Real-Time Overhead Water Monitoring:
Lessons from a Crude Unit Case Study

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ABSTRACT

For refineries, measuring ammonia in overhead accumulator water is no longer just an analytical safeguard; it is a direct lever for profitability, process optimization, and corrosion control. Traditional grab sampling provides only sporadic visibility into real operating conditions, often leading to conservative treatment strategies, delayed adjustments, and uncertainty about the true ammonium chloride salt-formation temperature. Because small handling delays can shift measured ammonia levels, grab sampling limits operators' ability to run the crude unit at its most economical overhead temperature.

Online process analyzers provide continuous, real-time ammonia measurements, enabling the distributed control system (DCS) to automatically calculate the temperature for ammonium chloride salt formation. With this capability, refineries can safely push the atmospheric tower overhead temperature to the lowest feasible value, unlocking meaningful economic gains. Across the industry, every degree reduction in overhead temperature can add roughly \$1 million in annual profit. Refineries that have implemented closed-loop control report improvements in reliability, energy efficiency, and corrosion mitigation alongside the economic gains.

This presentation will review the analytical requirements, implementation considerations, and control system integration strategies that enable real-time determination of salt-formation temperature. A case study from a large West Coast refinery will demonstrate how continuous online monitoring transformed overhead accumulator optimization, reduced chemical consumption, improved dosing accuracy, and delivered measurable economic benefits. The session will highlight how moving beyond traditional grab sampling enables refineries to achieve higher profitability and more robust corrosion control through process-driven operations.

INTRODUCTION

Crude unit overhead corrosion costs the U.S. refining industry billions of dollars annually in equipment failures, unplanned outages, and premature retubing. The primary culprit is ammonium chloride salt, formed when ammonia and hydrogen chloride combine in the overhead system and deposit on metal surfaces. These hygroscopic deposits absorb moisture, creating localized acid concentrations that drive corrosion rates exceeding 200 mils per year on carbon steel. A single crude unit retubing event can cost $15-30 million and require weeks of lost production (1).

Figure 1 illustrates where this corrosion occurs within the refinery process flow. The crude distillation unit separates incoming crude oil into valuable product streams, but the overhead system, where vapors condense and accumulate, becomes the battleground between economic optimization and corrosion control. Operators face a difficult choice: run the overhead system hot to prevent salt formation, sacrificing product recovery and wasting energy, or run cool to maximize economic performance while risking accelerated corrosion damage.

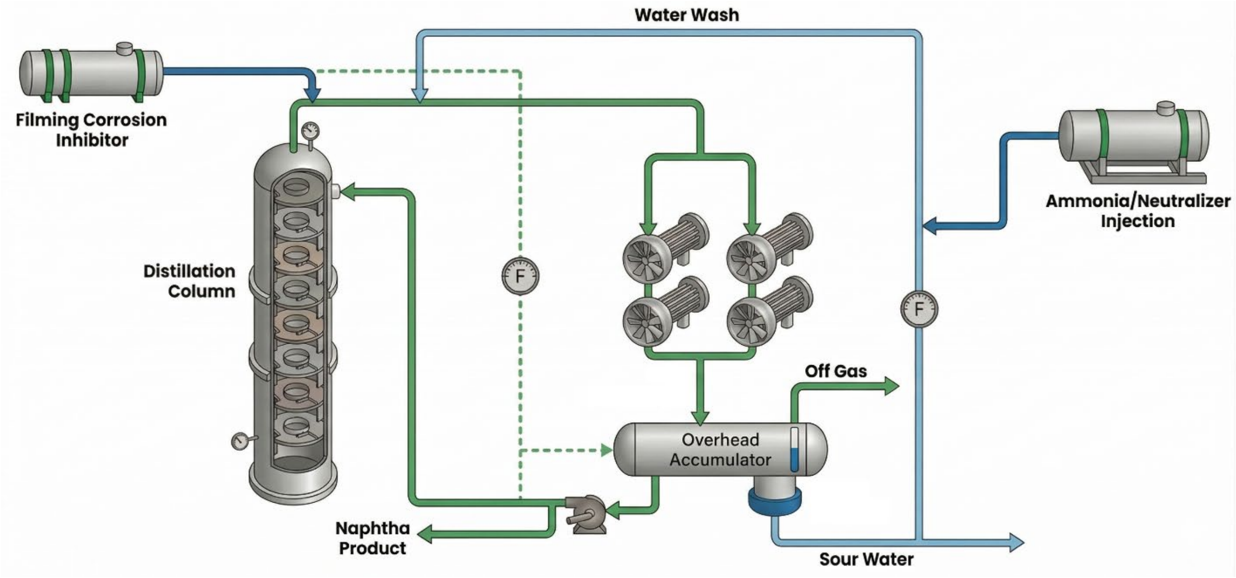


FIGURE 1. TYPICAL OVERHEAD CRUDE LAYOUT HIGHLIGHTING THE CRUDE DISTILLATION UNIT AND ITS OVERHEAD SYSTEM, WHERE AMMONIUM CHLORIDE SALT DEPOSITION AND CORROSION CAN OCCUR.

