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30 YEARS
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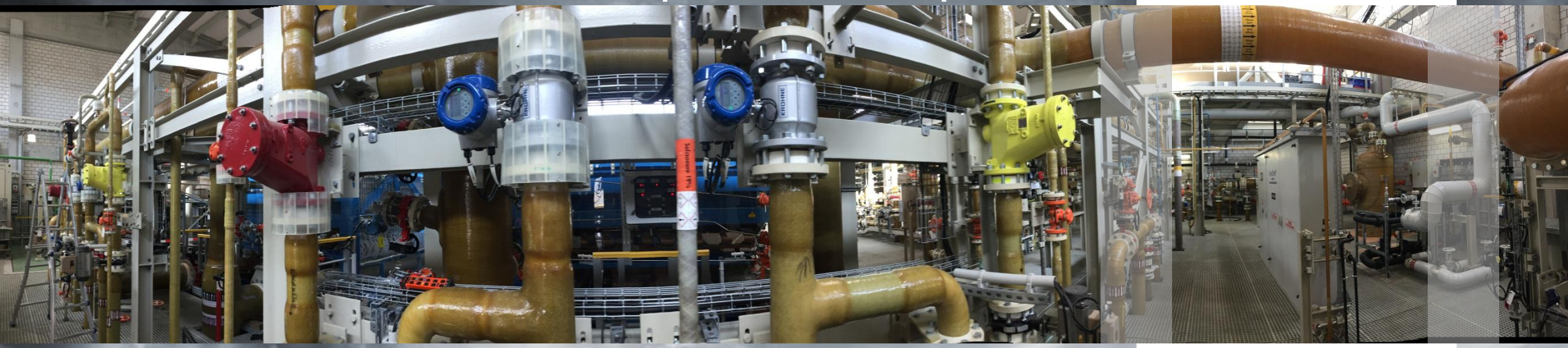
# on-line analyzer systems for safety and control of chlorine production plants



by Chris Du Bois

Exc. VP Systems Integration Div. AppliTek

by Thibaut Bettini

Project Engineer AppliTek

cloroSur

WORLD chlorine council

Buenos Aires
Argentina
Nov. 2016



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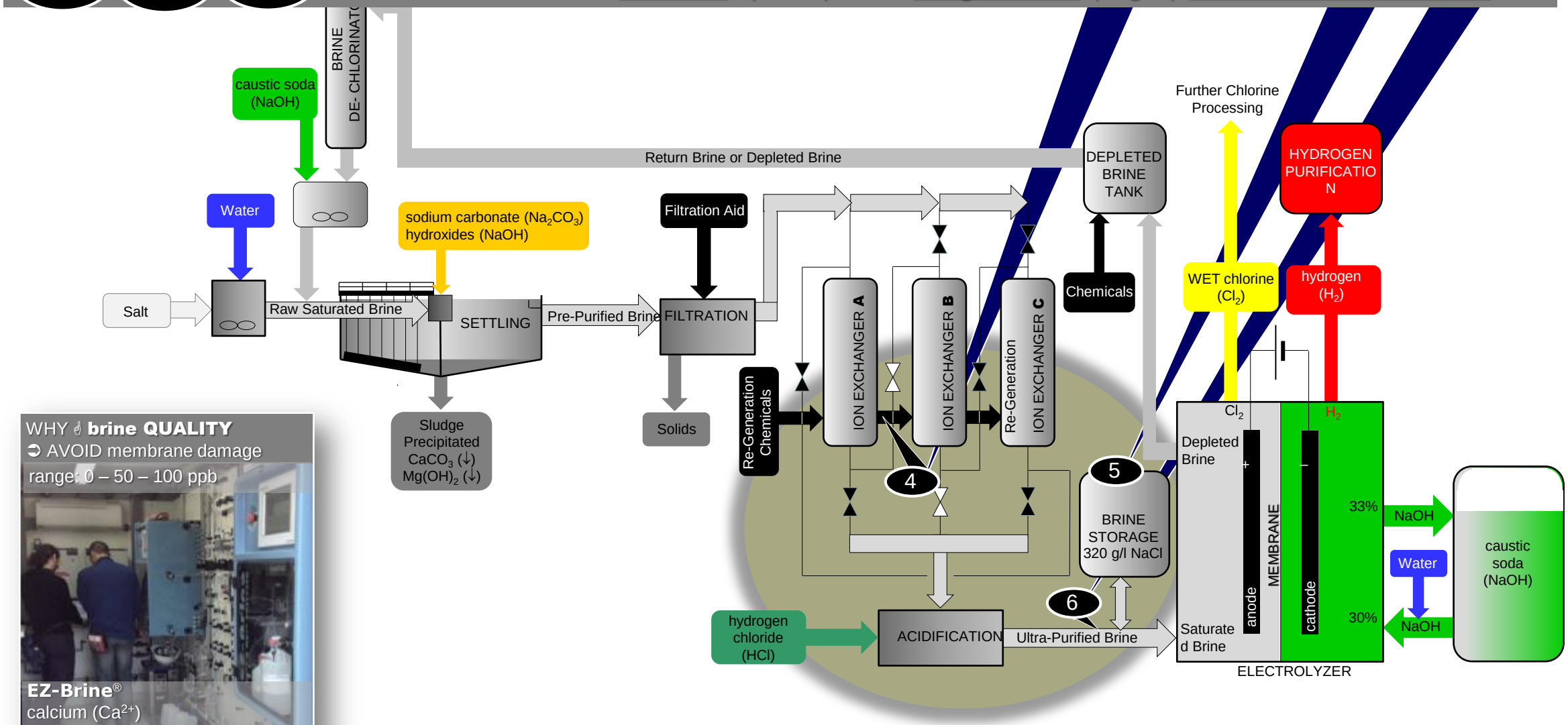
# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine




WHY ☝ **brine QUALITY**
➲ AVOID membrane damage
range: 0 – 50 – 100 ppb



**EZ-Brine®**
calcium ($Ca^{2+}$)
& magnesium ($Mg^{2+}$)
in Ultra-Purified Brine

## Where in Process ?



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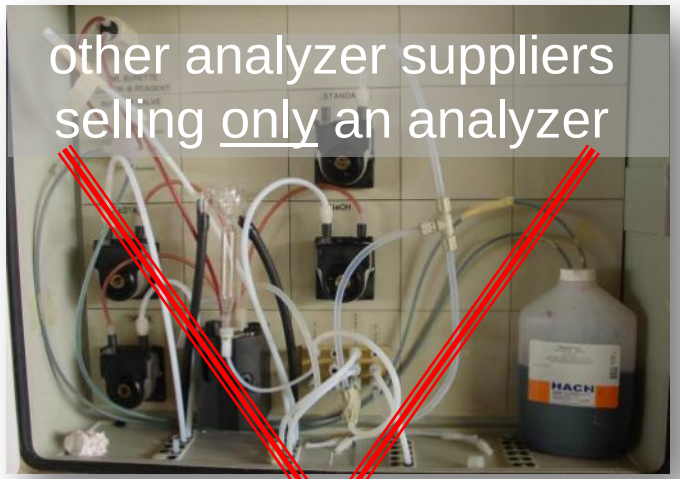
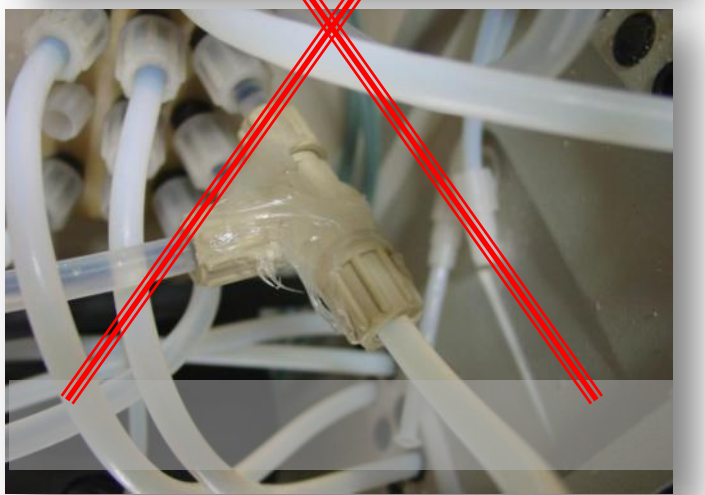
# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## AppliTek delivers an analyzer system guaranteeing analysis results



