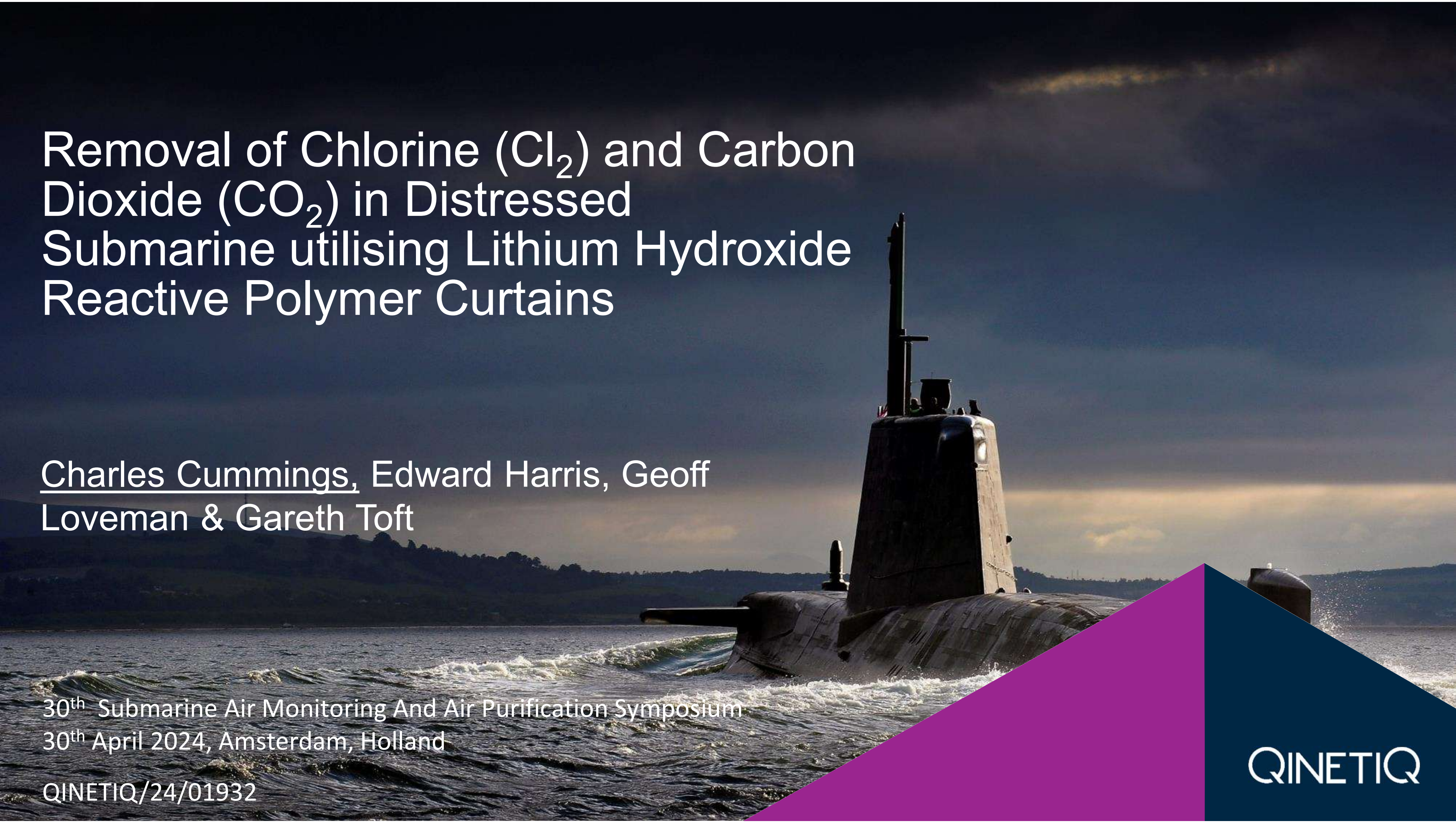

Removal of Chlorine (Cl_2) and Carbon Dioxide (CO_2) in Distressed Submarine utilising Lithium Hydroxide Reactive Polymer Curtains

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30th Submarine Air Monitoring And Air Purification Symposium
30th April 2024, Amsterdam, Holland

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Contents

1. Introduction

Chemistry (Atmospheres)

- QinetiQ
  - Science and Technology firm HQ in Farnborough, UK
  - Chemistry (Atmospheres) Team sit within Maritime Life Support, alongside Diving and Submarine Escape
  - Provide technical support and independent assurance
    1. Research and development
    2. Test and evaluation
    3. Fleet support
- Expertise in:
  1. Submarine ventilation modelling
  2. Atmosphere purification
  3. Atmosphere analysis and monitoring
  4. Equipment test and evaluation
  5. Air quality (toxicology) investigative trials

Background

- Distressed Submarine (DISSUB)
  - Submarine major incident has been declared
  - Submarine cannot manoeuvre
  - Submarine cannot operate routine life support systems including:
    - Oxygen generation
    - Carbon dioxide (CO_2) removal
    - Other contaminant removal
- Emergency Life Support
  - Oxygen generators (“oxygen candles”)
  - CO_2 removal via lithium hydroxide (LiOH) reactive polymer curtains (LiOH-RPC)

But what is the fate of other contaminants?

