Challenges in Managing Mercury in Field Development and Production

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Enhancing Sulfur Efficacy in Mercury Removal from Natural Gas Condensate and Produced Water

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Introduction – it is possible to utilize aqueous sulfides to elicit mercury removal in hydrocarbon matrices

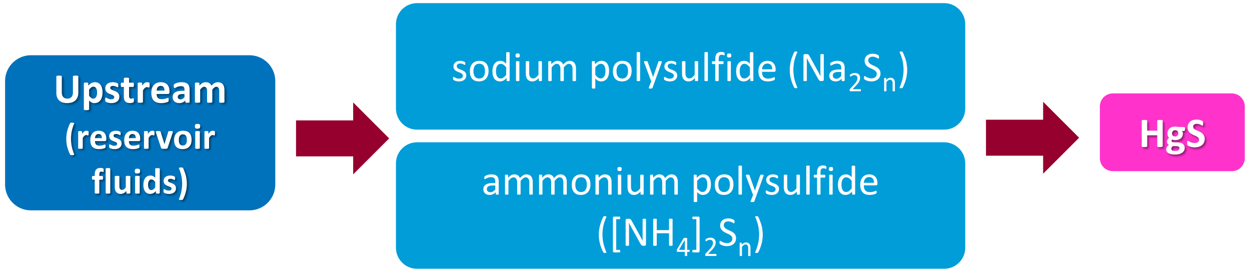
Literature; use of aqueous polysulfide solutions can effectively react with mercury compounds at near room temperature to form HgS;

Elemental Hg : $Hg^0 + S^{2-}_n \rightarrow \mathbf{HgS} + S^{2-}_{n-1}$

Organic Hg : $R–Hg–R' + S^{2-}_n \rightarrow \mathbf{HgS} + S^{2-}_{n-1} + R–R'$

Inorganic Hg : $HgCl_2 + S^{2-}_n \rightarrow \mathbf{HgS} + S^{2-}_{n-1} + 2Cl^-$

Patents; upstream processes; sodium polysulfide (Na_2S_n) and ammonium polysulfide ($[NH_4]_2S_n$) utilized for reducing mercury concentrations in reservoir fluids to below 100 ppb (wt).



Upstream (reservoir fluids)

sodium polysulfide (Na_2S_n)

ammonium polysulfide ($[NH_4]_2S_n$)

HgS

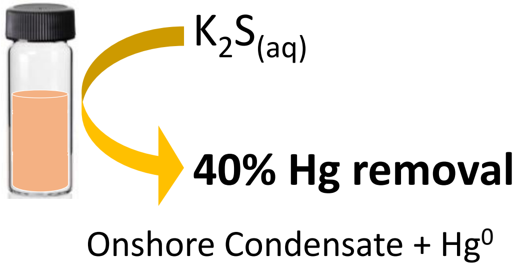
Percent mercury removal / %				
Aqueous sulfides		**Hg species**		
		Hg^0_{condy}	**$HgCl_{2condy}$**	**$Hg(NO_3)_{2PW}$**
Na_2S	Onshore	33	24	95
	Offshore	52	38	88
$(NH_4)_2S$	Onshore	40	50	93
	Offshore	25	23	87
K_2S	Onshore	33	9	94
	Offshore	33	33	64

NOTE Ratio of [mercury species] to [aq. sulfide] is *ca.* 1:1.

- Aqueous sulfides are effective in removing mercury(II) from produced water (PW)
- Also shows ability to remove mercury from condensate (condy)

Source: i. Yan, T. Y. Mercury Removal from Oils. Chem. Eng. Commun. 2000, 177 (Oct. 2014), ii. Yan, T. Y. US 4,915,818 Use of Dilute Aqueous Solutions of Alkali Polysulfides to Remove Trace Amounts of Mercury from Liquid Hydrocarbons (1990), iii. Yean, S.; Gallup, D. L.; Young, L. A.; Cooper, R. E.; Zielinski, M. B.; Emanuele, A.; Llewellyn, B. C.; O'rear, D. J. US 9,447,675 B2 In-Situ Method and System for Removing Heavy Metals from Produced Fluids (2016), iv. Wong, S.M.A.S and Salam, S. IPTC-24982-MS: Enhancing Mercury Removal in Hydrocarbon Fluids: Efficacy of Aqueous Sulfides Extraction in Natural Gas Condensate and Produced Water, Internat. Petroleum. Tech. Conf., Kuala Lumpur (Feb. 2025).

