Digester and Recaust Automatic Liquor Titrator Measurement Technology

Presented by

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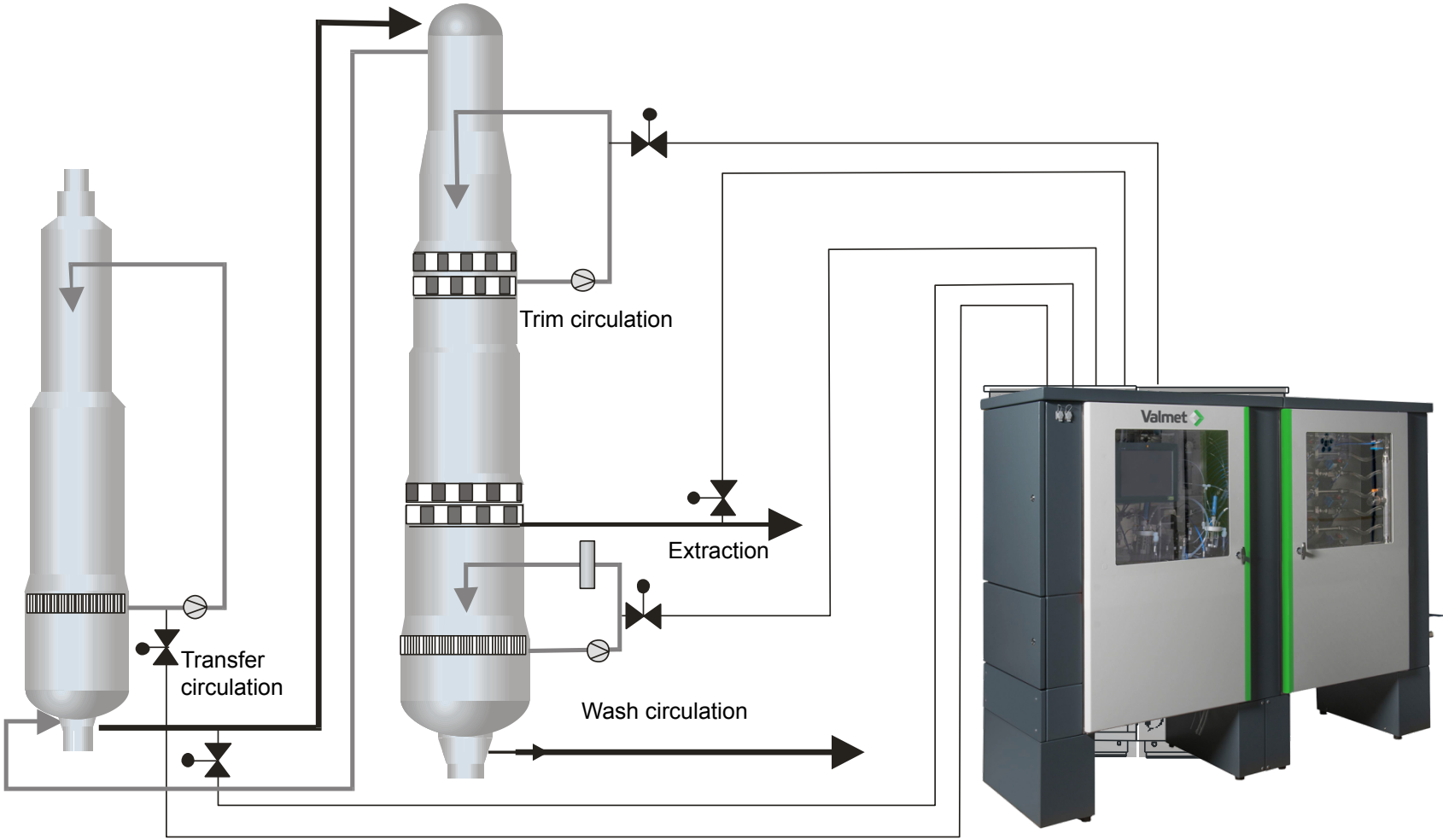
Cooking Liquor Titrator

- Standard analysis method for black liquor residual alkali
  - EA
- Complete white liquor analysis as an optional feature
  - NaOH, Na_2CO_3, Na_2S
  - Effective alkali (EA), Active alkali (AA), Total Titratable Alkali (TTA), Causticizing Efficiency (CE %), Sulphidity (S%)
- Analysis based on an inflection point titration that eliminates the effect of any pH electrode drift
- Sample Handling unit and Analysis unit can be separated to facilitate installation if needed.
  - There are some distance requirements that need to be considered if this option is used.

Typical sampling points for a continuous digester



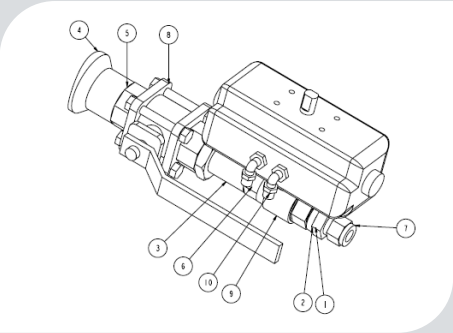
Process Samplers

Sample line:

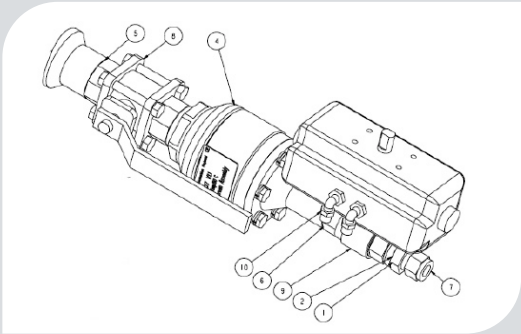
- Maximum: 16 lines
- AISI 316L

Samplers:

- Installation with a coupling welded to the process pipeline



Sampler SD 711
• White liquor or shive-free black liquor
• Sample line max. 100 m

