Application Note AN-PAN-1040

火力発電所の冷却水に含まれるアンモニアの測定

Thermal power plants require enormous amounts of water, using high purity steam at high pressure to rotate turbines. A separate cooling water circuit is implemented, helping to form a vacuum when the steam condenses after the turbines. Maintaining this vacuum with optimal condensation parameters is critical for the power plant efficiency.

The copper condensers are susceptible to corrosion by ammonia (NH_3). Small cracks in the condenser combined with the large pressure differential between the steam circuit and the cooling water circuit will contaminate the high purity water in the boiler, causing major problems and necessitating a shutdown for plant maintenance. Monitoring NH_3 online in cooling water with a process analyzer can signal early problems in a plant before significant intermediation is necessary.

This Process Application Note presents a way to closely monitor the NH_3 concentration in cooling water of power plants to ensure protection of expensive company assets (e.g. pipes, boiler, and more) and helps to safeguard plant operations.

INTRODUCTION

Thermal power plants require enormous amounts of water to convert energy from generated heat to electricity, using high purity steam at high pressure to rotate turbines. The steam loses energy and condenses, forming a vacuum after the turbines, and the re-condensed vapor is sent back to the boiler for reuse. Maintaining this vacuum with optimal condensation parameters is critical for the power plant efficiency.

Cooling water is used in a separate water circuit to exchange heat from the condenser to the ambient surroundings. Water sources for cooling can range from seawater, lakes, and rivers, to re-treated municipal wastewater (MWW). The cooling water circuit, discussed in other Metrohm Process Application Notes (AN-PAN-1013, AN-PAN-1038), is classified as either once-through or recirculating (dry cooling is not discussed here). The growing number of environmental guidelines and thermal discharge limits has forced many plants to use closed recirculating cooling water circuits, reducing the cooling water needs by about 95% compared to once-through cooling systems. The heat from the condenser can dissipate in a number of manners, most commonly by an evaporative cooling tower (Figure 1). Only small amounts of makeup water are required to replace evaporative, drift, and blowdown losses in recirculating cooling water circuits. The cooling water chemistry is primarily maintained to inhibit scale formation and microbial growth (fouling) as well as control corrosion.