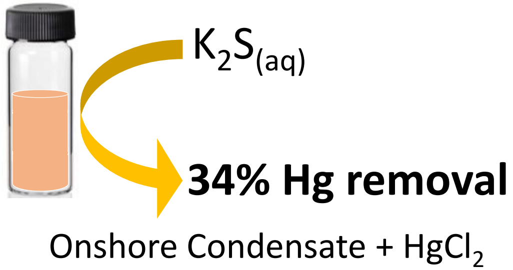
The use of an acid together with an aqueous sulfide improves the Hg removal in condensate samples



$K_2S_{(aq)}$

40% Hg removal

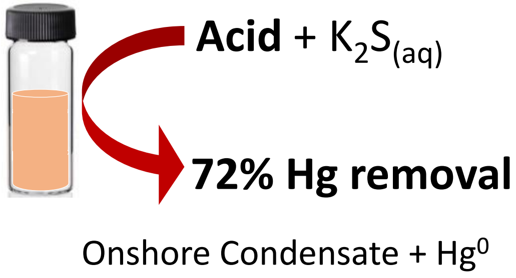
Onshore Condensate + Hg^0



$K_2S_{(aq)}$

34% Hg removal

Onshore Condensate + $HgCl_2$

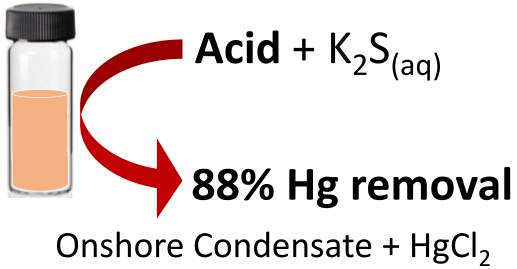


Acid + $K_2S_{(aq)}$

72% Hg removal

Onshore Condensate + Hg^0

(Increase of *ca.* 32%)



Acid + $K_2S_{(aq)}$

88% Hg removal

Onshore Condensate + $HgCl_2$

(Increase of *ca.* 54%)

NOTE

i. Sample matrix: onshore condensate, with initial [Hg^0, $HgCl_2$]= 3,000 ppb wt.

ii. Ratio of S^{2-} to Hg^{2+} was 1.7:1 (excess sulfides)

$$\text{Mercury compounds } (\textit{i.e. } Hg^0, HgCl_2) \xrightarrow[\textit{(Aqua Regia)}]{\textit{oxidized}} Hg^{2+}$$

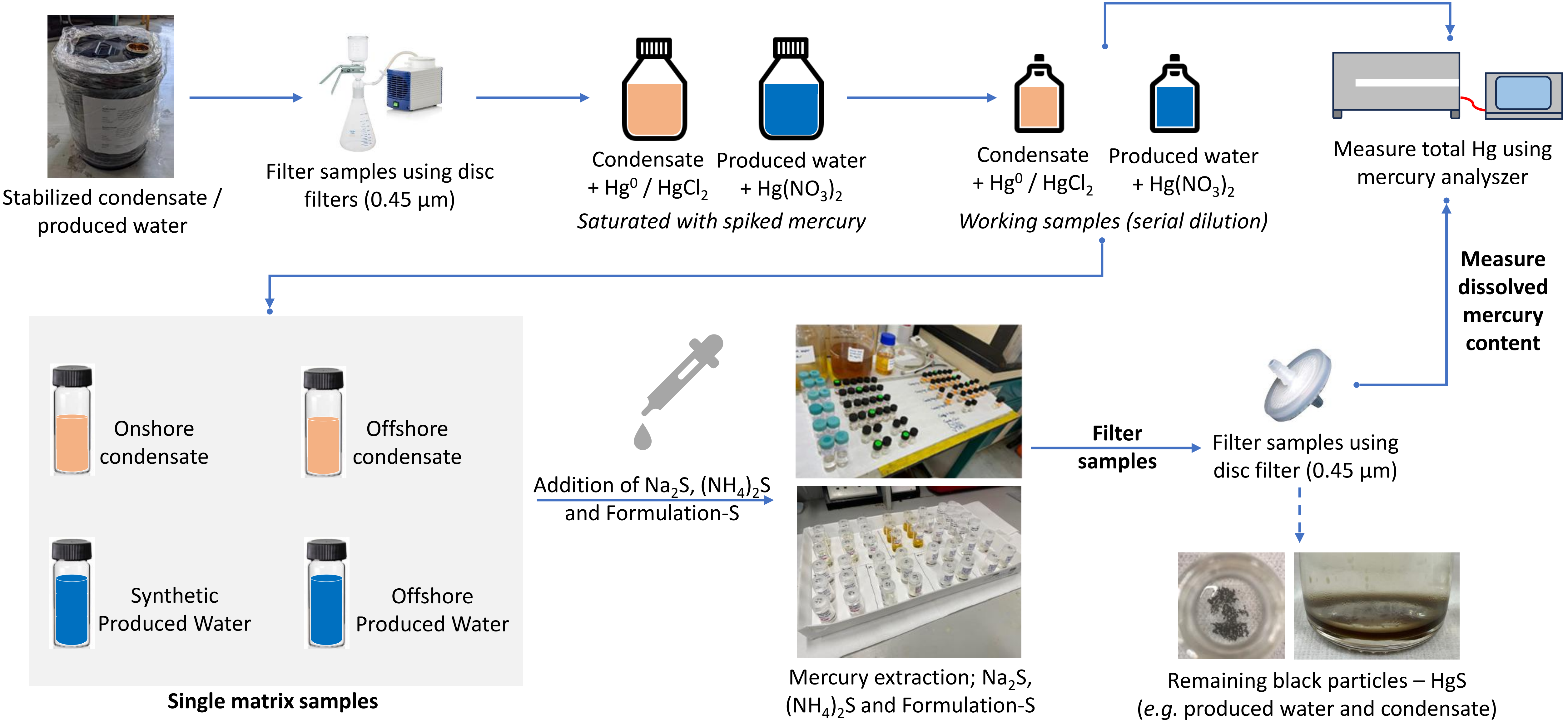
$$Hg^{2+} + S^{2-} \longrightarrow HgS$$

