# Control of Ion Exchange in Brine Purification Process using **EZ-Brine®**

CloroSur Technical Seminar

abiclor

cloroSur


WCC Safety Workshop

WORLD chlorine council®

by Chris Du Bois
Exec. VP Systems Integration

presented by Thibaut Bettini

November
14 -16th 2018
Quinta Real hotel
Monterrey Mexico

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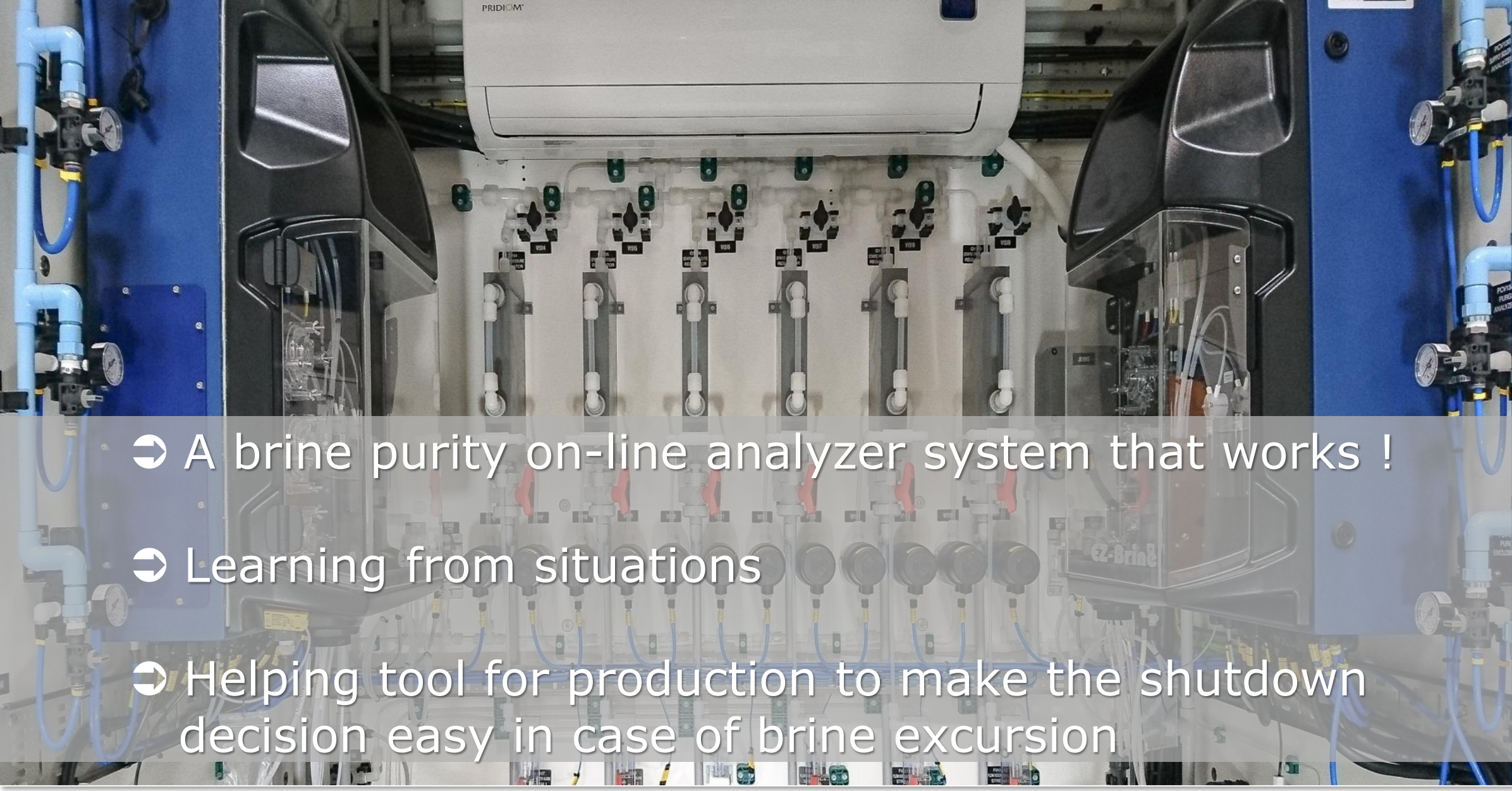

- A brine purity on-line analyzer system that works !
- Learning from situations
- Helping tool for production to make the shutdown decision easy in case of brine excursion

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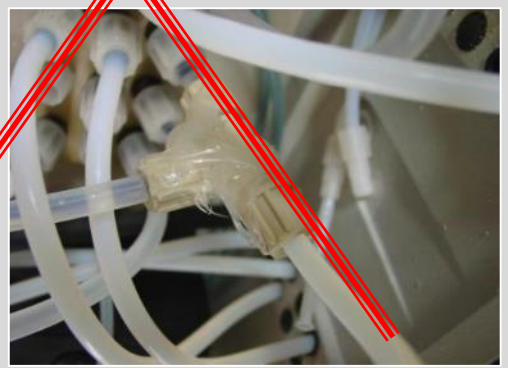
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !



Good Analysis Result

= Analyzer

+ Application

+ Preconditioning

AppliTek delivers an analyzer system guaranteeing analysis results

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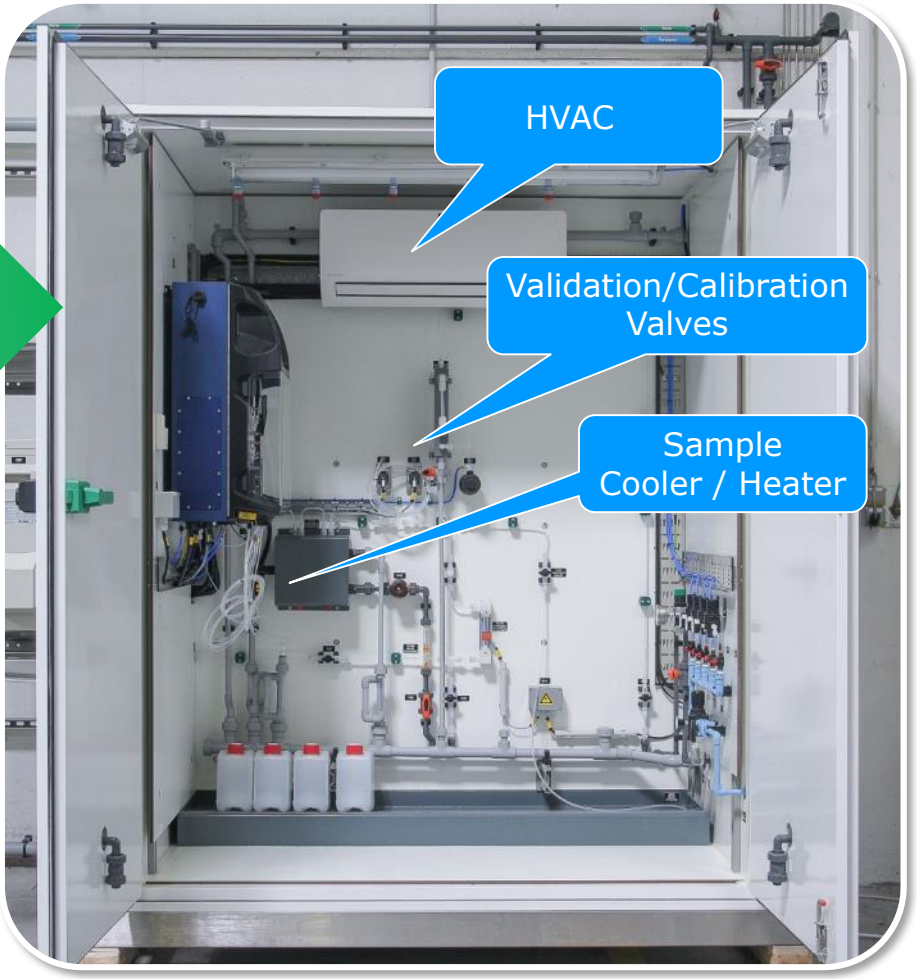
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !

Good Analysis Result

= temperature control of sample and **EZ-Brine**® analyzer

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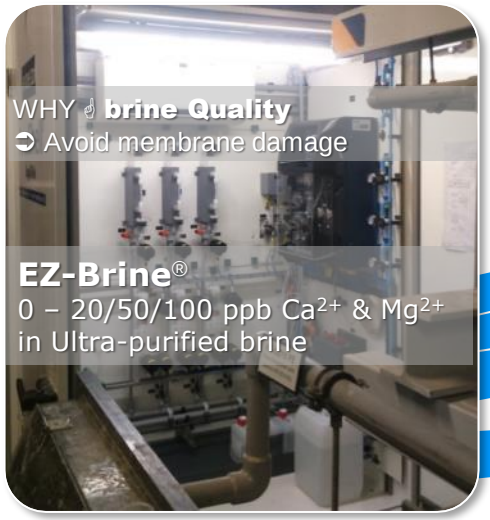
# EZ-Brine® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !

## Where in Process ?




Vacuum
BRINE DE- CHLORINATOR
caustic soda (NaOH)
Water
Salt
Raw Saturated Brine
sodium carbonate ($Na_2CO_3$) hydroxides (NaOH)
SETTLING
Sludge Precipitated $CaCO_3$ (↓) $Mg(OH)_2$ (↓)
Pre-Purified Brine
Filtration Aid
FILTRATION
Solids
Return Brine or Depleted Brine
DEPLETED BRINE TANK
Chemicals
Re-Generation Chemicals
ION EXCHANGER A
ION EXCHANGER B
Re-Generation ION EXCHANGER C
STOP
BRINE STORAGE
320 g/l NaCl
hydrogen chloride (HCl)
ACIDIFICATION
Ultra-Purified bine
Further Chlorine Processing
WET chlorine ($Cl_2$)
HYDROGEN PURIFICATIO N
hydrogen ($H_2$)
$Cl_2$
$H_2$
Depleted Brine
anode
MEMBRANE
cathode
33%
30%
NaOH
Water
NaOH
caustic soda (NaOH)
ELECTROLYZER
Shut Down

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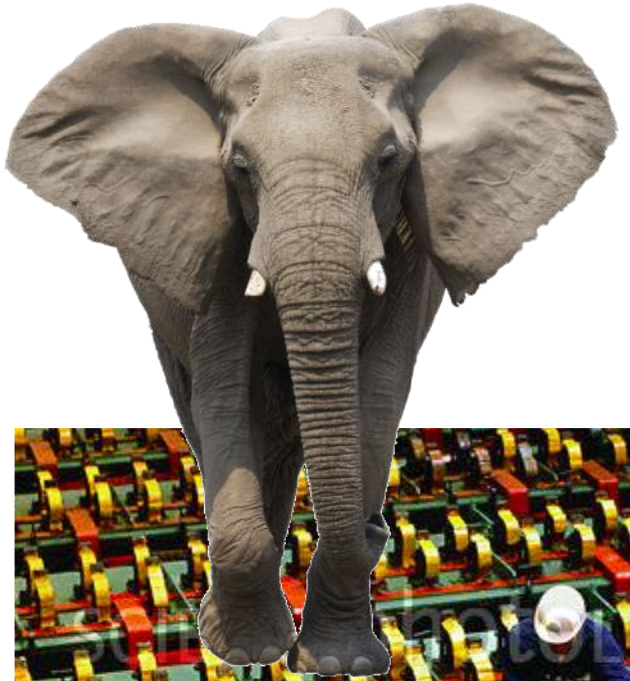
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

control of elephant



control of mosquito

Importance of on-line brine control

amalgam chlorine plant

Challenge!

