An evaluation of monoethanolamine degradation and mitigation

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Introduction

- Atmosphere contaminants
 - Duty of care
 - Control
- Carbon dioxide (CO₂)
 - Consumable vs. regenerable
 - Amine based regenerable system
 - Monoethanolamine (MEA)
- NH₃ produced from MEA degradation









Introduction

- Degradation propagates further degradation
 - Auto-oxidation
 - Free-radical metal ions

Factors

- Temperature
- Impurities
- CO₂ loading
- Mitigation
 - Inhibitor
 - Bind to impurities, potentially act as a passivator
 - Filtration
 - Removal of impurities and decomposition by-products
- Can we do better?





The effect of CO_2 loading and temperature on MEA degradation¹

[1] Davis J. and Rochelle G., Thermal degradation of monoethanolamine at stripper conditions, Energy Procedia, 1, pp. 327-333, 2009

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Bubmarine Delivery Agency



Experimental









Experimental

Inhibitor	Chemical functionality		
1	Alcohol, carboxylic acid		
2	Sulfoxide, amide, aromatic		
3	Alcohol, pyridine-like		
4	Pyridine-like, thioether		
5	Azo, secondary amine, aromatic		
6	Secondary amine, sulfoxide		
7	Alcohol, ester		

Sorbent	Description		
1	Activated carbon (Granular)		
2	Activated carbon (Pellet)		
3	NH_3 enhanced functionalised activated carbon (Pellet)		
4	Zeolite		
5	Porous resin for cation & anion ion exchange		
6	Cation ion exchange resin (strong)		
7	Cation ion exchange resin (weak)		



Results - Baseline

- No inhibitor or filtration
 - Degradation rate constant 1.64 x 10⁻⁸ s⁻¹



NH₃ release from 4.5 M MEA solution during an experiment





Results - Inhibitors



Prospective inhibitor degradation rates





Results - Inhibitor 1 & 4

		Test sc			
Experiment	Inhibitor	MEA (M)	Inhibitor Concentration (mM)	k' (x10 ⁻⁸ s ⁻¹)	
Test 12	None	4.5	0	4.74	
Test 13a			2	4.08	
Test 13b	Inhibitor 1		20	2.15	
Test 13c			200	0.13	
Test 14a	Inhibitor 4		2	0.65	
Test 14b			20	0.15	



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Inhibitor 1 & 4

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Results - Filter media - recirculation

- Sorbent 1 with Inhibitor 1
 - Initially showed no clear improvement
- Sorbent 1 with Inhibitor 4
 - Precipitated out





Results - Filter media - recirculation

- Reduced inhibitor concentration
- Sorbent 4 caking

	Test solution composition		Filter bed		k'
Experiment	MEA (M)	Inhibitor 1 (mM)	Sorbent	Mass (g)	x 10 ⁻⁸ (s ⁻¹)
Test 17		20	-	-	0.89
Test 18a	4.5	20	Sorbent 1	10	1.23
Test 18b		200			1.16
Test 19a		20	Sorbent 2		2.51
Test 19b		200			0.91
Test 20a		20	Sorbent 3		2.15
Test 20b		200			1.52
Test 21a		20	Sorbent 5		0.60
Test 21b		200			0.74
Test 22a		20	Sorbent 6		1.15
Test 22b		200			0.42
Test 23a		20	Combout 7		0.78
Test 23b		20	Sorbent /	2	1.35

Results - Dual sorbent beds

- Pelletised sorbent 2 plus
 - Sorbent 4
 - Sorbent 5
 - Sorbent 6
 - Sorbent 7
- All dual beds underperformed with 20 mM inhibitor
- At 200 mM all dual beds outperformed sorbent 1 alone, with the exception of sorbent 2 | 5
- Sorbent 2 | 7 best performing 0.27 x 10⁻⁸ s⁻¹



Conclusions

- Inherently MEA will degrade over time and this is exacerbated by temperature and the presence of impurities
- Impact on degradation: Inhibitor >> sorbent = CO₂ loading
- Inhibitor 1 was the most appropriate for the application in the system. Inhibitor 4 performed better but raised toxicity concerns and precipitated out of solution
- Sorbent 1 was outperformed by several alternative sorbent medias
- Dual sorbent beds, with synergistic functionalities, yielded the best performance



Acknowledgements

Charles Cummings

UK MOD atmosphere control stakeholders

Chemistry (Atmospheres) Team





This work was undertaken as part of the Maritime Strategic Capability Agreement between the Naval Authority Group and QinetiQ



Any questions