Ammonia plays a dual role in this system. Refineries intentionally inject ammonia-based neutralizers to control pH and prevent acidic corrosion from hydrogen chloride formed during crude oil desalting and distillation. However, excessive ammonia creates the precursor for salt formation. The optimal operating window is narrow, dynamic, and invisible to operators relying on periodic grab sampling that provides results hours after collection.

This uncertainty forces conservative operating strategies. Refineries maintain large safety margins, often 15-25°F above the calculated salt formation temperature, to compensate for what they cannot see between grab samples. These margins protect against corrosion but sacrifice substantial economic value. For a large crude unit, each degree of overhead temperature reduction is worth approximately $1 million per year in increased liquid recovery and reduced energy consumption.

The solution lies in continuous online monitoring. Real-time measurement of ammonia, chloride, pH, and iron concentrations provides operators with the visibility needed to optimize overhead temperature while maintaining corrosion protection. This paper presents a case study from a large West Coast refinery demonstrating how process analyzers transformed overhead operations, enabled a 20°F temperature reduction, and delivered measurable economic benefits while improving reliability and corrosion control.

THE CHEMISTRY OF OVERHEAD CORROSION

The reaction between ammonia and hydrogen chloride follows a straightforward equilibrium:

$NH_3\,(g) + HCl\,(g) \rightleftharpoons NH_4Cl\,(s)$

At high temperatures, this equilibrium favors the gaseous reactants. As the temperature decreases, the equilibrium shifts toward the solid salt. The temperature at which solid ammonium chloride first begins to form, known as the salt point or ionic dew point, depends primarily on the partial pressures of ammonia and hydrogen chloride in the vapor phase. Higher concentrations of either gas raise the salt point, meaning salt can form at higher temperatures. Lower concentrations lower the salt point, allowing the overhead system to operate at a cooler temperature without risk.

Figure 2 illustrates this relationship. The curved boundary represents the salt formation temperature as a function of amine and HCl partial pressures. Above the curve, ammonia and hydrogen chloride remain as separate vapor species. Below the curve, solid salt forms. The vertical distance between the operating temperature and the salt formation curve, shown as Salt +ΔT, represents the safety margin that protects the system from deposition.

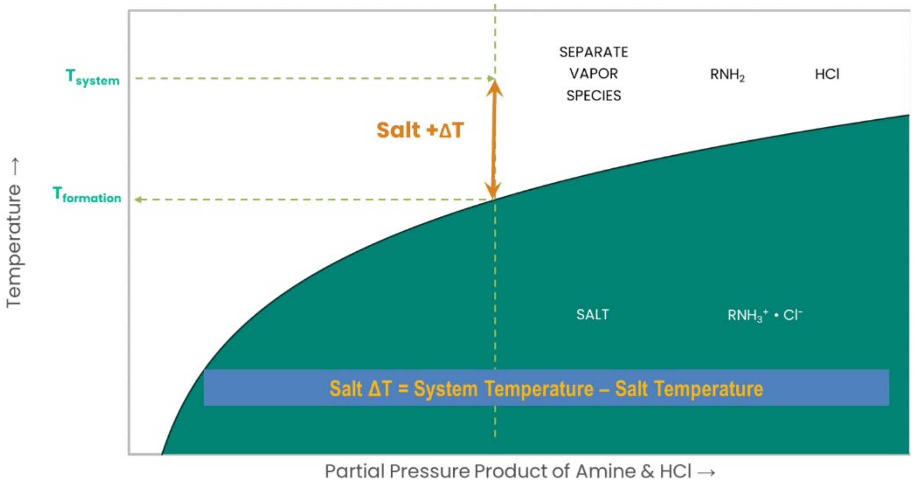


FIGURE 2. SALT FORMATION CURVE SHOWING THE RELATIONSHIP BETWEEN PARTIAL PRESSURE, TEMPERATURE, AND THE OPERATING MARGIN (SALT ΔT).

This relationship creates both the problem and the opportunity in overhead corrosion control. If operators know the exact salt formation temperature at any given moment, they can set the overhead temperature just high enough to prevent deposition while maximizing the economic benefit of lower operating temperatures. The difficulty lies in accurately and continuously determining the salt point.

