

A photograph of a submarine on the water, viewed from a low angle. The submarine is dark and has a conning tower with various antennas and sensors. The sky is dark and cloudy, with some light breaking through near the horizon. The water is dark with white foam from the submarine's wake.

Research into Alternative Adsorbents for Atmospheric Control of Monoethanolamine and Ammonia on Royal Navy submarines

Edward Harris

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Agenda

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2 Experimental

3 Analysis method

4 Results and discussion

COTS Adsorbents

Acid-impregnated resins

5 Conclusions and Acknowledgments

Introduction

- Elevated levels of carbon dioxide (CO₂) in enclosed environments poses a significant hazard to exposed personnel
- Royal Navy submarines use monoethanolamine (MEA) to remove CO₂ from the atmosphere
- MEA and its breakdown product, ammonia (NH₃) can contaminate the atmosphere
- MEA and NH₃ are hazardous to health
- MEA and NH₃ can be oxidised to NO_x in the catalyst burner
- Strong acid cation (SAC) ion-exchange resin beds adsorb these contaminants
- An evaluation of COTS adsorbents and in-house acid-impregnated resins has been conducted

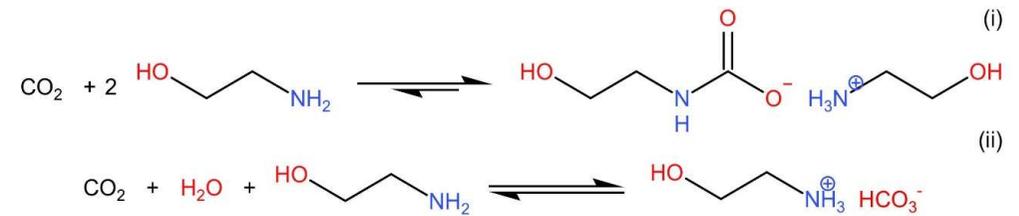


Figure 1: Formation of (i) MEA-carbamate (ii) MEA-bicarbonate

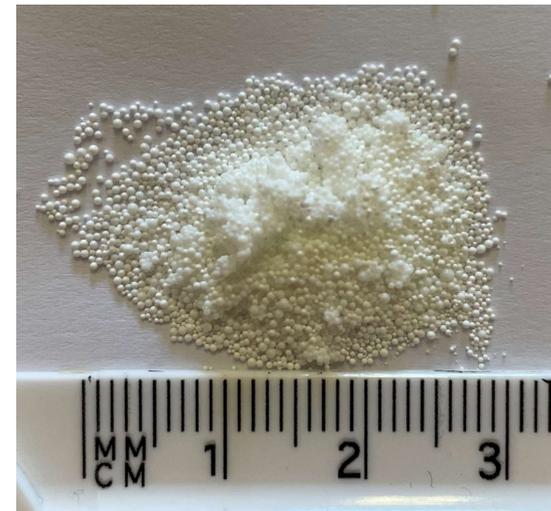


Figure 2: Example of resin size

Experimental

- **Nine COTS adsorbents**

- **Charcoals**

- Unfunctionalised

- Charcoal 1

- Functionalised (proprietary)

- EMCEL 131.05.1

- EMCEL 131.74.1

- Functionalised (phosphoric acid)

- Ammonosorb

- **Ion-exchange resins**

- SAC

- DOWEX® 50W8X

- SAC resin 1 (current in-service)

- Chemsorb® 620-60

- Multigard® 3800

- **Weak acid cation (WAC)**

- DOWEX® MAC-3

- **Acid-impregnated resin**

- Commercially available resin, Resin 3, impregnated with phosphoric acid via different methods