Figure 1: Distressed Submarine

Figure 2: Oxygen candle and LiOH-RPC

Introduction

$$2Cl^{-}_{(aqueous)} \rightarrow Cl_{2\ (gas)} + 2e^{-}$$

$$2H^{+}_{(aqueous)} + 2e^{-} \rightarrow H_{2\ (gas)}$$

- Chlorine (Cl_2) can be produced from the electrolysis of seawater
- Generated from any exposure live wires or battery terminals (>2V)
- Elevated levels of chlorine poses a significant hazard
  - UK workplace exposure limits: 0.5 ppm for 15 min
  - USA NIOSH exposure limit: 0.5 ppm for 15 min
  - Immediate Danger to Life and Health limit: 10 ppm
- Some navies have adopted 1 ppm submarine escape limit

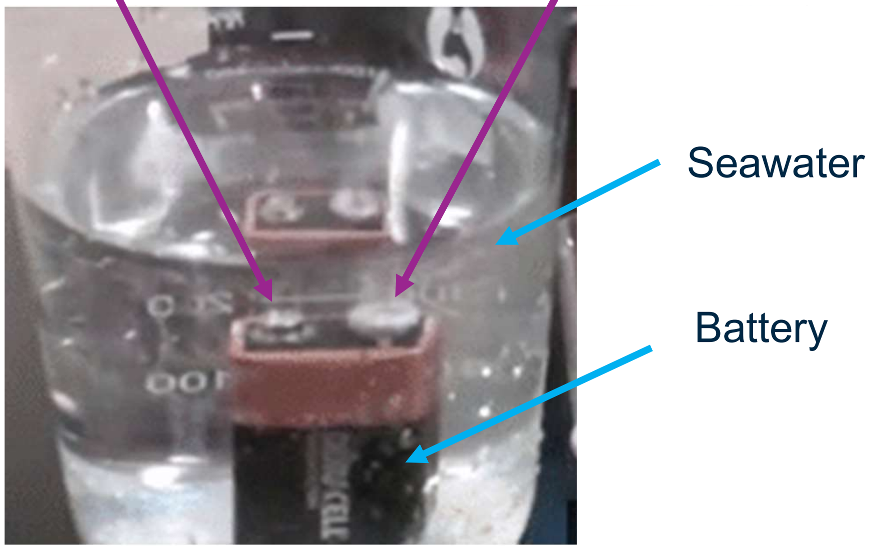

Figure 3: Chlorine and hydrogen generation

Our goal was to characterise Cl_2 removal on the laboratory small scale

Introduction

- Cl_2 removal
  - Cl_2 removal should be facilitated by LiOH RPC
- Quantify Cl_2 removal on LiOH RPC
  - On the laboratory scale…. Cl_2 removal?
  - How quick? – Chemical kinetics, capture rate?
  - How much? – Capacity?
  - What is the influence of CO_2?
  - Does curtain storage time affect removal?

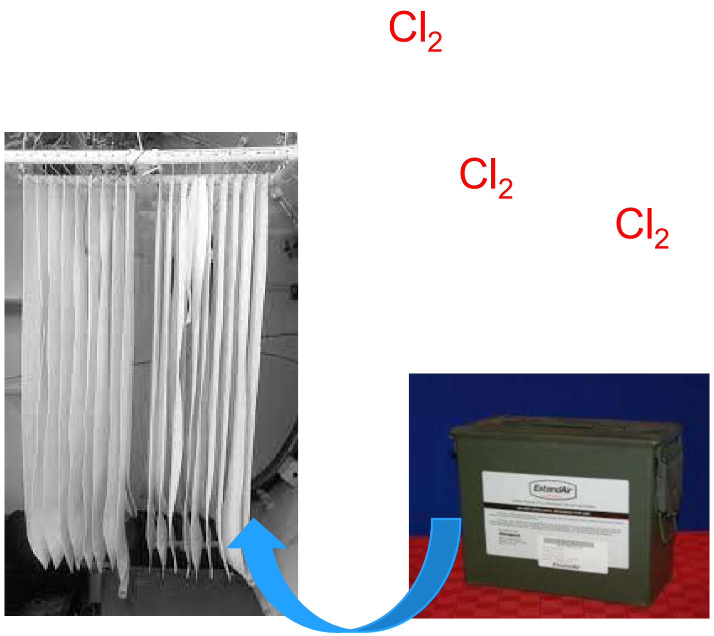

Figure 4: Chlorine capture via LiOH RPC and box containing 70 sheets

- Direct reaction

$$Cl_2 + 2LiOH \rightarrow LiCl + LiClO + H_2O$$

- Reactive via intermediate

$$2Cl_2 + 2H_2O \rightarrow HClO_2 + 3HCl$$

$$HClO_2 + LiOH \rightarrow LiClO_2 + H_2O$$

$$HCl + LiOH \rightarrow LiCl + H_2O$$

2. Experimental

Experimental – Apparatus and materials

- Apparatus
  - 158 L test chamber
  - Cl_2 and CO_2 monitoring via electrochemical and IR sensors
  - The tank contents were recirculated at 2 $L.min^{-1}$
- Source contaminants
  - Cl_2 gas was generated from a permeation device
  - Pure CO_2 gas was injected direct from a cylinder