ⓘ Field Proven Best Available Technology

Analysis Result =

Analyzer

+ Application

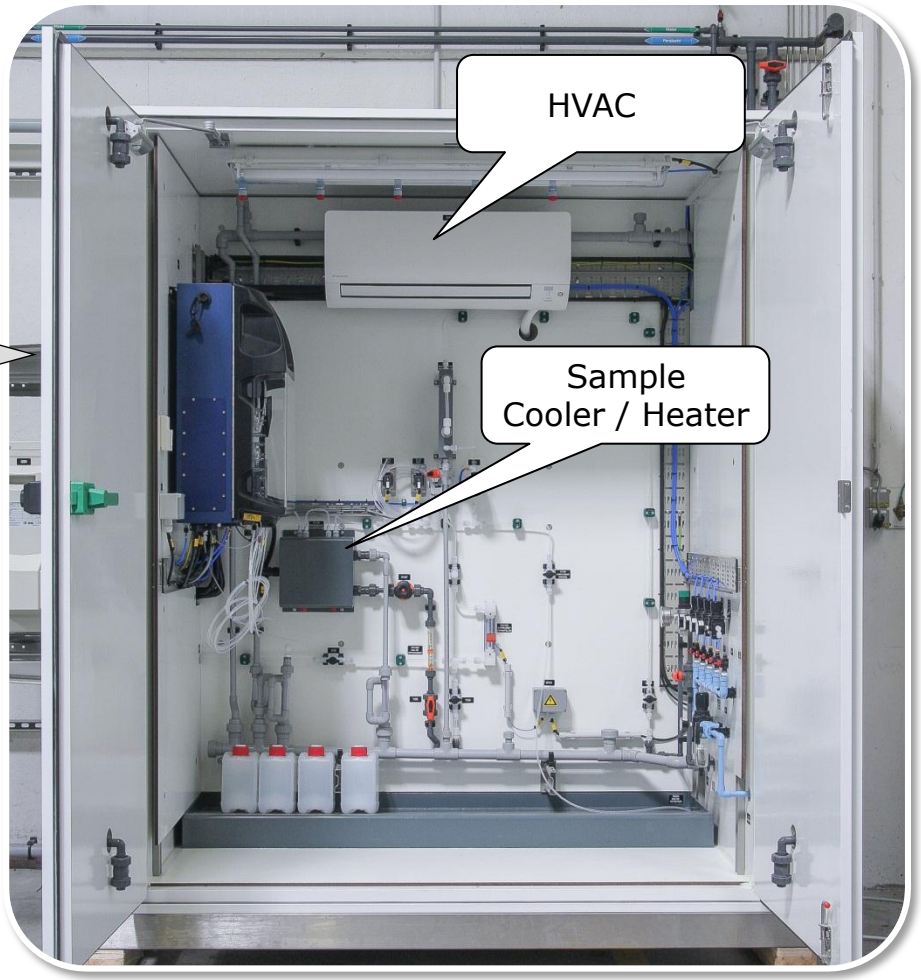
+ Preconditioning

WHY on-line **EZ-Brine®** ?

# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## AppliTek delivers an analyzer system guaranteeing analysis results


temperature control
sample + analyzer




ⓘ Field Proven Best Available Technology

Why on-line **EZ-Brine®** ?

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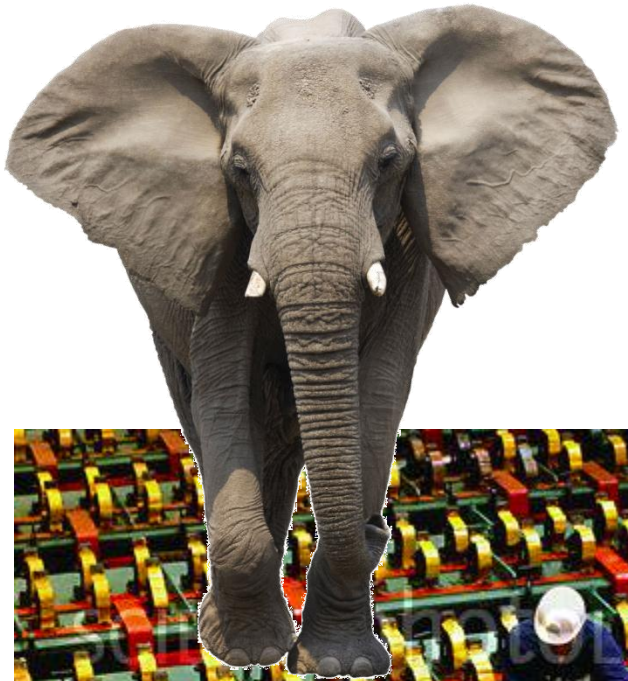
# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

control of elephant



control of mosquito

amalgam chlorine plant

Challenge!

membrane chlorine plant



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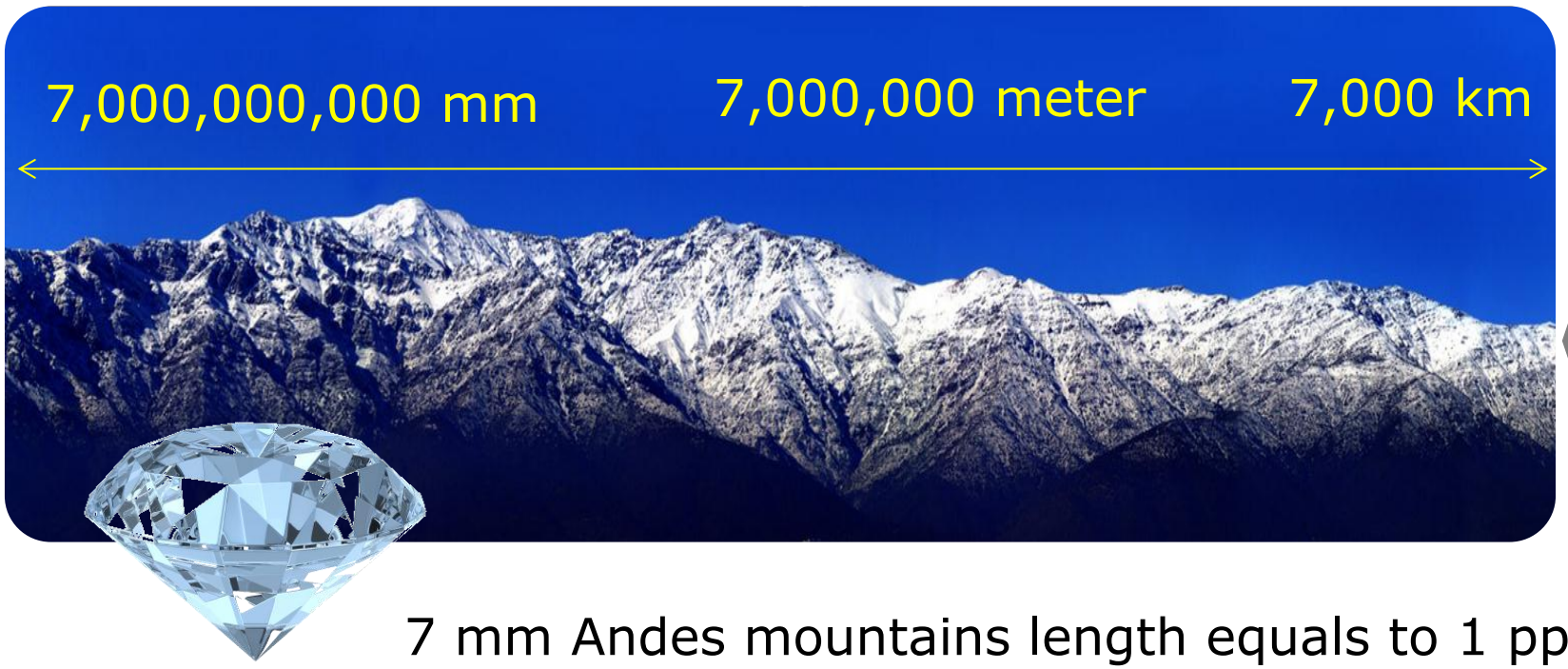
# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