When conditions shift and the operating temperature falls below the salt formation curve, the consequences are severe. Figure 3 shows this scenario: as the system enters the salt-formation zone (negative ΔT), hygroscopic salt deposits form on metal surfaces. These deposits absorb moisture and create localized pockets of hydrochloric acid, driving corrosion rates of 50 to 200 mils per year on mild steel.

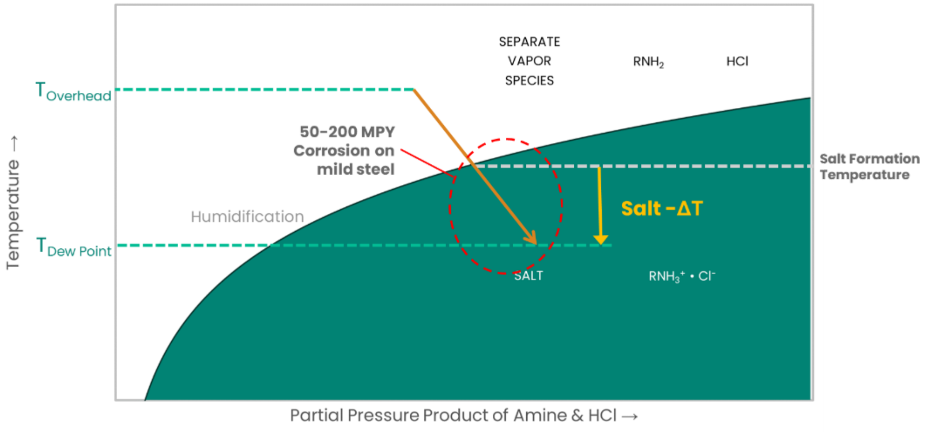


FIGURE 3. SALT FORMATION AND CORROSION RISK WHEN OPERATING TEMPERATURE FALLS BELOW THE SALT POINT (NEGATIVE ΔT).

Industry practice addresses this uncertainty through conservative safety margins. Refineries typically maintain overhead temperatures at least 25°F above the calculated salt point under normal conditions. This buffer provides protection, but also represents the cost of uncertainty. As an example, if a refinery operated with a 40°F margin when a 25°F margin would suffice, they are leaving money on the table with every barrel processed. The challenge is that without continuous visibility into actual salt point conditions, refineries cannot determine the true minimum safe margin.

ONLINE AMMONIA MONITORING TECHNOLOGY

Without continuous visibility into ammonia levels, refineries cannot determine the true minimum safe margin. Grab sampling provides sporadic snapshots that may not capture the true state of the overhead system. Sample handling introduces errors, analytical delays obscure real-time conditions, and by the time a result arrives in the control room, conditions could have changed.

Online process analyzers, such as the 2060 TI Ex Process Analyzer (Figure 5), address this challenge. Rather than collecting grab samples and transporting them to a laboratory, these analyzers continuously sample from the overhead system and measure the ammonia and iron concentrations simultaneously. This shift from periodic to continuous measurement transforms overhead corrosion control from a reactive, conservative practice into a proactive, data-driven operation.

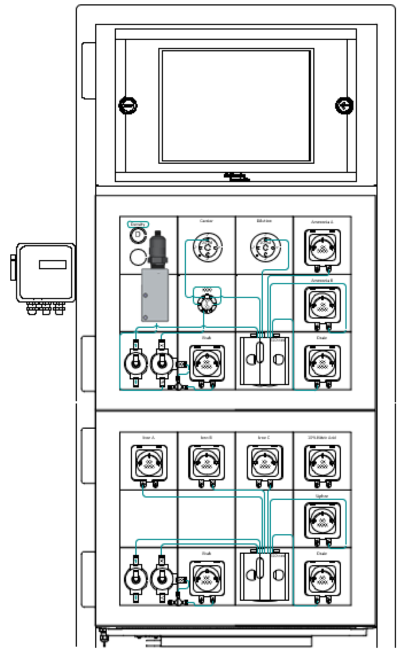


FIGURE 6. 2060 TI EX PROCESS ANALYZER FOR ONLINE AMMONIA AND IRON PHOTOMETRIC MEASUREMENTS IN OVERHEAD ACCUMULATOR WATER.