- **Oxidant** (*i.e. Aqua Regia*) **enhances mercury extraction** by **oxidizing Hg^0 and $HgCl_2$ to Hg^{2+}**, followed by **complexation with S^{2-} to form HgS**. Oxidants are widely used for mercury extraction (*e.g.* acid digestion) in standard methods (*e.g.* EPA, ISO).
- **Improving Hg^{2+} availability** before sulfide complexation **enhances mercury extraction** efficiency.
- However, introducing acids into process streams is **impractical** due to operational and safety concerns.

➡ **Sulfide that is capable of performing oxidation without the need of an acid; Formulation-S**

Source: Wong, S.M.A.S and Salam, S. IPTC-24982-MS: Enhancing Mercury Removal in Hydrocarbon Fluids: Efficacy of Aqueous Sulfides Extraction in Natural Gas Condensate and Produced Water, Internat. Petroleum. Tech. Conf., Kuala Lumpur Feb. 2025

Experimental workflow: Sample preparation, Hg removal tests, and total mercury analysis (n ≥ 2)



Stabilized condensate / produced water

Filter samples using disc filters (0.45 µm)

Condensate + Hg^0 / $HgCl_2$

Produced water + $Hg(NO_3)_2$

Saturated with spiked mercury

Condensate + Hg^0 / $HgCl_2$

Produced water + $Hg(NO_3)_2$

Working samples (serial dilution)

