Institution: University of Plymouth

Unit of Assessment: Agriculture, Veterinary and Food Science

Title of case study: Measurement, modelling and optimisation of dual porous materials and pore fluids for optimising the design and changing structure of porous materials for industry

1. Summary of the impact

This case study outlines how research at Plymouth University in soil science has been extended to a new way of measuring and characterising porous solids and their pore fluids by generating realistic simulated three-dimensional void networks and is now being used across a wide range of industry sectors. The research has been pioneered, patented and marketed and is available to industry via the products Pore-Cor™ and PoreXpert™. The approach has impacted nationally and internationally across a range of sectors including energy companies such as EDF and paper production such as Hewlett Packard. It has improved efficiency and operations in industry such as in nuclear reactors and led to a University spin out company.

2. Underpinning research

The Environmental and Fluid Modelling research group (EFMG) led by Professor Peter Matthews (Reader 01/08/1984 – 31/08/2008, Professor 01/09/2008- to date) has pioneered a new way of modelling porous materials, and the behaviour of liquids and gases within them. The standard implicit approximation, the capillary bundle model, still prevalent in the research literature but unrealistic for nearly all porous materials, is to assume that the pores are like a bundle of very narrow drinking straws, all of different sizes but not connected to each other. The EFMG has developed a method of constructing simulations containing three-dimensionally interconnected voids, which match the water retention characteristics of soil, or the mercury intrusion characteristics of other materials (Matthews et al., 2006). The capillary bundle approximation is even worse for porous materials which comprise an interconnected network of small pores (meso-porosity) connected throughout into matrices of even smaller pores (micro-porosity). Important examples of such 'dual porous' materials are soil, high performance paper coatings, and the graphite, known as Gilsocarbon, used in the UK's 14 Advanced Gas Cooled nuclear reactors. The method of constructing a model of such dual-porous pore systems is common to all such materials, but is mathematically very complicated and experimentally very demanding to measure. A major development of the dual porous approach was funded by the BBSRC's £1.1m Soil Programme for Quality and Resilience (BB/E001793/1), of which Matthews was overall project leader (P.I.). The mathematically demanding method of construction is common to all dual porous materials (Laudone et al 2013). Current developments for soil involve including hydrophobicity (NERC NE/K004212/1, £0.9m, Matthews as P.I.) and modelling nitrate pools (BBSRC BB/K001566/1, £0.4m, Matthews as Co.I.). It has just been described in a special issue of the European Journal of Soil Science (Laudone et al, 2013.)

Once the void structure has been simulated, it is sufficiently realistic and quantitatively matched to the dual porous material that it can be used for many other purposes (Gribble et al., 2011). For example, Laudone et al (2011) have used it to determine the distance between the micro-biological 'hotspots' in soil that reduce the greenhouse gas nitrous oxide, from the main flow pathways through the soil. This distance is critical to the way in which the bacteria protect themselves from flooding or drought, and is pertinent to the agricultural management of soils to reduce nitrous oxide emissions.

With regard to porous matrix paper coatings, the modelling approach has been used by Omya AG to develop dual porous paper coating formulations. The macro-porosity allows rapid movement of ink, and the capillarity (suction) of the micro-porosity ensures very fast adsorption and drying in very fast, large scale ink-jet printing machines which will soon take over entirely from offset-litho.

An understanding of the pore structure of Gilsocarbon is critical in being able to predict the radiolytic oxidation, and hence mass loss, within the UK's AGR nuclear reactors. The owners, EDF, wish to obtain an extra 9 years of life for each of its reactors beyond their planned lifetimes, and are funding a £200k research programme at Plymouth to measure and model future mass loss within the reactor cores.

The software 'PoreXpert' is now being marketed and sold through the Plymouth University spin-out company PoreXpert Ltd. Two patents have been filed to protect areas of intellectual property not already published in the scientific literature. The software has begun to achieve wide take-up world-wide for materials including ceramics, catalysts, membranes and filters.

Total research income to support this is research has been £3m+, much of which has directly or indirectly funded the development of software. Sources of funding include the NERC Environmental Diagnostics programme, NE/K004212/1, EPSRC GR/K70489 and BBSRC BB/E001793/1, BB/E001793/1, industry, and purchasers of the software.

