



2024 Brimstone Sulfur Symposium

Finding NiMo: Diving into a Tail Gas Treatment Alternative

September, 12th, 2024

Johann Le Touze & Jamie Maddie



Axens
Powering integrated solutions

Content

1. Introduction to Axens
2. Tail Gas Treatment Catalysts
3. Catalyst Specifications
4. Performance Evaluation

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Sulphur Recovery Catalysts – Some Key Figures

4 markets
covered



OIL
REFINING



PETROCHEMICALS



GASES



ALTERNATIVES &
RENEWABLES



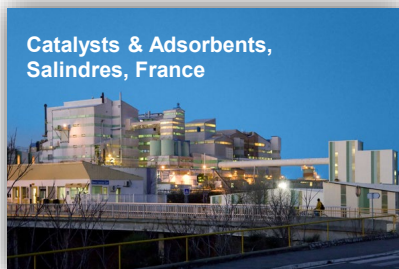
~ 4,000

Tons of Sulphur Recovery Catalysts
produced each year

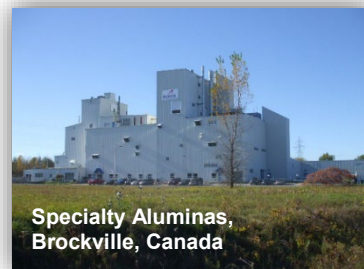


4

Production Sites



Catalysts & Adsorbents,
Salindres, France



Specialty Aluminas,
Brockville, Canada



Catalysts,
Calvert City, USA

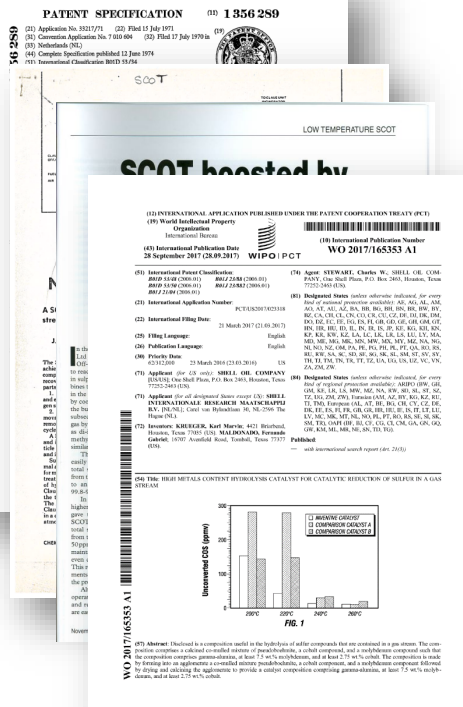


Catalysts,
Dammam, KSA

Content

1. Introduction to Axens
- 2. Tail Gas Treatment Catalysts**
3. Catalyst Specifications
4. Performance Evaluation

TGT Catalyst History



1971

1st patent on TGT technology and reduction catalysts based Group VI (Mo) and/or Group VIII (Co, Ni) metals

1973

New patent published on TGT technology and CoMo catalysts

1989

Axens' 1st Conventional TGT catalyst
CoMo/Al₂O₃ catalyst (beads)

2004

Axens' 1st Low Temperature TGT catalysts
High CoMo/Al₂O₃ catalyst (beads or ML extrudates)

2015

Axens' 1st low-density Conventional TGT catalyst
CoMo/Al₂O₃ catalyst (beads)

2016

New patent published on high CoMo content catalysts

2024



30+

DIFFERENT CoMo-based TGTU CATALYSTS

You might think that the industry
is full of “CoMo-nists”!