Measure total Hg using mercury analyszer

Onshore condensate

Offshore condensate

Synthetic Produced Water

Offshore Produced Water

Single matrix samples

Addition of Na_2S, $(NH_4)_2S$ and Formulation-S

Mercury extraction; Na_2S, $(NH_4)_2S$ and Formulation-S

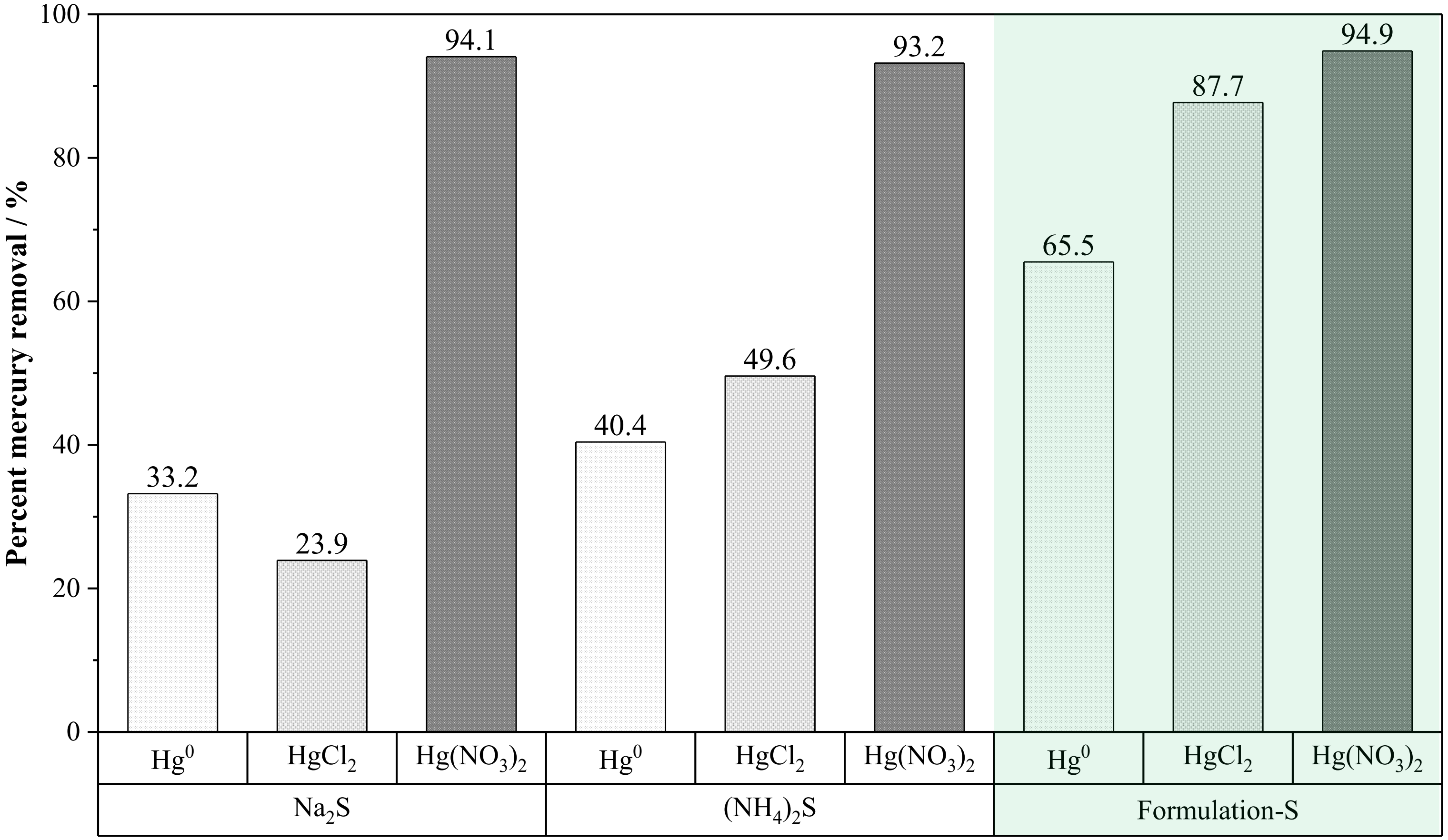
Filter samples

Filter samples using disc filter (0.45 µm)

Measure dissolved mercury content

Remaining black particles – HgS (*e.g.* produced water and condensate)

Onshore sample set: Formulation-S resulted in highest overall Hg removal vs aqueous sulfides (Na_2S, $(NH_4)_2S$)