membrane chlorine plant

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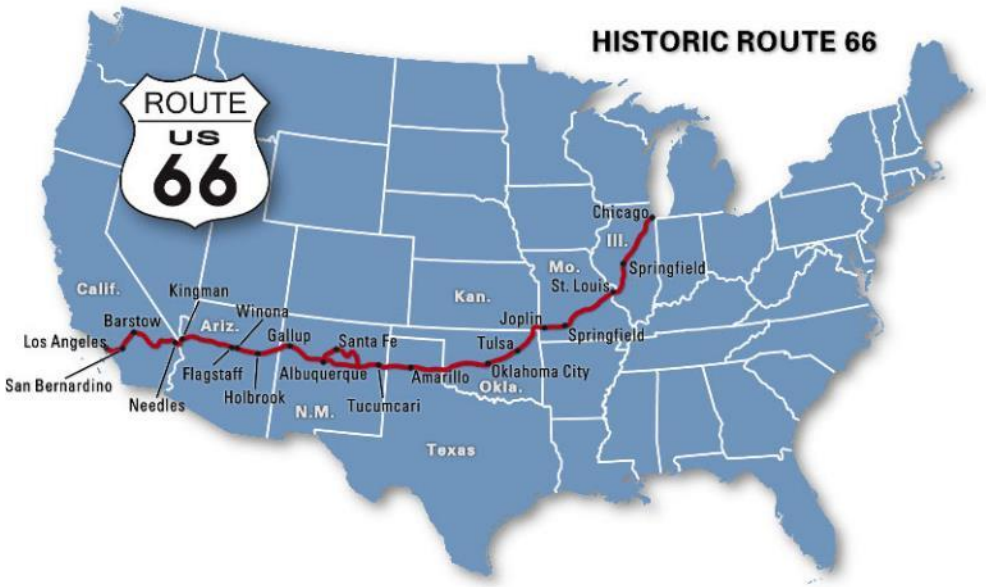
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

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 ( 1 )  diamond on route 66

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


2,448 miles ( 3,940 km )

1 ppb equals finding 0.15” (3.9mm)
~ one carat diamond

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !

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

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

- Electrical Power Cost Increase
- Membrane Replacement Cost ( typical life-time > 5 years )
- Shut down Cost ( production loss )
- Labor Cost

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !

colorimetric measurement using hydroxynaphthol blue color indicator (HNB) in conformance with ASTM 3500-Ca

- 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

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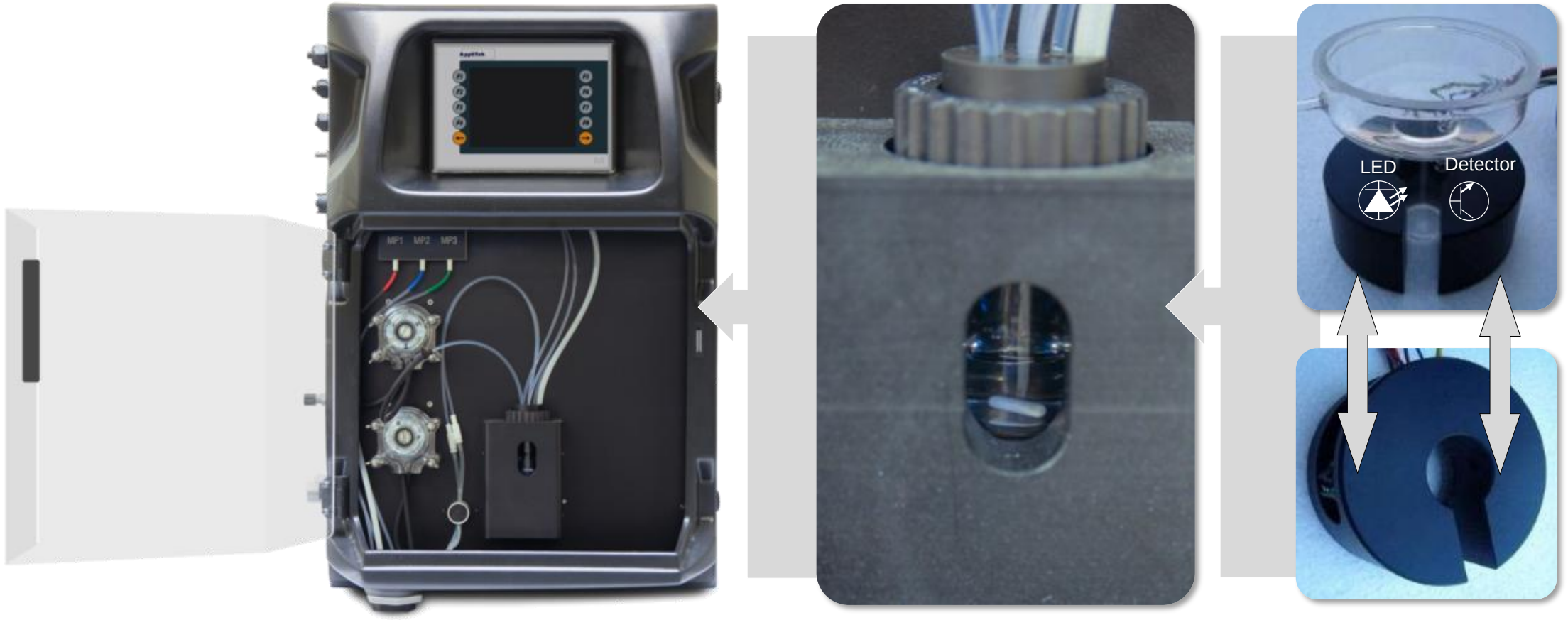
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