typical **EZ-Brine®** range: 0 – 20 **ppb** $Ca^{++}$ & $Mg^{++}$ (detection limit < **1 ppb**)

1 **ppb** = 1 **p**art **p**er **b**illion

1 **ppb** equals finding approx. one coin in the Andes mountains

+20 **ppb** of $Ca^{++}$ & $Mg^{++}$ in brine can already damage your membrane chlorine production




7 mm Andes mountains length equals to 1 ppb



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# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

on-line $Ca^{2+}$ & $Mg^{2+}$ control has a Direct Financial impact.

membrane damage by $Ca^{2+}$ & $Mg^{2+}$ is non-returnable → high costs !



➔ Electrical Power Cost Increase

➔ Membrane Replacement Cost (typical life-time > 5 years)

➔ Shut down Cost (production loss)

➔ Labor Cost

## Why **EZ-Brine®** ?

# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## Analysis Colorimetric method

- injection of brine sample in **EZ-Brine®** analyzer
- addition of Sodium hydroxide (NaOH) buffer → Alkaline
- addition of color reagent (HNB) → red complex
- Initial absorbance value is measured at (λ) 610 nm
- addition of EDTA → RED complex is destroyed → blue
- Final Absorbance value is measured at (λ) 610 nm
- calculation of result: Lambert Beer's Law

$ABS = \epsilon \cdot b \cdot C$

$\epsilon$ = molar absorptivity (l . cm-1. mol-1)
b = path length (cm)
C = concentration (mol/liter)

measuring range: 0 – 20 – 50 - 100 ppb $Ca^{++}$ & $Mg^{++}$

detection limit: better than 0.6 ppb

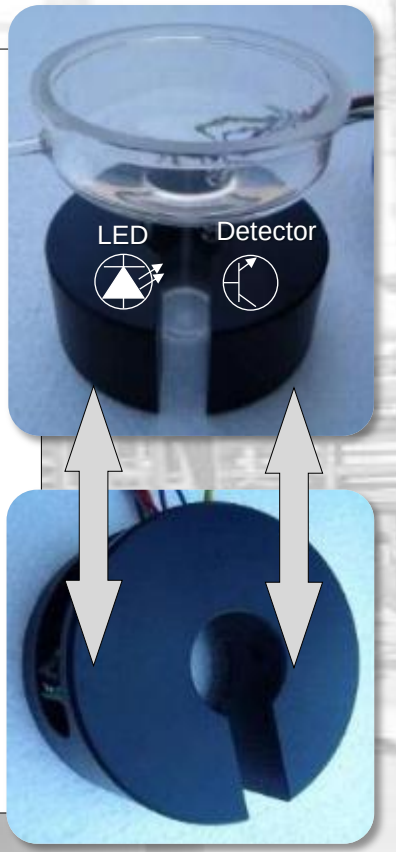
analysis frequency: 1 analysis / 8 minutes

How **EZ-Brine®** ?

# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## Unique Colorimetric Design:

special highly sensitive photometer driven by a unique algorithm




## How EZ-Brine® ?



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# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

Purified BRINE

| Time | Stream | ABS0 (mAu) | ABS1 (mAu) | ABS2 (mAu) | ABS21 (mAu) | Result (ppb $Ca^{++}$ & $Mg^{++}$) | room temperature (°C) |
|---|---|---|---|---|---|---|---|
| 07:05:44 | 0 | -27.47 | 849.59 | 854.37 | 45.77 | 14.75 | 23.3 |
| 07:00:54 | 0 | -27.30 | 852.14 | 856.96 | 45.94 | 14.87 | 23.2 |
| 06:56:03 | 0 | -27.11 | 856.94 | 861.41 | 45.81 | 14.78 | 23.3 |
| 06:51:13 | 0 | -27.81 | 858.92 | 862.72 | 45.19 | 14.33 | 23.3 |
| 06:46:22 | 0 | -27.48 | 863.60 | 867.05 | 45.05 | 14.23 | 23.3 |

| Average (ppb $Ca^{++}$ & $Mg^{++}$) | Stdev (ppb $Ca^{++}$ & $Mg^{++}$) |
|---|---|
| 14.59 | **0.29** |

## Results **EZ-Brine®**

Purified BRINE spiked with 20ppb of Calcium ($Ca^{++}$)

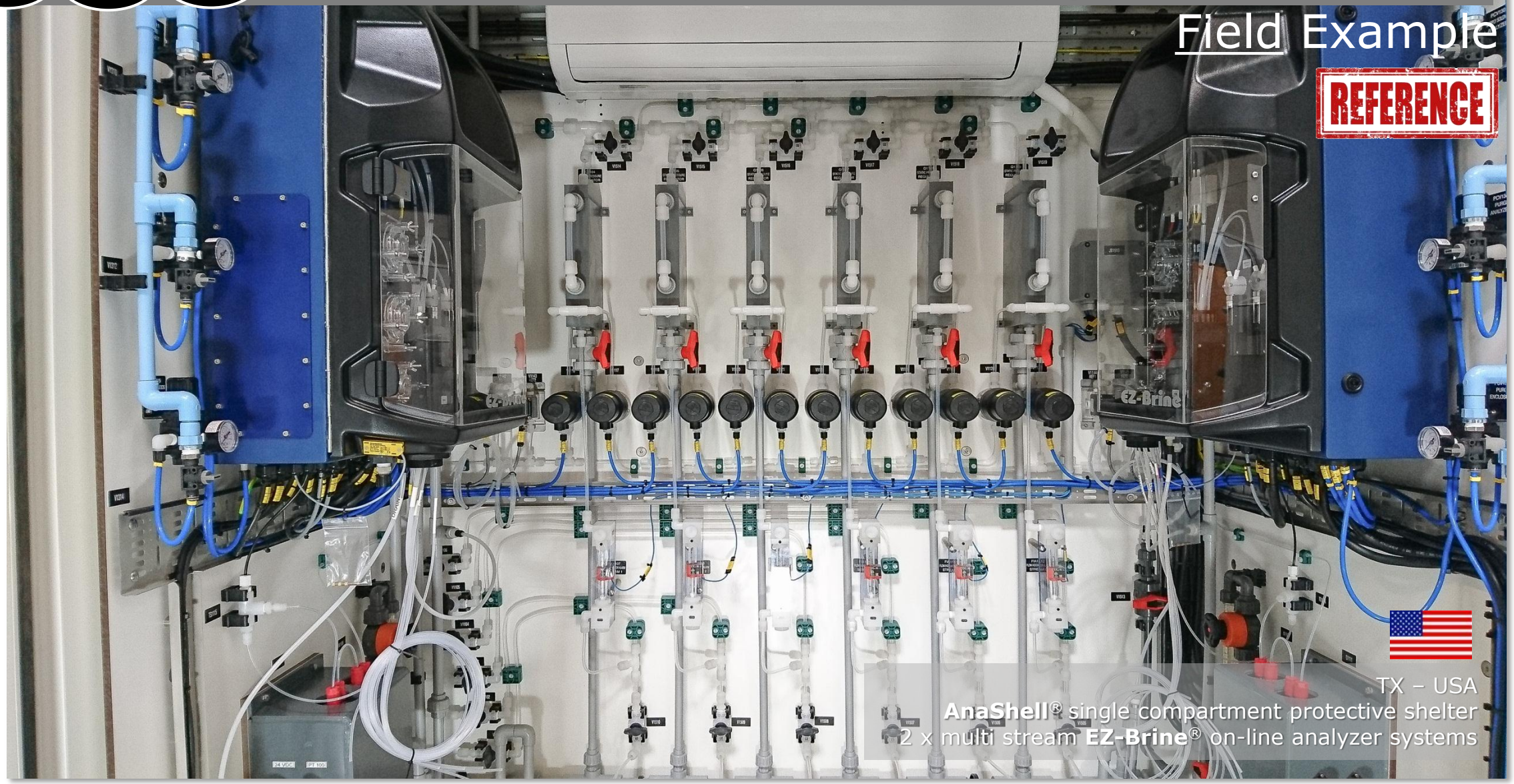
| Time | Stream | ABS0 (mAu) | ABS1 (mAu) | ABS2 (mAu) | ABS21 (mAu) | Result (ppb $Ca^{++}$ & $Mg^{++}$) | room temperature (°C) |
|---|---|---|---|---|---|---|---|
| 06:41:32 | 0 | -26.76 | 846.94 | 880.02 | 75.32 | 36.02 | 23.1 |
| 06:36:42 | 0 | -27.01 | 849.95 | 883.41 | 75.85 | 36.41 | 23.3 |
| 06:31:51 | 0 | -27.21 | 852.03 | 886.06 | 76.55 | 36.91 | 23.8 |
| 06:27:01 | 0 | -26.33 | 855.56 | 888.59 | 75.68 | 36.28 | 22.8 |
| 06:22:10 | 0 | -26.17 | 860.56 | 893.14 | 75.43 | 36.11 | 22.6 |