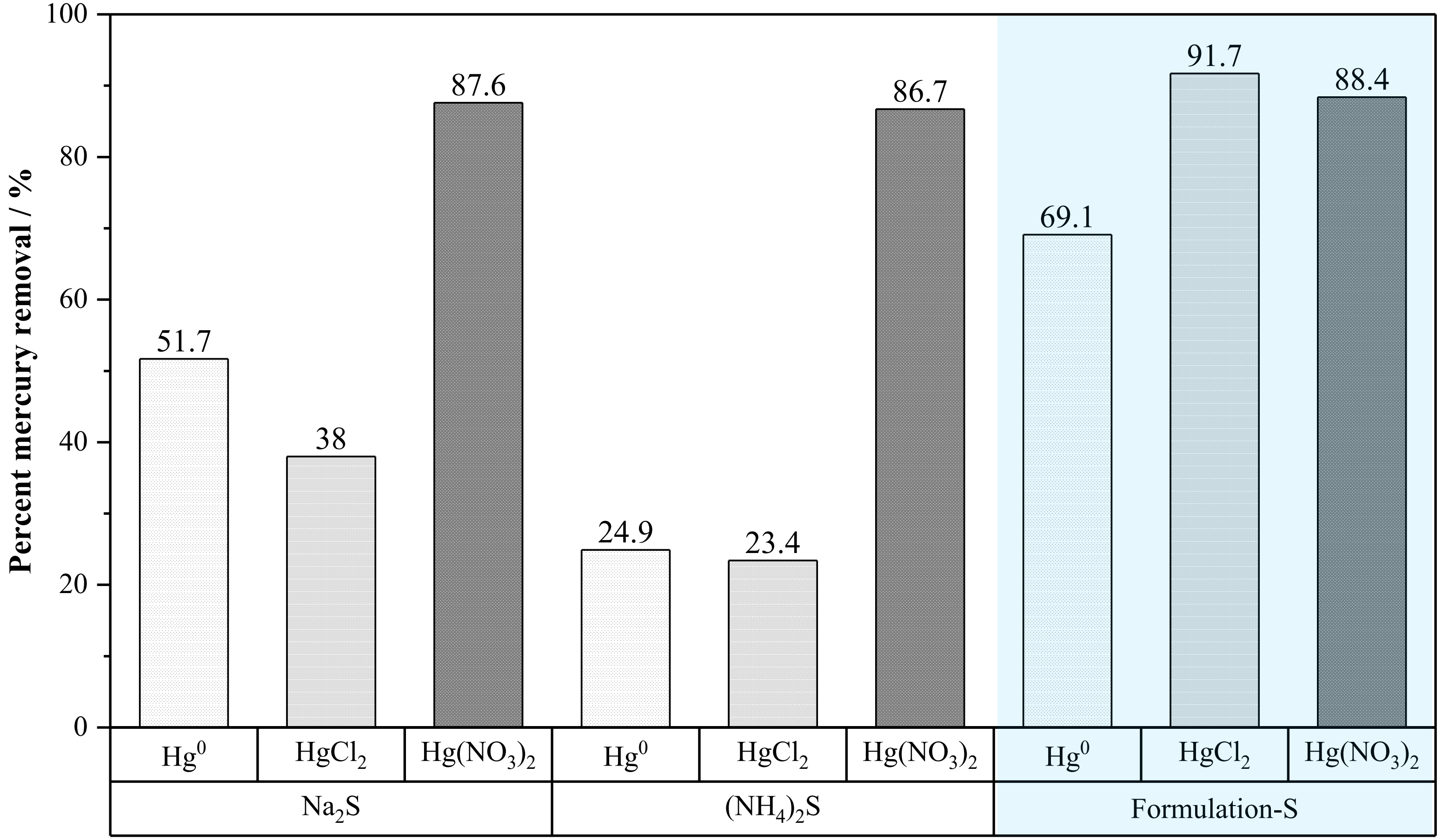


Order of percent Hg mercury removal

- Hg^0 in condensate
  - F-S > $(NH_4)_2S$ > Na_2S
- $HgCl_2$ in condensate
  - F-S > $(NH_4)_2S$ > Na_2S
- $Hg(NO_3)_2$ in syn. prod. water
  - F-S > Na_2S > $(NH_4)_2S$
- Both F-S and aq. sulfides show
  - **high level of Hg^{2+} removal** in syn. prod. water,
  - but **varying levels of removal** in condensate,

Percent mercury removal in **onshore condensate** (single-matrix) containing Hg^0 and $HgCl_2$, and **synthetic produced water** containing $Hg(NO_3)_2$. Results adjusted to account for mercury loss. Initial mercury concentration for each sample was *ca.* 1,000 ppb wt. Each percentage represents a samples size $n \geq 2$.