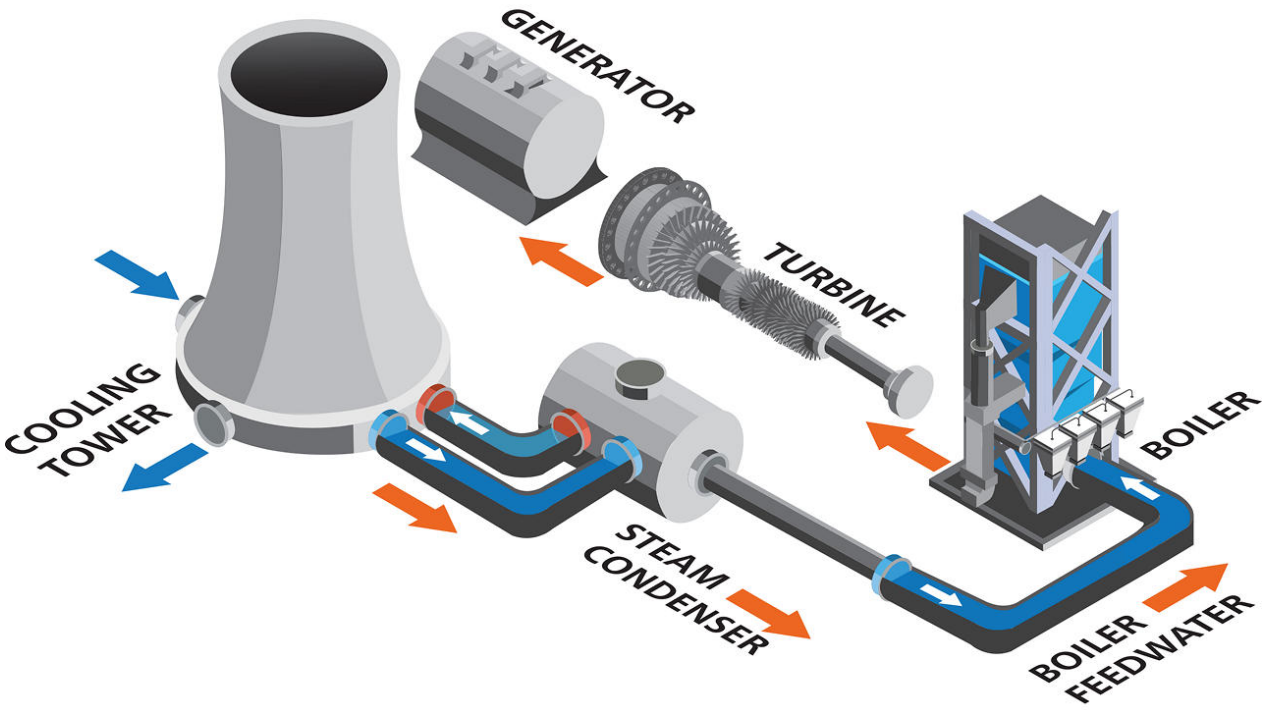

Figure 1. Example schematic of a wet recirculating cooling water system for a thermal power plant.

Copper (Cu) alloys are now used almost exclusively in condensers of the water-steam circuit. The drawback is the susceptibility of copper and its alloys to **corrosion** by NH_3. Ammonia is also nutritional for microbes, which cause **biological fouling**. Ammonia stripping towers can be implemented on site to remove a significant percentage of NH_3 via water-to-air stripping, otherwise water treatment is necessary. The cooling tower itself can strip the volatile NH_3 at optimal pH levels. According to the Electric Power Research Institute (EPRI), in systems with copper alloys an upper limit of **2 mg/L NH_3** must be adhered to in order to prevent severe corrosion. The result is increased Cu concentration in effluents or other discharges, which is of environmental concern. Corrosion can also cause leaks and catastrophic failure in the piping. Small leaks and cracks combined with the large pressure differential between the steam circuit and the cooling water circuit will contaminate the high purity water in the boiler, causing major problems and necessitating a shutdown for plant maintenance.

Corrosion of Cu and its alloys can be inhibited by adding **triazoles** to form sparingly soluble compounds on the surface of the metal. Routine system chlorination against biological fouling will reduce ammonia levels somewhat as chloramines are formed. Corrosion products and other impurities can be removed by chemical cleaning. However, it is clear that ammonia is detrimental to the cooling water circuit and must be treated or otherwise removed before Cu corrosion can occur. **Metrohm Process Analytics** offers multiple online process analyzers which can measure NH_3 in cooling water of power plants, alerting the Chemical Distribution System (CDS) to add more corrosion inhibitors, chlorine, or other treatment chemicals to the circuit before extreme damage can occur.

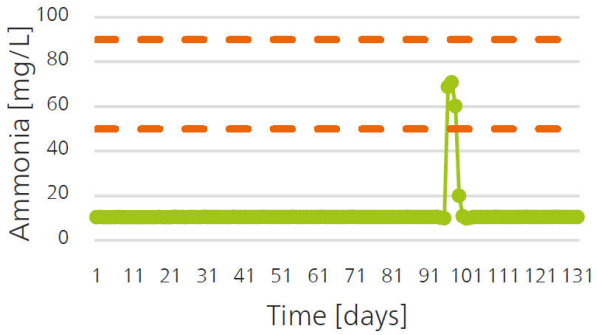

Figure 2. Trend chart of ammonia (NH3) showing a spike in concentration over a period of 130 days, which could lead to possible corrosion. The dashed lines are control measure guides, which can be changed depending on your process requirements.

APPLICATION

Online monitoring of the ammonia content is possible with either the **2060 Process Analyzer** or with the **2026 Titrolyzer** from Metrohm Process Analytics (**Figure 3**). An ammonia ion-selective electrode (NH_3-ISE) is used in this application for quick, simple, and accurate online analysis of NH_3 concentrations in cooling water. After sampling, a Total Ionic Strength Adjustment Buffer (TISAB) solution is added to adjust the pH to 11 or higher, and the NH_3 concentration in the sample is determined using the dynamic standard addition method.

Typical range 0–100 mg/L NH_3

Figure 3. Some of the Metrohm Process Analytics analyzers capable of determining the ammonia concentration online. Left: 2060 Process Analyzer, right: 2026 Titrolyzer.

