**Institution:** University of Kent

**Unit of Assessment:** 8: Chemistry

**Title of case study:** Project Earthlight: Enhancing the UK's Defence Strategy for the Immobilisation and Degradation of Chemical Warfare Agents through Absorbent Polymer Technologies

**Period when the underpinning research was undertaken:** 2012-2020

**Details of staff conducting the underpinning research from the submitting unit:**

| Name(s): | Role(s) (e.g. job title): | Period(s) employed by submitting HEI: |
|---|---|---|
| Dr Simon Holder | Reader in Organic Chemistry | 1999-present |

**Period when the claimed impact occurred:** 2018-2020

**Is this case study continued from a case study submitted in 2014?** No

**1. Summary of the impact** (indicative maximum 100 words)

The safe decontamination of chemical warfare agents (CWAs) is a major challenge for defence agencies in the UK. Most are destructible by hydrolysis in a laboratory, but the prior requirement of their storage and transport is extremely hazardous. Researchers in Chemistry at Kent have designed and synthesised a new composite material that can absorb and degrade up to 54 times its own weight of a range of CWAs. The simple absorbent material (100kg) has been manufactured at Kent and stockpiled by the Ministry of Defence's Defence Science and Technology Laboratory (DSTL) as an interim security measure whilst an industrial tender has gone out to manufacture the composite on a larger scale. This gives the Ministry of Defence a material that immobilises CWA stockpiles and degrades them on site. By acting as an advising consultant, Dr Holder contributed to DSTL's decision-making strategies and thinking, which underpinned and helped facilitate the development and manufacture of the product.

**2. Underpinning research** (indicative maximum 500 words)

Chemical warfare agents (CWAs) have been illegal, according to the Chemical Weapons Convention (1997), for the past forty years. Nevertheless, CWAs have been used in Iraq (1988), Japan (1995), Syria (2013), Malaysia (2017), and the UK (2018) throughout this period. For this reason, the UK has been, and continues to be, involved in the transport and destruction of CWAs, including the destruction of 1,000 metric tons of CWAs and precursors during the Syrian Civil War in 2013. Most CWAs, typically in liquid form, are destructible by hydrolysis in a laboratory, but the prior requirement of their storage and transport is extremely hazardous; they are lethal in mg doses, any spillage can easily result in fatalities. The ideal solution to this problem would be a material that simultaneously immobilises a CWA whilst degrading it on site, minimising contact with civilian and military personnel.

In **March 2013**, the Ministry of Defence's Defence Science and Technology Laboratory (DSTL) issued a call for research proposals to develop new polymers that could absorb and degrade chemical warfare agents – Reactive Super Polymeric Absorbents (rSPAs). In particular, the DSTL was seeking a practical material to be developed and sourced in the UK that could treat liquid nerve agents both in the laboratory and in the field on scales from millilitres to litres, thereby making transport safer and potential subsequent use more difficult. Since **2012**, Holder and his research group at Kent had been working to develop incorporate absorbent polymer materials in radio-frequency identification (RFID) sensor systems (in collaboration with the School of Engineering at Kent). This led to a growing interest and expertise in the absorbent properties of polymers within the group **[R1, R2]**. In recognition of their existing combined knowledge of absorbent polymers and contemporary catalysts, Holder and Blight were awarded joint research grants from DSTL to investigate the feasibility of developing such materials.

Between **2014** and **2018**, a Kent research team comprised of Holder, Blight, and two DSTL-funded PhD students studied the initial synthesis of absorbent polymer systems. The team conducted extensive absorption studies on the use of polystyrene-based networks containing ionic groups with a range of organic solvents. These studies demonstrated that this traditional design for superabsorbent polymers would not work for CWAs. In **July 2016**, Holder attended a conference where a talk on pHIPEs led to the realisation that such materials, utilising porous polymers that showed high compatibility with the CWAs, would function as good absorbents. In **2016-18**, the team conducted investigations of various pHIPE systems with different compositions, cross-linking densities and porosity **[R3]**. The investigations led to the development of a material that was mechanically stable, compressible, and super-absorbent, absorbing and immobilising up to 54 times its own weight of CWAs **[R3]**. Between **2018** and **2020**, the team (including a DSTL-funded PDRA) demonstrated that the material could be synthesised on the kilogram scale (previously it was synthesised on the gram scale) and then 10s of kg scales **[f]**. Between **2015** and **2018**, the team also trialled a number of known metal-organic framework (MOF) compounds for their catalytic degradation of CWA simulants **[R4]**. These MOFs were further tested at DSTL against actual CWAs, and a candidate was identified that was then directly incorporated into the pHIPE successfully at Kent, leading to the pHIPE-MOF. In **2018**, the Kent-produced pHIPE-MOF composite was tested against a CWA by staff at DSTL, and it showed a high level of absorption and degradation of the CWA within seven days, with no need for the addition of any other reagents (including water) **[R5]**.