Offshore sample set: Formulation-S resulted in highest overall Hg removal vs aqueous sulfides (Na_2S, $(NH_4)_2S$)



Order of percent Hg mercury removal

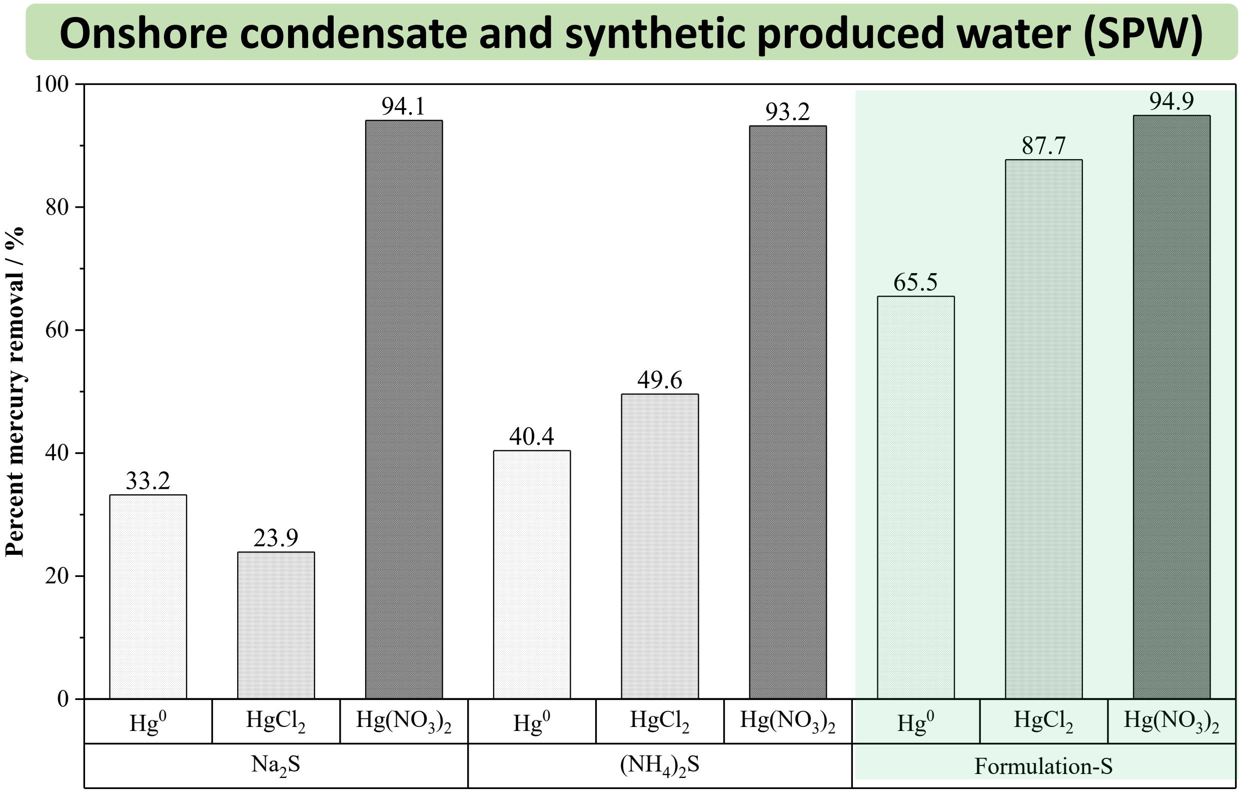
- Hg^0 in condensate
  - F-S > Na_2S > $(NH_4)_2S$
- $HgCl_2$ in condensate
  - F-S > Na_2S > $(NH_4)_2S$
- $Hg(NO_3)_2$ in syn. prod. water
  - F-S > Na_2S > $(NH_4)_2S$