- Methods included the use of different solvents and extraction techniques

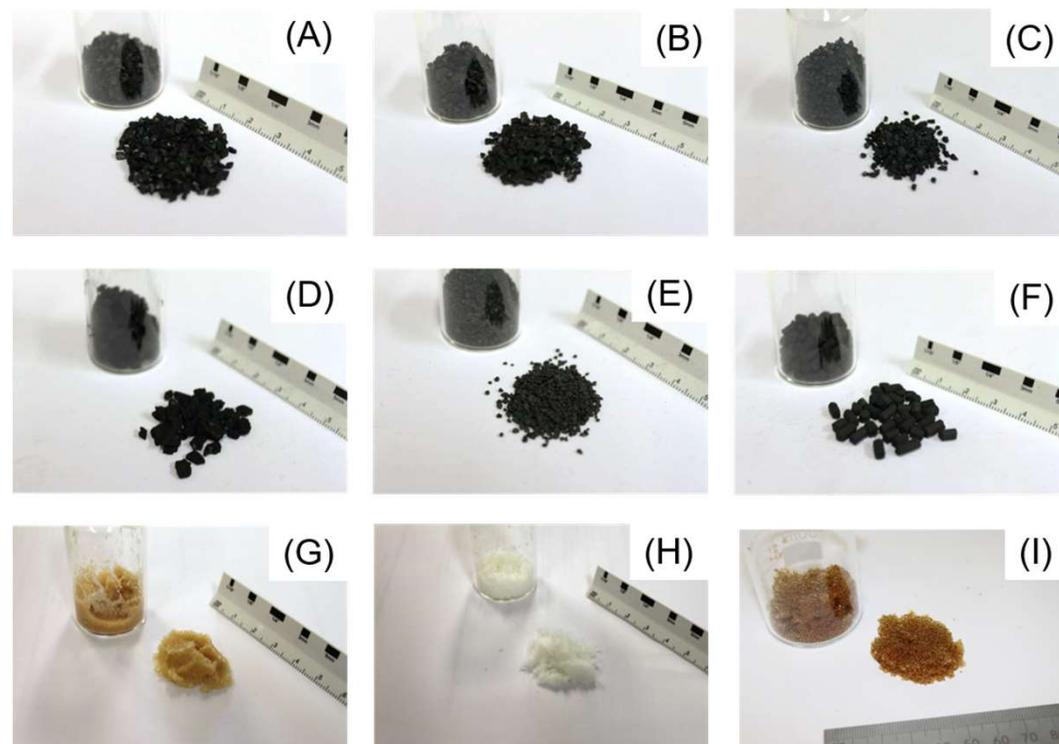


Figure 3: COTS Adsorbents: (A) Charcoal 1, (B) EMCEL 131.05.1, (C) EMCEL 131.74.1, (D) Chemsorb® 620-60, (E) Multigard® 3800, (F) Ammonosorb, (G) DOWEX® 50W8X, (H) DOWEX® MAC-3, (I) SAC resin 1

Experimental

- NH_3 adsorption test apparatus
 - NH_3 standard with humidified air
 - Adsorbent bed (10 mm)
 - FTIR detector (Gaset DX4040)
 - 0.03 s residence time
 - 75 ppm NH_3
- MEA adsorption test apparatus
 - Vaporised MEA blended with humidified air
 - Adsorbent bed (10 mm)
 - FTIR detector (Gaset DX4040)
 - 0.03 s residence time
 - 30 ppm MEA



Figure 4: Experimental apparatus for NH_3 tests

Experimental

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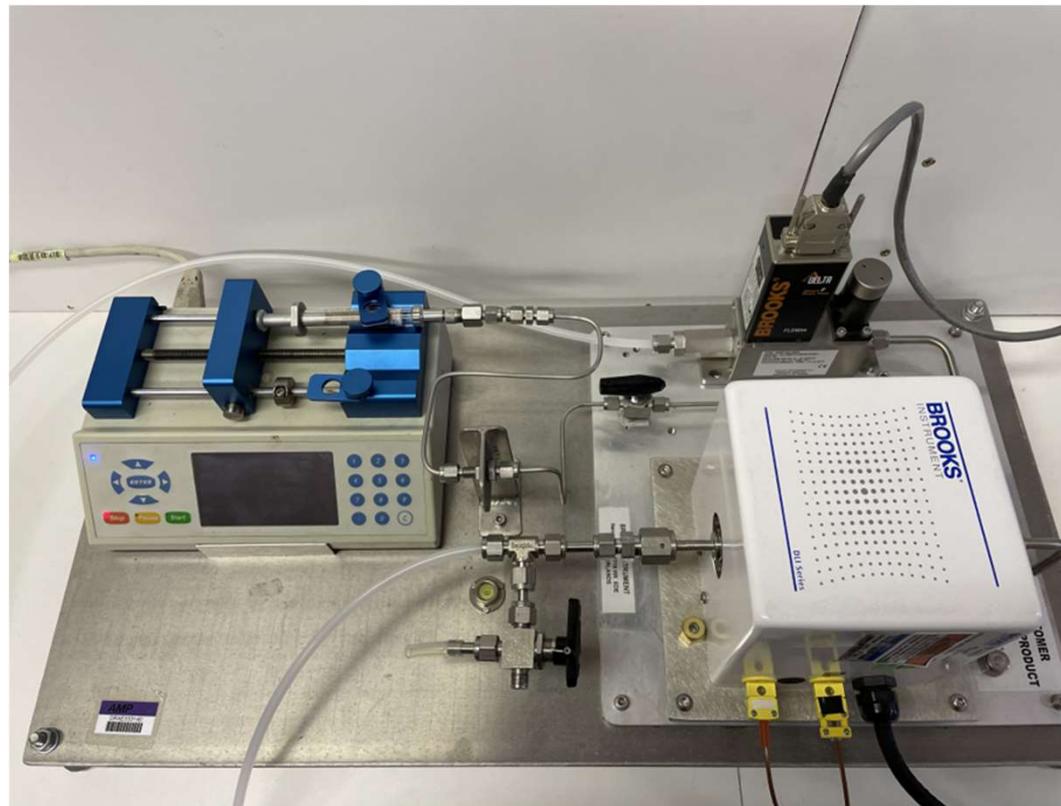