Photometric analysis provides a reliable foundation for continuous measurements of ammonia and iron in overhead accumulator water. The sample matrix contains dissolved hydrocarbons, emulsified oils, suspended solids, and varying salt concentrations that can interfere with electrode-based methods. Ion-selective electrodes (ISE), while suitable for clean aqueous samples, are susceptible to fouling and interference from organic compounds commonly present in overhead systems. Photometric methods isolate the target analyte through reactions specific to ammonia or iron, minimizing matrix effects and providing the accuracy, selectivity, and response time needed for real-time monitoring in refineries.

The Berthelot method determines ammonia concentration through a colorimetric reaction. Ammonia in the sample reacts with hypochlorite and phenol in the presence of a nitroprusside catalyst to form indophenol blue, a stable-colored compound. The intensity of the blue color, measured at 610 nm, is directly proportional to ammonia concentration. The reaction is highly selective for ammonia and performs reliably across the concentration range typically encountered in overhead water, from tens of ppm to several thousand ppm.

The TPTZ (2,4,6-tripyridyl-s-triazine) method measures dissolved iron at the sub-ppm to low-ppm levels typically encountered in overhead water during normal operation. TPTZ reacts with ferrous iron to form a blue-purple complex that absorbs strongly at 590 nm. Iron in overhead water originates from corrosion of upstream piping and equipment. Rising iron levels indicate metal loss, whether from acid attack, salt deposition, or velocity-accelerated corrosion.

While ammonia measurement enables predictive control of the salt-formation temperature, iron trending shows whether that control strategy is protecting the system. Together, these two measurements provide operators with leading and lagging indicators of overhead corrosion risk.

ANALYZER OPERATION AND MAINTENANCE

An online analyzer delivers on its ROI only if it operates reliably without constant operator intervention. The analyzer is part of a complete system that includes sample conditioning equipment, the analyzer itself, reagents, and a data communication pathway. Each component plays a role, and understanding how they work together is essential for a successful installation.

The sample system is the foundation, and getting it right during installation prevents most of the problems encountered in service. Industry studies have shown that up to 80% of analyzer issues stem from sampling system design rather than the analyzer itself (2). The sample take-off point should be located at the overhead accumulator liquid outlet or condensate line slipstream. A fast-loop configuration, where process fluid continuously circulates past the analyzer sample tap and returns to the process, is strongly preferred over dead-end arrangements that require lengthy purge cycles before each measurement. Sample conditioning must include cooling when the overhead water temperature exceeds the analyzer's limits and filtration to protect the optical cell from fouling. Locating the grab sample point on the same line as the analyzer prevents discrepancies between online and laboratory results that undermine operator confidence.

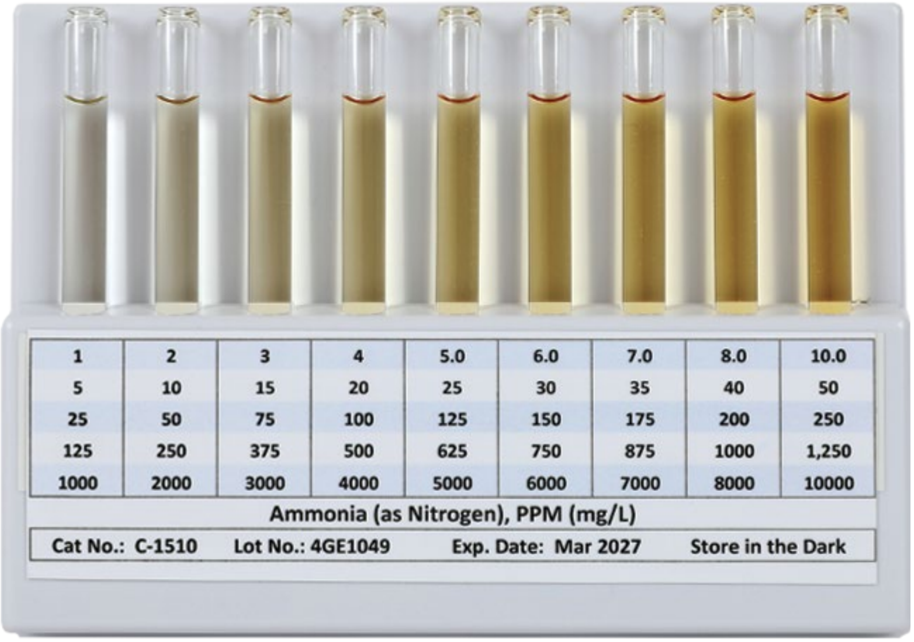
Process analyzers maintain accuracy through automatic compensation and intelligent sample validation. An integrated density meter continuously monitors the incoming sample stream and skips analysis cycles when the sample becomes oil-rich rather than water-phase, protecting the optical cell from hydrocarbon contamination. Reagent blanking continuously corrects for hypochlorite degradation, maintaining measurement accuracy between reagent changes. In the Berthelot method, hypochlorite serves as a key reagent in the colorimetric reaction with ammonia. Hypochlorite is inherently unstable and degrades over time due to temperature, light exposure, and contact with trace contaminants. Reagent blanking compensates for this by periodically measuring the reagent baseline without sample present and applying a correction factor to each analysis cycle, ensuring that changes in reagent strength do not introduce systematic error into ammonia results. Automatic calibration routines use known standards to preserve precision over weeks of operation. Reagent level sensors alert operators before supplies run low, and self-diagnostic functions monitor system health, allowing the analyzer to operate unattended while delivering consistent results.