**A brine purity on-line analyzer system that works !**

Unique Colorimetric Design:
special highly sensitive photometer driven by a unique algorithm

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !


| **EZ-Brine**® sample temperature | Result (ppb $Ca^{2+}$ & $Mg^{2+}$) |
|---|---|
| 10 °C | 95.4 |
| 15 °C | 87.4 |
| 20°C | 81.4 |
| 25°C | 75.5 |
| 30°C | 71.0 |
| 35°C | 67.1 |

Is the sample temperature controlled before injection into the analyzer prior to analysis?

The **EZ-Brine**® analyzer has a Peltier-type sample cooler/heater to control the sample to constant temperature within ± 1°C prior to sample injection and analysis.

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !

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** |

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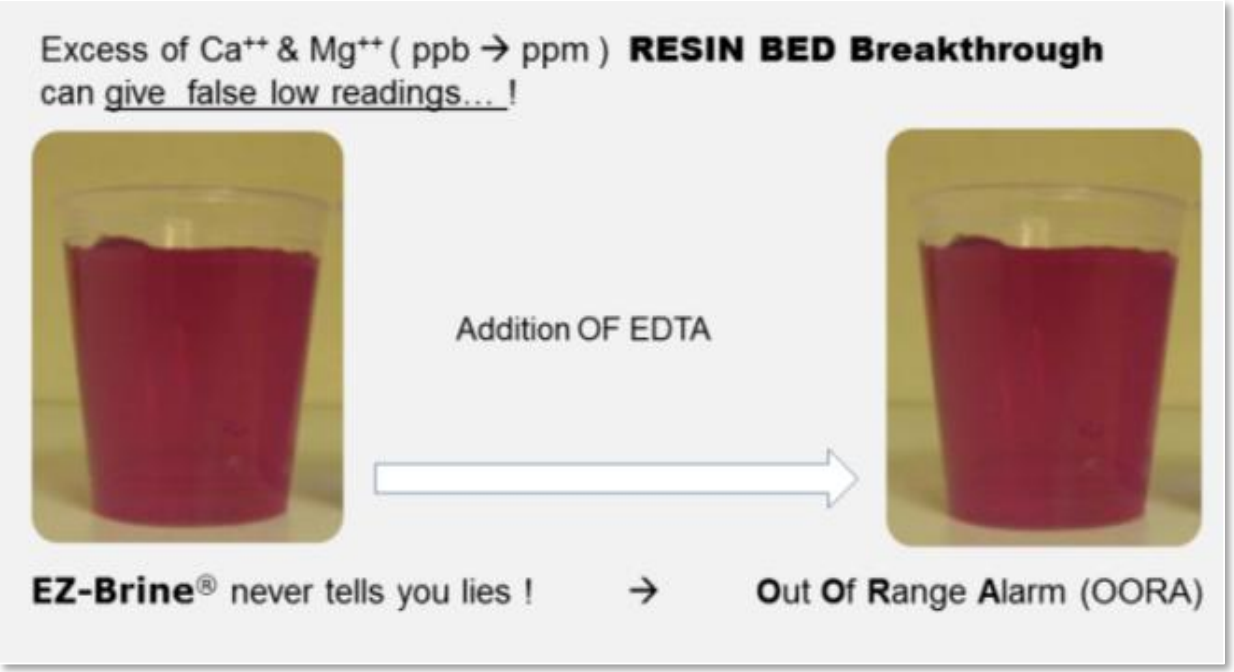
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

**A brine purity on-line analyzer system that works !**

Can you have a False Low Reading due to saturation of the Ion Exchangers "Resin Bed Breakthrough"?
Excess of $Ca^{2+}$ & $Mg^{2+}$ (ppb --> ppm level)

Danger for destroying your membranes!
Unnoticed Resin Bed Breakthrough causes Permanent Membrane Damage!

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

**A brine purity on-line analyzer system that works !**

Is un-dissolved Ca & Mg being measured?
Do we perform an acidification step prior to analysis?

