Focke Self-assessment of research 2009 - 2016

My research has a strong applied flavour as it is mostly funded by industry. It also means that we cannot publish everything we do. In this self-assessment I present some of my best contributions where the original idea was my own and I was the driver to get the work done.

My five most cited papers in each of Carbon Technology, Chemical and Polymer Technology and Pyrotechnics were cited 79, 205 and 61 times respectively (Google Scholar).

Carbon technology. My best contributions in carbon technology relate to the use of expandable graphite in flame retardant applications and for the synthesis of graphite nanoplatelets. We used commercially sourced expandable graphite as our ultimate targets are commercial applications. The first step was to properly characterise these materials [1]. Our key finding was that the commercial products are not just pure graphite intercalation compounds with sulfuric acid species intercalated as guest ions and molecules in between intact graphene layers. We proposed a more realistic model in which graphite oxide-like layers are also randomly interstratified in the graphite flakes. These graphite oxide-like layers comprise highly oxidized graphene sheets which contain many different oxygen-containing functional groups. Our model explains the high oxygen to sulfur atomic ratios found in both elemental analysis of the neat materials and in the gas generated during the main exfoliation event.

We invented an elegant method for making medium density graphite foams with high thermal conductivity [2]. It is based on the exfoliation of expandable graphite in a pitch precursor.

Next we explored graphite as a flame retardant, together with known and novel intumescents, in polyolefins [1, 3-7]. The most striking result was obtained in plasticised PVC [8]: Formulations containing 20 wt.% expandable graphite behaved as if they were literally non-flammable in cone calorimeter testing. We also managed to develop a rotomoulding process that yields flame retarded and antistatic components using a double dumping process [9]. Unfortunately expandable graphite only allows black-coloured materials. So we explored its replacement with modified vermiculite. This mineral also exfoliates explosively but the onset temperature had to be reduced to match the degradation temperature of the polymers. We succeeded in doing this [10, 11] and work is continuing to tailor this mineral for flame retardant applications.

Clay and polymer additive technology. I specialise on using thermal analysis techniques to study (a) the oxidation behaviour of materials targeting either the inhibition or enhancement of the rates of degradation or combustion; and (b) the release rates of migrating or volatile actives such as volatile corrosion inhibitors and insect repellents.

We showed that volatile corrosion inhibitors (VCI) show very complicated vapour-liquid phase equilibria. Those based on amine-carboxylic acid adducts feature negative azeotropes [12, 13]. The VCI products we developed are commercially used to protect rolled steel sheeting.

We also developed oxo-degradation technology based on anionic clay technology [14, 15]. A variant of this approach was used commercially for a period of time. The idea was to allow littered plastic film, especially plastic shopping bags, to rapidly photodegrade when exposed to the sun. Industry expressed concern that this kind of material could have negative impact on recycling but we showed that such worries are misplaced. It proved possible to re-stabilise polyethylene containing these oxo-prodegradants by adding suitable anti-oxidants [14].

Using our expertise in chemical and polymer technology, we have developed a range of novel products for malaria vector control:

- Betacyfluthrin-based polypropylene bed nets that pass all the WHO requirements [16]
- Particle-stabilised insecticide for indoor residual spray that outlast DDT in laboratory trials [17, 18]

- A patented low cost wall lining that has just successfully completed four years of field trials [19, 20]. Licensing of this product is currently being negotiated.
- Mosquito-repellent textiles based on bicomponent fibres are presently in scale-up trial phase. [21]
- A provisional patent was lodged on a particularly effective topical mosquito repellent blend that also kills insects. This azeotropic formulation provided more effective protection for a longer time than the best commercial repellents in MRC bioassay tests [22].

