Sarthak Urankan | Adsorbent Purification Solutions for Refining and Petrochemicals

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Why Remove the Trace Contaminants?

• Get better yields from your expensive catalysts
  – Nobel metal catalysts (isomerization, reforming, selective hydrogenation, complete saturation) – prevent sulfur compound poisoning
  – Polymerization catalysts (Ziegler Natta, Metallocene)

• Meet or exceed product specifications
  – Polymer grade olefins – water, arsine and mercury, COS, CO₂, CO and O₂ and other oxygenates
  – Copper strip product specifications – sulfur compounds

• Protect equipment (plant and pipelines)
  – Chloride removal to minimize corrosion
  – Mercury attack of equipment and cold boxes

• Environmental – toxicity and for emission controls (Increased toxicity awareness, Tighter TLV limits / tighter emission standards)
  – Mercury, sulfur compounds
Contaminants of Concern In Petroleum Refineries

Legend
- Mercury
- Water
- Arsine
- Oxygenates
- Fluorides
- Sulfur Compounds
- Chlorides

Desalted Crude Oil

Crude Distillation

Gas Concentration → Amine Guard → H₂ Plant → Polybed™ PSA

Light Straight Run

Hydrotreating

Naphtha

Gas Oil

Atmospheric Distillation

Kerosene

Middle Distillate

Vacuum Distillation

From FCC

From FCC

Hydrotreating

Light Naphtha Isomerization

Catalytic Reforming

Hydrotreating

C₄ Isomerization

SHP

Alkylation

FCC

Amine Guard

H₂ Plant

Polybed™ PSA

LPG

Propylene

Jet Fuel

Diesel

Kerosene

Gasoline

LPG

Propylene

UOP 8080C-2
UOP Purification Solutions

UOP continues to develop **new technology solutions** to meet industry demands.

- Catalytic Reforming
  - **Net Gas Chloride Adsorbents + CLR-304**

- Metal Oxide Sulfur Guard Beds
  - **ADS-120**

- Specialty Hybrid Adsorbents
  - **AZ-300/AZ-400** for purification of reactive streams

- Metal Sulfides Mercury Guard Beds
  - **GB-347**
Chloride Management for Catalytic Reforming – Reactor Section

Possible locations for chloride gas or LPG Treaters

Possible location for stabilizer liquid chloride Treaters

Reformate to:
- Gasoline Pool, or
- Aromatics Recovery

UOP Addresses Corrosion and Plant Safety in the Entire Reforming Process
UOP Chloride Management Portfolio

UOP is the Supplier that...

- Manufactures the major types of chloride adsorbent, including promoted aluminas, molecular sieves and mixed metal oxides

- Provides an unbiased recommendation of single or combination products to most cost effectively address your technical needs

- Are not only adsorbent experts but also have extensive knowledge of the Catalytic Reforming process and catalyst itself

<table>
<thead>
<tr>
<th>UOP Product</th>
<th>CLR-204</th>
<th>CLR-304</th>
<th>CLR-454</th>
<th>PCL-100/ PCL-200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Material</td>
<td>Promoted Alumina</td>
<td>Mixed Metal Oxide</td>
<td>Molecular Sieve</td>
<td>Molecular Sieve</td>
</tr>
<tr>
<td>Service</td>
<td>Net Gas and LPG</td>
<td>Net Gas</td>
<td>Net gas</td>
<td>Stabilizer Feed, Liquid Phase</td>
</tr>
<tr>
<td>Green oil Formation</td>
<td>Very low</td>
<td>Negligible</td>
<td>Reduces green oil and removes organic chloride</td>
<td>N/A</td>
</tr>
<tr>
<td>Adsorption capacity</td>
<td>Preferred product for HCl &amp; reduces organic chloride formation</td>
<td>Excellent capacity for HCl, does not make organic chlorides</td>
<td>Good for HCl &amp; preferred for organic chlorides</td>
<td>Good for HCl &amp; for organic chlorides</td>
</tr>
</tbody>
</table>
Net Gas Chloride Treaters –
Two Case Studies & Key Technical Issues

CLR-204 vs Promoted Alumina

- Feed: H₂ gas
- Operating temperature: 40 °C
- Operating pressure: 1,200 KPa
- Start-up mid 2009