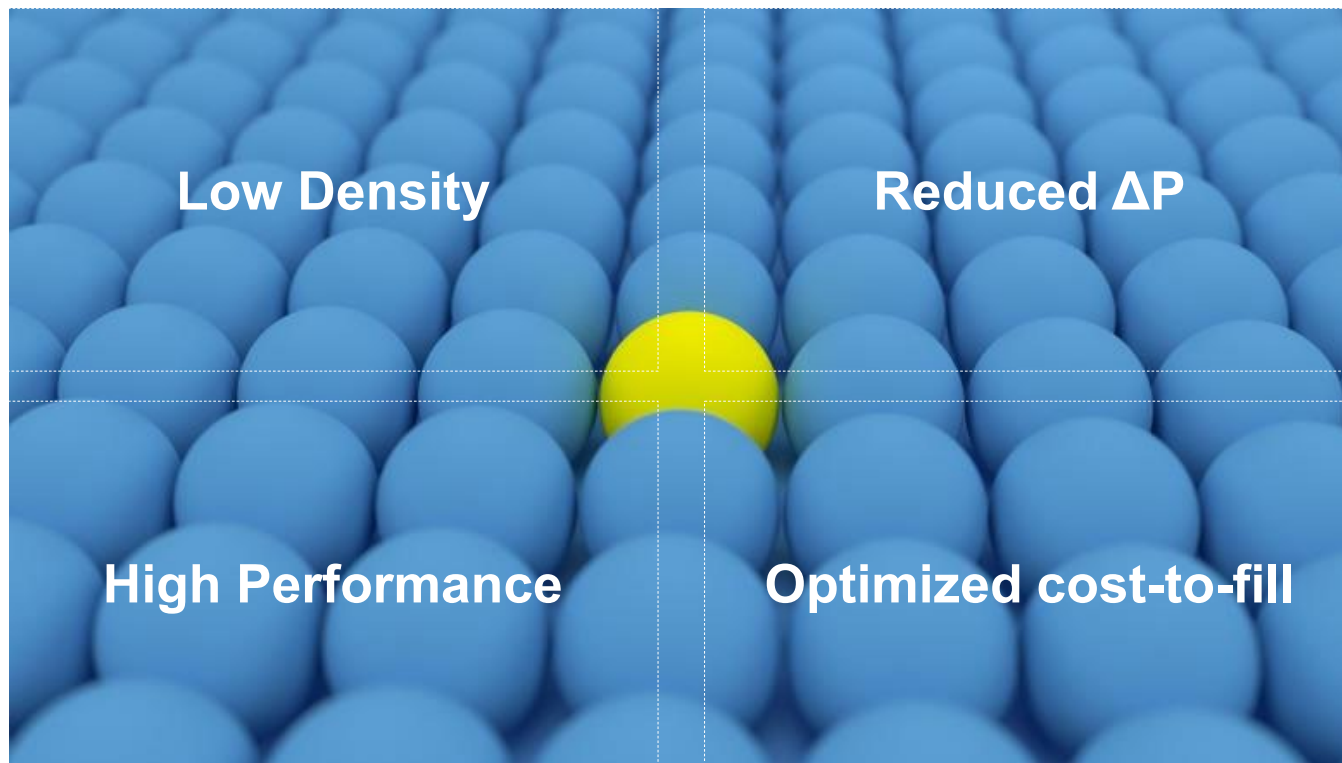
A high-speed photograph of a yellow ball splashing into blue water, creating a large, dynamic splash. The text "Market needs novelty & disruption!" is overlaid in white.

Market needs novelty & disruption!