3. References to the research (Plymouth staff in **bold**)

1. **Laudone, GM**.,**Matthews, GP.,** Gregory, AS., Bird, NRA., & Whalley, WR. (2013) 'A dual-porous, inverse model of water retention for the study of biohydrological processes in soil' *European Journal of Soil Science*, 64, pp. 345-356
   Peer reviewed journal, Impact Factor 2.651

2. **Laudone, GM., Matthews, GP**., Bird, NRA., Whalley, WR., Cardenas, LM. & Gregory, AS. (2011) 'A model to predict the effects of soil structure on denitrification and N_2O emission' *Journal of Hydrology* 409 (1-2), pp. 283 – 290
   Peer reviewed journal, Impact factor 2.964

3. Gribble, CM., **Matthews, GP., Laudone, GM.,** Turner, A., Ridgway, CJ., Schoelkopf, J. & Gane, PAC. (2011) 'Porometry, porosimetry, image analysis and void network modelling in the study of the pore-level properties of filters' *Chemical Engineering Science* 66 (16), pp. 3701 - 3709
   Peer reviewed journal, Impact factor 2.964

4. **Matthews, GP., Laudone, GM.,** Gregory, AS., Bird, NRA., De G Matthews, AG. & Whalley, WR. (2010) 'Measurement and simulation of the effect of compaction on the pore structure and saturated hydraulic conductivity of grassland and arable soil' *Water Resources Research* 46 (5), WO5501 13pp, Peer Reviewed journal, Impact Factor 3.149

5. **Price, JC., Matthews, GP**., Quinlan K, Sexton J. & Matthews A. G de G. (2009) 'A Depth Filtration Model of Straining within the Void Networks of Stainless Steel Filters' AIChE Journal 55 pp. 3134-3144
   Peer reviewed journal Impact Factor 2.493

6. **Bodurtha, P.**, **Matthews, GP.**, **Kettle, JP** and **Roy, IM**. (2004) 'Influence of anisotropy on the dynamic wetting and permeation of paper coatings' Journal of Colloid and Interface Science 283 pp. 171-189
   Peer reviewed journal Impact Factor 3.172

4. Details of the impact

The highly marketable intellectual property that has emanated from this fundamentally soil science research (outline patent submitted 2012) has been commercially protected and professionally exploited through Pore-Cor^{TM} and succeeded by PoreXpert^{TM} software. The software can be used to optimize the design of porous materials, or predict properties such as ageing and formation damage by generating three-dimensional void networks which closely match the full percolation characteristic and porosity of any meso- and macro-porous material. It has already been used in the study of catalysts, oil reservoir rock, paper coatings, soil, ceramics, pharmaceuticals and filters.

After 2 years of development, PoreXpert Ltd was set up in November 2012. This spin-out is partly owned by Frontier IP Group, which has a partnership agreement with the University of Plymouth. As a result of channel agreements, PoreXpert is being distributed by Thermo Fisher Scientific, Milan, to all users of its Pascal mercury porosimeters worldwide, and to all customers of Porometer nv, Ghent.

At a research level Pore-Cor and PoreXpert straddle the sample size at which individual pore level effects can be integrated and up-scaled to core and field scale – an important step forward in understanding soils. The software is highly demanding of experimental data, because it fits the percolation characteristic in its entirety. Such demands have led to the installation of improved soil physics apparatus at Rothamsted Research, Harpenden, which now monitors sample shrinkage during the measurements of the water retention characteristic.

The software has found resonance with commercial companies and researchers alike and through sale and use of the software, commercial impact has been made, much of which is confidential to clients. Clients include fundamental agricultural researchers such as Rothamsted Research and climate modellers at the Met Office. Furthermore the software technology is proving to be transferable from agricultural soils to all meso- and macro-porous material with industrial applications including high performance paper coatings (e.g. the next generation of Hewlett Packard ink-jet papers, with designed coatings supplied by Omya AG), stainless steel filters for aeronautical and military applications (Porvair Filtration), soil structure under clover and terrestrial nitrous oxide production (Rothamsted Research, BBSRC), leakage of pollutant oil through soil (British Gas and Transco), catalysts (Johnson-Matthey), porous ceramics (Delta-T Devices), oil reservoir sandstones (British Gas and British Petroleum), security systems for bank note transport (Spinnaker International) and gas mask filters (Questair). Major Energy Companies, such as EDF, are utilising it and have invested in both its development and exploitation. The approach is also now being used to up-scale soil hydrophobicity transitions to a level which are being incorporated into the Meteorological Office JULES climate-change dependant hydrological model (NE/K004212/1).