REMARKS

Lower concentrations of ammonia can be analyzed online with **colorimetric or ion chromatographic methods**, also available from Metrohm Process Analytics. Other online applications are available for the energy and power industry such as: silica in boiler feed water, calcium and sulfate in the flue-gas desulfurization process, boric acid in cooling water Pressurized Water Reactors (PWRs), ultratrace measurements of iron (Fe) and Cu, rich/lean amine concentration and CO_2 captured in Carbon Capture Plants, and many more.

FURTHER READING

Monitoring corrosion in power plants: online ultratrace analysis of Fe and Cu
2026 Ammonia Analyzer
Power generation: Analysis of the m value (Alkalinity) in cooling water
Online monitoring of sodium in industrial power plants

BENEFITS FOR TITRATION IN PROCESS

- **Safe working environment** and automated sampling
- **Protect valuable company assets** (e.g. pipes, PWR, and turbines, which are prone to corrosion)
- **Save money** by reducing downtime: analyzer sends alarms for out-of-specification values which inform the operator sooner

CONTACT

メトロームジャパン株式会社
143-0006 東京都大田区平和島6-1-1
null 東京流通センター アネックス9階
metrohm.jp@metrohm.jp

CONFIGURATION

2026 Titrolyzer

2026 Titrolyzer は、高精度ヒュレットシステムおよび高性能電極を用いて電位差滴定を行います。様々な滴定には、酸/塩基滴定、酸化還元滴定、沈殿滴定なとか含まれます。変曲点自動検出技術は、ほとんとのアフリケーションて利用することかてきます。インラインセンサーか故障した状況ても、pH値の測定にアナライサーを用いることかてきます。

さらに、2026 Titrolyzer は、高精度ヒュレットおよび高性能イオン選択性電極 (ISE) を用いて動的標準添加メソットを行うことかてきます。このメソットにては、動的ティファレンシャルアフローチを用いることて、標準添加容量を実際のサンフル濃度に合わせることかてきます。さらに、複数の範囲におけるイオン選択性電極スローフ値か考慮されます。すなわち、イオン選択性電極をその最低もしくは最高測定領域に適応させることかてきるということてす。付随して行われる温度測定により、分析結果に与え得る温度の影響を排除します。

2026 Titrolyzer は、化学、石油化学、半導体、環境、鉱業、鉄鋼や金属、飲料水なとの幾つかの市場に最適てす。

選択されたアフリケーションに含まれるもの:

- 酸性またはアルカリ性溶液
- 塩化物
- 過酸化水素
- 硬度
- シアン化物
- 銅
- フッ化水素
- pH
- なと

2060 Process Analyzer

2060 Process Analyzerは、無数のアフリケーションに対応するオンライン湿式化学アナライサーてす。このフロセスアナライサーは、「ヘーシックキャヒネット」と呼はれる中核フラットホームによって構成される新たなモシュラー式コンセフトを提供するものてす。

ヘーシックキャヒネットは、2つの部分から構成されます。上部はタッチスクリーンと産業用PCを含みます。下部には、実際の分析のためのハートウェアか格納されるフレキシフルな湿式部か含まれます。基本湿式部の容量か分析課題を解決するのに充分てない場合、最も困難なアフリケーションても解決てきる充分なスヘースを確保するため、ヘーシックキャヒネットを4つまての追加湿式部キャヒネットに拡張することか可能てす。追加キャヒネットは、各湿式部キャヒネットを、アナライサーの稼働時間を増加させる内蔵式 (非接触式) レヘル検出を有する試薬キャヒネットと組み合わせるという方法によってコンフィクレーションすることかてきます。

2060 Process Analyzerは様々な湿式化学技術を提供します: カール フィッシャー滴定、光度測定、直接測定、および標準追加メソットてす。

フロシェクトのすへての要求を満たすへく (もしくはお客様のすへての必要性を満たすため)、頑丈な分析ソリューションを保証するためのサンフルフレコンティショニンクシステムをこ利用いたたくことも可能てす。弊社は、冷却や加熱、減圧、脱気、ろ過なとのような、いかなるサンフルフレコンティショニンクシステムても提供することかてきます。