| Average (ppb $Ca^{++}$ & $Mg^{++}$) | Stdev (ppb $Ca^{++}$ & $Mg^{++}$) | Accuracy (ppb $Ca^{++}$ & $Mg^{++}$) |
|---|---|---|
| 36.35 | **0.35** | **1.75** |

# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## Field Example

REFERENCE




TX – USA

**AnaShell®** single compartment protective shelter
2 x multi stream **EZ-Brine®** on-line analyzer systems

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CELEBRATING 30 YEARS 1985 - 2015

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# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## Field Example

REFERENCE

TN – USA
**AnaShell**® single compartment protective shelter
2 x multi stream **EZ-Brine**® on-line analyzer systems

# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## Field Example

REFERENCE

Frankfurt - Germany
**AnaShell**® protective shelter including double stream **EZ-Brine**® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

## Field Example


LA - USA
**AnaShell®** protective cabinet
2 x **EZ-BRINE®** on-line analyzer system for
$Ca^{++}$ & $Mg^{++}$ in ultra-purified brine

# 4 5 6 EZ-Brine® on-line calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-Purified brine

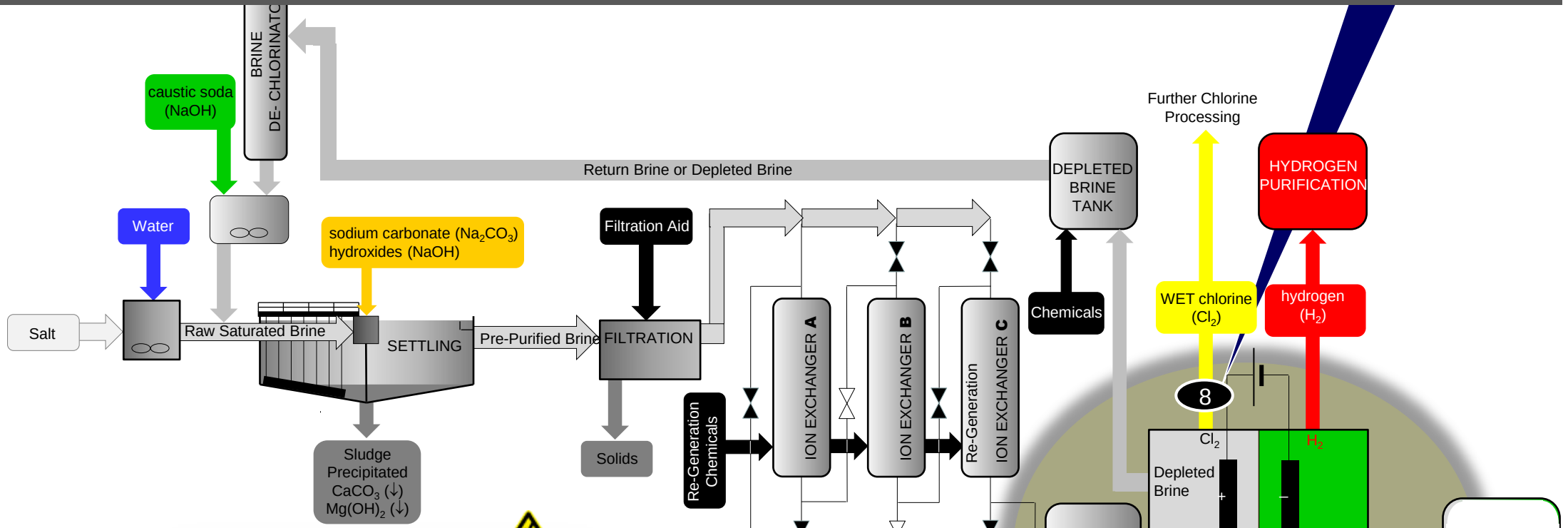
## Field Example

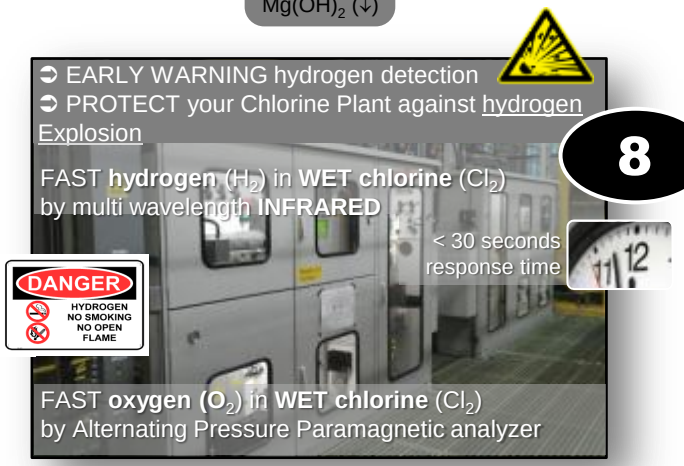




Samutprakarn - Thailand
**AnaShell®** single-compartment protective shelter
1 x **EZ-Brine®** on-line Analyzer system for Ca++ & Mg++ in ultra-purified brine

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed




## Where in Process ?

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

WORLD chlorine council — March 2011 / Number 17 — http://worldchlorine.org

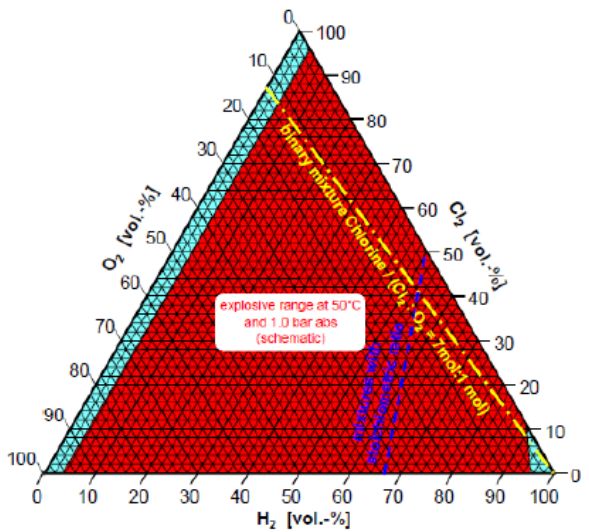
## Global Safety Team Newsletter

*News about the Global Safety Team* (Page 3)

*Hydrogen-chlorine low explosibility limits* (Page 4)

*Learning from incidents* (Page 4)

*Useful Links* (Page 7)




Explosion diagram of the ternary mixture $H_2/Cl_2/O_2$

references a study on " hydrogen-chlorine low explosibility limits ", performed by the laboratory of the safety engineering department of BASF in Ludwigshafen, Germany.