Utility requirements include instrument air, electrical power, and a waste drain. Instrument air maintains positive cabinet pressure, preventing corrosive vapors from reaching electrical components. The IP66-rated cabinet enables outdoor installation without climate-controlled enclosures. Communication uses standard 4-20 mA signals or Modbus for straightforward DCS integration. Most systems operate 30 days or more between reagent changes, minimizing routine maintenance requirements.

IMPLEMENTATION CASE STUDY

The large West Coast refinery operates two crude distillation units. Each unit operates under different constraints, creating distinct overhead chemistry profiles. This variability means that a single monitoring approach or fixed operating procedure cannot adequately address the risk of overhead corrosion, even within the same refinery.

Prior to implementing online monitoring, operations relied on grab samples to measure ammonia levels. Figure 7 shows an ammonia comparator (Nesslerization) color comparison chart used by operators during grab sampling. Each tube represents a known ammonia concentration, from clear (low ammonia) through progressively darker yellow to deep gold (high ammonia). Operators visually match their sample against the standard colors to estimate ammonia content. This simple, familiar method has been used in refineries for decades. However, it has significant limitations, including subjective visual estimation, accuracy that depends on lighting and operator experience, and a delay from collection to analysis.



1	2	3	4	5.0	6.0	7.0	8.0	10.0
5	10	15	20	25	30	35	40	50
25	50	75	100	125	150	175	200	250
125	250	375	500	625	750	875	1000	1,250
1000	2000	3000	4000	5000	6000	7000	8000	10000

Ammonia (as Nitrogen), PPM (mg/L)

Cat No.: C-1510 Lot No.: 4GE1049 Exp. Date: Mar 2027 Store in the Dark

FIGURE 7. OPERATOR AMMONIA TEST USING AN AMMONIA COMPARATOR (NESSLERIZATION) COLOR COMPARISON CHART, SHOWING RANGE FROM CLEAR (LOW AMMONIA) TO GOLD (HIGH AMMONIA) (3).

In 2025, the large West Coast refinery installed process analyzers on both crude units to enable continuous monitoring of overhead water. The 2045 TI Ex Process Analyzer was selected for its hazardous area certification, outdoor installation capability, and proven performance in refinery service. Figure 8 shows the installed analyzer, mounted adjacent to the overhead accumulator, with sample conditioning equipment visible in the foreground. The installation provides continuous ammonia and iron measurements that feed directly into the DCS for real-time salt point calculation and temperature control.

FIGURE 8. 2045 TI EX PROCESS ANALYZER INSTALLATION AT A LARGE WEST COAST REFINERY.

ANALYZER VALIDATION AND PERFORMANCE

Before transitioning to automated control, the analyzer's performance was validated through calibration verification and comparison with laboratory grab sample results. This validation period established operator confidence in the continuous measurement data and confirmed the analyzer's accuracy under actual refinery operating conditions.

Calibration verification demonstrates the analyzer's ability to maintain accuracy over the full measurement range. Figures 9 and 10 show the ammonia and iron calibration curves with an R^2 of 0.9974 and 0.9997, respectively. These calibration curves demonstrate excellent linearity across the range encountered during normal operation for these analytes.

