



PURASPEC CLEAR

Chloride guards



Johnson Matthey
Inspiring science, enhancing life

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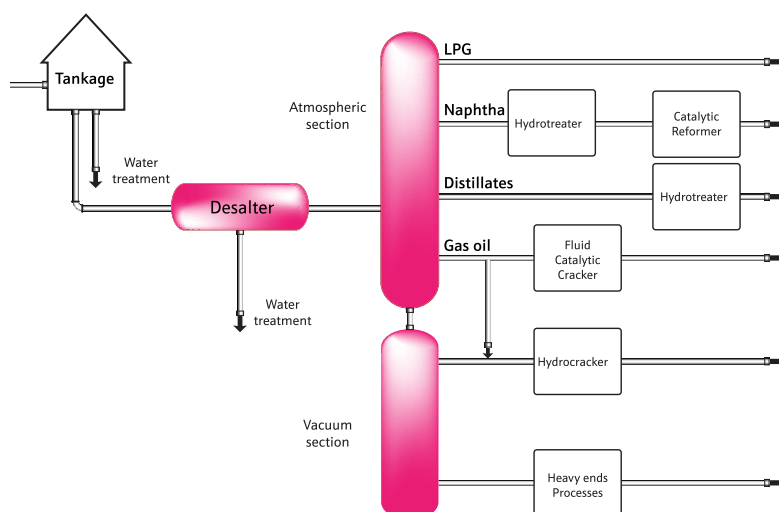
Chlorides in a refinery

Where does it come from?

Chlorides are introduced into the refinery flowsheet in several ways. Some crude sources can bring both inorganic and organic chloride content. Desalter processes and chemical additives are used to remove chlorides and prevent corrosion and fouling caused by these chlorides. The other major source is from the Catalytic Reforming Unit (CRU). This unit upgrades straight run naphtha value for use in the gasoline pool or as petrochemical feedstock. Chlorides are injected onto CRU catalyst to attenuate acid function required to provide the best naphtha property enhancement. These chlorides are not permanently held on the catalyst and progress into the product streams, which are primarily hydrogen-rich offgases, stabilized naphtha, and LPG.

Why is it important?

Chlorides have significant effect on the integrity of refinery equipment, particularly around and downstream of the CRU. This is critical on the hydrogen-rich product as it is typically used as a key hydrogen feedstock for a number of high value units around the refinery. Two major issues come from not addressing chloride content in CRU product streams: corrosion and fouling, and for RCl removal.



Corrosion

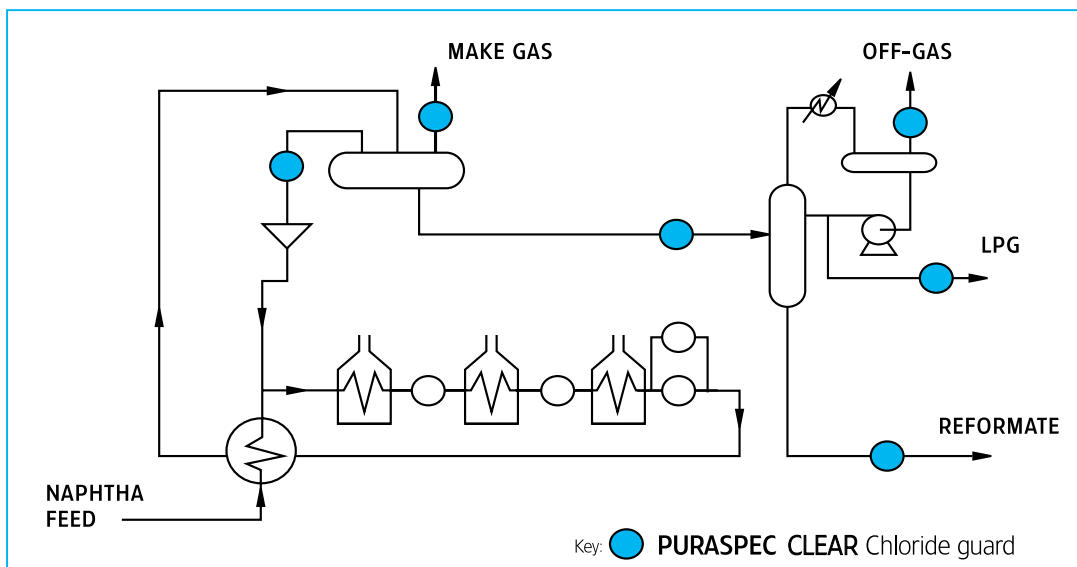
Stress corrosion cracking of stainless steel (particularly 300-series) can be an issue for downstream hydrogen users. For example, many refiners report corrosion issues within feed-effluent exchangers in hydrotreating & hydrocracking units that utilize CRU-produced hydrogen. Within the CRU, the product stabilizer tower falls victim to tray and vessel corrosion. Equipment corrosion results in the need for more frequent inspection and equipment replacement, increasing risks and costs for the refiner.