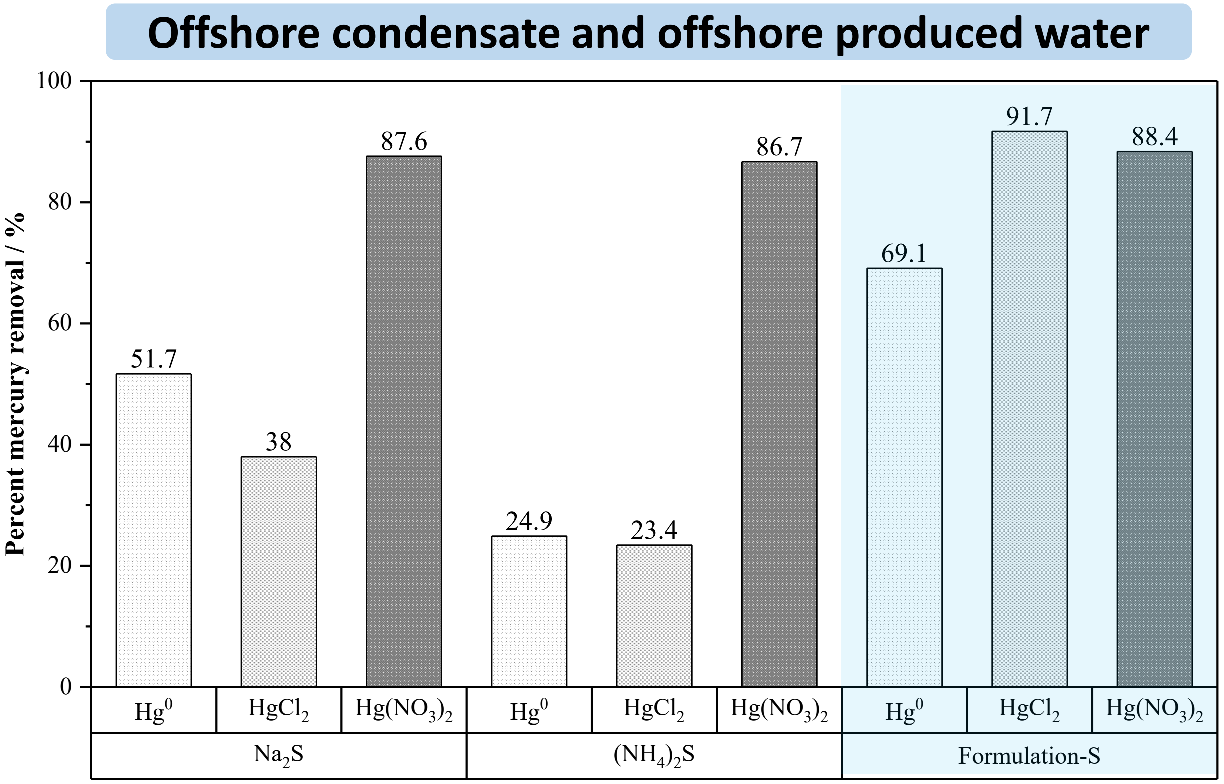
- Both F-S and aq. sulfides show
  - **high level of Hg^{2+} extraction** in syn. prod. water,
  - but **varying levels of extraction** in condensate,

- Similar trend observed with the onshore sample set.

Percent mercury removal in **offshore condensate** (single-matrix) containing Hg^0 and $HgCl_2$, and **offshore produced water** containing $Hg(NO_3)_2$. Results adjusted to account for mercury loss. Initial mercury concentration for each sample was *ca.* 1,000 ppb wt. Each percentage represents a samples size $n \geq 2$.

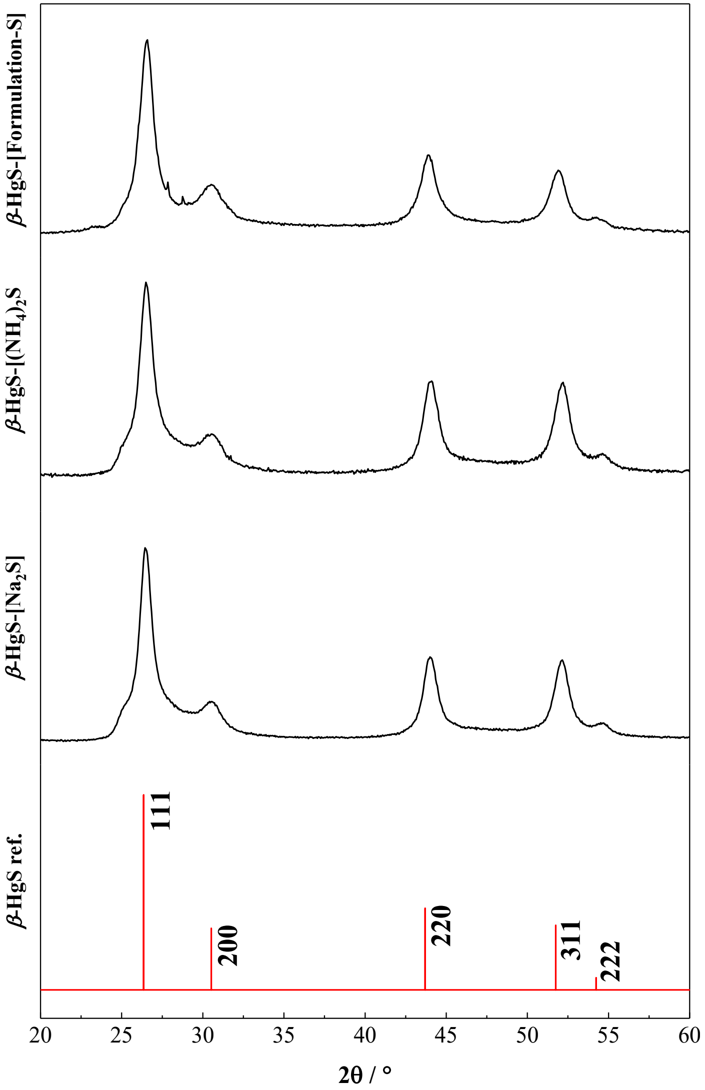
Formulation-S resulted achieved highest overall Hg removal for both onshore and offshore sample sets