Content

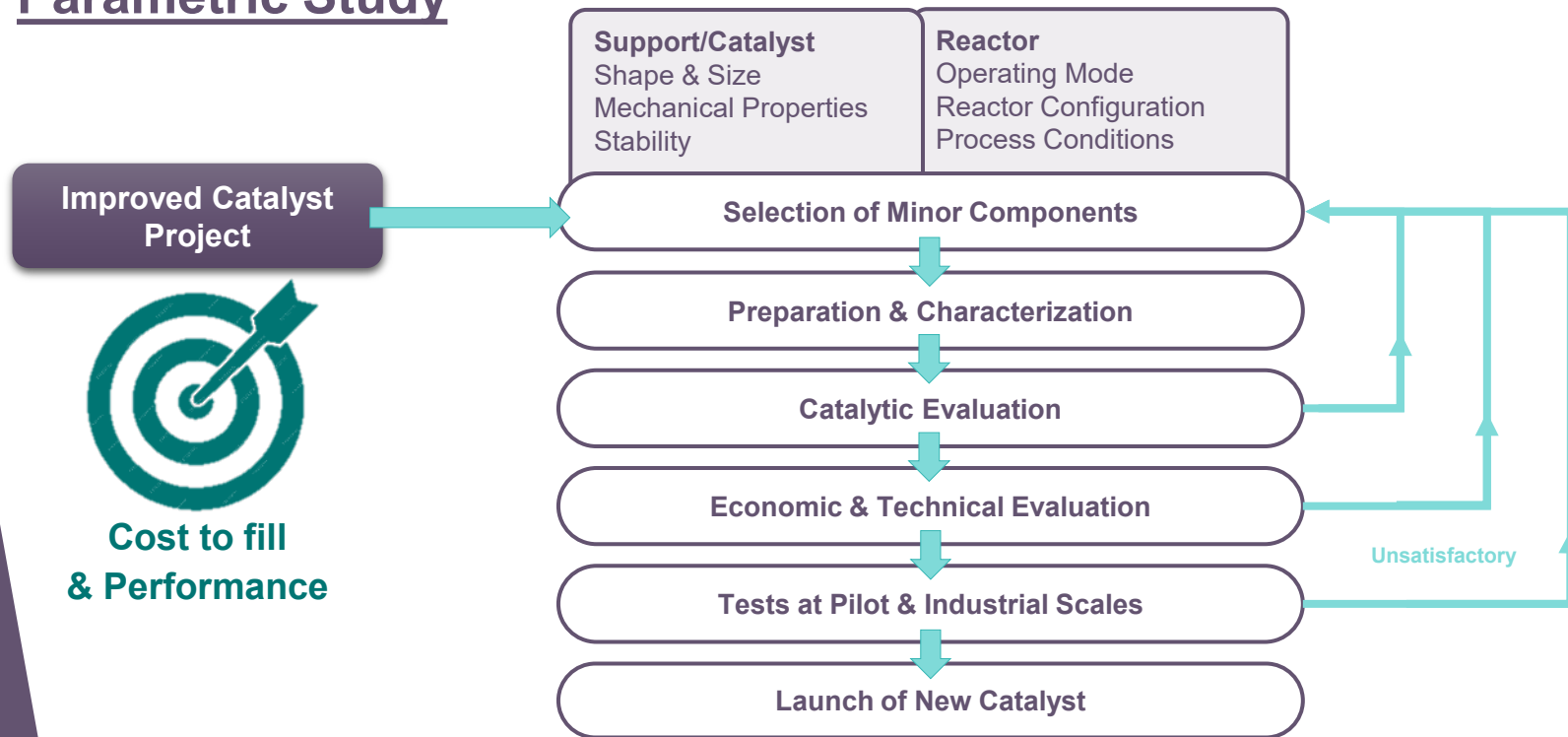
1. Introduction to Axens
2. Axens' TGT Catalyst
- 3. New Catalyst Specifications**
4. Performance Evaluation

In Quest of a New TGT Catalyst which offers...