The conclusion of the study: maximum allowable value of 3 ± 0.2 % $H_2$ in $Cl_2$ at 50°C

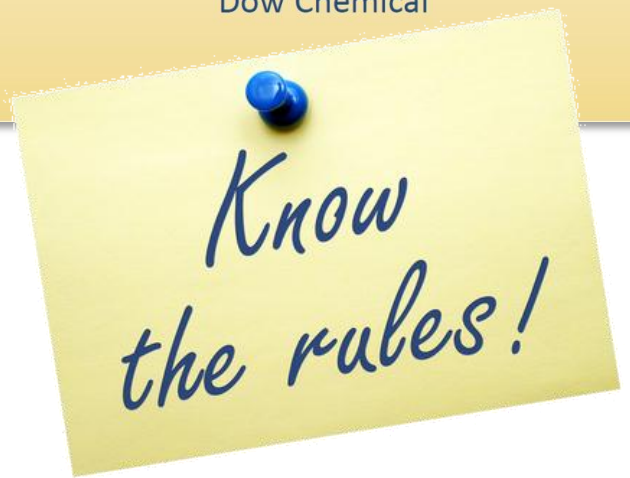
Lesson learned after Explosion in drying section of a membrane electrolysis unit: the absolute necessity to have a fast detection of hydrogen concentration increase at the outlet of the cells plus an additional monitoring system of the possible membrane damages
(voltage / current, quality of products …)

## Why on-line $H_2$ in hot-wet Chlorine ?

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed


Cardinal Rules

2014 Global Safety Team- Safety Workshop
Vic McMurray
Dow Chemical




## Why on-line $H_2$ in hot-wet Chlorine ?

## n°1 Cardinal Rule of safe production of chlorine by WCC

**Remain in safe concentration range for hydrogen in chlorine**

- **Explosion risk if hydrogen concentration in chlorine between about 4 and 93 %** (precise values vary in function of pressure, temperature, presence of other constituents …)
- **In addition to preventative actions, monitoring via on-line analysers is mandatory**:
  - Some hydrogen is produced in the cells, but quantity can increase (bad brine quality) and there can be some mixing with chlorine (damaged membrane or diaphragm …)
  - concentration of hydrogen increases also when chlorine is liquefied …
- Hydrogen is also produced anywhere there is steel corrosion

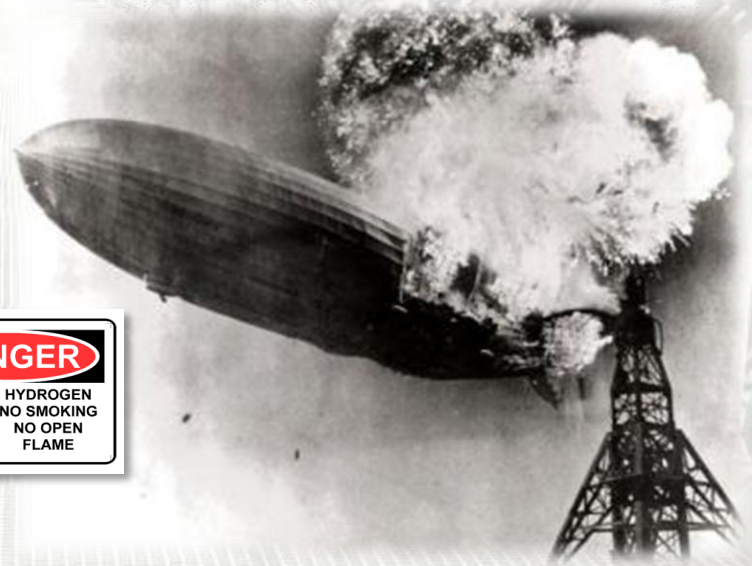
# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Misconceptions !

- hydrogen is a light gas ⟹ No Risk
- hydrogen is not an hydrocarbon ⟹ No Risk

## Why on-line $H_2$ in hot-wet Chlorine ?

May 6, 1937 Lakehurst, New Jersey USA
Hindenburg disaster





Explosion risk

Plant Safety
Critical Equipment

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

High $H_2$ present

High Energy present

Defined as: General Purpose Zone ( Non-explosion Proof )

Low voltage

High Current = High Energy

High Electrical Current → NO electrical Ex Proof Technology possible

chlorine Electrolysis Process

on-line Hydrogen Analyzer system

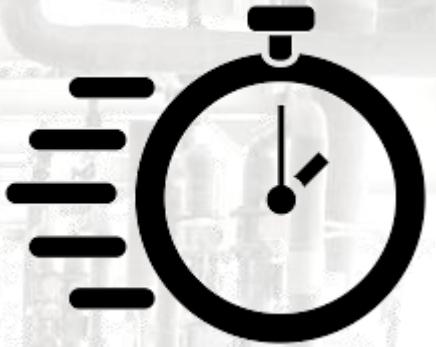
SAFETY FIRST

- Field Proven Technology
- Fast Response (T90 = 15 seconds)
- Good results during start-up Cell Room
- HAZOP approved

Fast on-line analysis of hydrogen ($H_2$) in hot-wet chlorine ($Cl_2$) gas to keep the gas matrix within the flammability limits.

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

FAST

hydrogen is not waiting to ignite until you are ready with analysis !!!
Every second counts !!!

Response time of < 35 seconds $T^{90}$
Do not install an analyzer systems that needs minutes to show results

$T^{90}$ = time needed to detect 90% of Full Scale range when you switch from 0 to 100% at sample point



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# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## by Gas-Chromatograph (GC) 1

- Discontinuous measurement
- Long analysis time (several min.!)
- Can only be used for Quality Control
- Cannot be used for Process Control
- Cannot be used for SAFETY
- Complex Technology
- High Maintenance
- Low Up-time

## by Thermal Conductivity (TC) 2



UV light

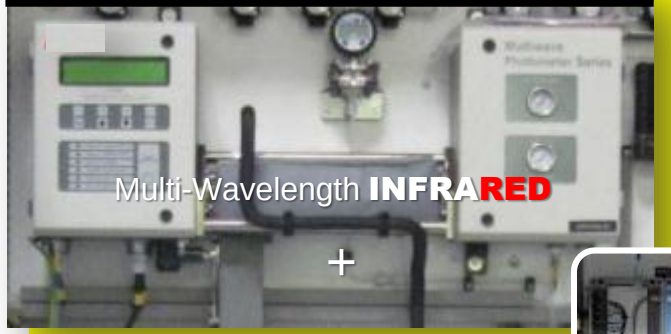
$H_2 + Cl_2 \Rightarrow 2\ HCl$

differential measurement

Δ Delta TC before - and after oxidation by UV

- Not Selective measurement for $H_2$
- Calibration Matrix - dependable
- Does not react first 6 – 12 min. after Plant Start-up
- Cannot be used for SAFETY during Plant Start-up