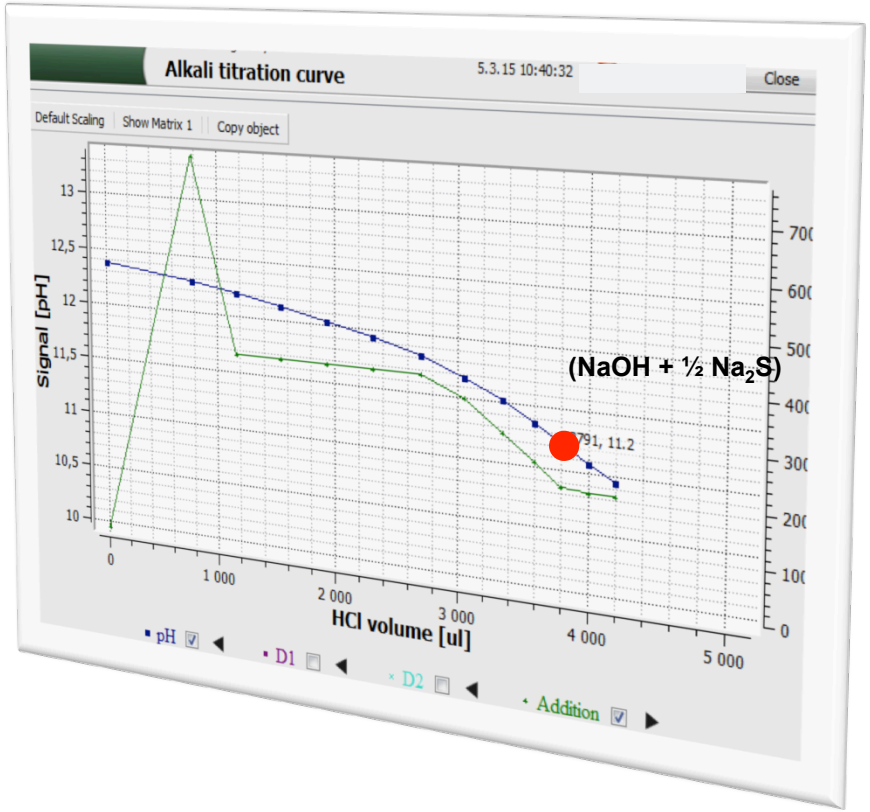


Sampler SD 712
• Shive-containing liquors
• Sample line max. 30 m

Analysis method

Black liquor

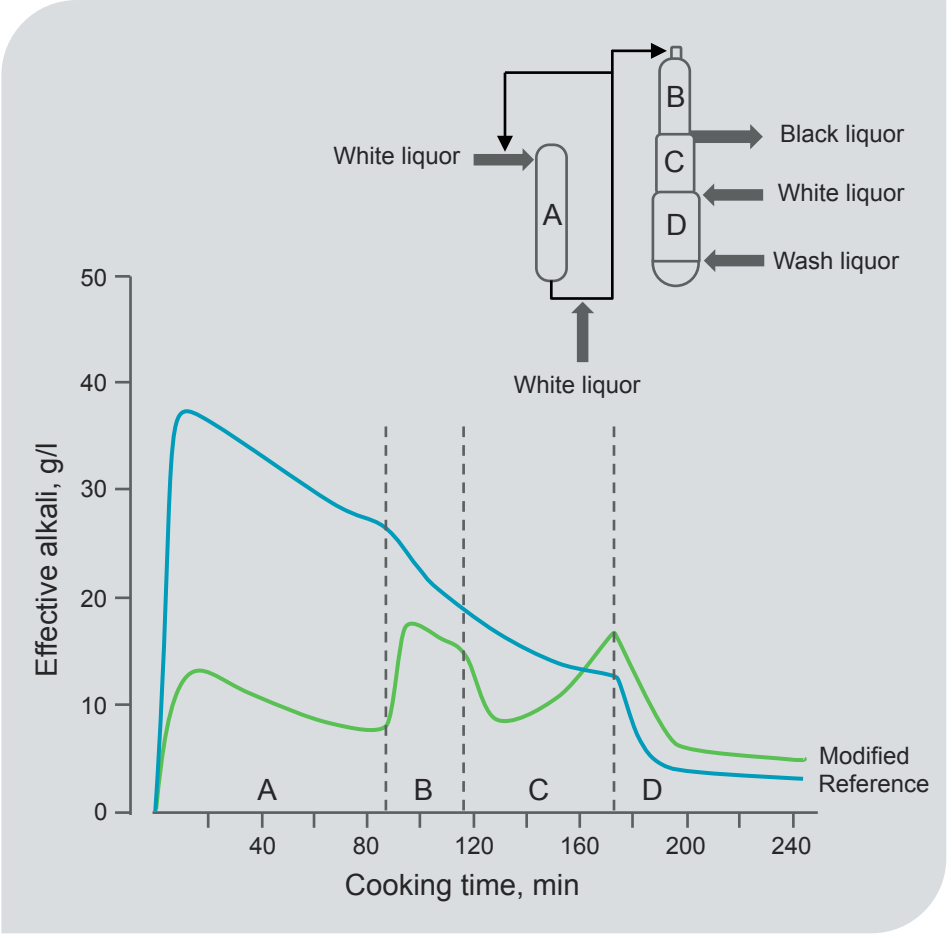
- SCAN N 33:94
- Potentiometric titration with hydrochloric acid (HCl)
- Sodium carbonate is added to give a better inflection and buffer the titration solution
- Autocalibration feature for adaptation to changing process conditions
- Possible to use pH end point titration if desired.
  - Requires regular pH probe calibration



Managing the alkali profile

Reliable and dependable measurement information

- Automatic sampling and analysis for real liquor chemistry results
- Absolute measurements
- Managing the alkali charge and profile
- System point of view for operators
- Seamless integration into process and mill
- High frequency measurements