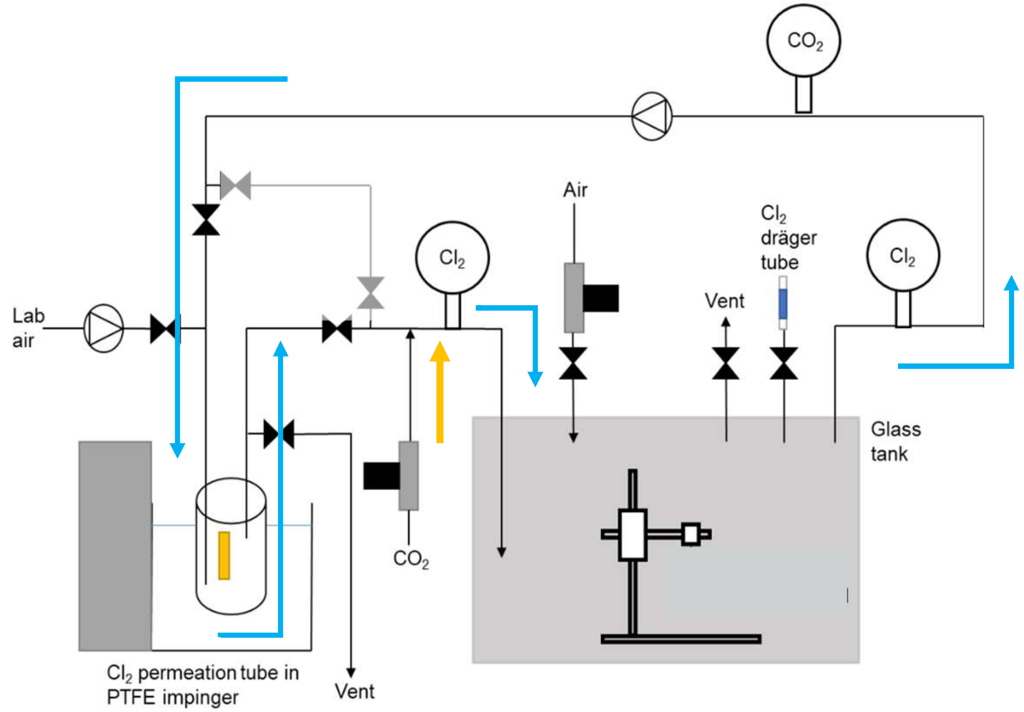

Figure 5: Test Apparatus - Cl_2 and CO_2 filling

Experimental – Apparatus and materials

- Apparatus
  - 158 L test chamber
  - Cl_2 and CO_2 monitoring via electrochemical and IR sensors
  - The tank contents were recirculated at 2 $L.min^{-1}$
- Source contaminants
  - Cl_2 gas was generated from a permeation device
  - Pure CO_2 gas was injected direct from a cylinder
- LiOH RPC
  - All LiOH RPC were cut into 10 x 10 cm
    1. In-date LiOH RPC samples were from Micropore Corp. (~3 y) – **Majority Tests**
    2. CO_2-saturated LiOH RPC (in-date)
    3. Limited tests on an out-of-date (~14 y) LiOH RPC samples