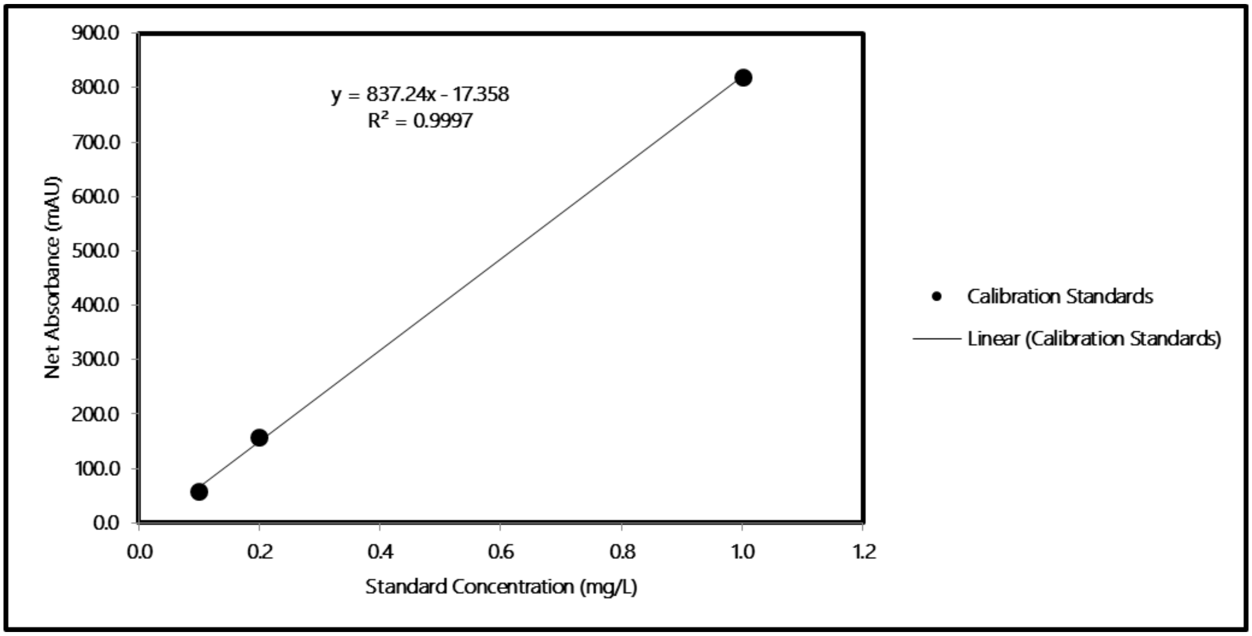


FIGURE 9. IRON CALIBRATION CURVE DEMONSTRATING LINEARITY (R^2 = 0.9997) ACROSS THE MEASUREMENT RANGE.

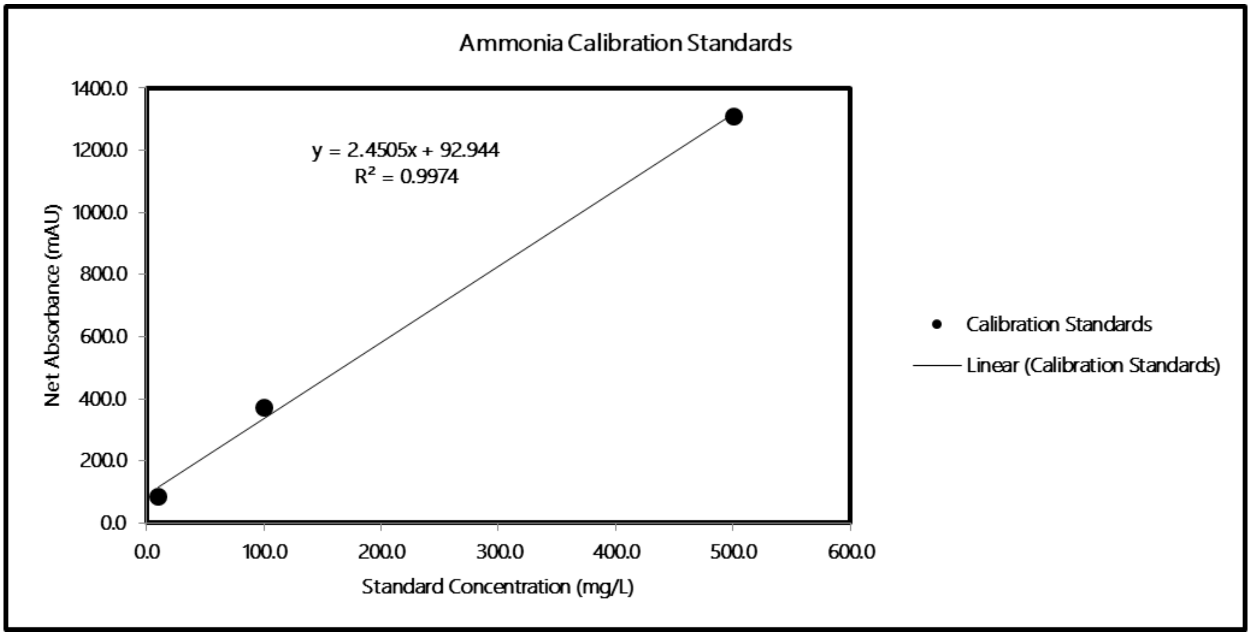


FIGURE 10. AMMONIA CALIBRATION CURVE DEMONSTRATING LINEARITY (R^2 = 0.9974) ACROSS THE MEASUREMENT RANGE.