## by Multi-Wavelength INFRARED (MW-IR) 3





UV light

$H_2 + Cl_2 \Rightarrow 2\ HCl$

$H_2$ and $Cl_2$ forms HCl by UV

HCl is measured by MW-IR

% HCl stoechiometrically equal to $H_2$

- Selective measurement for $H_2$
- Calibration Matrix - independable
- Fast Response (T90 < 20 seconds)
- Shows Good results @ Plant Start-up
- Best Available Technology
- Field Proven – High Up-time

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

Thermostatically controlled electrically traced thick wall PFA insulated sample bundle

Process Valve by Customer

DIP-tube # 1 Main Header

Sample Take Off Point ( STOP )

%$^{vol}$ HCl stoechiometrically equals to $H_2$

4 – 20 mA

HCl analysis ( corresponds to $H_2$ )

Multi-wavelength IR analyzer

UV reactor

$H_2 + Cl_2 \rightarrow 2HCl$

Salt Washing
Water Removal
Salt Filtration
Pressure Control
Flow Control
Sample Aspiration
Flame Arrestors

Calibration

Preconditioning

HMI

Human Interface

DANGER
ELECTRICAL HAZARD. Authorized personnel only

Drain

Drain Pump

FIELD

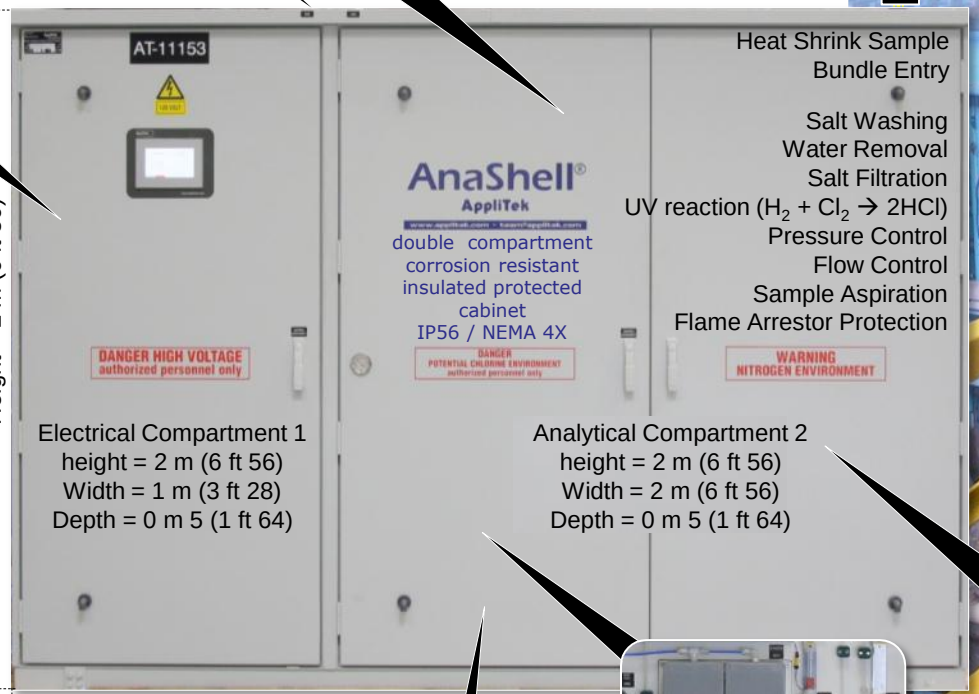
**AnaShell®** corrosion resistant protective cabinet

SAFETY FIRST

## How on-line $H_2$ in hot-wet Chlorine?

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed




Height = 2 m (6 ft 56)

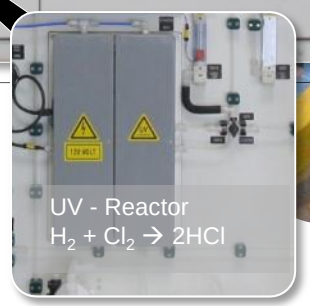
Width = 3 m (9 ft 84)

Heat Shrink Sample Bundle Entry

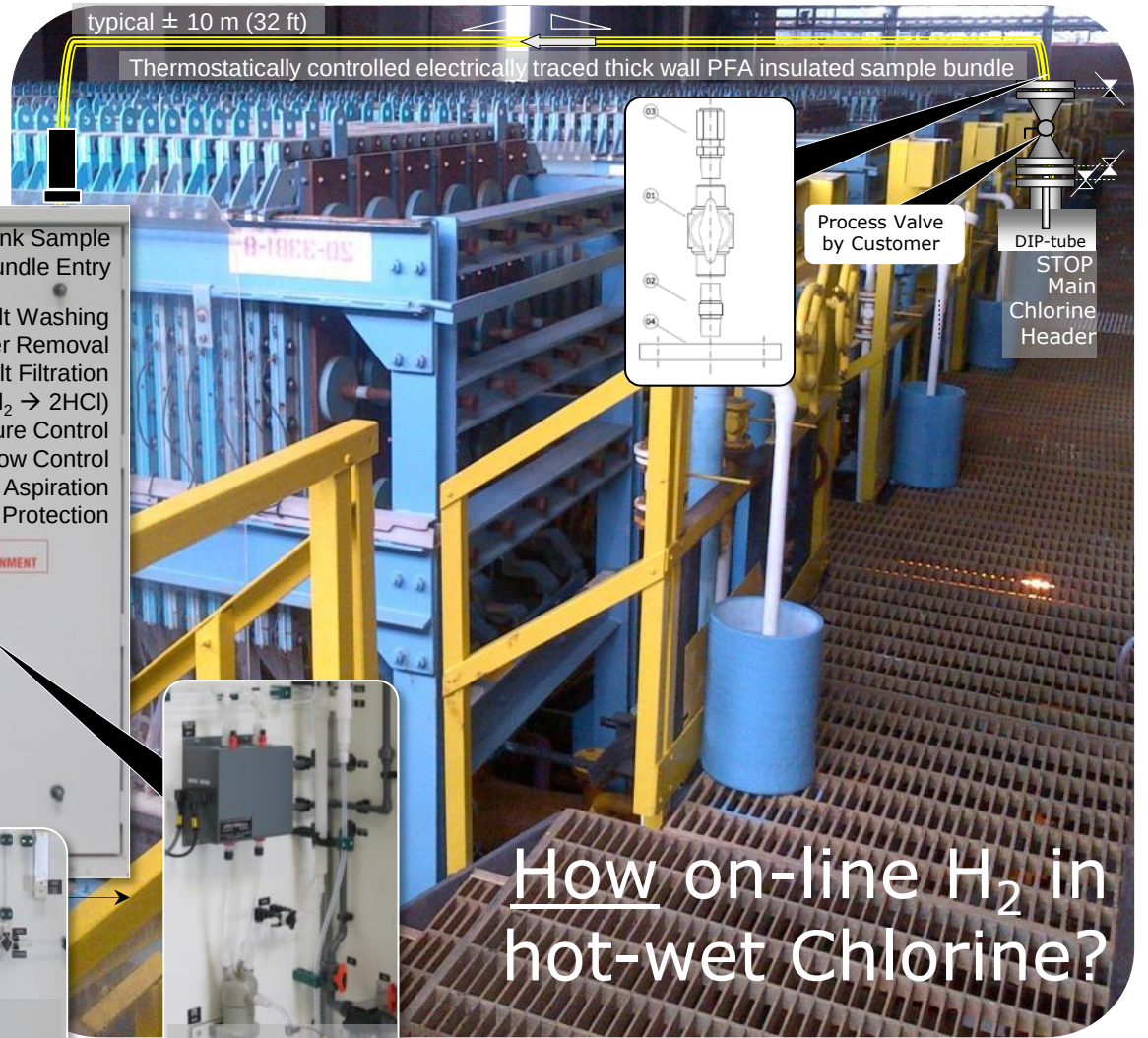
Salt Washing
Water Removal
Salt Filtration
UV reaction ($H_2$ + $Cl_2$ → 2HCl)
Pressure Control
Flow Control
Sample Aspiration
Flame Arrestor Protection