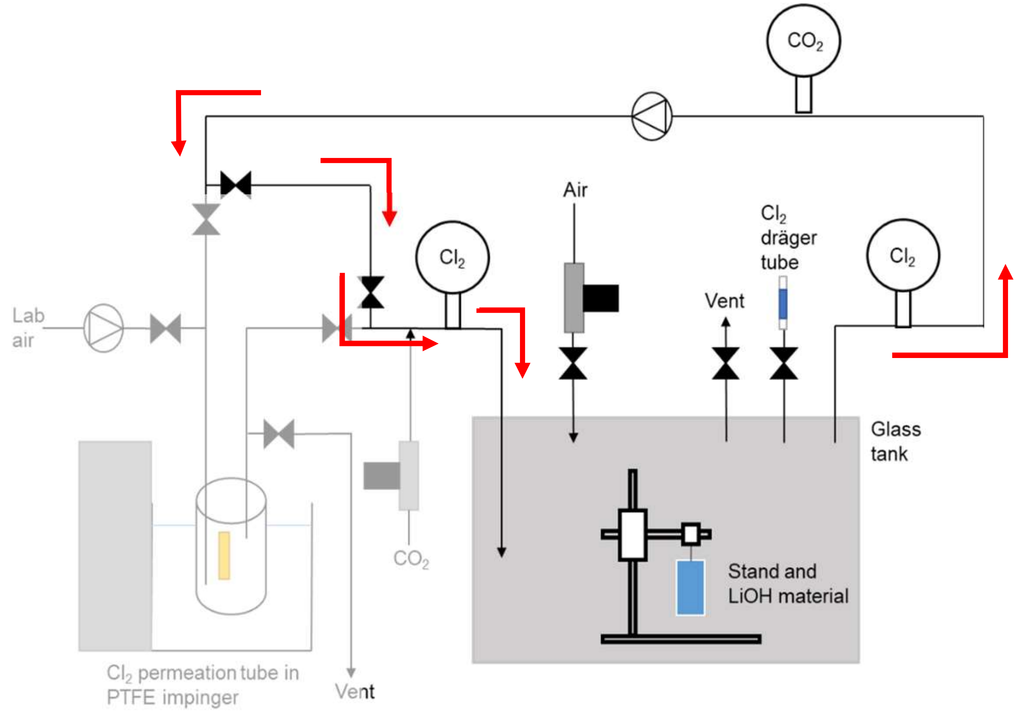

Figure 6: Test Apparatus - Cl_2 and CO_2 removal

Experimental – Apparatus and materials

Cl_2
gas sensors

LiOH RPC

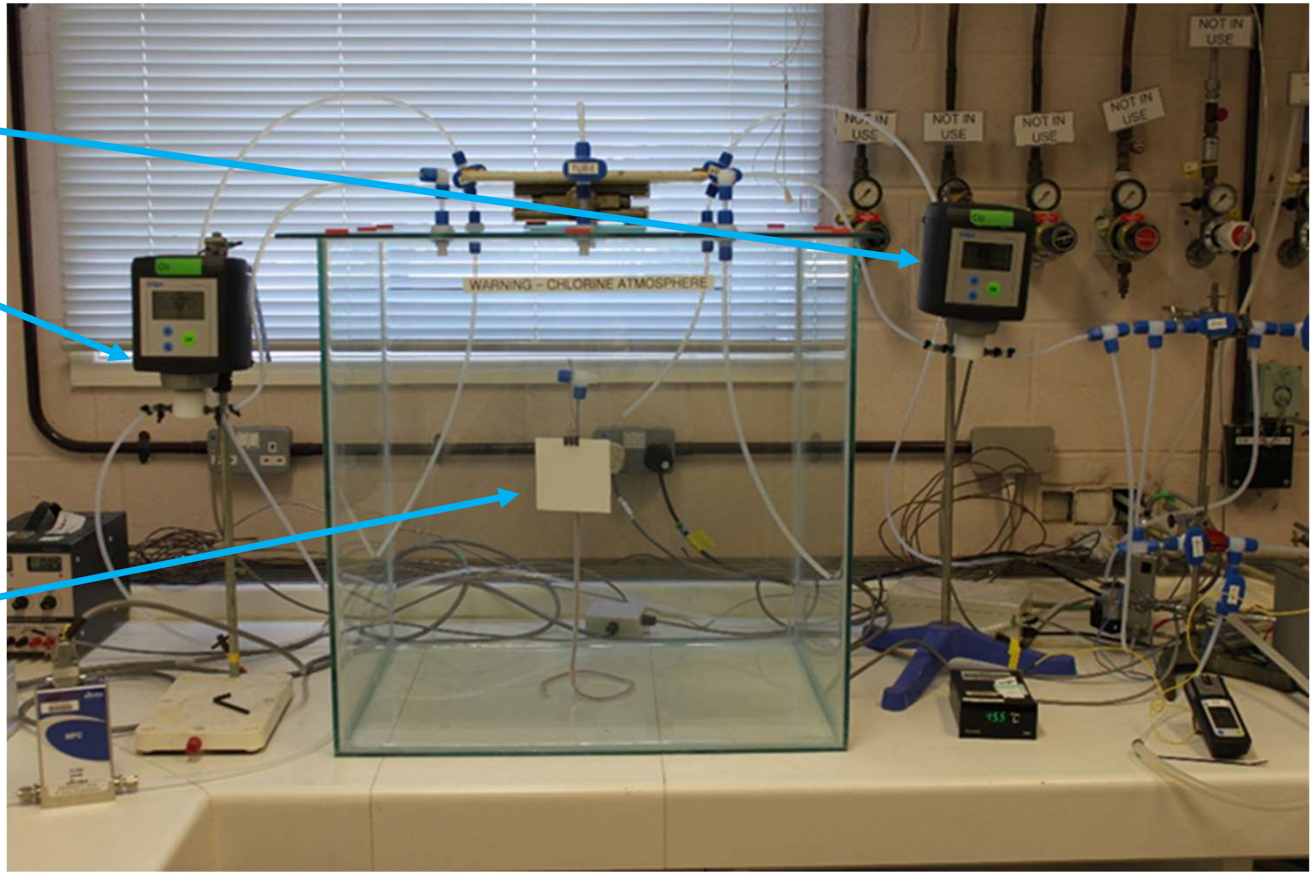

Figure 7: Photograph of test apparatus

Experimental – Data analysis

- LiOH RPC contaminant removal kinetics
  - Pseudo first order rate law

$$\boldsymbol{Capture\ Rate} = \frac{d[contaminant]}{dt} = k'_{obs}[contaminant]$$

$$k'_{removal} = k'_{obs} - k'_{background}$$

  - $k'_{removal}$ is likely a product of a number of processes (Langmuir kinetics) including:
    1. Mass transport
    2. Adsorption
    3. Direct reaction
    4. Exhaustion LiOH
    5. Reaction via intermediates…
  - Lab exp ≈ Box deployment in 80 m^3 compartment
  - Capacity calculated from literature and test data
  - 2 repeat experiments

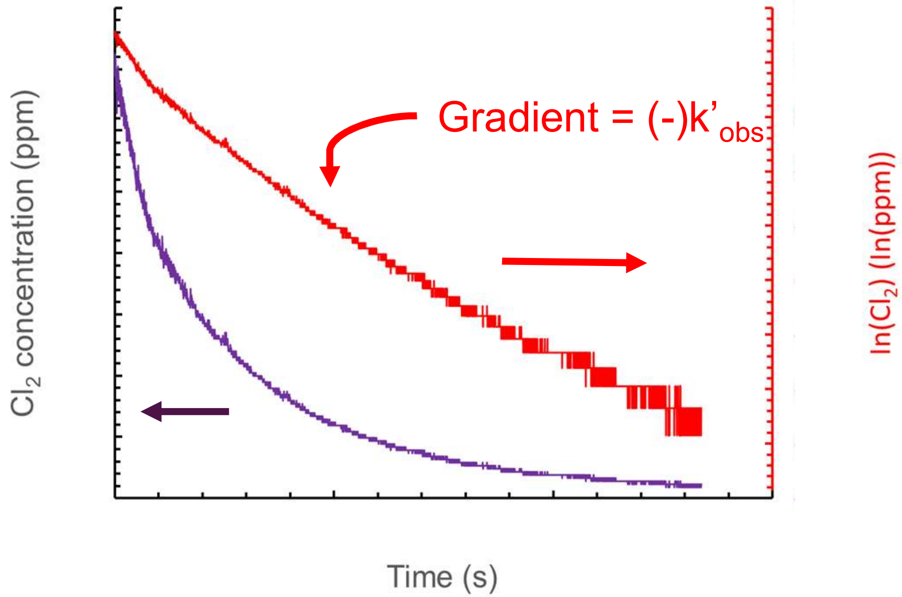

Figure 8: Example Cl_2 removal plot and analysis

3. Results and Discussion – Cl_2 and CO_2 removal on in-date LiOH RPC

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Results and discussion – Cl_2 removal

- k'$_{removal}$ for Cl_2 was 1.24 $\times10^{-6}$ $s^{-1}.cm^{-2}$
- Cl_2 capture rate for box deployment in a 80 m^3 compartment was calculated:
  - 53 $mL.h^{-1}.box^{-1}$ at 1 ppm Cl_2
- Gravimetric analysis showed only a small mass increase of ~1.24 g was detected during experiments.