Centralized system

Liquor Titrator Structure

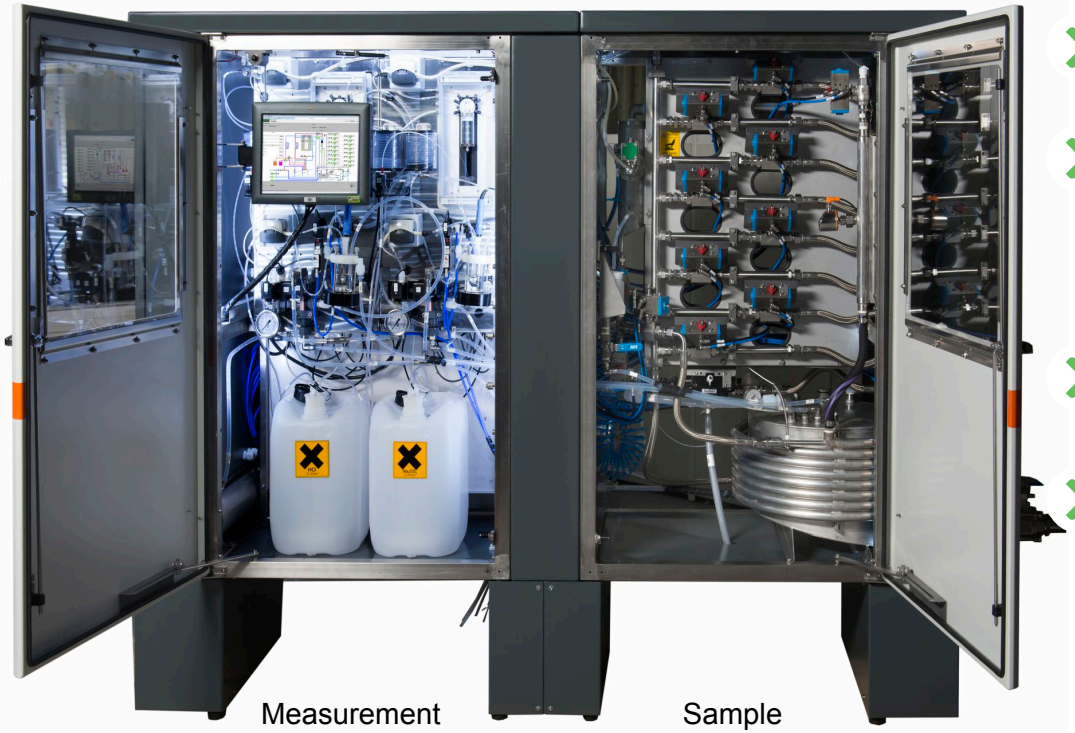
Flushing water

Cooling water

Analysis water

Instrument air

Electricity



Measurement unit

Sample handling unit

Touch screen interface

Pneumatically controlled samplers
- Valmet SD-712
- Valmet SD-711

Sample back to sewer

Measurement results:

Black liquor: EA

White liquor: NaOH, Na_2S, Na_2CO_3, EA, AA, TTA, CE%, S%

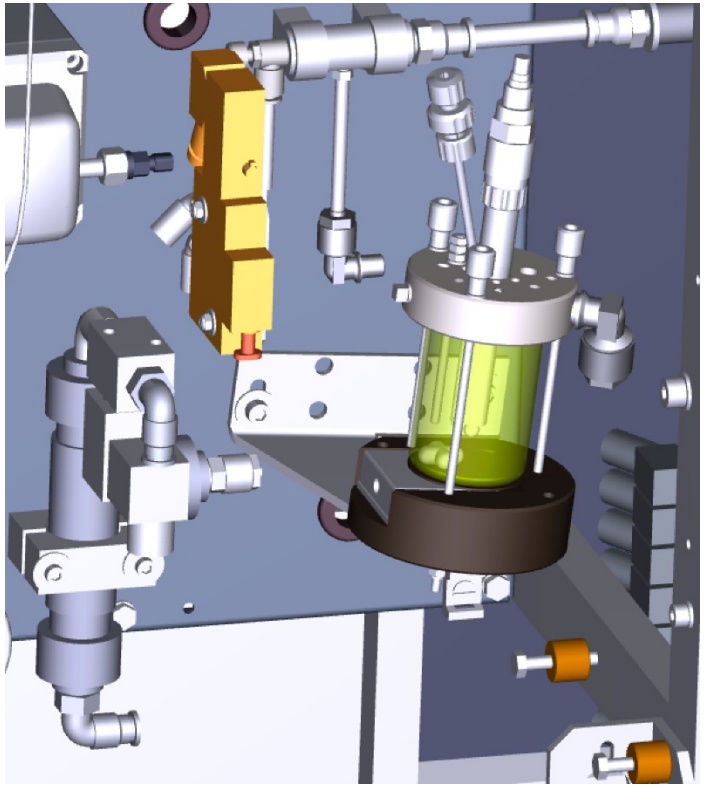
Cooking Liquore Titrator Analysis Unit

Sample Analysis Waste & H2S Vapor Removal

Empties Analysis Cup after tests

Evacuates Vapors from Analysis cup during white liquor titration

Vented externally via connection @ analyzer bulk head



Ejector unit

Sample Analysis unit

Sealed Analysis Unit

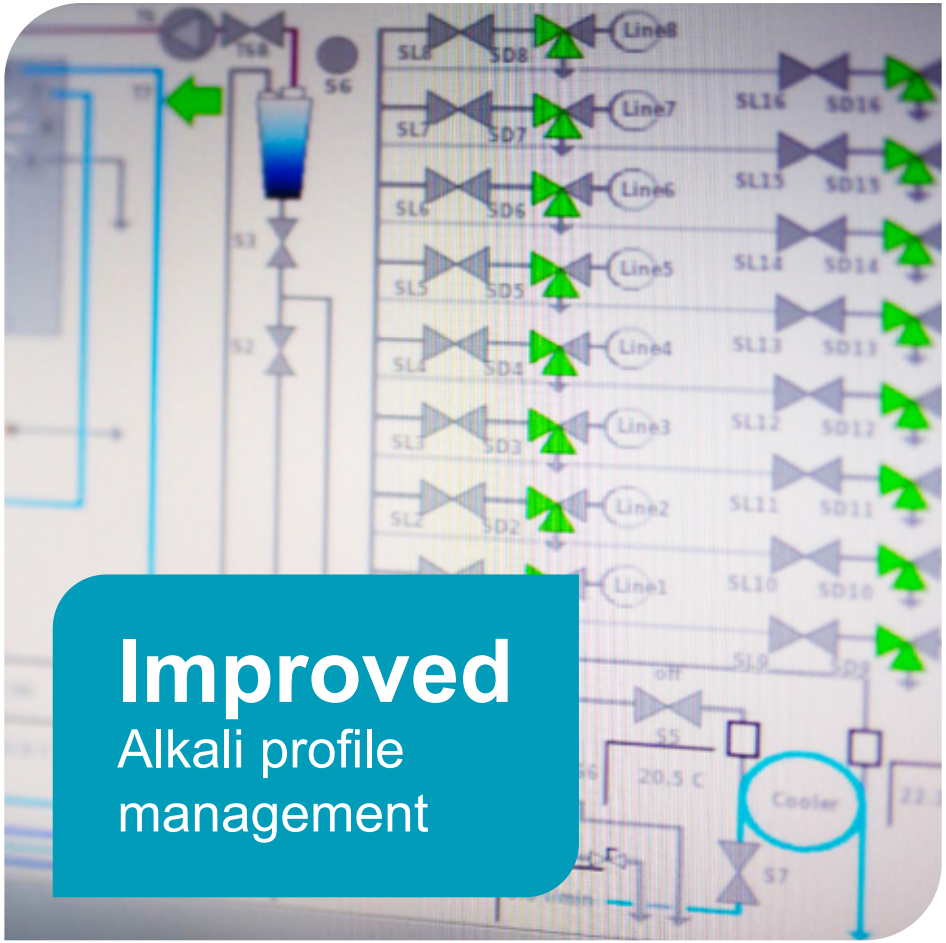
Liquid and vapors removed by ejector

H2S cannot escape into Analyzer

Accurate results from day one

Based on reliable measurement

- An effective cooking management tool
- Better pulp quality and production control
- Easy installation without need for calibration
  - Only calibrate new pH probe
- Large reference base
- Field-proven results



Safe and convenient

The multipoint analyzer concept

- Simple installation, cost-effective maintenance
- Centralized location of most critical sample handling and components
- Minimized exposure to equipment in harsh environments
- Automatic self-cleaning system
- Industry-standard communication alternatives and protocols

Automatic Sampling Liquor Titrator

- Alkali Titrator runs the Scandinavian test method in order to perform the ABC titration for white liquor samples
- Black liquor circulations can be sampled automatically also. The titrator can be configured to run a titration to measure the A point, or it can be setup to run to an endpoint pH in order to match the lab unit in obtaining the EA result.
- No calibration is required since it is running the same or very similar test as the lab. This allows the operator or control scheme to utilize the data within a week of start-up.
- The liquor profile across the digester can be stabilized
- Corrections for inaccuracies in the chip feed rate, moisture content, or even poor chip quality can be corrected by measuring the residual alkali as early in the digester as possible.
- The final alkali content can me measured in the wash zone in order to ensure proper residual levels that will protect against lignin re-precipitation and also corrosion issues.

Caustic Plant Liquor Titrator

Online measurements available from day one

- Provides actual liquor chemistry titration results
- No calibration needed – online measurements available from day one
- Measurement Capabilities:
  - Dissolving Tank green liquor
  - Weak Wash
  - Green liquor to slaker
  - Slaker/1st causticizer lime mud slurry
  - Final causticizer lime mud slurry
  - Final white liquor to the digester
  - NEW Recovery Boiler Reduction
- Automatic flushing and acid washing sequences
- Can be used to measure manual liquor samples
- Rugged design ensures high uptime (98%) and low maintenance (clear maintenance program)

Analysis method

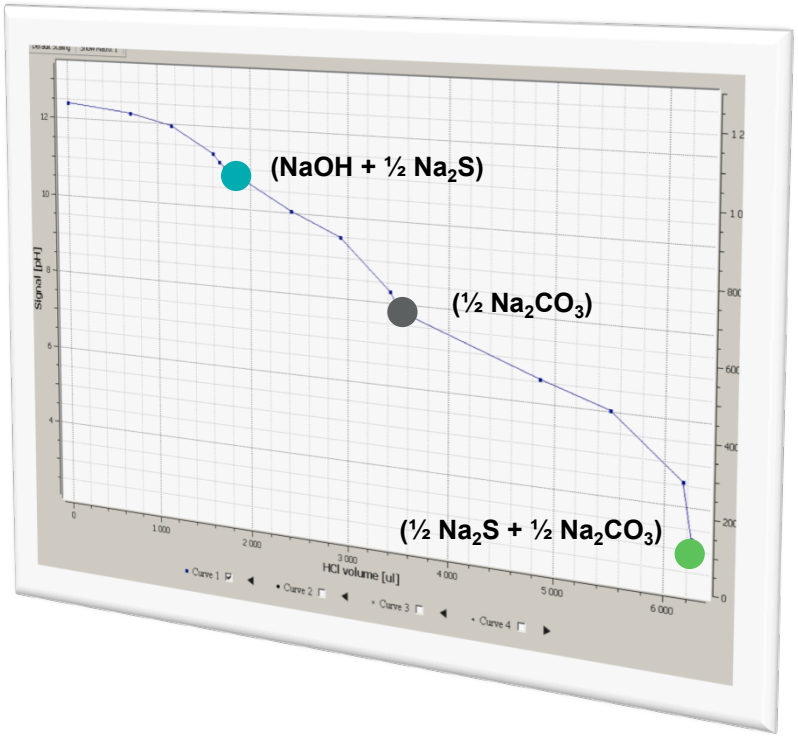
White liquor

- SCAN 30:85
- 2 ml sample is titrated with 1.0 N HCl – an electrode registers pH
- Reactions for the three equivalence points