Repeatability data from standard analysis confirms the analyzer maintains consistent performance between calibration events, supporting the extended maintenance intervals that reduce operational burden. Table 1 summarizes precision metrics from twelve consecutive replicate measurements of calibration standards.

TABLE 1. ANALYZER PRECISION DATA FROM REPLICATE STANDARD ANALYSIS (n=12)

Replicate	**Ammonia Standard (100 mg/L)**	**Iron Standard (0.50 mg/L)**
1	74	0.48
2	75	0.49
3	75	0.50
4	77	0.50
5	76	0.50
6	75	0.50
7	80	0.50
8	80	0.50
9	75	0.50
10	75	0.50
11	74	0.50
12	75	0.51
Mean	75	0.50
Std. Dev.	**2.07**	**0.01**
%RSSD	**2.72%**	**1.44%**
%Recovery	**75.92%**	**99.67%**

The iron method achieves measurement precision of 1.44% RSD and near-perfect recovery. The ammonia method demonstrates 2.72% RSD with 75.92% recovery. The lower ammonia recovery reflects the volatility of ammonia in aqueous standards rather than measurement error. This is a well-understood characteristic of ammonia analysis that does not affect the method's ability to accurately track relative changes in process samples.

Comparison of online analyzer data with laboratory grab-sample analysis validated measurement accuracy in the actual process matrix. Figure 11 shows a correlation between analyzer readings and grab-sample results over an extended period of operation.

FIGURE 11. CONTINUOUS ANALYZER DATA (BLUE) COMPARED TO LABORATORY GRAB SAMPLE RESULTS (RED OVERLAY), SHOWING PROCESS VARIATIONS INVISIBLE TO PERIODIC SAMPLING.

The red overlay represents grab sample values, while the blue trace shows continuous analyzer measurements. The analyzer tracks process variations that grab sampling cannot capture, revealing the dynamic nature of overhead ammonia levels that periodic sampling misses entirely. During periods when grab samples were collected, the analyzer and laboratory results were closely aligned, confirming measurement accuracy. More importantly, the continuous data reveals significant short-term variations between grab sample points. These variations would remain invisible to operators relying solely on periodic laboratory analysis. This visibility into real-time process dynamics became the foundation for implementing closed-loop control.

CONTROL SYSTEM INTEGRATION

The installation of online ammonia analyzers on both crude units fundamentally changed overhead operations. With continuous measurements feeding the DCS, the refinery gained real-time visibility into overhead chemistry that was impossible with periodic grab sampling.

Figure 12 shows a typical DCS trend display with all four analyzer measurements: ammonia (blue), chloride (yellow), pH (purple), and iron (cyan). The analyzer provides continuous pH measurements, chloride measurements every 5 minutes, ammonia measurements every 15 minutes, and iron measurements every hour. This multi-parameter monitoring reveals the dynamic interactions between overhead chemistry variables. When pH declines, operators can observe the corresponding ammonia response. When chloride levels shift, the impact on the risk of salt formation becomes immediately visible. Iron trending provides continuous feedback on corrosion activity.