Electrical Compartment 1
height = 2 m (6 ft 56)
Width = 1 m (3 ft 28)
Depth = 0 m 5 (1 ft 64)

Analytical Compartment 2
height = 2 m (6 ft 56)
Width = 2 m (6 ft 56)
Depth = 0 m 5 (1 ft 64)



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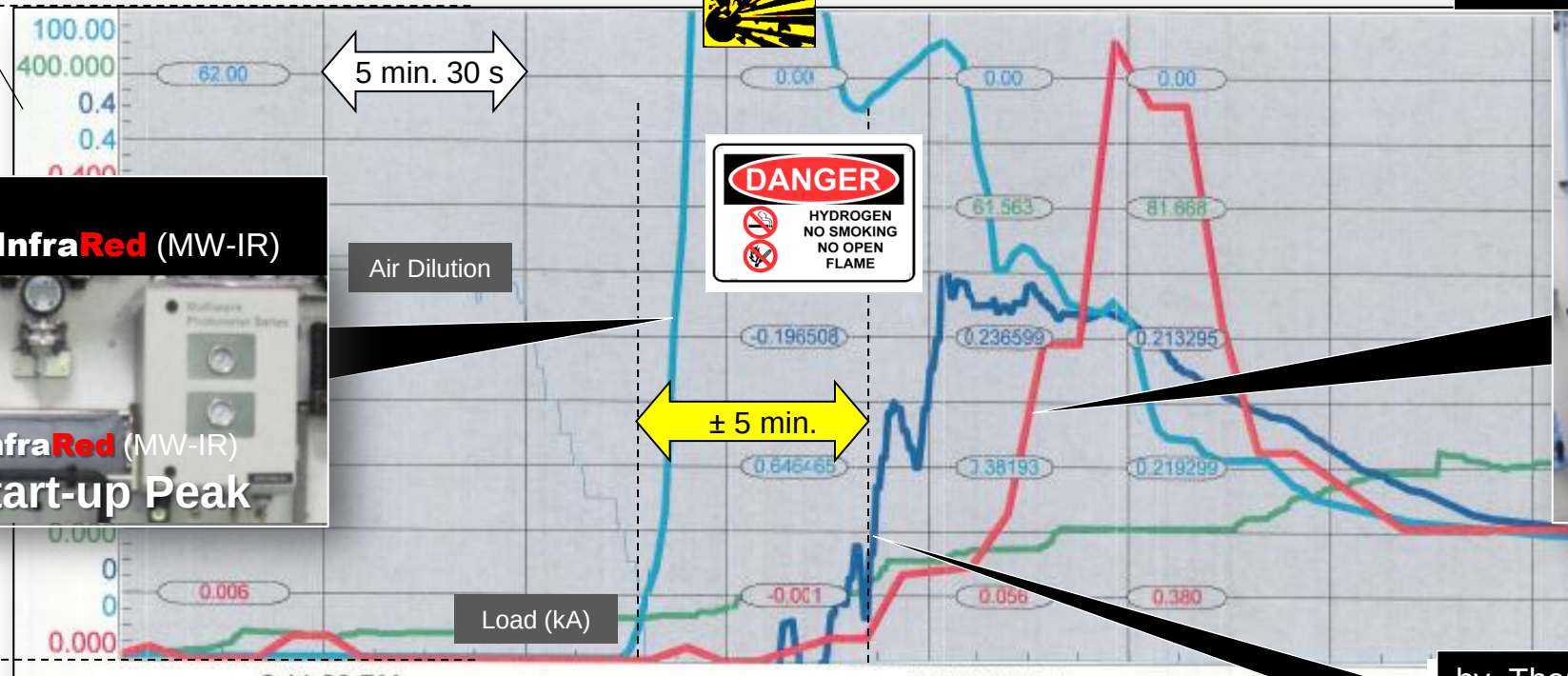
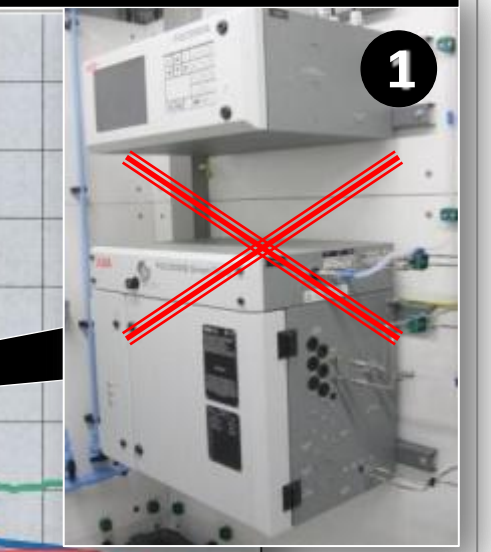
# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Start-up Membrane type Chlorine Plant

0.4% $H_2$ in $Cl_2$

by Multi-Wavelength **InfraRed** (MW-IR)

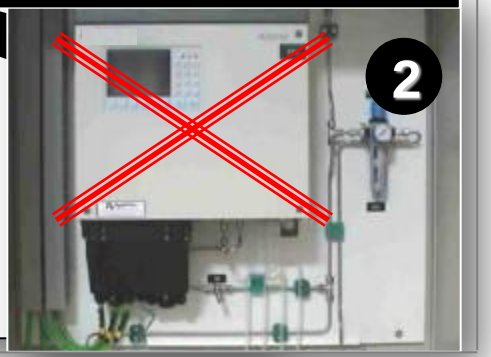




by Gas-Chromatograph (GC)




0% $H_2$ in $Cl_2$

by Thermal Conductivity (TC)



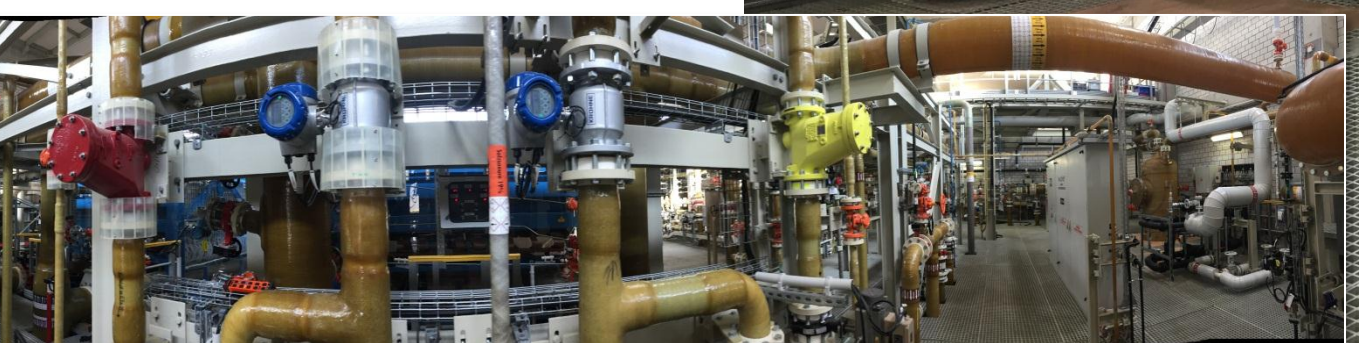

| Name | Description | Value | Level | Status | Aut | Plot Min | Plot Max | Units |
|---|---|---|---|---|---|---|---|---|
| | Air Feed to Cl2 Header | | Good | Good | | 0.00 | 100.00 | % |
| | Total KA | | Good | Good | | 0.000 | 400.000 | KA |
| | H2 in Wet Cl2 | | Good | Good | | 0 | 0.4 | % |
| | H2 in Wet Cl2 (Backup) | | Good | Good | | 0 | 0.4 | % |
| | Wet Hydrogen GC | | | | | 0 | 0.4 | % |
| | Cellroom H2 | | Good | Good | | 0.000 | 0.400 | Pct. |