**3. References to the research** (indicative maximum of six references)


**[R1]** Rumens, C. V., Ziai, Mohamed A., Belsey, K., Batchelor, John C., and **Holder, Simon J**. (**2015**). 'Swelling of PDMS Networks in Solvent Vapours; Applications for Passive RFID Wireless Sensors.' *Journal of Materials Chemistry* C, 3: 10091-10098. https://doi.org/10.1039/C5TC01927C

**[R2]** Belsey, K. E., Parry, A. V. S., Rumens, C. V., Ziai, M. A., Yeates, S. G., Batchelor, John C., and **Holder, Simon J**. (**2017**). 'Switchable disposable passive RFID vapour sensors from inkjet printed electronic components integrated with PDMS as a stimulus responsive material'. *Journal of Materials Chemistry* C, 5(12): 3167-3175. https://doi.org/10.1039/C6TC05509E

**[R3]** Wright, Alexander J., Main, Marcus J., Cooper, Nicholas J., Blight, Barry A., and **Holder, Simon J.** (**2017**). 'Poly High Internal Phase Emulsion for the Immobilization of Chemical Warfare Agents'. *ACS Applied Materials and Interfaces* 9(37): 31335-31339. https://doi.org/10.1021/acsami.7b09188

**[R4]** Kalinovskyy, Y., Cooper, N. J., Main, M. J., **Holder, Simon J.**, and Blight, B. A. (**2017**). 'Microwave-assisted activation and modulator removal in zirconium MOFs for buffer-free CWA hydrolysis'. *Dalton Transactions* 45: 15704-15709. https://doi.org/10.1039/C7DT03616G

**[R5]** Kalinovskyy, Y., Wright, A. J., Hiscock, J. R., Watts, T. D., Williams, R. L., Cooper, N. J., Main, M. J., **Holder, S. J**., and Blight, B. A. (**2020**). 'Swell and Destroy: A Metal–Organic Framework-Containing Polymer Sponge That Immobilizes and Catalytically Degrades Nerve Agents'. *ACS Applied Materials and Interfaces* 12: 8634-8641. https://pubs.acs.org/doi/abs/10.1021/acsami.9b18478


**Grants**

**[G1]** Defence Science and Technology Laboratory (DSTL) grants (**2014-20**). The research project led by Holder was funded by three DSTL grants. Total value: £558,947.

**4. Details of the impact** (indicative maximum 750 words)

Following the successful development of the absorption and degradation capabilities of the pHIPE-MOF at DSTL, in **January 2019** DSTL ordered 150kg of the pHIPE-MOF from the University of Kent to be used in an interim capability by the Ministry of Defence (MoD). In **2019-20**, a large-scale manufacturing process based on the research by the University of Kent team **[R3-R6]** was initiated. In **June 2020**, Project Earthlight commenced to secure the manufacture and supply of pHIPE-MOF to the MoD. In summarising the benefits of the Kent research and input (further detailed below), Defence Equipment and Support (DE&S), a stakeholder of DSTL closely involved with the project, stated that the 'knowledge transfer process between the University of Kent, DSTL and DE&S and its resulting conception of Project Earthlight has fostered the generation of new knowledge, practices and strategy within the DSTL for the UK's defence against chemical warfare agents', and highlighted that the research has 'facilitated an improved provision of materials to absorb nerve agents' **[g]**.

**Enhancing the knowledge and defence strategies of the DSTL**

In response to the successful demonstration of the absorption and degradation capabilities of the pHIPE-MOF at DSTL in **2018**, DSTL confirmed that the research undertaken at Kent by Holder's team had changed their knowledge. Specifically, they highlighted that the advance of the pHIPE-MOF reflected 'the first time that a material capable of both absorbing and breaking down these materials has been developed' **[a]**. As DSTL stated, the dual function of the pHIPE-MOF (absorption and immobilisation) 'reduces the need to use substantial quantities of corrosive chemicals for the decontamination of nerve agents', and is 'itself inexpensive and straightforward to produce' **[a]**. DSTL also confirmed that 'By detoxifying chemical warfare agents, the pHIPE-MOF system enhances health and safety protocols'; adding that 'Logistically, it is beneficial to take one material which can be effective against a range of hazardous chemicals' and to have 'the ability to add the pHIPE-MOF combination in the field and walk away with the knowledge that the toxic component will be broken down in a known timeframe' **[a]**.