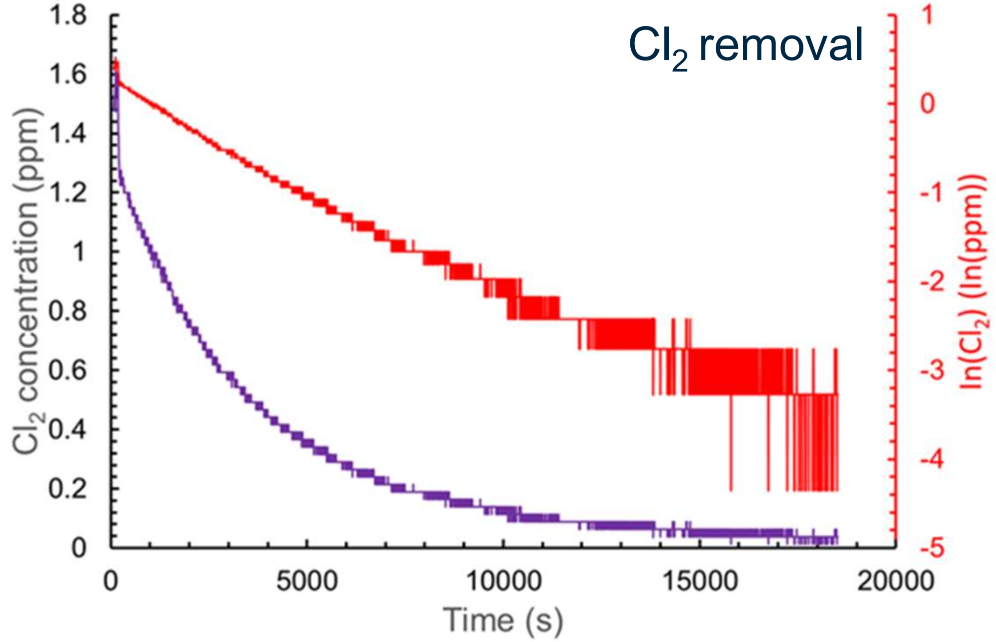

Figure 9: Cl_2 removal by LiOH-RPC

Results and discussion – CO_2 removal

- Data consisted of two regions, the first from 30-1250 s and second from 1250 s onwards
- $k'_{removal}$ for CO_2 removal was 0.76 x10^{-6} $s^{-1}.cm^{-2}$
- Cl_2 removal rate constant was 61% faster than that of CO_2.
- CO_2 capture rate for box deployment in a 80 m^3 compartment was calculated:
  - 250 $mL.h^{-1}.box^{-1}$ at 0.7 % CO_2

CO_2 capture >> Cl_2 capture

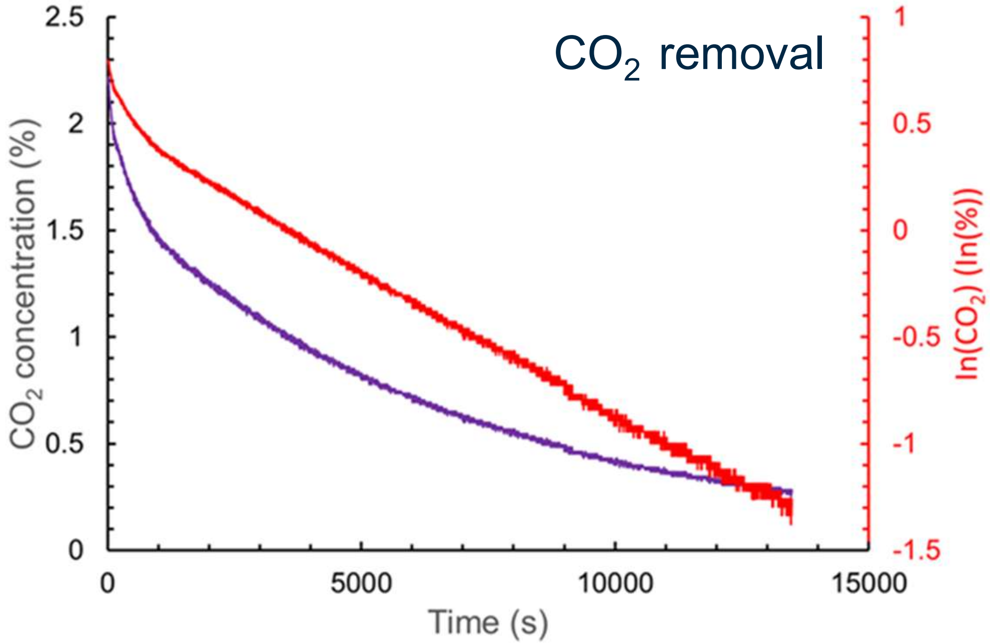

Figure 10: CO_2 removal by LiOH-RPC

Results and discussion – Cl_2 and CO_2 removal

- Repeat experiments were conducted with CO_2 and Cl_2
- The mean $k'_{removal}$ for each contaminant was:
  - Cl_2: 1.51 $\times10^{-6}$ $s^{-1}.cm^{-2}$
  - CO_2: 0.74 $\times10^{-6}$ $s^{-1}.cm^{-2}$
- The rate constant of Cl_2 removal increased by 20% in the presence of CO_2 due to changes in:
  - Temperature
  - Humidity
  - Convection (mass transport)
- Contaminant capture rate for box deployment in a 80 m^3 compartment with was calculated:
  - 240 $mL.h^{-1}.box^{-1}$ at 0.7 % CO_2
  - 69 $mL.h^{-1}.box^{-1}$ at 1 ppm Cl_2