EP1: NaOH + Na2S + Na2CO3 + 2HCl
-> NaHS + Na2CO3 + 2 NaCl + H2O pH 10.6

EP2: NaHS + Na2CO3 + HCl
-> NaHS + NaHCO3 + NaCl pH 8.4

EP3: NaHS + NaHCO3 + 2 HCl
-> 2 NaCl + H2S + H2O + CO2 pH 3.8



Calculations of Results

Effective Alkali	**EA**	**EA = NaOH + 1/2 Na_2S** **EA = A * NM / V**
Active Alkali	**AA**	**AA = NaOH + Na_2S** **AA = (2A - 2B + C) NM / V**
Total Titratable Alkali	**TTA**	**TTA = NaOH + Na_2S + Na_2CO_3** **TTA = C * NM / V**
Causticizing Degree	**CE%**	**CE% = NaOH * 100 / (NaOH + Na_2CO_3)** **CE% = (2 B - C) * 100 / (4B - C - 2A)**
Sulfidity	**S%**	**S% = Na_2S * 100 / (NaOH + Na_2S)** **S% = (2B - C) * 100 / (2A - 2B + C)**
Sodium Carbonate	**Na_2CO_3**	**Na_2CO_3 = (2B - 2A) * NM / V**
Sodium Hydroxide	**NaOH**	**NaOH = (2B - C) * NM / V**
Sodium Sulfide	**Na_2S**	**Na_2S = (2A - 4B + 2C) * NM / V**

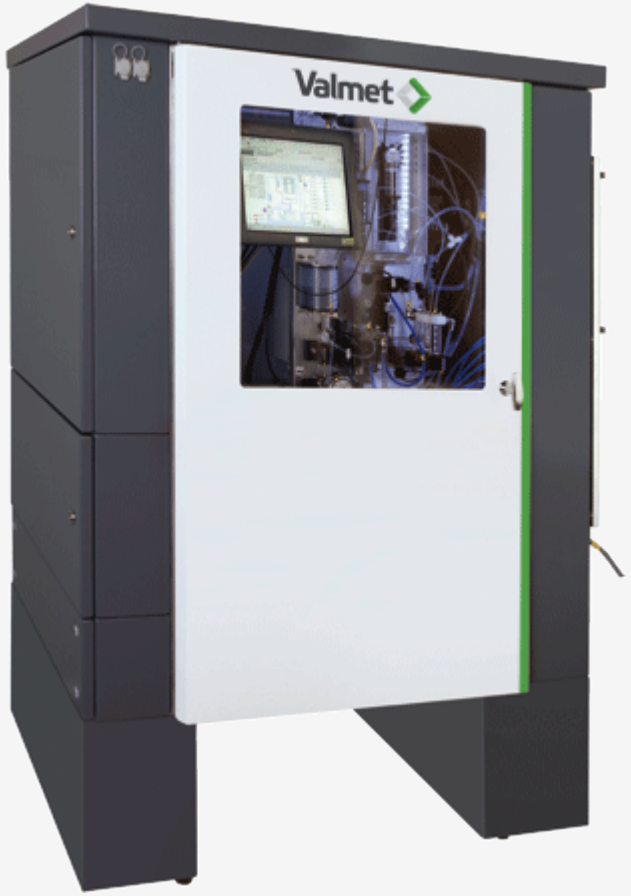
A = Titration volume at equivalence point 1 (EP1)
B = Total titration volume at eq. point 2 (EP2)
C = Total titration volume at eq. point 3 (EP3)
N = HCl normality
V = Sample volume

M = Molecular weight
- if result is computed as Na_2O, M = 31
- if result is computed as NaOH, M = 40

Caustic Plant Liquor Titrator

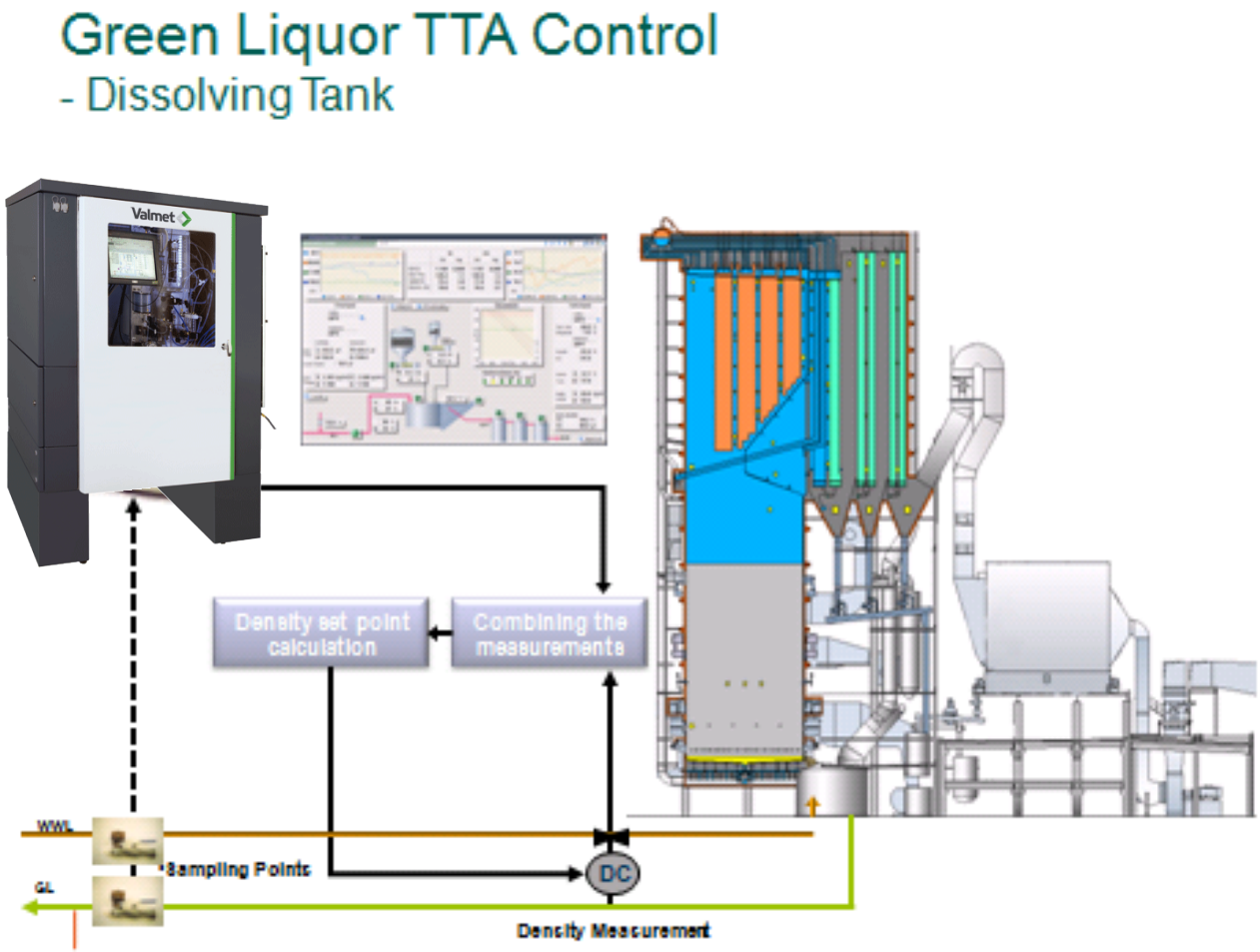
For Employee Safety!

