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Cycling-Up without Carryover: Truth or Dare?

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The Reasons for this Investigation

- The National Research Council of Canada deemed that the potential for technologies that will allow boilers to operate at higher cycles was such that it funded a two-year \$400k research project through its Industrial Research Assistance Program (NRC-IRAP).
- Tannins prevent foaming at high TDS. This has been observed for over a century, but not understood.
- ASME or ABMA guidelines as to maximum conductivity in boiler water are constantly exceeded in tannin-treated boilers and yet carryover, as measured by condensate conductivity, remains extremely low.



Three Key Points

- 1. There are many misconceptions about carryover, especially about the causes for its occurrence at high cycles/high dissolved solids.
- 2. Understanding the behavior of bubbles in boilers brings scientific clarity and truth to the matter.
- 3. Cycling-up is possible for those who dare to use the right chemistry. If you could double the conductivity in your boiler, how much water and energy would you save?



Key Point 1: Understandings (and Misunderstandings) of Carryover

- Surface-active substances enter the boiler, reduce the surface tension, and create stable bubbles that accumulate at the surface.
- The high temperature and high pH of the boiler will readily saponify vegetal or animal O&G.
- At high-cycles, most boiler polymers will degrade, sometimes into small surfaceactive fragments.



- Caused by variations and sudden demands for steam
- Leads to a lower pressure and a surge of boiling
- Highly dependent on the presence of nucleation sites and already existing bubbles
- Contrary to surfactants, the accumulation of salts typically found in boilers leads to an increase in surface tension.
- An accumulation of certain ion pairs (but not others!!) inhibits bubble coalescence. Smaller bubbles predominate and are the root cause of high TDS carryover.

Keypoint 1: Even the Best Steam Experts Don't Get It Right! Stills from Steam Boilers - The Inside Story Part 8 - TDS Control

From: https://www.youtube.com/watch?v=VgJH_HYlyDQ





The simulated picture of large bubbles under a foamy surface is wrong!!!!





Keypoint 2: From 1924 to 1943, C. W. Foulk of Ohio University Pioneered Studies to Understand Foaming at High TDS In Boilers



FIGURE 2. FOAM ON SOLUTION OF SODIUM CHLORIDE IN WATER TUBE BOILER Left, 5000 and right, 30,000 p. p. m. of sodium chloride





FIGURE 1. WATER TUBE BOILER

From: Foulk, C. W. and J. W. Ryznar (1939). "Foaming of Boiler Water." Industrial & Engineering Chemistry 31(6): 722-725.

Keypoint 2: An "Anomaly" of Water that Is yet to Be Fully Understood

First observations in:

• Foulk, C. (1924). "Foaming of Boiler Water." Industrial & Engineering Chemistry 16(11): 1121-1125.

Complex investigations and attempts to unravel the physico-chemical mechanisms started only in the 1960's, but got more mysterious in 1993 and continue to this day:

- Marrucci, G. "A theory of coalescence." Chemical engineering science 24.6 (1969): 975-985.
- Craig, V., et al. (1993). "Effect of electrolytes on bubble coalescence." Nature 364(6435): 317.
- Duignan, Timothy T. "The surface potential explains ion specific bubble coalescence inhibition." Journal of Colloid and Interface Science 600 (2021): 338-343.



Keypoint 2: 1993 – Only Certain Ion Pairs Will Inhibit Coalescence!



FIG. 2 Effect of electrolytes on bubble coalescence. NATURE · VOL 364 · 22 JULY 1993



FIG. 1 The percentage coalescence observed for a stream of nitrogen gas bubbles rising in a range of aqueous electrolyte solutions at 21-23 °C. 100% coalescence corresponds to no change in opacity relative to pure water; 0% coalescence is at the point where no further change in opacity was observed.





Key Point 2: This Is What It Looks Like





Keypoint 2: Why Size Matters... for Bubbles: Rising Speed

Terminal speed of a spherical bubble is proportional to the square of its radius: $v=(2/9)\rho g R^2/\mu$

g is the gravitational acceleration (m/s2) R is the radius of the spherical particle (m) ρ is the difference in density between the gas and the liquid (kg/m3) N.B. In high-pressure boilers the difference is greatly reduced and so is the speed, this explains why the TDS limits are lower μ is the dynamic viscosity (kg/m*s) v is the velocity (m/s)





Key Point 2: Consequences of Small Bubble Size: High Steam Fraction in Water

- The concentration at which coalescence is inhibited (the Critical Coalescence Concentration or CCC) is different for different salts and salt mixtures.
- For a given output of steam, smaller bubbles rise more slowly, so there will be a greater proportion of steam in the boiler water (gas holdup).
- This foamy mass is more susceptible to rapid expansion with small variations in pressure. It will also give false level readings on sight-glasses because its density is much lower than water.