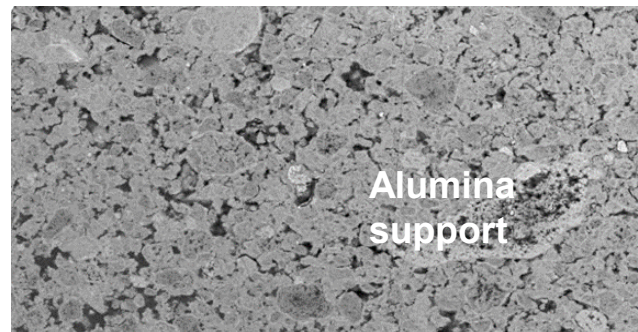
Catalyst Development

Parametric Study



TGT Catalysts Carriers

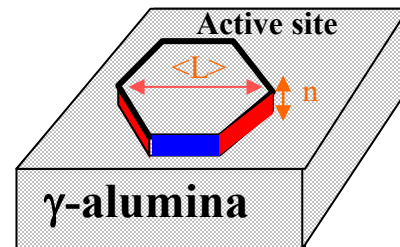
- To achieve the required properties of a catalyst (activity, stability, tolerance to impurities, mechanical resistance...), the alumina selection is based on the following criteria:
 - ▶ **Chemical purity** of the alumina (Na_2O , SO_4 , Cl , NO_3 ..)
 - ▶ **Textural properties** (specific surface area, pore volume, macroporosity)
 - ▶ **Acidity level**



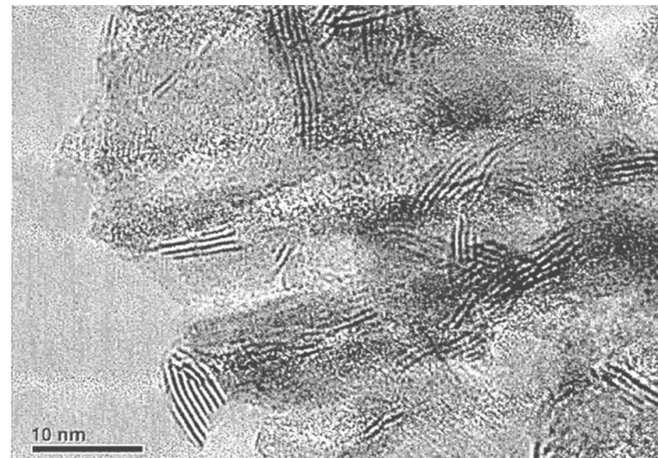
Alumina Carrier

■ Alumina carrier roles for TGT catalysts:

- 1) **Dispersion** of the active phase
- 2) Creation of the **highest contact surface** between active phase and tail gas
- 3) **Optimize distribution of pore sizes**
- 4) **Mechanical strength**



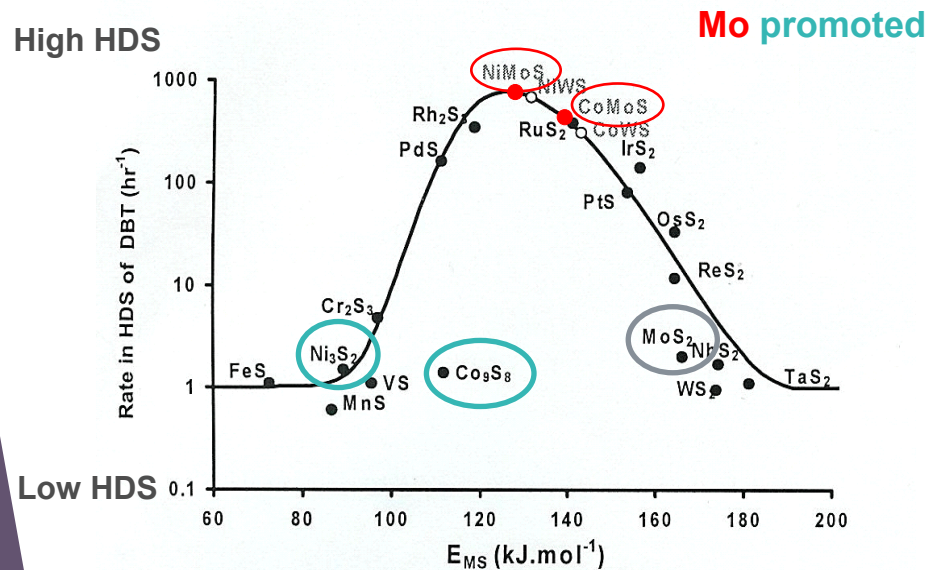
Transmission Electron Microscopy (TEM)
of a TGT catalyst