- With automated liquor sample collection preparation and testing, operators and laboratory personnel are exposed less to the safety hazards of manual sample collection
- Eliminate need for operators or laboratory personnel to collect dissolving tank/caustic plant samples for TTA/Density or smelt spout sampling for reduction.
- Automated liquor sampling, sample preparation and testing allows time for operators and laboratory personnel to:
  - Work Safer!
  - Focus on managing the process
  - Improve housekeeping in process areas
  - Assume additional operational tasks
  - Perform more value added tests



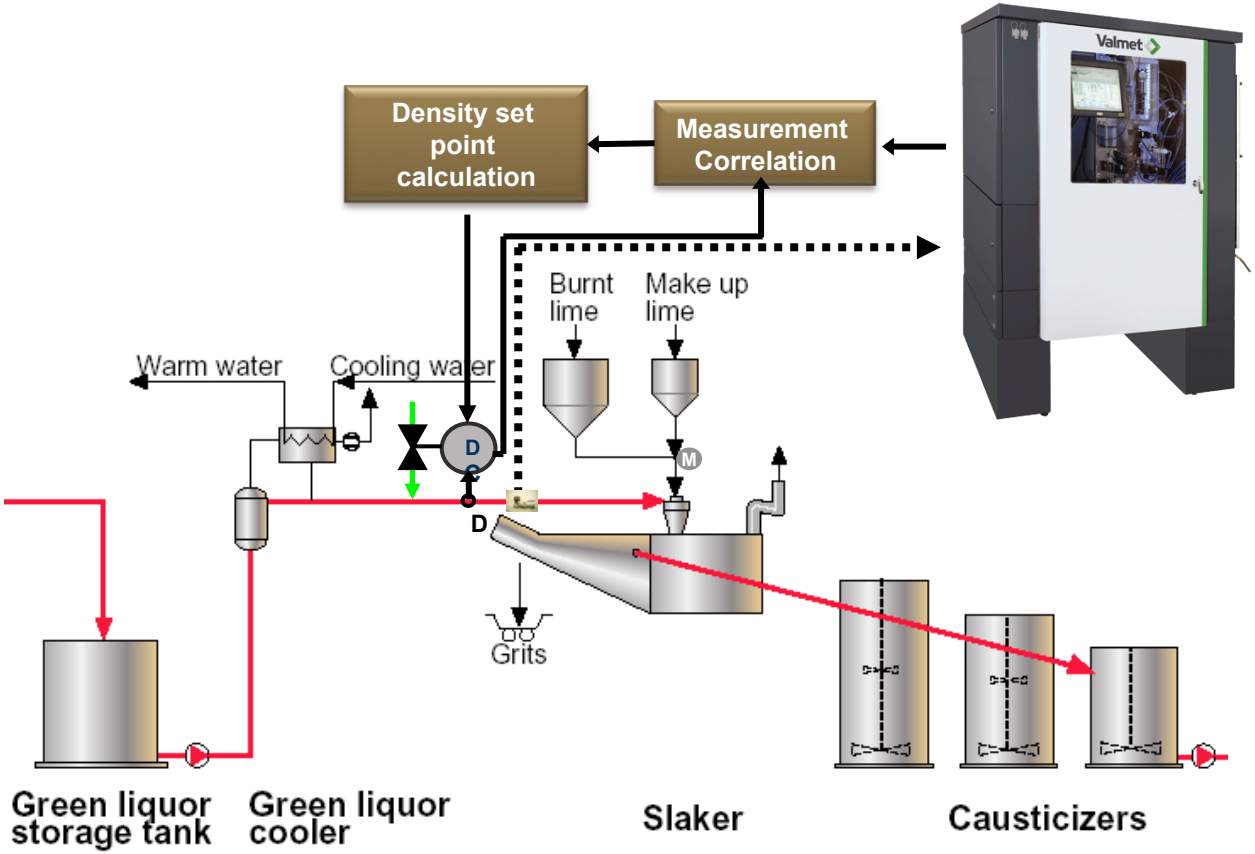
Green Liquor TTA Control – Dissolving Tank

- Best Results are achieved with density control at the Recovery Boiler Dissolving Tank AND at the Slaker
- Alkali analyzer measures TTA and correlates result to density. Density setpoint is sent to existing denisty controls
- Manipulated Variables
  - Weak Wash Flow
- Control Variables
  - Green Liquor Density
  - Green Liquor TTA