Figure 5: Direct Liquid Injector - Vapour Generator

Analysis Method

- Percentage breakthrough of NH₃ and MEA at the outlet of the filter bed was calculated by Equation 1
- Sorbent capacities at specific breakthrough (10, 25 & 50%) were calculated with Equation 2
- When 50% breakthrough was not seen. Equation 3 used to estimate maximum sorbent capacity

$$\% \text{ Breakthrough} = \frac{[\text{Conc}]_{\text{outlet}}}{[\text{Conc}]_{\text{inlet}}} \cdot 100$$

Equation 1

$$q_b = \frac{F}{m} \int_0^{t_b} [\text{Conc}]_{\text{inlet}} - [\text{Conc}]_{\text{outlet}} \cdot dt$$

Equation 2

$$q_b = q_{\text{max}} \times \frac{t \times c'}{(1 + t \times c')}$$

Equation 3

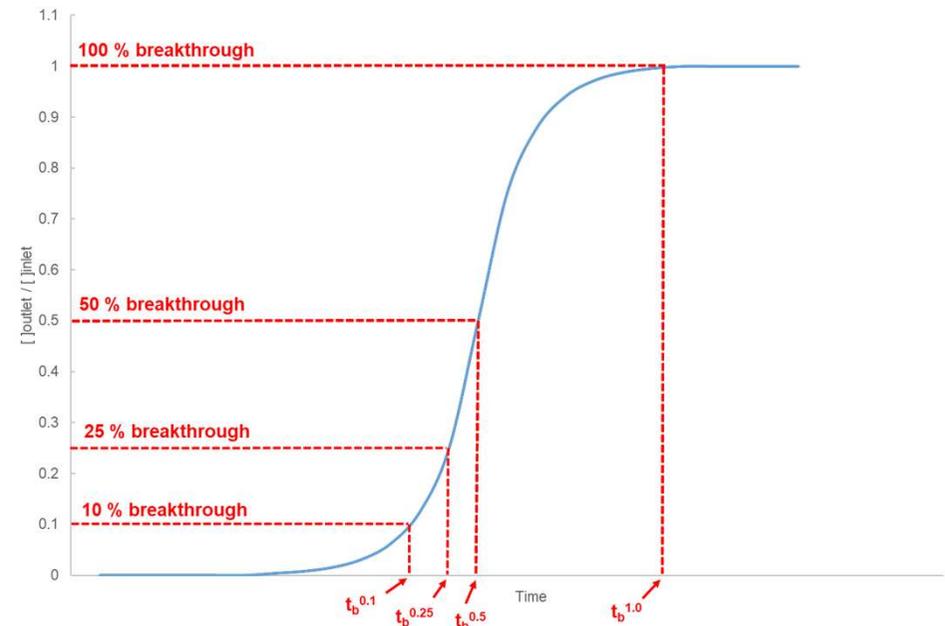


Figure 6: Ideal breakthrough curve

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Results and Discussion – COTS adsorbents (NH₃)