Fouling

Inorganic chloride can, in the presence of adequate ammonia, form ammonium chloride salts. These salts can cause plugging in the CRU stabilizer tower as well as in downstream hydrotreater exchangers.

Fouling will limit unit rates and cause the need for additional maintenance operations, affecting operability and profitability for a refiner.





How should refineries handle these issues?

The use of fixed-bed chloride removal media is the industry standard to protect refinery processes against the impact of chlorides from the CRU. These beds are designed to remove chloride content from process gases and liquids. Chloride guard beds are most typically installed on the naphtha (stabilized or unstabilized), LPG, offgas, and make gas streams. A variety of material options exist but a customized offering of high performance materials is necessary to truly address the issue cost-effectively and with minimal impact to operability.

What makes an effective chloride guard?

Chloride guards are specially designed to provide the maximum value to the refiner. Key characteristics for a chloride removal solution are:

- High chloride capacity
- Low/no side reaction tendency
- Optimum mass transfer characteristics
- Robust to wetting, fouling, and chloride spikes

A CLEAR solution

PURASPEC™ CLEAR™ chloride guards presents, **PERFORM™**, **ARMOR™** and **PURASIEVE™**, a suite of customized solutions to maximize value for the refiner.

Johnson Matthey's **PURASPEC CLEAR** product line is:

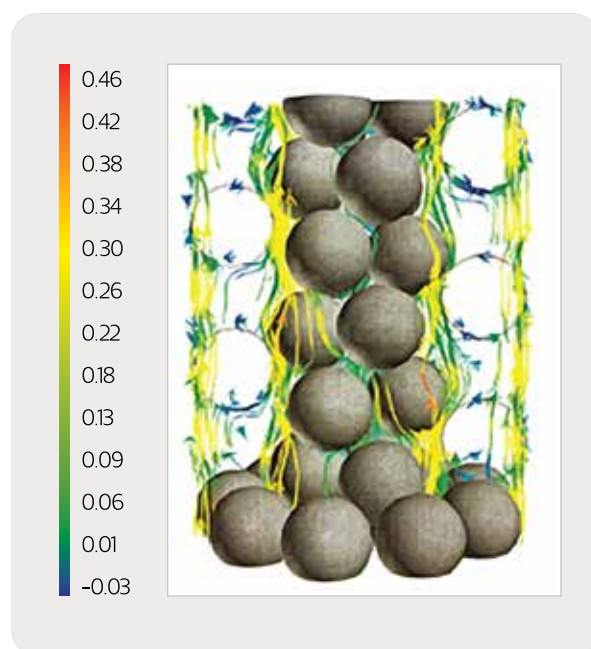
- Diverse to offer specialized product solutions based on the specific operation.
- Technically superior to deliver the highest chloride capacity in the market.
- Cost-effective to minimize budgetary impact and life cycle cost.
- Engineered to eliminate costly impacts of organic chlorides or green oil formation.
- Robust to difficult applications (hydrocarbon fouling, liquid entrainment).



CLEAR PERFORM

Bimetallic chemical absorbents

Products in the best-selling **PERFORM** line contain two active metal phases to provide maximum functionality for HCl and RCl removal. For typical catalytic reforming units, which have total chloride content <10 ppmv, this product can effectively remove both HCl and RCl completely and provide the longest run lengths achievable in the industry. They are best formulated to eliminate side-reaction formation and have performed well in difficult applications.



CLEAR PERFORM case study

Make gas application

Background

A large East Asian refinery was having issues with the operational life time of their make gas chloride guard. Short bed life was proving to be a costly expense for their operation. The refinery trialled four separate brands of chloride removal materials over the course of several years in an effort to understand which material would perform best in their application.

Chloride guard performance

The catalytic reformer make gas application can be generally summarized in the below table.

Parameter	Value
Unit type	CCR
Feed	Make gas
Typical flowrate	60,525 Nm ³ /hr
Operating temperature	25–40 °C
Operating pressure	20 bara

The outlet specification given by the refinery was no more than 1 ppmv total chloride, at which point they would trial a new material. The refinery found that when **PERFORM** material was in service, the units preformed for up to four times as long as the competitor products.