- Competitive alumina product experience - 4 months lifetime
- Severe green / red oil problem

- CLR-204 - 7.5 months lifetime*
- No green oil problem

* Adsorbent change-out due to turnaround

CLR-204 vs Mixed Metal Oxide

- Feed: H₂ gas (MW ~7.5)
- Operating temperature: 35 °C
- Residence time: 20 seconds
- Start-up mid 2010

- Mixed metal oxide – ~5.5 months lifetime (~ 50% of stoichiometric capacity)

- CLR-204 – 6 months lifetime
- No green oil problem

Product Performance Can Vary Tremendously – Depending Upon Operating Conditions

Not All The Promoted Aluminas Perform The Same – Every Treater Is Unique

Theoretical Adsorption Capacity ≠ Capacity Commercially Achieved
Mixed Metal Oxide, CLR-304 – Chloride Adsorbent for Net Gas

Chloride on Spent Adsorbent in Dynamic Lab testing

Distance into Adsorbent Bed

% HCl Capacity

Inlet 25% 50% 75% Outlet

CLR-304

CLR-204

Oligomerization Reactivity Comparison

Commercial std. promoted alumina

CLR-204

CLR-304

Green Oil

UOP CLR-304 is UOP’s Highest Chloride Capacity and Lowest Green Oil Production Product
UOP Purification Solutions

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  - GB-347

UOP Can Help You Meet Your Future Technology Needs
Sulfur Removal Adsorbents: Non-Regenerative

- For C₅+ hydrocarbons sulfur compound removal, hydrotreating and/or Adsorbent sulfur guard beds are used
  - NON-regenerative adsorbents are used to achieve ultra low sulfur levels
  - UOP offers all major options and helps our customers select the product best suited to their specific needs
    - ADS-11L (Nickel)
    - ADS-120 and ADS-130 (Copper)
    - ADS-280 (Zinc)
  - Simplified sulfur guard bed chemistry
    - $M + H_2S \rightarrow MS + H_2O$
    - $MO + H_2S \rightarrow MS + H_2O$
      - MO = metal oxide, MS = metal sulfide
      - Metal oxide → metal sulfide

UOP Offers a Complete Portfolio of Sulfur Guard Beds Including Copper, Nickel and Zinc Products
Sulfur Guard Bed for Paraffin Isomerization Unit – A Case Study

N. American Refinery: Sulfur Guard Bed; upstream of UOP Paraffin Isomerization

- Product Installed: ADS-120
- Feed Rate: 100 m³/hr
- Operating temperature: 118 °C
- Feed sulfur design: 1 ppmw

ADS-120 handled an unexpected NHT upset extremely well

- The refiner claimed a 1 day NHT upset and estimated feed sulfur at ~ 70 ppmw
- Spent samples (10 samples from various parts) were tested - EVERY SAMPLE had achieved stoichiometric sulfur capacity during the upset
- Back calculated the feed sulfur was 350 ppmw if upset only lasted for 1 day – 5x times vs. customer estimation and 350 X design feed sulfur!
- The ADS-120 bed had captured all the sulfur; previous experience with other products were NOT so good
- Customer reordered ADS-120 as a recharge in addition to replacement for a Catalytic Reformer Sulfur Guard Bed as well

Robust Product Performance is Critical in Order to Handle Process Upsets
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Olefin Treating: Challenges

Removal of impurities from olefins, using adsorption, is significantly more difficult than from paraffins

- Adsorbent reactivity can impact operational safety and performance
- Strong olefin adsorption on molecular sieves can release sufficient heat to start a dangerous polymerization reaction

Olefin Treating: Solutions

Some Strategies to overcome these problems and reduce the concerns:

- Adsorbent selection to exclude the reactive olefin stream (ODG-442)
- Use of hybrid adsorbents (AZ-300/ AZ-400) – that have a low heat of adsorption, are not reactive towards the process stream and has adequate contaminant capacity
- Use of chemisorbents – such as low reactivity promoted aluminas or metal oxides to selectively scavenge targeted contaminants (COS, mercury, arsine)
Low Catalytic Reactivity Adsorbents are a “Must Have” for Sensitive Olefin Purification Applications