- The best performing adsorbents were the three ion-exchange resins
- Capacities
 - SAC resin 1 – $q_b^{0.1}$: 27.7 mg.g⁻¹
 - DOWEX 50WX8 – $q_b^{0.1}$: 13.8 mg.g⁻¹
 - DOWEX MAC-3 – $q_b^{0.1}$: 13.8 mg.g⁻¹
- Acid functionalisation was a driver for adsorption
- Suggests NH₃ adsorption was primarily a chemisorption process

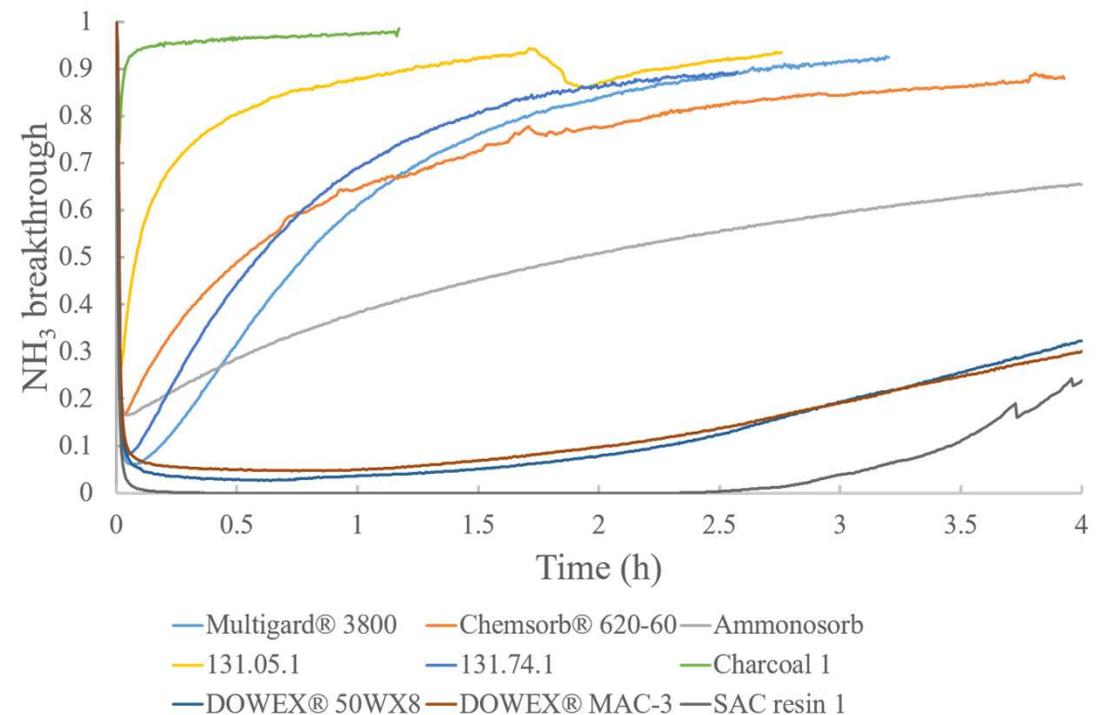


Figure 7: NH₃ breakthrough of COTS adsorbents

Results and Discussion – COTS adsorbents (MEA)

- The best performing adsorbents were the activated charcoals
- Capacities
 - Multiguard 3800 – $q_b^{0.5}$: 49.7 mg.g^{-1}
 - SAC resin 1 – $q_b^{0.5}$: 38.4 mg.g^{-1}
 - Charcoal 1 – $q_b^{0.5}$: 34.4 mg.g^{-1}
- Physical properties were a driver for adsorption
- Suggests MEA adsorption was primarily a physisorption process
- SAC resin 1 highlighted that ion-exchange resins can facilitate physisorption if they have the suitable physical properties