Based on the bed lives achieved with the tested materials, the refinery decided to load **PERFORM** material due to its superior lifetime performance. The subsequent **PERFORM** material loading surpassed the performance of the first test, with an operational life time of 499 days. Results of the tests and subsequent install are summarized in Figure 1.

Superior total chloride removal

The chloride removal performance offered by **PERFORM** is the best in the market due to the advanced functionality of the material. Refiners around the world have seen the benefit that **PERFORM** chloride guards can offer in unit reliability and profitability. This is a function of the following features:

- Maximum active content, yielding highest total chloride removal capacity
- Optimized structure to utilize entire granule
- Robust to continuous events of hydrocarbon wetting and fouling
- Inherent acidification protection to prevent green oil and organic chloride formation

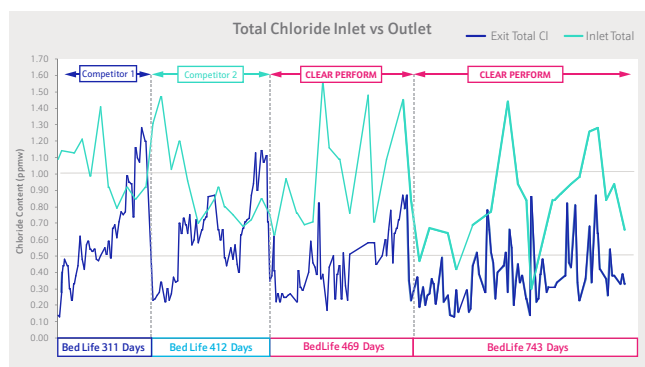


Figure 1. Total chloride inlet vs. outlet

CLEAR PERFORM case study

Stabilizer feed application

A large Asian refinery was experiencing losses in process profitability due to shortened Chloride Guard bed life and an inability to maintain a desired 0.5 ppmw exit specification. In an effort to evaluate available materials, they trialled **PERFORM** along with two competitor materials, given a maximum outlet specification of 1.0 ppmw.

Chloride guard performance

The catalytic reformer unstabilized reformat application can be summarized in the below table.

Application information	
Unit type	CCR
Feed	Unstabilized reformat
Typical flowrate	190 Nm ³ /hr
Operating temperature	35-50°C
Operating pressure	23.3 bara

All three materials tested were seen to remove HCl from the inlet stream, yet in the case of both competitor products the total outlet chloride continued to rise. **PERFORM** had maintained the desired 0.5 ppmw specification for total chloride and never reached the 1.0 ppmw that competitive materials breached within the first year (figure 2). **PERFORM** performed reliably for its entire life cycle even during periods of inlet chloride spikes.

The chloride removal performance offered by **PERFORM** liquid-phase products is the best in the market due to the advanced functionality of the material. Refiners around the world have seen the benefit that **PERFORM** chloride guards can offer in unit reliability and profitability. This is a function of the following features:

- Maximum active content yielding highest total chloride removal capacity
- Optimized size and structure to provide best mass transfer characteristics in liquid phase
- Inherent acidification protection to prevent green oil and organic chloride formation