Enhance the adsorbent potential by reducing:

- Adsorbent reactions with the process stream
  - Coking
  - Side reactions & new contaminants created
- Safety concerns due to exothermic side reactions

Adsorbent Reactivity, Should be a Key Factor in Product Selection
AZ-400 is UOP’s Highest Capacity Hybrid Adsorbent for Demanding Olefin Purification Applications

AZ-400 hybrid adsorbent is especially effective, for the hard to remove, less polar contaminants

**Butene-1 Comonomer Treaters for LLDPE/ HDPE Plant**

- **Bed on Adsorption**
  - Butene-1 to Polymerization Reactor
  - CH$_3$OH, Carbonyls, MTBE, Peroxides

- **Bed on Regeneration**
  - N$_2$ at 240°C
  - H$_2$O

**AZ-400 is UOP’s Highest Capacity Hybrid Adsorbent for Olefin Containing Streams**

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>% Capacity Improvement Over AZ-300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl Sulfide</td>
<td>50%</td>
</tr>
<tr>
<td>Acetone</td>
<td>40%</td>
</tr>
<tr>
<td>C3 Mercaptan</td>
<td>30%</td>
</tr>
<tr>
<td>T-Butanol</td>
<td>20%</td>
</tr>
</tbody>
</table>

**UOP High Capacity Hybrid Adsorbent: AZ-400**
UOP continues to develop **new technology solutions** to meet industry demands

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Mercury in the Hydrocarbon Chain

Upstream
Exploring, drilling and producing crude oil and natural gas

Midstream
Processing, storage and transportation

Downstream
Refining oil and gas into fuels and chemicals

Amalgamation versus chemical reaction – two different Hg removal pathways: regenerative and non-regenerative

- UOP can provide both regenerable and non-regenerable adsorbents for R&P applications, which allows for flexible flow sheet location choices, and sometimes used in combination to provide an economical MRU solution

1. UOP Regenerable HgSIV™ adsorbents: amalgam formation
   - Ag° + Hg° = HgAg

2. UOP GB non-regenerable adsorbents – metal sulfide products for liquid applications (GB-346S, GB-346HPS, GB-347) and 500 series products for gas phase (unsulfided options are also available)
   - 2CuS + Hg = HgS + Cu₂S
Adsorbent Purification Solutions for Refining and Petrochemicals

- UOP adsorbents are an effective, and economical, method for purification of process streams in Refineries, Petrochemical processes and Natural Gas Conditioning

**Factors to consider in adsorbent selection**
- Adsorbent capacity and selectivity
- Adsorbent reactivity
- Process reliability and safety
- Continuous Product and Process Innovation
- World-wide Tech service support
- Multiple manufacturing facilities located world-wide to satisfy our customers needs
- UOP Modular solutions for timely, guaranteed performance

Single Point Responsibility (Adsorbents & Services) Similar to Managing Licensor Concept
Q&A
UOP Offers a Complete Range of Contaminant Removal Solutions

**Molecular Sieves**
- Use of a small pore zeolite enables exclusion of reactive species and is very effective for dehydration
- Other contaminants may need a larger pore (such as a 4A, 5A, or 13X type) which may adsorb a reactive carrier stream thus a preload step may be required
- Careful selection of base material helps control high surface energy and active sites to meet adsorption requirements in reactive streams

**Hybrid Adsorbents**
- Engineered homogenous combination of a promoted alumina and a large pore zeolite
- Combines high selectivity for light acid gases with low olefin reactivity (low heat of adsorption of hydrocarbons) and high capacity for polar molecules makes these products ideally suited for purification of olefinic streams

**Promoted Aluminas**
- Activated aluminas are synthetic transitional phase aluminas with a tailored pore structure to facilitate rapid chemisorption, resulting in a short mass transfer zone
- Low affinity for reactive hydrocarbons, thus a preload step not needed
- Light acid gases such as CO₂, H₂S & COS are removed by chemisorption to very low concentrations