Fig. 8 Qualitative comparisons between strong $(CaCl_2 \cdot 2H_2O)$ and Na_2SO_4 and moderate (NaCl and MgSO₄ · 7H₂O) electrolytes

From: Sujan, Ajay, and Raj K. Vyas. "Estimation of transition concentration of aqueous mixtures of single and binary electrolytes for bubble coalescence inhibition." *Chemical Papers* 72.10 (2018): 2539-2559.



Key Point 2: Consequences of Small Bubble Size: Droplet Ejection

- Pressure differential between the inside and outside of a spherical bubble is inversely proportional to its radius: Pi - Po = 2σ/R. (Laplace's law).
- Very small bubbles have extremely high pressures and will eject droplets when they burst.
- As small droplets have a low terminal falling speed, it takes only a weak flow to carry them in the steam lines.

 σ is the surface tension (N/m) P is the presssure (subscipt i is inside, o is outside) (Pa or N/m²) R is the radius (m)





From: Kientzler, C. F., et al. "Photographic investigation of the projection of droplets by bubbles bursting at a water surface." *Tellus* 6.1 (1954): 1-7.



Key Point 2: Showtime! Consequences of Having Many Small Bubbles: Nucleation and Bubble Growth

- Small bubbles will act as nucleation sites for steam-to-vapor transition whenever the pressure is lowered.
- 2. The small bubbles will rapidly expand to create carryover. (The demonstration here is with dissolved gas, but the effect is the same with boiling.)





Key Point 2: Various Ways of Measuring Coalescence: Microscopy





Figure 1. Bubble coalescence as observed in pure water (top) and coalescence inhibition in solutions at higher electrolyte concentrations. The inside diameter of the capillaries is 2 mm.

From: Christenson, H. K., et al. "Electrolytes that show a transition to bubble coalescence inhibition at high concentrations." *The Journal of Physical Chemistry C* 112.3 (2008): 794-796.



Key Point 2: Various Ways of Measuring Coalescence: Turbidity



Figure 2. Schematic of Bubble Coalescence Apparatus. Small bubbles are produced at the frit and rise in the column passing through the constriction that promotes bubble collisions. In pure water they rapidly coalesce such that the bubbles breaking the laser beam are large and few in number. In this case, most of the light is transmitted and strikes the detector. When coalescence is inhibited, the bubbles remain small and numerous, resulting in a large amount of scattering and low light intensity at the detector.

From: Henry, Christine L., et al. "Ion-specific coalescence of bubbles in mixed electrolyte solutions." *The Journal of Physical Chemistry C* 111.2 (2007): 1015-1023.



Key Point 2: Various Ways of Measuring Coalescence: Gas Holdup



From: Sujan, Ajay, and Raj K. Vyas. "Estimation of transition concentration of aqueous mixtures of single and binary electrolytes for bubble coalescence inhibition." *Chemical Papers* 72.10 (2018): 2539-2559.



Key Point 2: Various Ways of Measuring Coalescence: Image Analysis

Viewing chamber

Sampling tube



Figure 3. Bubble viewer in operation (left) and a schematic of the bubble viewer (right).

From: Sovechles, J. M. and K. E. Waters (2015). "Effect of ionic strength on bubble coalescence in inorganic salt and seawater solutions." AIChE Journal 61(8): 2489-2496.



Figure 6. Example bubble size images in (a) distilled water, (b) 0.01 M CaCl₂, (c) 0.02 M CaCl₂, (d) 0.04 M CaCl₂, (e) 0.06 M CaCl₂, and (f) 0.10 M CaCl₂, (g) 0.20 M CaCl₂, and (h) 1.0 M CaCl₂.



Key Point 2: Our Way – Patent Pending

- Uses boiling water and steam rather than air or gas bubbles
- Production of uniform bubbles at a hot metal surface
- Detection of bubble-size by three different means

From: Sujan, Ajay, and Raj K. Vyas. "Estimation of transition concentration of aqueous mixtures of single and binary electrolytes for bubble coalescence inhibition." *Chemical Papers* 72.10 (2018): 2539-2559.



Key Point 2: Consequences of Inhibition of Bubble coalescence

- Smaller bubbles rise more slowly
- They accumulate in the water mass and increase its gas holdup
- They serve as nucleation sites for sudden boiling
- When they burst, they eject droplets that get carried in the steam

From: Sujan, Ajay, and Raj K. Vyas. "Estimation of transition concentration of aqueous mixtures of single and binary electrolytes for bubble coalescence inhibition." *Chemical Papers* 72.10 (2018): 2539-2559.



Key Point 3: Daring to Cycle-Up and Go Above the Limits

What one of the biggest players in the field of water treatment is saying:

"The American Boiler Manufacturers Association (ABMA) recommendations for boiler water limits are provided in Table 16-1. These guidelines should not be considered absolute. Some systems cannot tolerate operation at these concentrations; others operate continuously at significantly higher concentrations."

Possible Strategies:

- 1. Reduce boiler chemicals that add to ionic strength, especially those that will produce doubly charged ions such as SO_4^{2-} (the reaction product of sulfites) or HPO_4^{2-} . This is a sure shot, but the gains are likely limited.
- 2. Add antifoam agents?