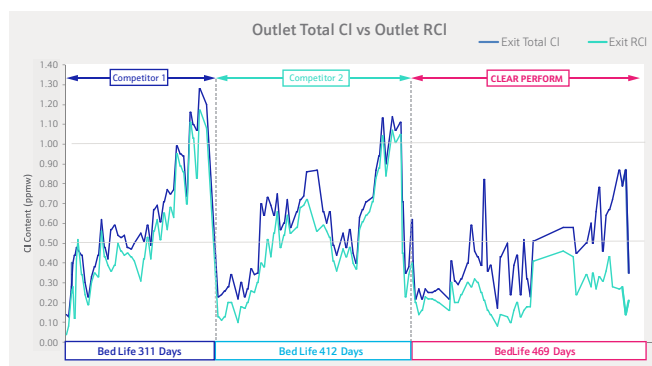
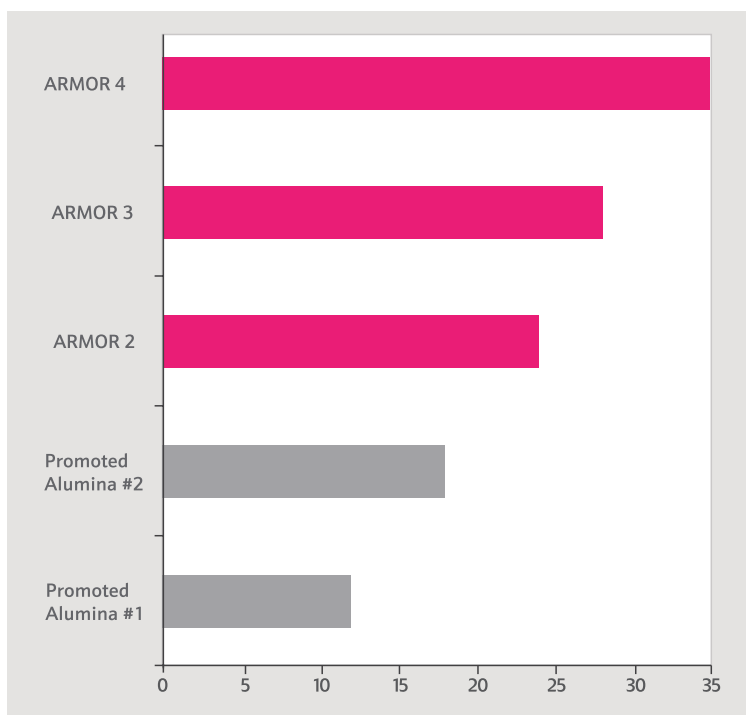


Figure 2. Outlet total chloride vs. outlet RCL

CLEAR ARMOR

Featuring Al_2O_3 -free promoted absorbents

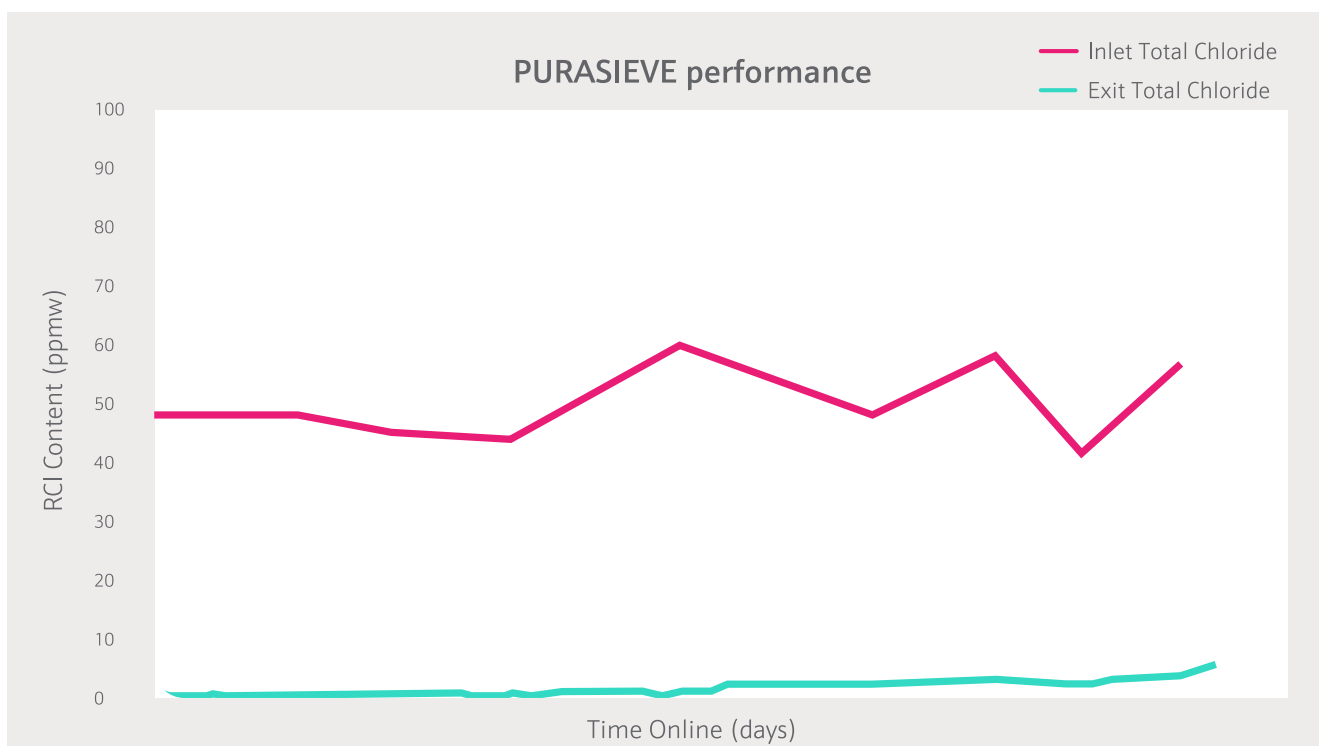
High alumina containing chloride guards, such as promoted aluminas that are pervasive in the market, have long been known as offenders for side reactions such as organic chloride formation and green oil formation. Johnson Matthey formulated products such as **ARMOR** to use a non-alumina support that has negligible acid function to best prevent detrimental side reactions in-service. These products also outperform all competitive materials for HCl removal, making them an easy choice for a full-bed or as part of an optimized solution.