**Metal Oxides & Sulfides**
- Critical applications for hydrocarbon streams
- Trace arsine and phosphine removal from hydrocarbon streams to protect sensitive noble metal or polymerization catalysts
- Specialty applications - such as mercury & sulfur compound removal
- Trace CO, O₂ scavenging from ethylene and N₂
UOP HPG-300 MOLSIV™ Adsorbent for Improved Paraffin Isomerization Feed Treating

HPG-300 offers increased capacity for contaminants compared to current generation Butamer and Penex adsorbents. Key customer benefits include:

- Ability to increase throughput in existing feed driers by as much as 30% without contaminant breakthrough
- Ability to tolerate higher feedstock impurities and help olefin content
- Less frequent regenerations in existing vessels will save operating costs and result in longer adsorbent life

UOP HPG-300 Adsorbent has Higher Contaminant Capacity & Ability to Tolerate Higher Feed Olefins
Arsine Adsorbent Performance: Lab and Commercial Tests

- Non-UOP arsine guard adsorbent produces high boiling residue at 30°C
- UOP GB-238 arsine guard is non-reactive at a higher temperature (50°C)

Arsine Adsorbent Lab Testing

A combination of enhanced porosity along with lower reactivity enable the GB-238 to outperform a typical non-UOP adsorbent with a similar metal content, helping achieve

- Safer operation
- and longer life
Innovative CS₂ Removal from Petrochemical Naphtha

• Petrochemical grade naphtha requires reduced CS₂ in order to reduce poisoning of pygas hydrotreating catalysts and equipment corrosion in ethylene Plants
  – There is an increased global attention on CS₂ content of petrochemical naphtha

• UOP CS2-100 is a unique molecular sieve adsorbent which features:
  – High CS₂ adsorption capacity
  – Regenerability for long term usage

• A thermal swing adsorption (TSA) system with CS2-100:
  – Has much lower capital cost versus a traditional Hydrotreating unit
  – Is able to remove CS₂ to very low levels (e.g. <1 ppm)
Modular CS$_2$ Removal Solution: Certainty in All Aspects

- Low operating cost
- Consistently low CS$_2$ in product
  - Optimize cycle time based on feed
  - Does not depend on liquid feed composition
- Trouble-free operation
  - Thermal swing adsorption (TSA) concept is proven commercially
- Modular fabrication and supply
  - Quality via controlled environment
  - Quick and certain delivery schedule
  - Turnaround schedule
  - Cost
- Guaranteed Performance
  - CS$_2$ = <1.0 wppm;
  - Adsorbent Life = 2 to 5 years
CS$_2$ in Petrochemical Naphtha – Ethylene Plant Implications

• Limits on CS$_2$ in Petrochemical naphtha date back to 2014 when naphtha industry agreed to report CS$_2$ level – particularly influenced by Japanese isoprene producers$^4$
  – Issues with CS$_2$ in regard to the pygas hydrogenation unit were reported as far back as the 10th Ethylene Producers Conference in 1998$^1$

• CS$_2$ passes through the cracking furnaces largely unaffected
  – It passes through the traditional alkali wash process in ethylene crackers, which is used to remove sulfur specifics from these processes

• CS$_2$ concentrates in the C$_5$+ pyrolysis gasoline
  – Further processing options in the ethylene plant:
    • Send C$_5$+ to pygas hydrogenation$^2$
    • Extract C$_5$’s from pygas (isoprene extraction unit – there have been reports of polymerization catalyst deactivation, as well as severe CS$_2$ corrosion in such units)
    • Hydrogenate the C$_5$s for recycle cracking
Refinery & Petrochemicals – Purification of Trace Contaminants

Case Studies:

- Catalytic Reforming Net Gas Chloride removal
- Sulfur Guard beds – for Paraffin Isomerization, Benzene Saturation and Catalytic Reforming
- Purification of Reactive Olefin Streams
Ethylene Plant Cracked Gas and Cracked Liquid Solutions

- **EPG-2**
  - Dehydration
  - Break-up resistant
  - Low reactivity

- **3A-EPG**
  - Dehydration
  - Superior mass transfer

- **EPG-N**
  - Ammonia removal

- **UOP HgSIV™ Adsorbent Capabilities**
  - Mercury removal
  - Same dryer size
  - Existing and New Units

**Use Layers of Multiple MOLSIV™ Adsorbents to Remove Multiple Contaminants**