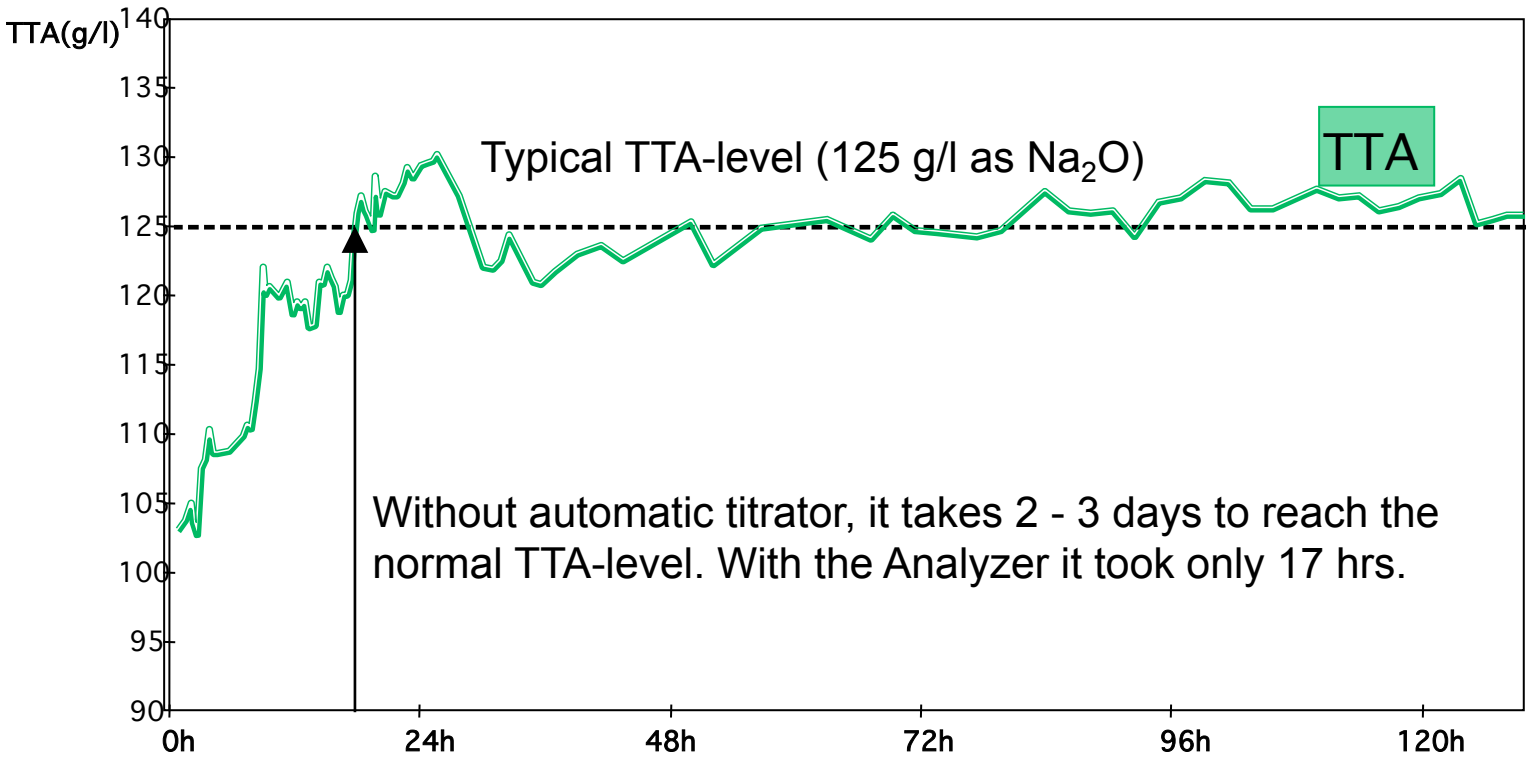


Green Liquor TTA Control - Slaker

- Requires Green Liquor Density Control at the slaker
- Goal is a stable and consistent green liquor TTA to the slaker to minimize variability and maximize lime addition
- Manipulated Variables
  - Weak Wash Flow
- Control Variables
  - Green Liquor Density
  - Green Liquor TTA



Causticizing Process Start-up



Causticizing Optimization %CE Control

- Incoming TTA Sets the Correct %CE Target Based on Goodwin's Curve
- Slaker Delta T Is Used for Quick Feedback to Lime Reactivity and is Modeled to the %CE
- Green Liquor Temperature can Also Be Controlled to Maximize the Slaker Temp Short of Boiling

Sampling points:

1 Green Liquor at dissolving tank

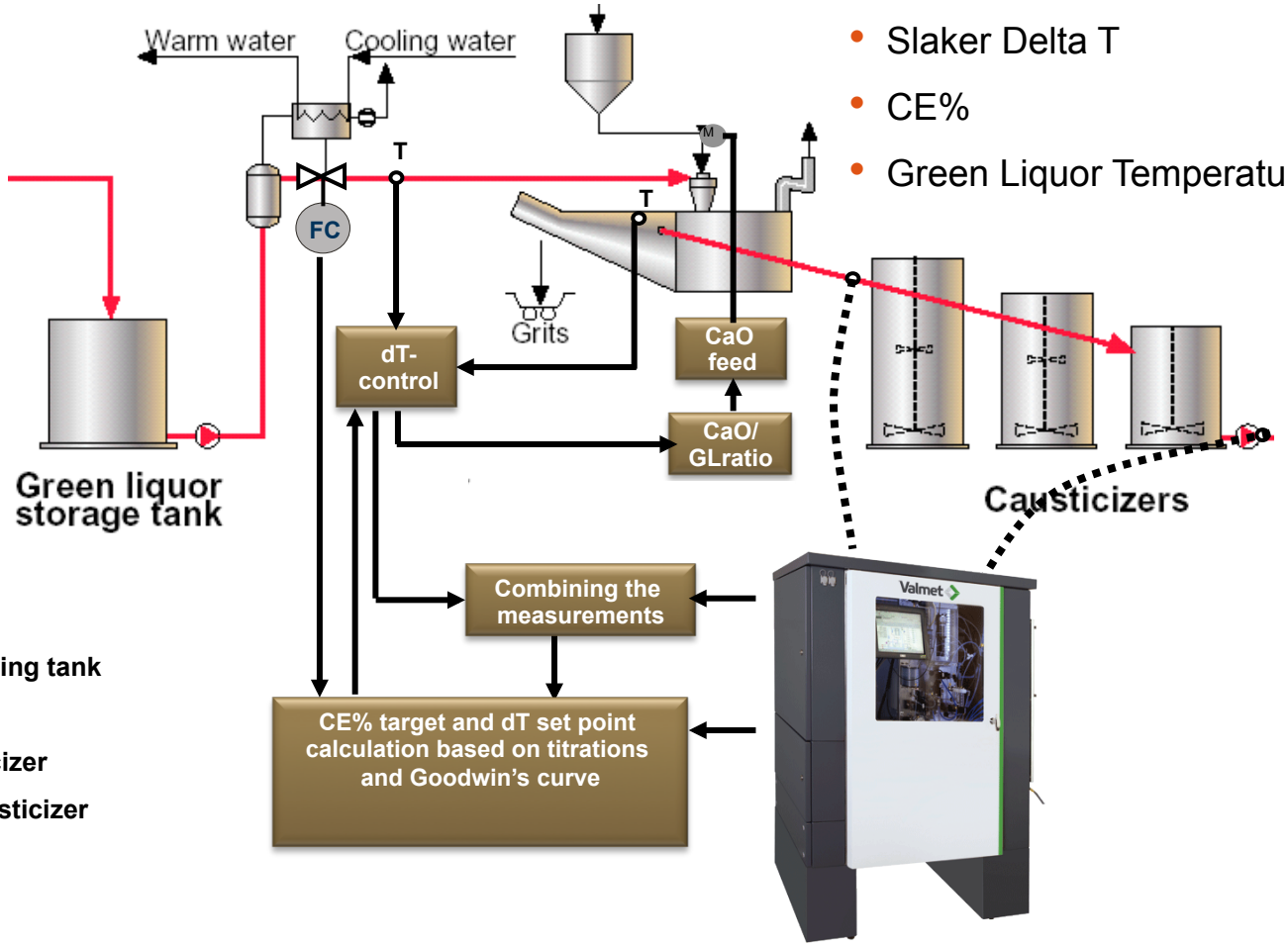
2 Green liquor to slaker

3 Lime milk at 1st causticizer

4 Lime milk after last causticizer

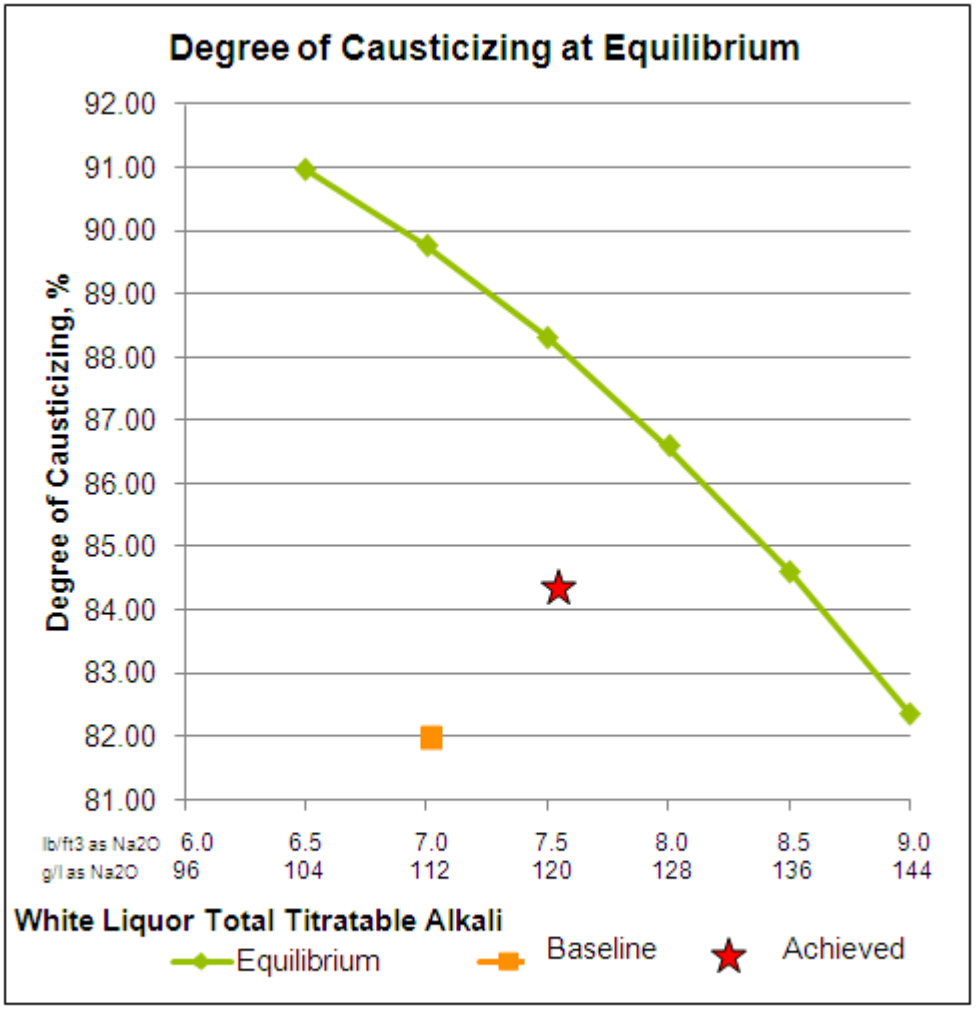
5 White liquor CE%

CE% Controls



- Manipulated Variables
  - Lime/Green Liquor Ratio
- Controlled Variable
  - Slaker Delta T
  - CE%
  - Green Liquor Temperature

Causticizing Optimization Results



Mill Base line:

82%

Achieved CE:

84.5%


Valmet
FORWARD