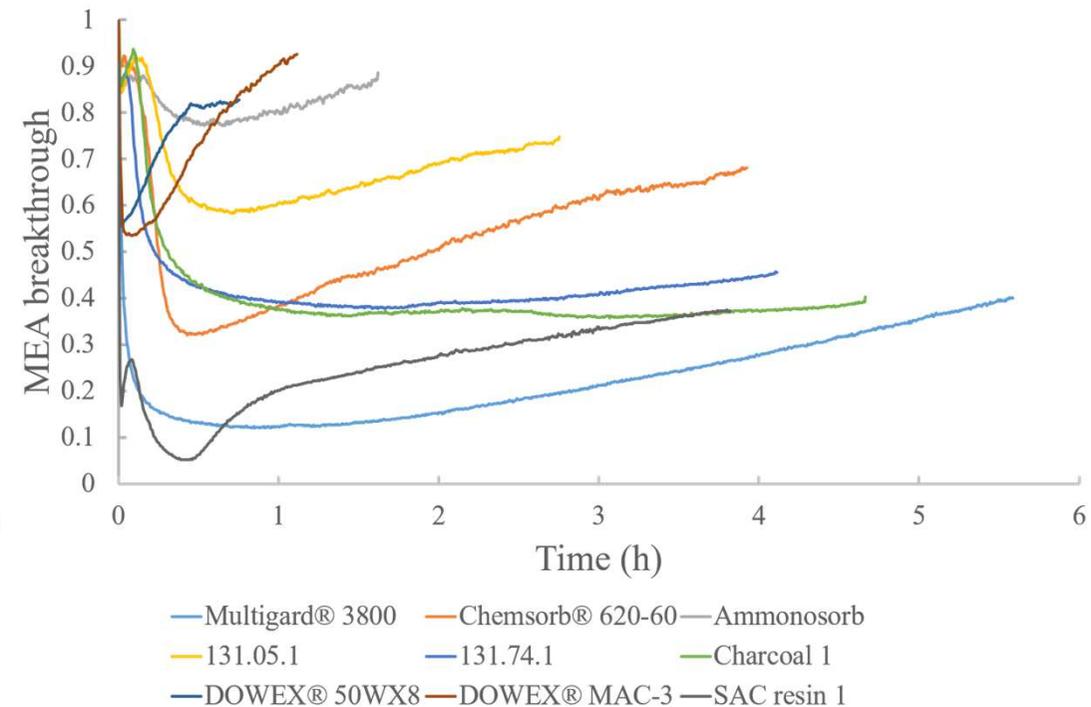


Figure 8: MEA breakthrough of COTS adsorbents

Results and Discussion – Acid-impregnated resin (NH₃)

- Preparation method had substantial effect on NH₃ capacity
- Capacities
 - Method 1 – $q_b^{0.1}$: 88.3 mg.g⁻¹
 - Method 4 – $q_b^{0.1}$: 56.3 mg.g⁻¹
 - Method 3 – $q_b^{0.1}$: 6.3 mg.g⁻¹
 - Method 2 – $q_b^{0.1}$: 3.6 mg.g⁻¹
- Method 2 & 3 resulted in little acid impregnation
- Method 1 & 4 had $q_b^{0.1}$ that were **3.2 and 2.0** times greater than SAC Resin-1
- Method 4 preferred as is a less complex method