In response to the material's successful development, as well as cost savings and safety benefits, DSTL 'decided to accept this formulation and develop it on a large scale' **[a]**. In order to determine the feasibility and cost of larger-scale syntheses and give the Ministry of Defence an interim Defence and Security capability, in **January 2019** DSTL ordered 150kg of the pHIPE from the University of Kent **[b, g]**. Roughly speaking, as 3.9kg of the composite can absorb and immobilise the contents of a standard chemical drum/barrel (208 L, 55 gal) of a nerve agent, 150kg has the potential to absorb 38 barrels (8000 L). By **December 2020**, DSTL received 100kg of the material 'for the provision of an interim capability, which can absorb chemical warfare agents' **[a]**.

**Informing the practice and capabilities of DSTL**

In **2019-20**, DSTL continued to explore the possibility of large-scale manufacture of the pHIPE-MOF in conjunction with the delivery of 100kg of the pHIPE from the University of Kent. As the Specialist Explosive Ordnance Disposal and Search (EOD&S), Exploitation and Countermeasures Project Manager at DE&S highlighted: 'alongside the production and receipt of the 100kg of material throughout 2019, Dr Holder acted as an advising consultant. Dr Holder provided DSTL and DE&S with additional informative material to inform us and our stakeholders with an understanding of the material, acted as an independent expert as we worked through and established the production methods and processes, and advised on potential companies to manufacture the pHIPE-MOF' **[c, g]**. In recognition of the opportunities that Holder's expertise afforded during this process, DE&S stated that: 'The application of his expertise and advice on key matters contributed to our thinking, and, as a result, informed and enhanced our decision-making processes and strategies as we sought to prepare for tender' **[g]**.

**Contributing to the manufacture and supply of pHIPE-MOF to the MoD**

In **June 2020**, DSTL acted to secure the manufacture and supply of the pHIPE-MOF system to the MOD by issuing a Prior Information Notice for Contracts in the field of Defence and Security for Project Earthlight **[d, g]**. The inception and notice of Project Earthlight highlighted the technology's readiness level for production and packaging, and set out the procurement processes, which began in **September 2020 [d, g]**. Acknowledging Holder's influence throughout this process, DSTL stated that: 'The production method for the MOF and pHIPE developed at Kent will be used as a basis for production on a large scale. The specifications outlined in the tender document such as absorbency (Q-value), timescale, testing protocols, and analysis of final MOF-pHIPE system are all based on the initial work carried out at Kent' **[a]**. In **November 2020**, two companies were invited to submit tenders for the production of the MOF-pHIPE material for the MoD **[f, g]**.

**5. Sources to corroborate the impact** (indicative maximum of 10 references)

**[a]** Defence Science and Technology Laboratory (DSTL) Questionnaire: Principal Scientist. This details the impact of the Kent research team on DSTL's prior processes, knowledge and understanding, practice, and future procedures and strategy (April 2020).

**[b]** Ministry of Defence Initial Tasking Order Form (2019). This details the requirements for the supply of 150kg of polyHIPE from the University of Kent.

**[c]** Tender process correspondence: Project Managers, Ministry of Defence and Defence Science and Technology Laboratory. This correspondence established the contributions made by Holder in facilitating the scale-up manufacturing process and supplying knowledge and assistance in developing the tender process.

**[d]** Ministry of Defence Prior Information (Contract) Notice. This sets out the contracting authority's (Ministry of Defence) purchasing intentions.

**[e]** Defence Science and Technology Laboratory Report. This is a DSTL report on the scale-up production produced by Holder and Dr Aaron Hillier for DSTL to demonstrate the feasibility of the scale-up process and to inform and guide the tender process for subsequent manufacturing.

**[f]** Invitation to Tender correspondence: Project Manager, Ministry of Defence. This details the companies approached to submit tenders for the manufacture of the polyHIPE-MOF.

**[g]** Testimonial: Specialist, Explosive Ordnance Disposal and Search (EOD&S), Exploitation and Countermeasures Project Manager, Defence Equipment and Support (DE&S). This details how the partnerships between Holder, DE&S, and DSTL resulted in the conception of Project Earthlight; informed new knowledge, practice, and strategy; and facilitated an improved provision of materials to absorb nerve agents.