From: https://www.watertechnologies.com/handbook/chapter-16-steam-purity

3. Use tannins?



Key Point 3: Antifoam Effect on Bubble Coalescence



Pure water (< 5 µs/cm)



Synthetic Boiler Water (20 ms/cm)



Synthetic Boiler Water (20 ms/cm) After addition of antifoam



Keypoint 3: The Trouble with Antifoams

There is lots of research and patents for antifoams in the 1940's and 1950's, by two scientists from Dearborn Chemicals. They are somewhat confused about the small bubbles: Are too many forming? Or are the small ones not coalescing?

The polyamide products developed worked, but they generally stop functioning within an hour or so and more must be fed. Tannins are here first mentioned as being necessary in the mixture and synergistic.





Key Point 3: Silicone-Based Antifoams Degrade and Dissolve at High pH!



Release of silicate into solution after prolonged conditions of high temperature and pressure. The antifoam effects are quickly lost!



Key Point 3: Polyglycols (including PGME) Also Degrade and Foam



CONTROL: Synthetic Boiler Water + Tannin Product after 120h at 180°C



Synthetic Boiler Water + Tannin Product + Polyglycolbased Antifoam at 0.1% after 120h at 180°C



Key Point 3: Effect of Tannins on Boiling Water and Carryover





Key Point 3: Tannins in an Experimental Boiler

Conditions: 125 – 150 psi (155-160°C)

Carry-over simulations:

- chemical (increase in conductivity using NaCl/NaOH)
- physical (increase vapor demand)

Threshold conductivity observed: 7 000- 8 000 µs/cm

Tannins were effective at a level of **8 ppm** in preventing carryover at the moment of injection as well as after ~20 hours of operation, and beyond conductivities of 10 000 μ s/cm.



Pilot scale boiler



Keypoint 3: Proposed Mechanism of Tannin-Antifoam Action

Two hypotheses:

- 1. The tannate anion is a β -type anion and its presence prevents the inhibition of coalescence due to the α -type anions.
- 2. Tannins form particles of the right size and hydrophobicity. Experiments indicate that the antifoam action of tannins manifests itself clearly only in the presence of Ca²⁺ or Mg²⁺ ions, with which they form insoluble complexes.



Possible mechanism of antifoam action of a soft calcium tannate particle illustrated in (a) or (d)

From: Bergeron, V. and P. Walstra (2005). 7 - Foams. Fundamentals of Interface and Colloid Science. J. Lyklema, Academic Press. 5: 7.1-7.38.



Key Point 3: Example of Savings Through Operation at High Cycles



<u>T</u>s

STEAM BOILERS WATER TREATMENT SAVINGS REVIEW 2022-08-30

CIUSSS DE L'ESTRIE - CHUS

jycloutier.csss-iugs@ssss.gouv.qc.ca

\$430,604

FLEURIMONT

Sherbrooke, Québec

Jean-Yves Cloutier

Cell.: 819-346-1110

Startup: January 4, 2009 TOTAL SAVINGS (*based on an inflation rate of 2% per year) 1 year 13 years 7 months \$27,898

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GHG (CO2 E	EQUIVALENT)	MAKE-U	P WATER	SEWER	WATER
1 year	13 years 7 months	1 year	13 years 7 months	1 year	13 years 7 months
136 t/year	1,847 t	2,395 m3/year	32,532 m3	2,732 m3/year	37,110 m3
\$17.00/t	\$21.99/t	\$0.50/m3	\$0.65/m3	\$0.50/m3	\$0.65/m3
\$2,317	\$35,763	\$1,197	\$18,476	\$1,366	\$21,084
SAME AS REMOVING FROM THE ROAD 30 MID-SIZE CARS	SAME AS REMOVING FROM THE ROAD 407 MID-SIZE CARS	SAME IN VOLUME AS 105 TANKER TRUCKS	SAME IN VOLUME AS 1,426 TANKER TRUCKS	SAME IN VOLUME AS 120 TANKER TRUCKS	SAME IN VOLUME AS 1,630 TANKER TRUCKS

FUEL (SAVINGS F	PER YEAR)		
Natural gas	71,712 m3/year	\$0.30/m3	\$21,514
SAME AS HEATING FO	OR 1 YEAR 57 RESIDENTIAL	HOUSES (1500 SQUARE	FEET)
FUEL (SAVINGS S	SINCE 13 years 7 months	s)	



FUEL (SAVINGS SINCE 11 years 2 months)					
Oil nº6	2,411,442 liter/year	\$0.68/liter	\$1,469,928		
Biomasse	16.571 t/vear	\$28.60/t	\$422,416		



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Three Key Takeaways

- 1. Carryover is a complex problem, and the technical literature can be misleading.
- 2. Understanding the behavior of bubbles in boilers brings some scientific truth to the matter.
- 3. You can dare to operate at higher cycles and save water, energy and reduce CO₂ emissions, but beware antifoams that may degrade and worsen the problem: Chose a proven chemistry.



Acknowledgements



Thank You!

Questions?

