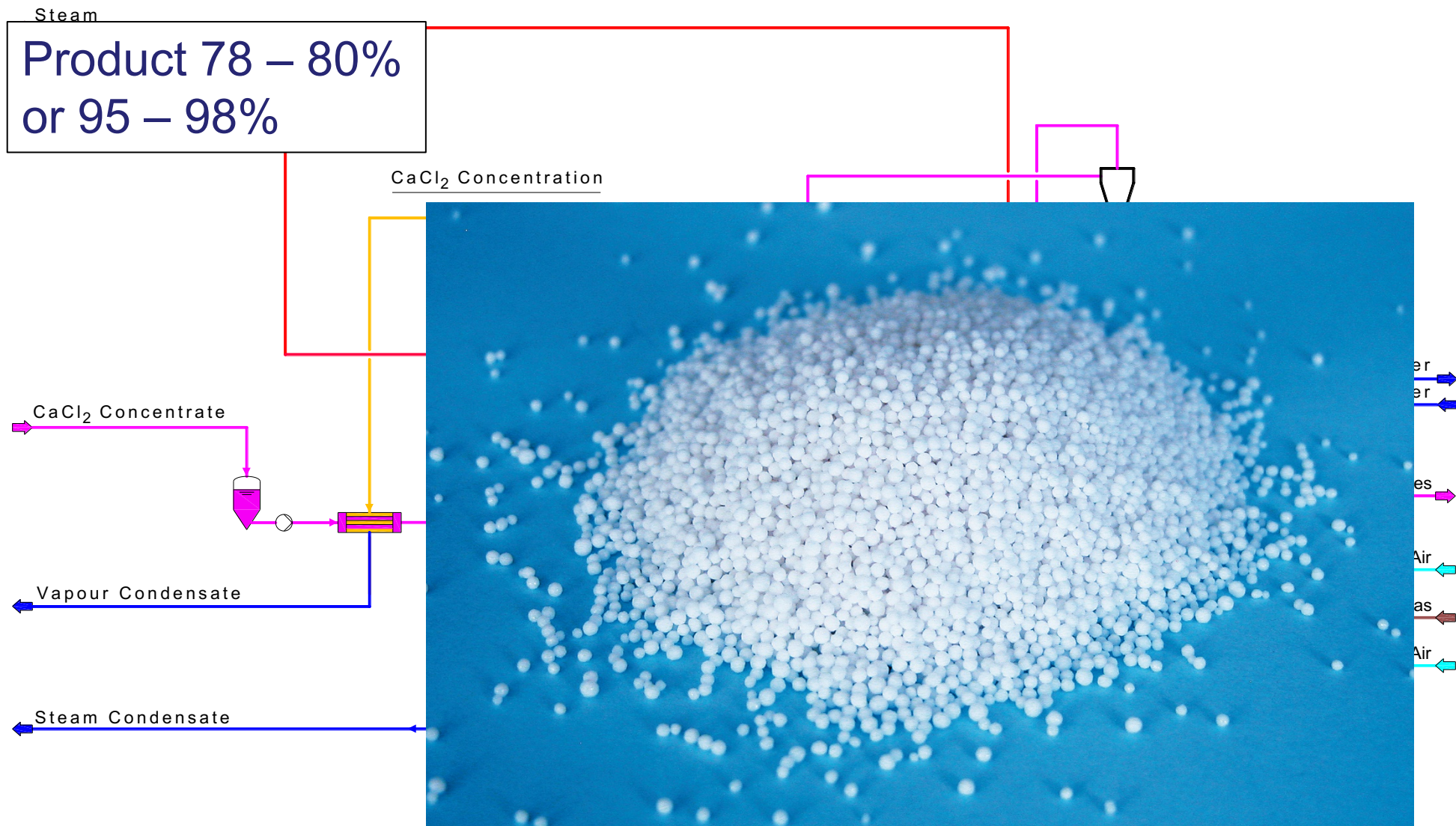


## What Else? Future Expansions!

- 💧 Recovery of Clean Calcium Chloride out of the Purge
- 💧 Recovery of Strontium Chloride out of the Purge Solution
- 💧 Recovery of Barium Chloride

**A new Definition of Zero Liquid Discharge!**

## CaCl<sub>2</sub> Production



## Summary

- 💧 Frac Water Treatment is a Challenging Task
- 💧 Changing Compositions and Unknown Constituents Request Flexibility and Good Know-how for the Treatment Methods
- 💧 It is Possible and Economic to Crystallize Valuable Salt in Road Salt Quality From Produced Water
- 💧 It is Possible to have no Liquid Waste Material at the end of the Treatment Chain
- 💧 More Valuable Products Make the Treatment Process an Environmental and Economical win-win Process for all Parties

# Thank you!

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