# Field Results

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE




Switzerland
**AnaShell**® double compartment protective cabinet
1 x single stream on-line Analyzer system for hydrogen in hot-wet chlorine

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE

LA – USA
**AnaShell**® triple compartment protective cabinet
1 x multi stream on-line Analyzer system for hydrogen in hot-wet chlorine

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

**REFERENCE**


Brazil

**AnaShell®** triple compartment protective cabinet
1 x multi stream on-line Analyzer system for hydrogen in hot-wet chlorine

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Example

**REFERENCE**



Argentina
**AnaShell®** double compartment protective cabinet
1 x multi stream on-line Analyzer system for hydrogen in hot-wet chlorine

8

# on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE


Belgium

**AnaShell**® triple compartment protective cabinet

1 x multi stream on-line Analyzer system for hydrogen in hot-wet chlorine

1 x single stream on-line Analyzer system for oxygen in hot-wet chlorine

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE


Banten - Indonesia
**AnaShell®** multi compartment protective cabinet
1 x on-line Analyzer system for hydrogen in hot-wet chlorine

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE


LA, USA

**AnaShell**® multi compartment protective cabinet

3 x on-line Analyzer system for hydrogen in hot-wet chlorine

( Multi Wavelength IR )

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE


LA, USA

**AnaShell**® multi compartment protective cabinet

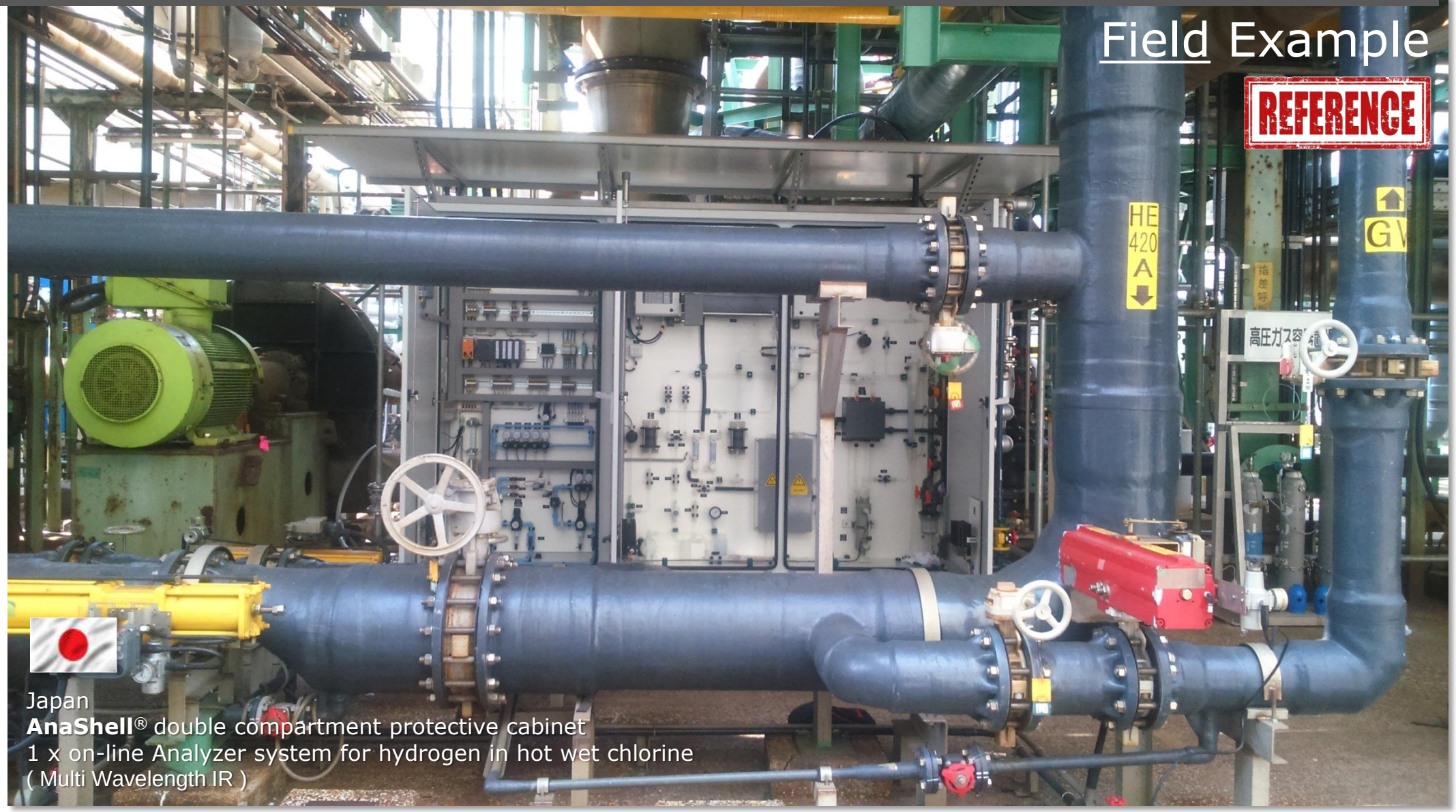
3 x on-line Analyzer system for hydrogen in hot-wet chlorine

( Multi Wavelength IR )

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE




Japan
**AnaShell**® double compartment protective cabinet
1 x on-line Analyzer system for hydrogen in hot wet chlorine
( Multi Wavelength IR )

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

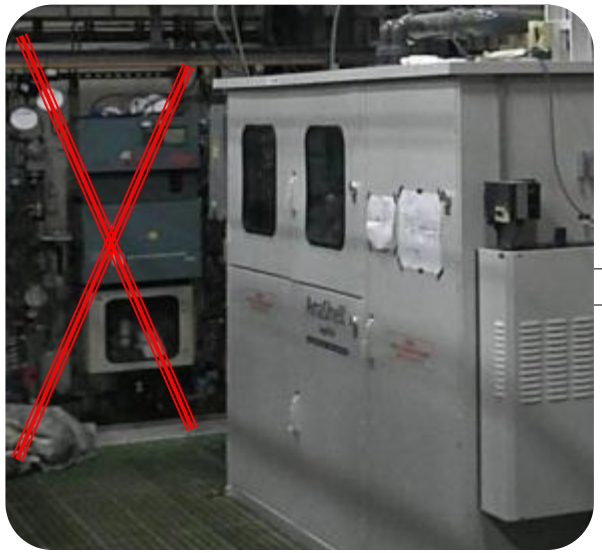
REFERENCE

Finland
2 x **AnaShell**® double compartment protective cabinet
2 x on-line Analyzer system for hydrogen in hot wet chlorine
( Multi Wavelength IR )

# 8 on-line hydrogen ( $H_2$ ) in hot-wet chlorine ( $Cl_2$ ) by Multi-Wavelength InfraRed

## Field Example

REFERENCE



The Netherlands
2 pc **AnaShell®** multi-compartment protective cabinets
1 x on-line Analyzer system for hydrogen in hot wet chlorine
( by multi-Wavelength IR )
1 x on-line Analyzer system for oxygen in hot wet chlorine
( by alternating pressure paramagnetic analyzer )

# References

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