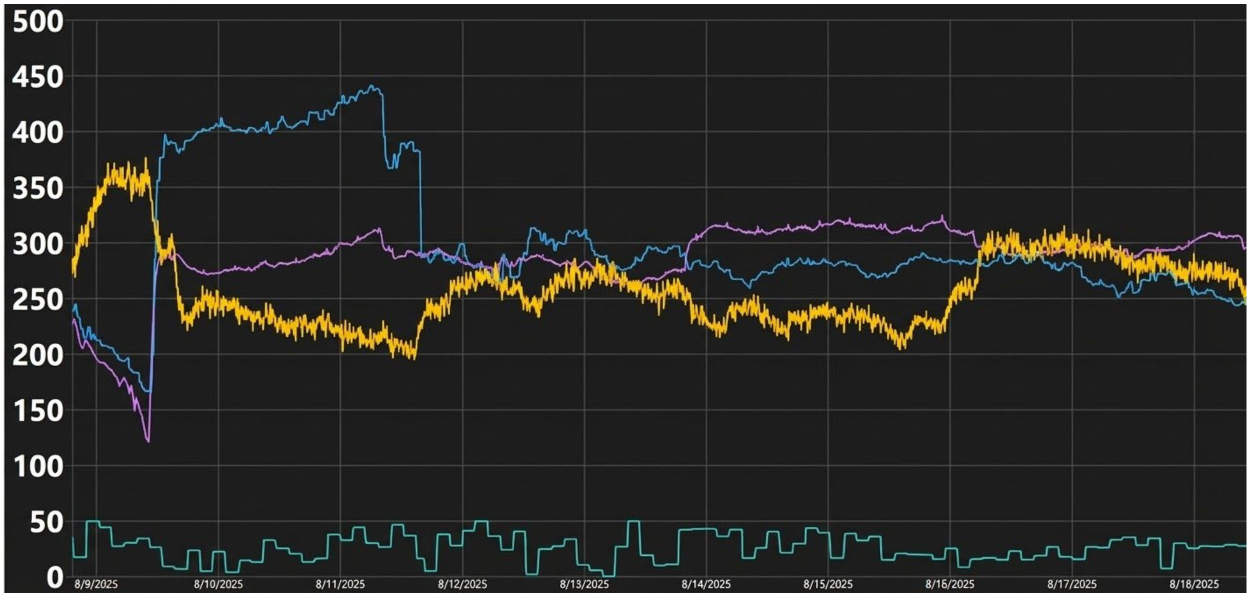


FIGURE 12. DCS TREND DISPLAY SHOWING CONTINUOUS MULTI-PARAMETER MONITORING: AMMONIA (BLUE), CHLORIDE (YELLOW), PH (PURPLE), AND IRON (CYAN). MEASUREMENT FREQUENCIES RANGE FROM CONTINUOUS PH MONITORING TO HOURLY IRON ANALYSIS.

The analyzer transmits all measurements to the DCS via standard 4-20 mA signals, and the DCS treats these values as standard process variables for trending, alarming, and control logic. With continuous visibility into overhead chemistry, the refinery implemented automated neutralizer dosing control based on real-time pH and ammonia measurements. Override controls revert to safe dosing rates if the analyzer fails. Today, both crude units operate with automated neutralizer dosing based on continuous analyzer data, maintaining optimal overhead chemistry through crude slate changes and process variability.

RESULTS AND BENEFITS

The implementation of online ammonia monitoring at a large West Coast refinery delivered measurable operational and economic improvements. The most significant achievement was optimizing overhead temperature while maintaining reliable corrosion protection.

With real-time visibility into overhead chemistry, operations could reduce ammonia injection rates and safely lower the overhead temperature by 20°F. This temperature reduction was achieved while maintaining the minimum 25°F margin above the salt formation temperature, demonstrating that conservative operating practices based on intermittent sampling were leaving substantial economic value unrealized.

Industry experience indicates that each degree of overhead temperature reduction is worth approximately $1 million per year in additional product recovery and reduced energy consumption for a large crude unit. The exact benefit depends on crude slate, product pricing, and operating conditions, but the direction is clear: tighter control of overhead chemistry enables refineries to operate closer to thermodynamic limits and capture economic value that traditional monitoring cannot access.

Beyond temperature optimization, reduced ammonia consumption lowered chemical costs and minimized the risk of corrosion from overtreatment. Continuous iron monitoring provided ongoing feedback on corrosion activity, allowing operators to verify that process changes maintained system integrity. Because iron accumulates in the overhead water as metal loss occurs over time, concentration trends reflect cumulative corrosion history rather than instantaneous process changes. A gradual decline in iron following process adjustments confirms that the control strategy is working, even if the response unfolds over days or weeks rather than hours. The overhead units no longer operate with the uncertainty in grab samples. Conditions are continuously visible, and the control system responds to chemistry changes in minutes rather than hours.

CONCLUSION

The crude unit overhead system presents a fundamental tension between corrosion protection and operating efficiency. Running hot prevents salt formation but sacrifices product recovery and wastes energy. Running cool maximizes economic performance but risks the consequences of uncontrolled corrosion. The key to resolving this is accurate, timely knowledge of overhead chemistry.

The experience at the large West Coast refinery demonstrates that continuous online monitoring transforms overhead corrosion control from a reactive, conservative practice into a proactive, data-driven operation. The ability to reduce overhead temperature by 20°F while maintaining reliable corrosion protection validates the economic case for real-time monitoring. Automated neutralizer dosing based on continuous pH and ammonia measurements eliminates the guesswork inherent in grab sampling, allowing operators to run closer to optimal conditions with confidence.

For refineries still relying on periodic grab samples and manual overhead management, the opportunity is clear. Technology exists to continuously monitor overhead chemistry and enable tighter process control. The economic benefits are substantial. The question is not whether to pursue real-time overhead monitoring, but when to begin.

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