CO_2 capture >> Cl_2 capture

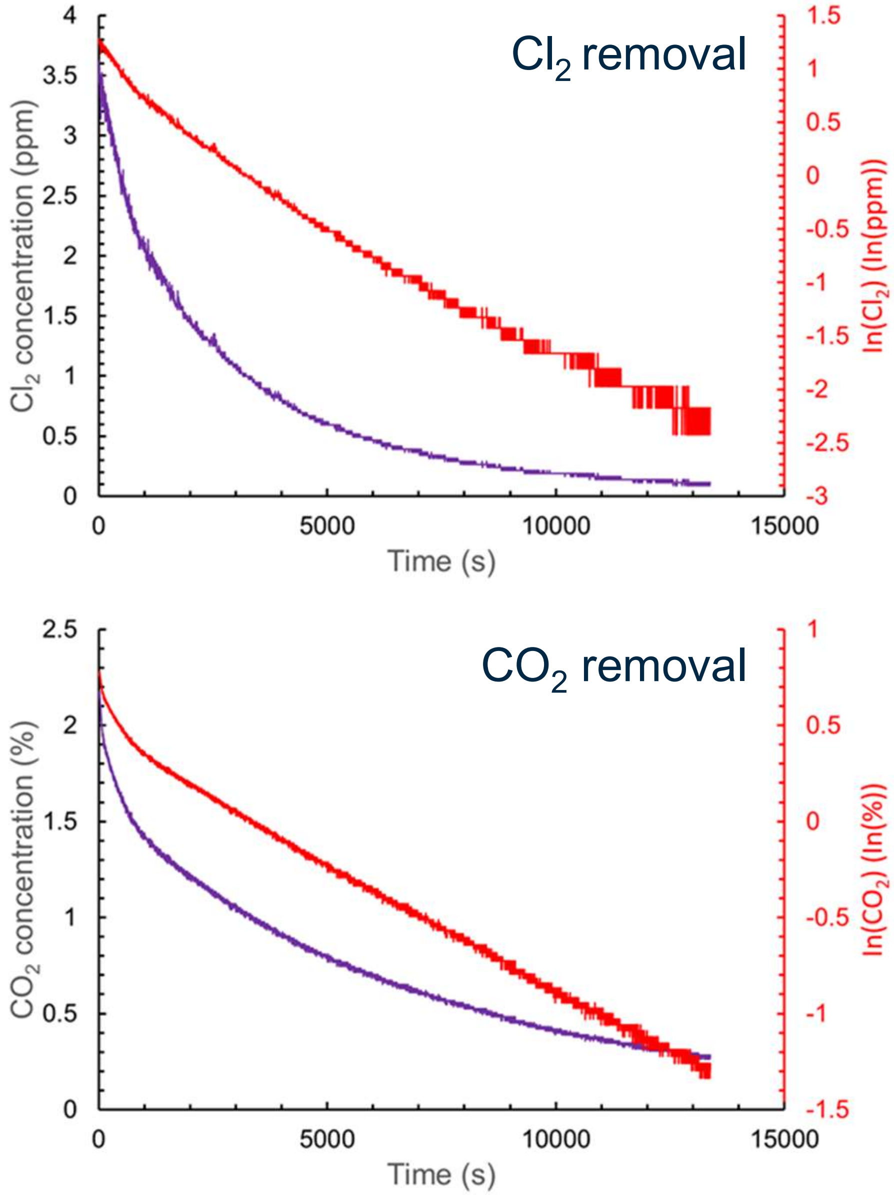

Figure 11: Simultaneous Cl_2 & CO_2 removal by LiOH-RPC

Results and discussion – Cl_2 and CO_2 capacity

- CO_2 capacity experiments were conducted on curtain materials.
- CO_2 maximum capacity of LiOH RPC is 847 $mg.g^{-1}$ (~92% saturated)
- Based on the data obtained an estimate of Cl_2 theoretical maximum capacity was calculated to be ~1366 $mg.g^{-1}$
- This is equivalent to ~7.7 kg of Cl_2 per box of LiOH curtains

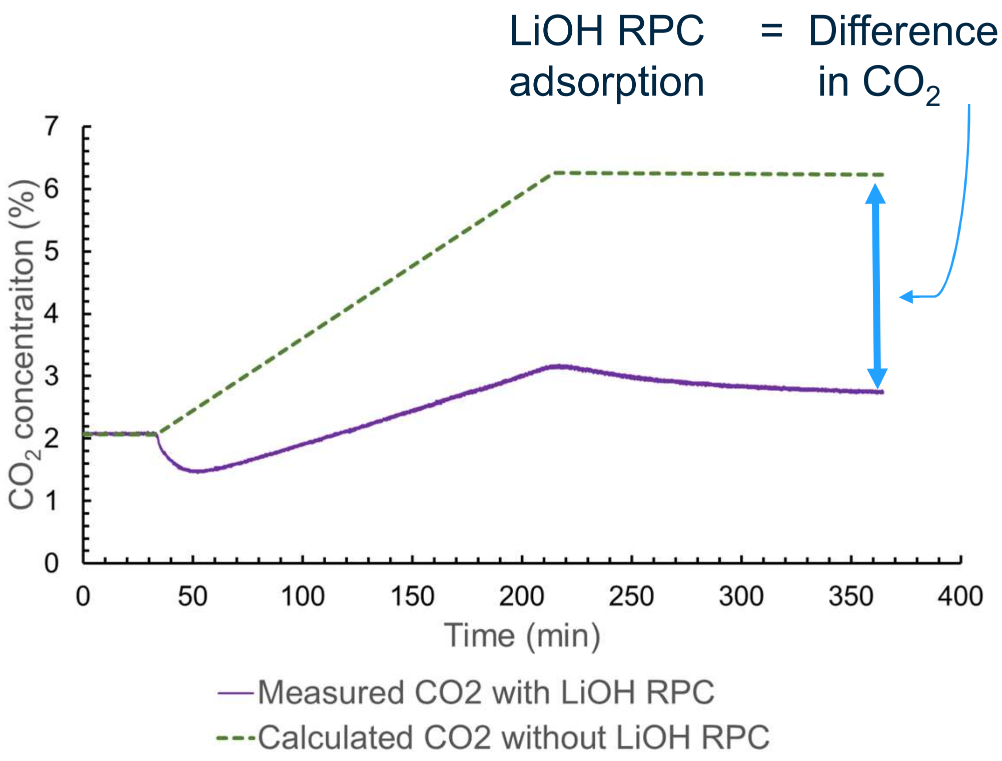

Figure 12: CO_2 capacity by LiOH-RPC

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3. Results and Discussion – Removal on CO_2 saturated LiOH RPC

Results and discussion – Cl_2 and CO_2 removal on CO_2-saturated LiOH RPC

- No CO_2 capture was observed (all LiOH converted to Li_2CO_3)
- $k'_{removal}$ of Cl_2 during the fully carbonated curtain tests was 0.28 $\times 10^{-6}$ $s^{-1}.cm^{-2}$
  - 77% less when exposed to only Cl_2
  - 81% less when exposed to Cl_2 and CO_2
- Cl_2 capture rate for box deployment in a 80 m^3 compartment with was calculated:
  - 8 $mL.h^{-1}.box^{-1}$ at 1 ppm Cl_2
- LiOH curtains saturated with CO_2 therefore continue to remove Cl_2 albeit at a reduced rate. Nevertheless, this could be beneficial in a DISSUB scenario