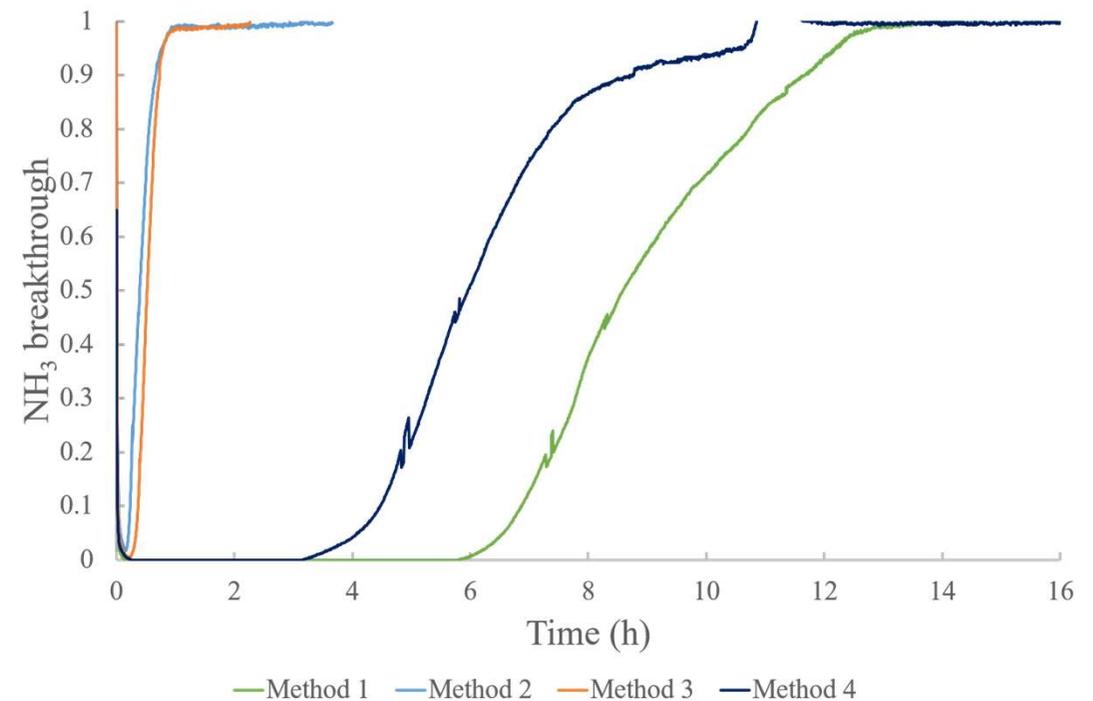


Figure 9: Effect of preparation method on NH₃ breakthrough of acid-impregnated Resin-3

Results and Discussion – Acid-impregnated resin (MEA)

- Same pattern in MEA capacity across different methods
- All resins had high MEA capacity in comparison to COTS
- Capacities
 - Method 4 – $q_b^{0.1}$: 91.1 mg.g^{-1}
 - Method 1 – $q_b^{0.1}$: 82.3 mg.g^{-1}
 - Method 2 – $q_b^{0.1}$: 54.6 mg.g^{-1}
 - Method 3 – $q_b^{0.1}$: 40.3 mg.g^{-1}
- Resin-3 has suitable physical properties for MEA adsorption
- Acid-impregnation further increases capacity
- Method 1 & 4 had $q_b^{0.1}$ that were **20 and 22 times** greater than SAC resin 1
- Method 4 gave best compromise between preparation cost and removal performance

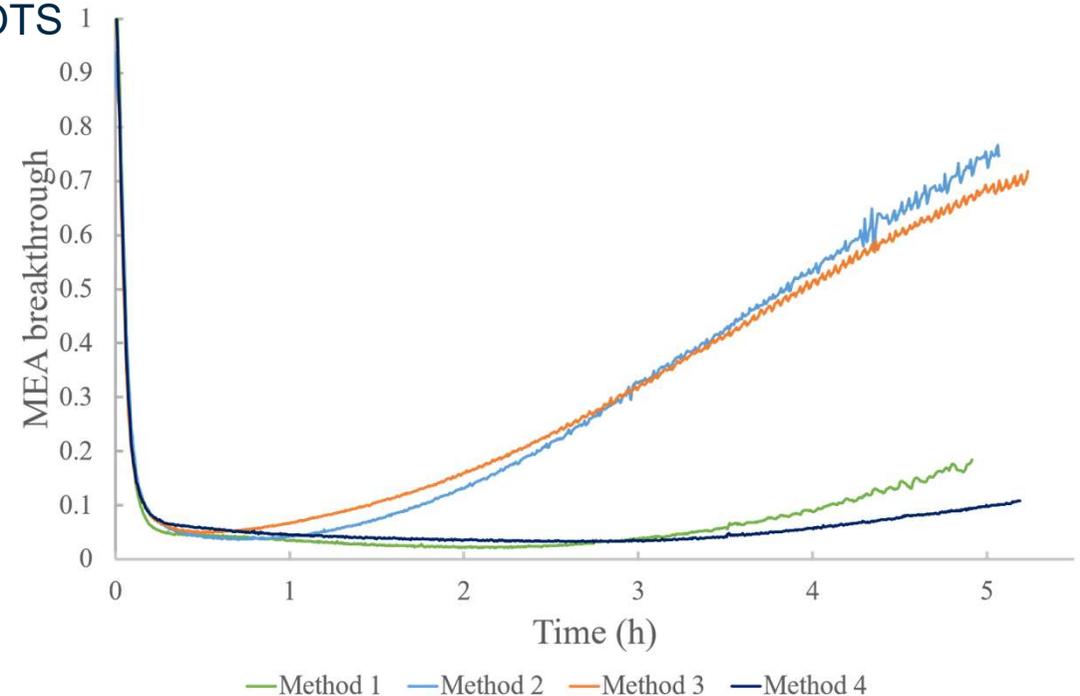


Figure 10: Effect of preparation method on MEA breakthrough of acid-impregnated Resin-3