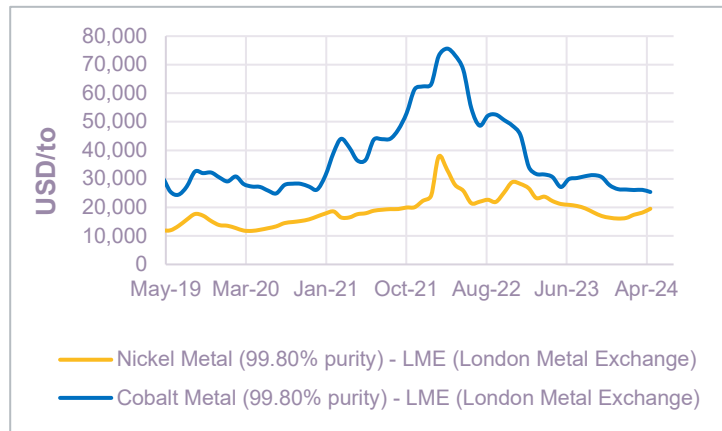
Active Phase

- Catalyst prepared as an **Oxide**, but operated in a **Sulfided State**
- Transition metals sulfides are the only ones to be active and stable in the presence of H_2S
- The catalytically active phase is a mixed sulfide:
 - ▶ **Mo** is promoted by **Co** (Co-Mo-S) or **Ni** (Ni-Mo-S).
 - ▶ Co and Ni are called **Promoters (Pr)**

Active Phase – Inspired by Axens' HDS Catalyst Pedigree



- **CoMoS & NiMoS** are more active than Co_9S_8 , Ni_3S_2 or MoS_2
- CoMoS for TGT is well known



Nickel Price < Cobalt Price
Less variations along with time

➔ Let's try NiMoS

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a) Catalyst Characteristics

A New NiMo Catalyst for TGT Application

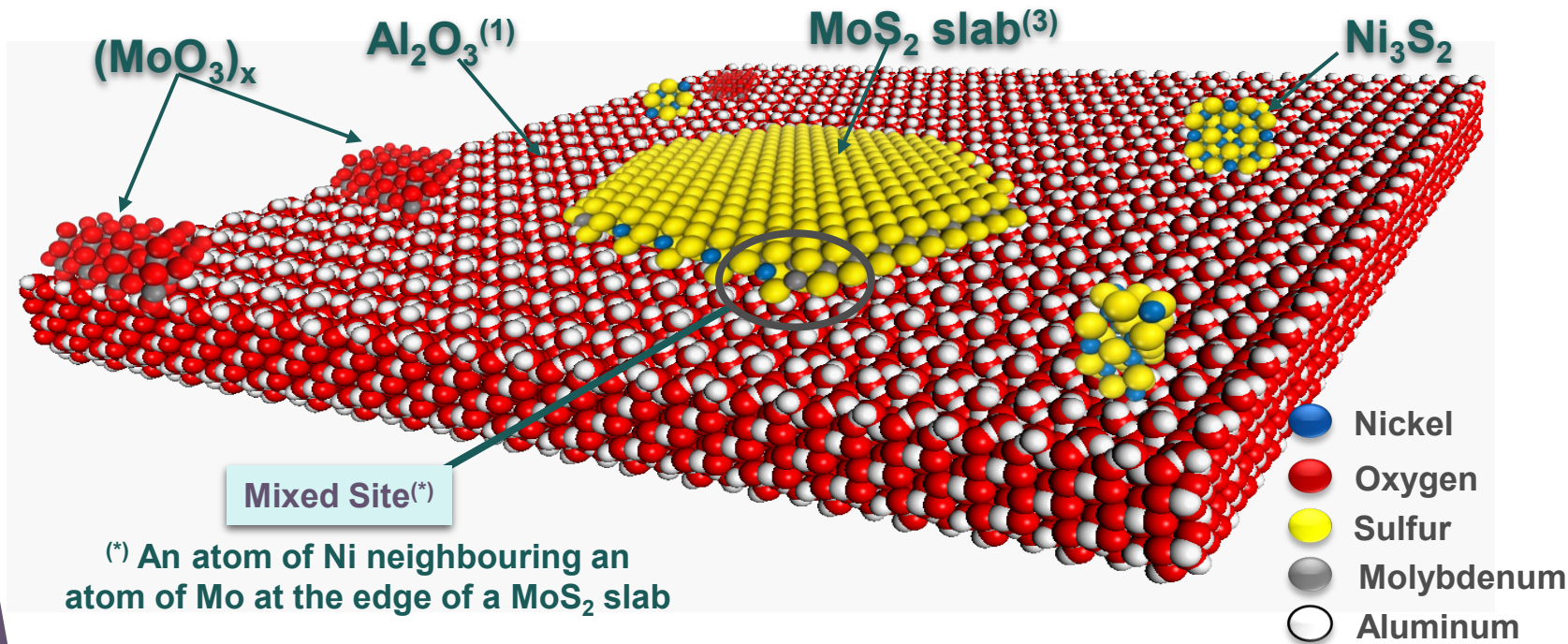
PARAMETER	New NiMo
Diameter	2.4 – 4 mm (3/32 to 5/32 in)
Sock Density	650 kg/m ³ (41 lb/ft ³)