Undisclosed Ca and Mg caused by a filtration or acidification problem in the process will not be measured by the photometric method. But once in the electrolyzer, it may dissolve after brine acidification and damage the membrane

The **EZ-Brine**® analyzer system has a built-in acidification step to dissolve any un-dissolved Ca & Mg prior to analysis

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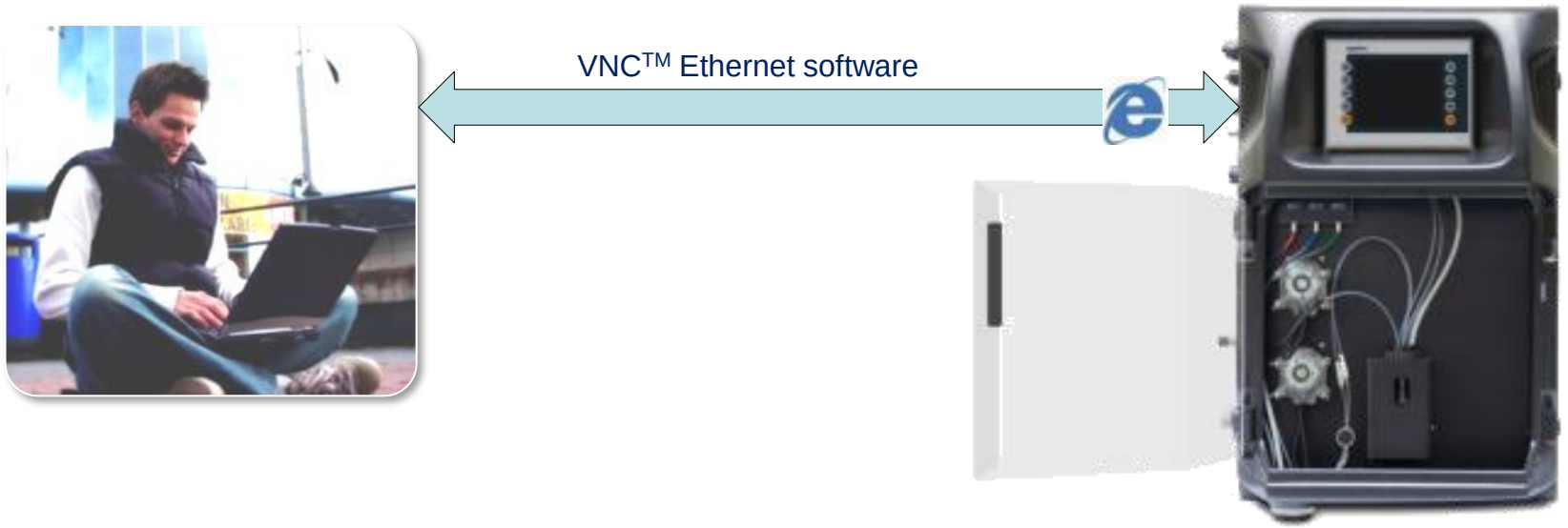
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## A brine purity on-line analyzer system that works !

Does your analyzer has bi-directional remote control?




The bi-directional control of the on-line **EZ-Brine**® analyzer touch screen can be remotely be taken over by another PC over a Local Area Network (LAN) using commonly available VNC™ Ethernet software

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

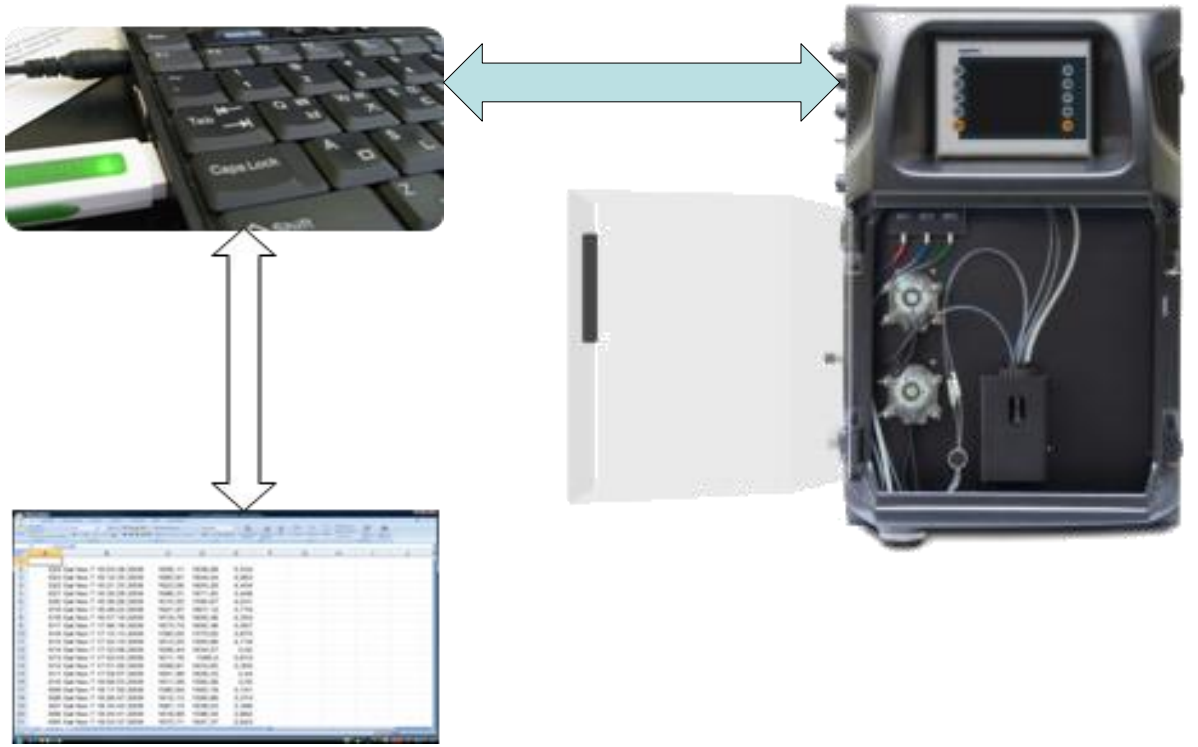
## A brine purity on-line analyzer system that works !