Conclusions

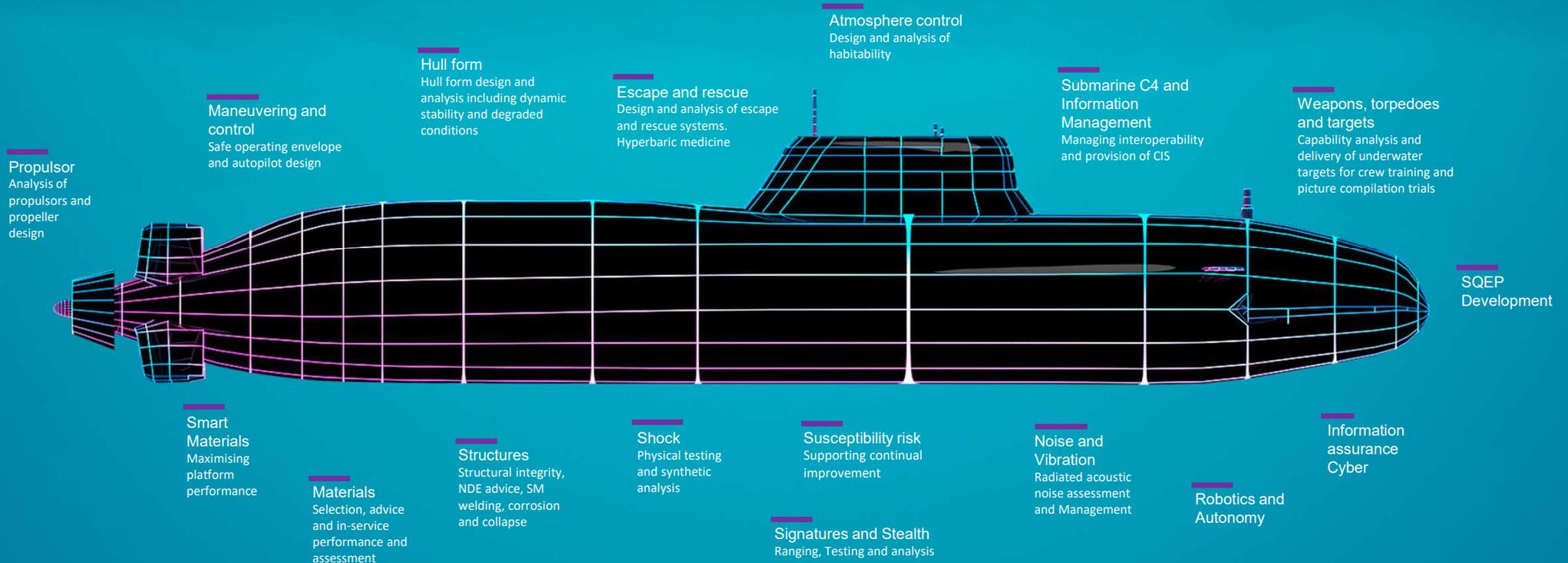
- NH_3 adsorption was primarily due to a chemisorption process between NH_3 and surface acid groups
- MEA adsorption was predominately due to a physisorption process
- Novel acid-impregnated resin samples were prepared and an optimised method was identified
- Resin samples produced had NH_3 and MEA capacities up to **3.2 and 22 times** greater than the best performing COTS adsorbent
- Resin prepared via Method 4 had the best compromise between preparation cost and removal performance

Acknowledgments

- This work was undertaken as part of the Maritime Strategic Capability Agreement between the UK MOD/Submarine Delivery Agency and QinetiQ.



And you for your attention...



Additional QinetiQ relevant capabilities used in submarine customer discussions

Physical and synthetic testing
Established testing facilities and support of in-country growth

Combat Safety
Understanding and articulating the susceptibility and risk of a platform

Acquisition and Through-life Support
Strategic enterprise modelling including requirements, project management and integrated logistics support

Integrated Survivability
Understanding submarine vulnerability through Survive® software modelling

Paramarine®
Renowned structural design and analysis software

Safety management
Advice and support in management of an enterprise wide safety ecosystem.

Training simulators
Design and build of SM control room simulators and blended training solutions