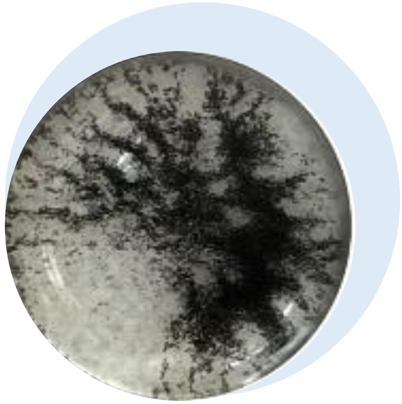


Percent mercury removal in **onshore/offshore condensate** (single-matrix) containing Hg^0 and HgCl$_2$, and **synthetic/offshore produced water** containing Hg(NO$_3$)$_2$. Results adjusted to account for mercury loss. Initial mercury concentration for each sample was *ca.* 1,000 ppb wt. Each percentage represents a samples size *n* ≥ 2.

Black precipitates formed in solution post mercury removal was identified as *β*-HgS (metacinnabar)

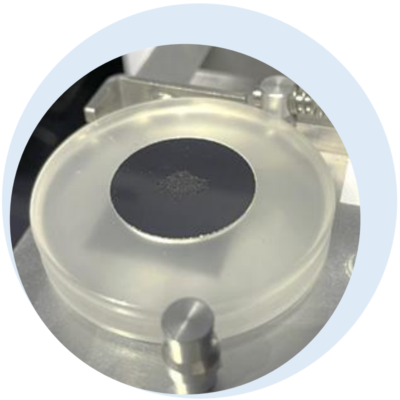


Diffractogram of black precipitates isolated from treatment of solution containing $Hg(NO_3)_2$.



β-HgS-[Na_2S]

β-HgS-[$(NH_4)_2S$]



β-HgS-[Formulation-S]

Pictured here on zero background sample holder

- ➢ All 3 diffractograms was **matched** to powder diffraction file of *β*-HgS – PDF 00-006-0261 (star quality) obtained from ICDD and exhibits cubic (zinc blende) phase of **metacinnabar**.

  NOTE Cinnabar (*α*-HgS), red HgS, exhibits hexagonal phase.

- ➢ **2 main polymorphs** of mercury(II) sulfide exist; *α*-HgS (red) and *β*-HgS (black). The metacinnabar variant results from precipitation.

Source: i. Simon, M.; Jonk, P.; Wuhl-Couturier, G.; Daunderer, M. Handbook of Extractive Metallurgy Chapter 17; Habashi, F., Ed.; Wiley-VCH (1997) Vol. Volume 2. ii. Wong, S.M.A.S and Salam, S. IPTC-24982-MS: Enhancing Mercury Removal in Hydrocarbon Fluids: Efficacy of Aqueous Sulfides Extraction in Natural Gas Condensate and Produced Water, Internat. Petroleum. Tech. Conf., Kuala Lumpur (Feb. 2025).

Summary and conclusion

- Formulation-S was able to attain mercury removal of
  - 65-69% (Hg^0) in condensate,
  - 88-92% ($HgCl_2$) in condensate,
  - 88-95% ($Hg(NO_3)_2$) in produced water,
- The formulation was able to remove mercury from both hydrocarbon and water matrices, suggesting it was **able to disperse/miscible in both matrices**,
- **Black precipitants** were observed to have formed via precipitation in treated samples,
- The black precipitate was identified to be **mercury(II) sulfide** (*i.e.* metacinnabar) from XRD analysis,
- This suggest the presence of a **reactive sulfide** species that is capable of performing oxidative complexation with the mercury species present in the sample matrix,
- The formulation can potentially be applied for **bulk-removal of mercury**.
- Room for further development and testing.

Thank you