Does your analyzer has a USB port for quick upload or download of data

➲ Data Logging
Result & Alarm data export
(1.000 results including sample stream, date & time)

➲ data curve export (last 30 analysis curves)

➲ **EZ-Brine**® program up- & download
The results can be recorded on a memory stick and used in a spreadsheet program such as Excel or any other data processing software



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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## Production helping tool to make the shutdown decision easy during brine excursion


Can you perform manual validation analysis?

The **EZ-Brine**® analyzer is equipped with two (2) pcs validation valves allowing manual analysis

The validation valves are installed prior to the temperature control. In that way the sample temperature is adjusted before analysis in the same way the on-line analysis are performed

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# **EZ-Brine®** on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

## Production helping tool to make the shutdown decision easy during brine excursion


known sample


Shut Down

?





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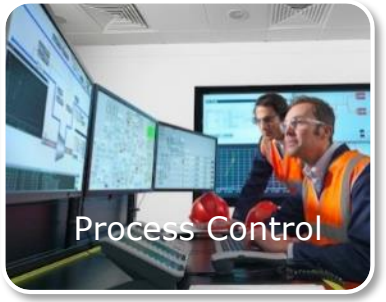
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

Field Example





USA
**AnaShell**® single compartment protective walk-in cabinet
2 x multi stream **EZ-Brine**® on-line analyzer systems

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Field Example


USA
**AnaShell**® single compartment protective walk-in cabinet
2 x multi stream **EZ-Brine**® on-line analyzer systems

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

Field Example


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

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

Field Example


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

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

Field Example


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

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

Field Example







Thailand
**AnaShell**® single-compartment protective shelter
1 x **EZ-Brine**® on-line Analyzer system for
$Ca^{++}$ & $Mg^{++}$ in Ultra-purified brine

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine

Field Example


Thailand
**AnaShell**® single-compartment protective walk-in cabinet
1 x **EZ-Brine**® on-line Analyzer system for
$Ca^{++}$ & $Mg^{++}$ in Ultra-purified brine

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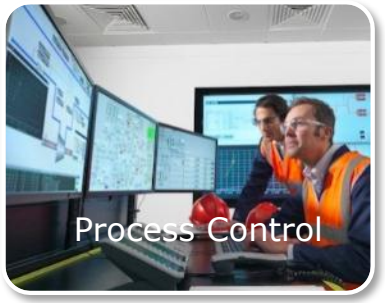
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine


Field Example




France
**AnaShell**® single-compartment protective walk-in cabinet
1 x **EZ-Brine**® on-line Analyzer system for
$Ca^{++}$ & $Mg^{++}$ in Ultra-purified brine

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# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine



Field Example


Hungary

**AnaShell**® single-compartment protective shelter
2 x **EZ-Brine**® on-line Analyzer system for
$Ca^{++}$ & $Mg^{++}$ in Ultra-purified brine

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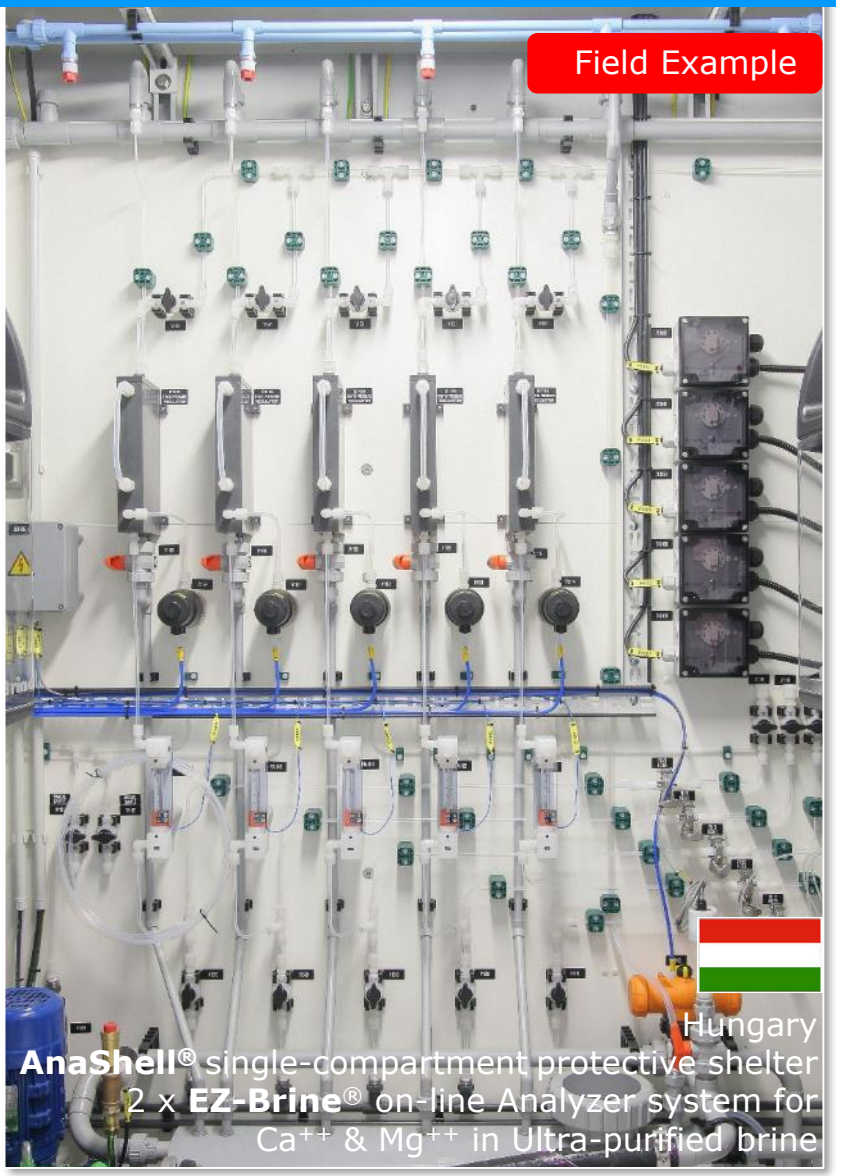