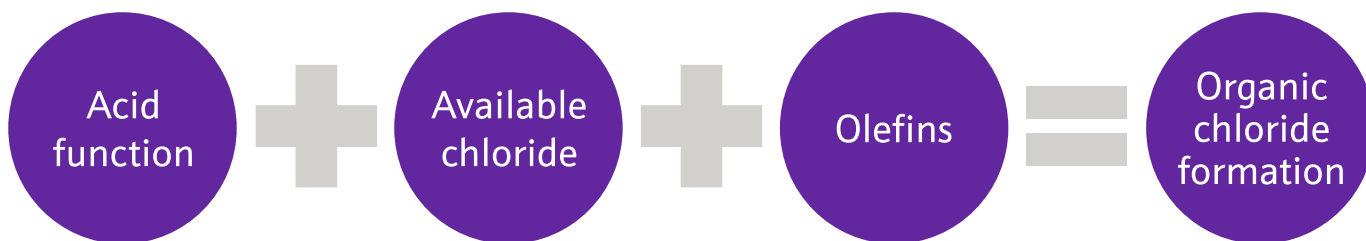
CLEAR PURASIEVE

Adsorbents & zeolites for total chloride removal

PURASIEVE comprise a series of materials that have inorganic chloride capacity but are specialized for organic chloride removal. These perform via either catalytic and/or physical mechanisms to eliminate organic chloride. These are most often paired with **ARMOR** and **PERFORM** products to provide an optimized total chloride removal solution. **PURASIEVE 2** is uniquely capable of handling high levels of organic chloride in both gas and liquid duties (100 ppmv gas, 50 ppmw liquid), which is much higher than most refinery chloride guard applications.



Chloride guard monitoring



Stream testing

Many refiners only measure for inorganic chloride content, leaving organic chloride content, which originates from the CRU process or created by an acidified chloride guard, undetected. This results in corrosion and fouling downstream without any warning to the operations staff. Therefore it is very important to have a methodology that adequately detects and quantifies both inorganic and organic chlorides. Johnson Matthey has long held the industry's best available monitoring techniques along with an on-call technical service staff to check readings at operating sites and provide summary and analysis of results. Johnson Matthey's on-site chloride monitoring kit can be used by engineers and operators for more frequent measurement of both organic and inorganic chloride compounds.

Changeout Guidance

Johnson Matthey offers assistance in estimating material changeout needs. By projecting in-service pickup in conjunction with an accurate chloride balance, it can be determined when chloride will likely break through. This is helpful for resource planning and material procurement.

Sample baskets to measure in-service chloride pickup

Sample baskets are available to measure in-service chloride pickup. In conjunction with other Johnson Matthey in-house evaluations, a bed profile can be determined. This is valid if the installation and sample baskets are both **PURASPEC** material. Johnson Matthey provides guidance for loading and retrieval of sample baskets.

Quality products, quality manufacturing

Johnson Matthey operates its manufacturing assets to meet the most stringent quality criteria. We ensure that all of our facilities meet stringent ISO global manufacturing standards. We ensure that only high quality raw materials are used in safe manufacturing environments to produce the best available products in the market. We also pride ourselves in customer focus, and can be flexible in delivery options around packaging, etc.



Johnson Matthey a company to believe in

Johnson Matthey has been a technology leader across various industries over the past several centuries. We have built ourselves as a provider of solutions to larger scale problems, and feel a real connectivity between what we provide and what our customers need. We take pride in being a sustainable company. We strive for environmental stewardship and are well on our way to achieving three key goals: achieve carbon neutrality, achieve zero waste to landfill, and halve key resources consumed per unit output.



For further information on Johnson Matthey, please contact your local sales representative or visit our website.
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