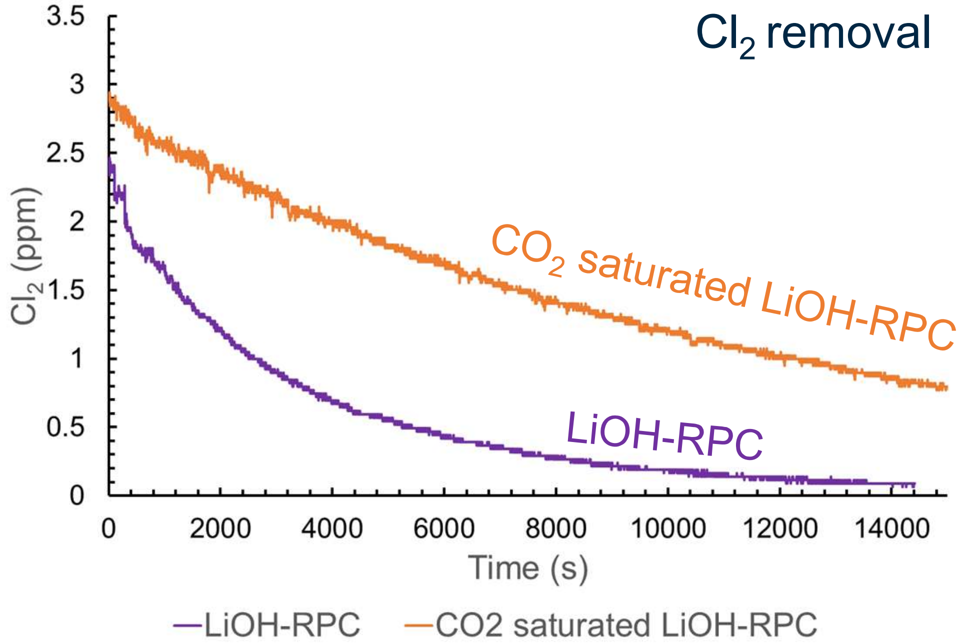

Figure 13: Cl_2 removal by (purple) LiOH-RPC and (orange) CO_2-saturated LiOH-RPC

3. Results and Discussion – Compartment modelling

Results and discussion – Compartment modelling

- Limited modelled Cl_2 concentration reduction in an 80 m^3 compartment with 1 box of LiOH RPC deployed, assuming that laboratory results scale linearly using equation:

$$In\left(\frac{[Cl_2]_0}{[Cl_2]_t}\right).\frac{1}{k'} = t'$$

- Initial compartment concentration of 3 ppm
  - No further Cl_2 generation
  - Using fresh LiOH RPC Cl_2 concentration reduced to 1 ppm in 1.1 hour
  - Using CO_2-saturated LiOH RPC Cl_2 concentration reduced to 1 ppm in 3.6 hour

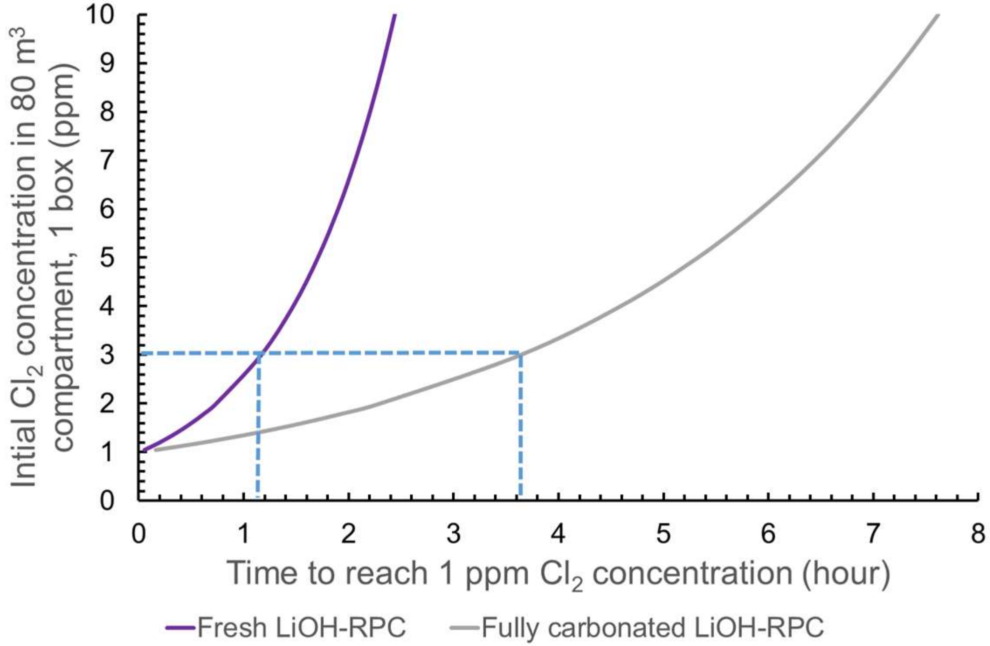

Figure 14: Modelled removal of Cl_2 removal by (purple) LiOH-RPC and CO_2-saturated LiOH-RPC (orange)

3. Results and Discussion – Removal on old batch of LiOH RPC

Results and discussion – Cl_2 and CO_2 removal on out-of-date LiOH RPC

- Removal on 14 year old LiOH RPC
- Cl_2 removal rate constant (1.22×10^{-6} $s^{-1}.cm^{-2}$) was comparable to newer LiOH RPC batch tested
- CO_2 removal rate constant was slightly higher (1.17×10^{-6} $s^{-1}.cm^{-2}$) than the newer batch tested
- These results suggest that there is variation in the rate of CO_2 removal by LiOH curtains that is not solely due to length of time since manufacture