Hungary
**AnaShell**® single-compartment protective shelter
2 x **EZ-Brine**® on-line Analyzer system for
$Ca^{++}$ & $Mg^{++}$ in Ultra-purified brine

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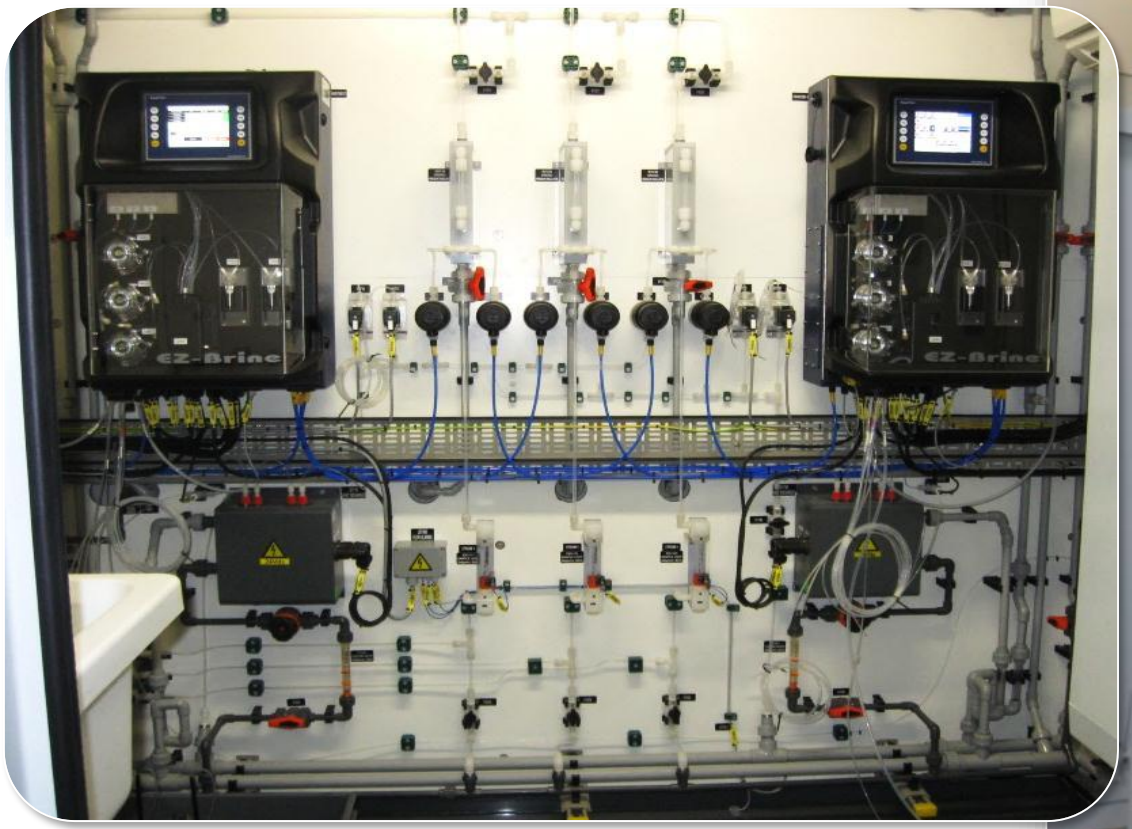
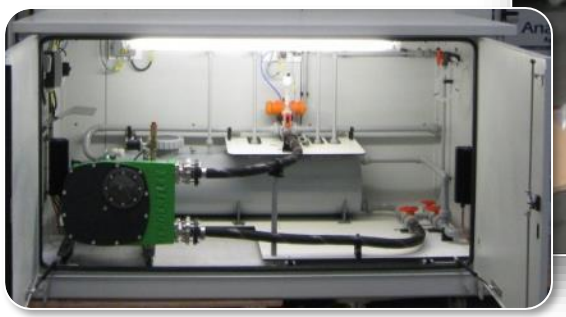
# **EZ-Brine**® on-line ppb level of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in Ultra-purified brine




Sweden
**AnaShell**® single-compartment protective shelter
2 x **EZ-Brine**® on-line Analyzer system for
$Ca^{++}$ & $Mg^{++}$ in Ultra-purified brine

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# up-stream on-line brine control – Avoid early membrane damage

## Raw - Saturated brine

high ppm level of $Ca^{2+}$ & $Mg^{2+}$ ( > 150 ppm )

1 SETTLING

Sludge Precipitated $CaCO_3$ (↓) $Mg(OH)_2$ (↓)

320 g / L

high ppm level of $Ca^{2+}$ & $Mg^{2+}$ ( ~ 5 ppm )

## Pre - Purified brine

FILTRATION 2

Re-Generation Chemicals

double or triple ION EXCHANGERS

## Ultra - Purified brine

Low ppb level of $Ca^{2+}$ & $Mg^{2+}$

pH CONTROL 3

hydrogen chloride (HCl)

brine FEED electrolyzers

### EZ-Clarifier®


0 – 1 g/L hydroxides ( NaOH )

0 – 1.5 g/L carbonates ( $Na_2CO_3$ )