The cross-disciplinary applicability of this research is illustrated by the example of its impact in the paper industry. Paper is coated to increase its brightness, improve printing characteristics, and generally improve its perceived quality for magazines and photographs. Whereas paper coatings used to be made from China Clay, the best modern coatings are made from calcium carbonate. The EFMG has been collaborating with Omya AG for several years to design ‘dual porous’ paper coatings – i.e. coatings made from micron-sized particles which themselves have their own internal nano-porosity. These paper coatings are now being used by Hewlett Packard for fast, high quality inkjet printing, which will ultimately entirely replace traditional offset litho printing.

The research has also developed to have impact on major energy companies such as EDF. The lifetimes of the UK’s AGR reactors are primarily governed by the rate at which the Gilsocarbon graphite in the reactor cores is oxidised, and loses mass, under the conditions of intense radiation and heat. This oxidation occurs despite the graphite being bathed in carbon dioxide – a normally reducing gas. EDF’s own Finite Element Analysis model cannot explain the ageing process, because it depends on the pore architecture within the graphite. EDF has invested in approximately £200k of applied research at Plymouth to elucidate this structure. Unexpectedly, the research has been as much experimental as modelling, because of the demands of the software. It has already influenced the approach of EDF to the prediction of the ageing / mass loss rate, and is being built into the Safety Case to the Office for Nuclear Regulation for the extended running of specific AGRs. Work on Gilsocarbon for EDF requires the separation of actual mercury intrusion from apparent mercury intrusion due to the destruction of the void network, and this can only be measured if a cyclic pressure cycle is used. Thermo Fisher is reprogramming the firmware and software for the Pascal porosimeter it has installed at Plymouth, and this modification will is being made available for all customers during 2013.

5. Sources to corroborate the impact

1. Written statement from Vice President Research and Development, Omya International AG, CH-4665 Oftringen, Switzerland. Use of PoreXpert software for design of nanoporous calcium carbonate based paper coatings used for ink-jet and other printing systems.

2. Written statement from Product Manager Microstructure, Thermo Fisher Scientific S.p.A,

20090 Milan, Italy. Use of PoreXpert for interpreting output from mercury porosimeters, integrated with standard instrument control software.

3. Newsletter from Product Manager Microstructure, Thermo Fisher Scientific S.p.A, 20090 Milan, Italy. The 'MicroTip' newsletter, emailed in January 2013 by the Product Manager to Thermo Fisher's 50 microstructure agents worldwide, announces collaborative agreement between Thermo Fisher Scientific and PoreXpert, and how agents can sell the software.

4. Screenshot of instrument control software. Shows Pore-Cor/PoreXpert data export button embedded into the 'Solid' control software of Thermo Fisher Pascal porosimeters.

5. Written statement from Managing Director, Porometer nv, B-9810 Eke, Belgium. Marketing and use of PoreXpert for interpreting the data output from porometers, for example for the modelling of gas particle and virus filtration, and consequent filter optimisation.

6. Screenshot of Porometer nv website homepage. Shows link to trial version of PoreXpert.

7. Newsletter by Soletek Trading Co Ltd, South Korea. Newsletter, distributed by Soletek in May 2013, announces integration of PoreXpert with Porolux porosimeters manufactured by Porometer nv.

8. Written statement from R&D Manager, EDF Energy Nuclear Generation Ltd, Gloucester GL4 3RS, UK. Description of extent of experimental and modelling work at Plymouth on the structure of Gilsocarbon, the main constituent of the cores of the fourteen nuclear reactors in the UK, and importance with regard to extending the safe lifetime of the reactors and hence enhancing the electricity generation capacity within the UK.

9. Screenshot of PoreXpert website testimonial page. The page http://www.porexpert.com/Testimonials.html shows testimonials from: Chemical Technology Manager, Ultraseal International, Coventry, UK; R&D Manager, QuestAir Technologies Inc, Canada; Research Professor, University of Padua; General Manager Tech. Service, World Minerals Inc., California; Postdoctoral Research Fellow, University of Nottingham, UK.