- New catalyst with a Nickel-Molybdenum (**NiMo**) active phase
- Low-density alumina support
- Optimized deposition & formulation of the metal active phase
- Reduced ΔP

Metal distribution on Ni-Mo-S Catalyst

A variety of species co-exist on the surface of the catalyst support.
Only the mixed sites of the MoS_2 slabs are most active.



(1) Catalyst Support

(3) Partially promoted by Nickel

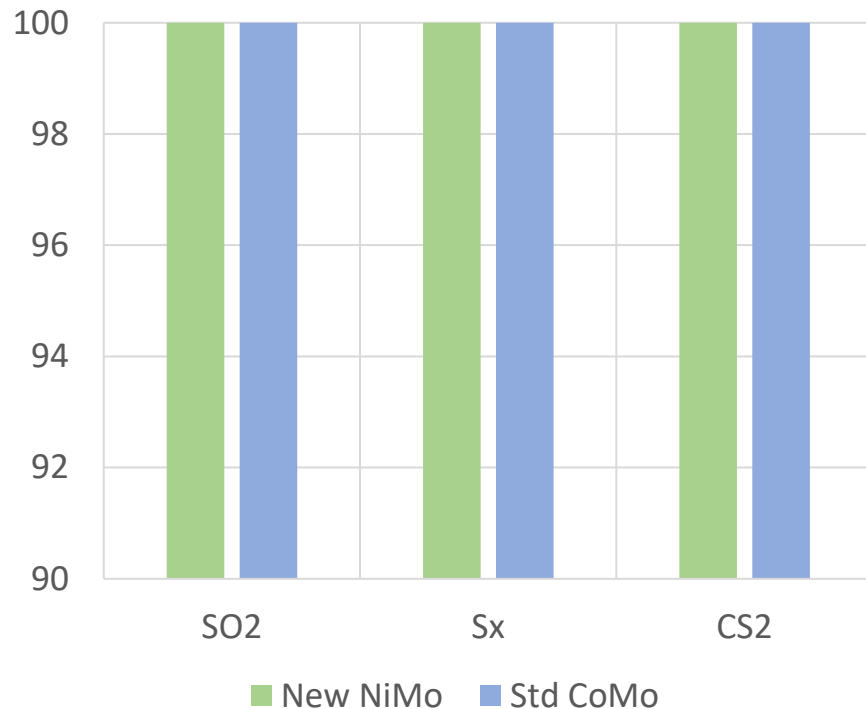
b) Catalyst Performance

Performance Evaluation – Experiment Conditions

- Catalyst evaluated under “**gas plant**” conditions at ASRL and Axens
 - ▶ “New NiMo” = NiMo catalyst with selected alumina support
 - ▶ “Std CoMo” = CoMo catalyst with selected alumina support and same metal content as “New NiMo”
- Tested in more stringent conditions than in refinery application
- Tested in Similar Operating Conditions in both labs (some % variations due to experiment setup limits)