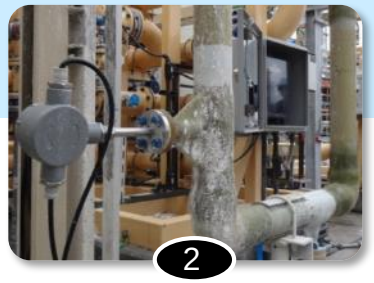
by **EZ-Settler®** + acid / base titration
( 2 points pH titration with self-finding inflection points )

### EZ-Brine®high


0 – 20 ppm $Ca^{2+}$ & $Mg^{2+}$
0 – 10 ppm $Mg^{2+}$
0 – 10 $Mg^{2+}$ by calculation

by photometric titration

### Turbidity




0 – 50 FTU / NTU
by Ultrasonic Turbidity

### EZ-Brine®


0 – 20 – 50 - 100 ppb $Ca^{2+}$ & $Mg^{2+}$

by colorimetric measurement using hydroxynaphthol blue color indicator (HNB) conf. ASTM 3500-Ca

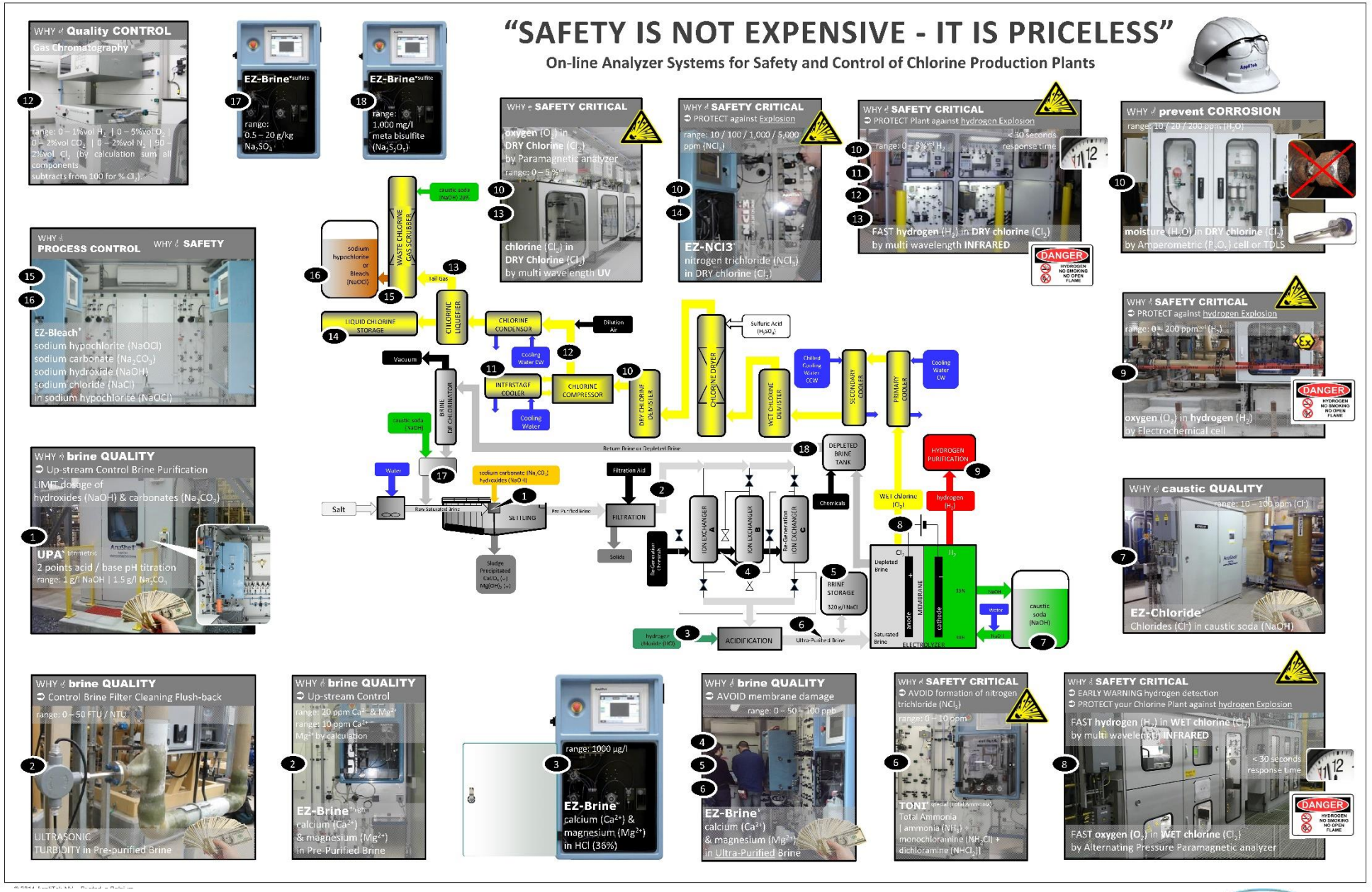
### TONI®special (Total Ammonia)


0 – 10 ppm TA
[ ammonia ($NH_3$) + monochloramine ($NH_2Cl$) + dichloramine ($NHCl_2$) ]
by colorimetric measurement using adapted Berthelot method conf. ASTM 450-NH3 F

### EZ-Brine®iodide


0 – 500 ppb iodide ( $I^-$ ) by calc.
0 – 500 ppb iodate ( $IO_3^-$ )
0 – 500 ppb iodide ( $I^-$ ) + iodate ( $IO_3^-$ ) by colorimetric measurement

# AppliTek your trusted partner in on-line brine control

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