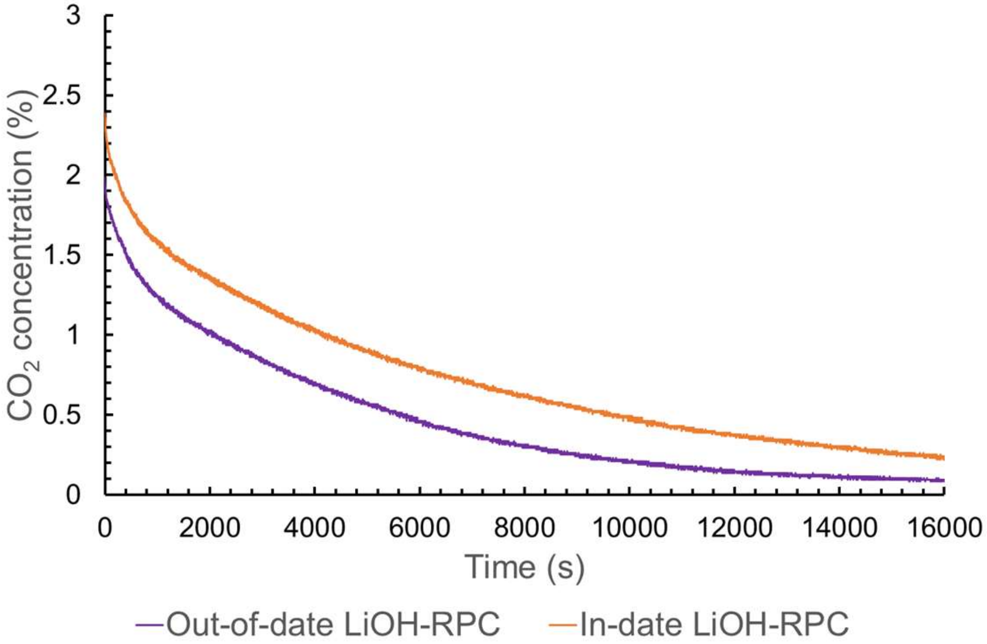

Figure 15: CO_2 removal by in-date and out-of-date LiOH-RPC

4. Conclusions

Conclusions

- Cl_2 and CO_2 removal on LiOH RPC
  - Cl_2 removal rate constant was 61% faster than that of CO_2 but the overall capture is less due to low Cl_2 concentration
  - Cl_2 rate constant increased a further 20% when CO_2 was present
  - LiOH RPC can potentially remove up to ~7.7 kg of Cl_2 per deployed box
- Removal on CO_2 saturated LiOH RPC
  - Fully carbonated curtains removed Cl_2 at reduced rate
  - This was 81% slower than fresh LiOH RPC when simultaneously exposed to Cl_2 and CO_2
  - The residual Cl_2 removal capability of fully carbonated curtains may be beneficial in a DISSUB
- Modelling of Cl_2 removal performance in a 80 m^3 compartment
  - Freshly deployed LiOH RPC will reduce Cl_2 concentration from 3 to 1 ppm in 1.1 h, CO_2 saturated LiOH RPC will take ~x3 times longer
- Removal on older batch of curtain materials
  - Older batch LiOH RPC had comparable Cl_2 and CO_2 removal rate capability

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Acknowledgments

Presenter would like to thank co-authors and Maritime Life Support

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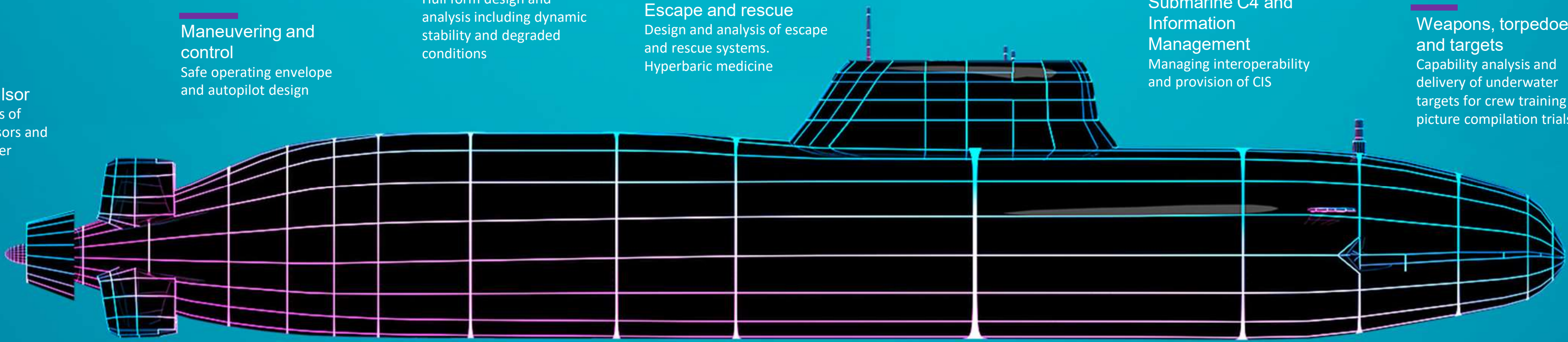
And you for your attention…



Propulsor
Analysis of propulsors and propeller design

Maneuvering and control
Safe operating envelope and autopilot design

Hull form
Hull form design and analysis including dynamic stability and degraded conditions

Escape and rescue
Design and analysis of escape and rescue systems. Hyperbaric medicine

Atmosphere control
Design and analysis of habitability

Submarine C4 and Information Management
Managing interoperability and provision of CIS

Weapons, torpedoes and targets
Capability analysis and delivery of underwater targets for crew training and picture compilation trials

SQEP Development

Smart Materials
Maximising platform performance

Materials
Selection, advice and in-service performance and assessment

Structures
Structural integrity, NDE advice, SM welding, corrosion and collapse

Shock
Physical testing and synthetic analysis

Susceptibility risk
Supporting continual improvement

Signatures and Stealth
Ranging, Testing and analysis

Noise and Vibration
Radiated acoustic noise assessment and Management

Robotics and Autonomy

Information assurance Cyber

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