Composition	H ₂ S	SO ₂	COS	CS ₂	H ₂	CO	CO ₂	H ₂ O	GHSV	Temperature
ASRL, mol%	0.8	0.3	0.05	0.05	2.0	2.0	15	40	1200 h ⁻¹	240°C, isothermal
AXENS, mol%	0.8	0.2	0.1	0.2	1.8	1.0	15	25	1200 h ⁻¹	240°C, isothermal

Performance Evaluation – SO₂/S_x/CS₂ Conversions



Results at 240°C & 1200 h⁻¹ GHSV

Tests at Axens & ASRL

New NiMo exhibits high performance

Performance Evaluation – CO & COS Conversions



Results at 240°C & 1200 h⁻¹ GHSV

ASRL confirms the high performance measured by Axens

Difference due to slight experimental deviation

New NiMo on par with Axens guarantees

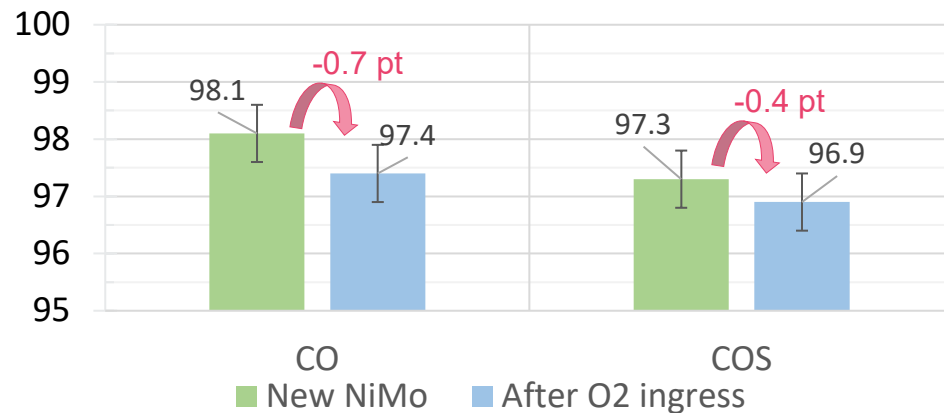
Standard guarantee range specified by customers

Performance Evaluation – Impact of Oxygen

- 3000 ppmv O₂ ingress testing at ASRL of New NiMo catalyst

Composition	H ₂ S	SO ₂	COS	CS ₂	H ₂	CO	CO ₂	H ₂ O	GHSV	Temperature	Sulfidation	Time on stream
ASRL, mol%	0.8	0.3	0.05	0.05	2.0	2.0	15	40	1200 h ⁻¹	240°C, isothermal	2/10% H ₂ S/H ₂ 320°C	8h

- SO₂ and CS₂ conversions at 100% before/after O₂ ingress



Proven O₂ resistance of
New NiMo catalyst

Conclusion

The new NiMo-based catalyst offers:

- **High Performance** at low temperature
- **Low density** thanks to new alumina support
- **Optimized deposition** of metal active sites
- **Balance cost / performances / lifetime**

**NiMo-based catalyst is a New Alternative
in the tail gas treatment catalyst market**

Acknowledgement



Thomas Serres
Catalyst R&D Team Manager

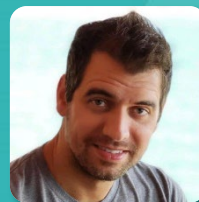


Mathieu Chevrier
*Global Market Manager
Claus & Adsorbents*



Guillaume Parer
*Acid Gas Technology
Group Manager*

**LET'S MEET
& CONNECT!**



Jamie Maddie
*Sulphur Recovery Technology
Engineer (USA)*

A vibrant underwater scene featuring Nemo, the orange clownfish, swimming near a large, textured brain coral. A thought bubble originates from Nemo, containing the text "YOU FOUND ME!". The background is filled with various other fish and coral structures.

**YOU
FOUND
ME!**

Axens
Powering integrated solutions



 axens.net



Thank you

Axens.net
a new digital
journey