Pyrotechnics. We achieved our objective to develop “green” pyrotechnic compositions for use as time delays and initiating compositions in chemical mine detonators. Formulations suitable for short-, medium- and long-time delay applications were developed [23-28]. The Mn-MnO_2 system [28] was patented as a “green” medium fast burning rate system. It is unique in that it features a metal reacting with its own “rust”! We also discovered a robust pyrotechnic formulation that combines a redox with an intermetallic reaction. This keeps the energy output at a plateau value over a relatively wide stoichiometric range [25].

The references for this section and lists of the best five publications on each topic can be found on our web site: http://www.up.ac.za/institute-of-applied-materials-iam

My five most cited papers in Carbon technology were together cited a total of 97 times according to Google Scholar:

- W Mhike et al. Thermally conductive phase-change materials for energy storage based on low-density polyethylene, soft Fischer–Tropsch wax and graphite. Thermochimica Acta 527 (2012) 75-82. Cited 37 times
- MH Makgato et al. Alkali-assisted coal extraction with polar aprotic solvents. Fuel Processing Technology 90 (4) (2009) 591-598. Cited 19 times
- WW Focke et al. Graphite foam from pitch and expandable graphite. Carbon 73, 41-50. Cited 16 times.
- WW Focke et al. Flexible PVC flame retarded with expandable graphite. Polymer Degradation and Stability 100 (2014) 63-69. Cited 13 times
- H Badenhorst et al. Modelling of natural graphite oxidation using thermal analysis techniques. Journal of thermal analysis and calorimetry 99 (1) (2010) 211-228. Cited 12 times

My five most cited papers in Chemical and Polymer technology were together cited a total of 205 times according to Google Scholar:

- WW Focke et al. The effect of synthetic antioxidants on the oxidative stability of biodiesel. Fuel 94 (2012) 227-233. Cited 56 times
- N Nhlapo et al. Surfactant-assisted fatty acid intercalation of layered double hydroxides. Journal of Materials Science 43 (3) (2008) 1033-1043. Cited 47 times
- B Magagula et al. Mn_2Al-LDH-and Co_2Al-LDH-stearate as photodegradants for LDPE film. Polymer Degradation and Stability 94 (6) (2009) 947-954. Cited 42 times
- HF Muiambo et al. Thermal properties of sodium-exchanged palabora vermiculite. Applied Clay Science 50 (1) (2010) 51-57. Cited 35 times
- PH Massinga et al. Alkyl ammonium intercalation of Mozambican bentonite. Applied Clay Science 49 (3) (2010) 142-148. Cited 25 times

My five most cited papers in Pyrotechnics were together cited a total of 61 times according to Google Scholar:

- K Ilunga et al. The effect of Si–Bi_2O_3 on the ignition of the Al–CuO thermite. Powder Technology 205 (1) (2011) 97-102. Cited 22 times
- L Kalombo et al. Sb_6O_{13} and Bi_2O_3 as oxidants for Si in pyrotechnic time delay compositions. Propellants, Explosives, Pyrotechnics 32 (6) (2007) 454-460. Cited 15 times
- D Swanepoel. Manganese as Fuel in Slow-Burning Pyrotechnic Time Delay Compositions. Propellants, Explosives, Pyrotechnics 35 (2) (2010) 105-113. Cited 13 times
- SM Tichapondwa et al. Suppressing H_2 evolution by silicon powder dispersions. Journal of Energetic Materials 29 (4) (2011) 326-343. Cited 7 times
- WW Focke et al. Chemical Engineering Communications 201 (2) (2014) 153-159. Cited 4 times

References

1. Focke, W.W.M., W.; Kruger, H. J.; Van Schalkwyk, R.; Lombaard, D.; Badenhorst, H. , *Thermal Analysis of Commercial Expandable Graphite Flame Retardants.* 2014.
2. Focke, W.W., et al., *Graphite foam from pitch and expandable graphite.* Carbon, 2014. **73**: p. 41-50.
3. Mhike, W., et al., *Flame retarding effect of graphite in rotationally molded polyethylene/graphite composites.* Journal of Applied Polymer Science, 2015. **132**(7).
4. Kruger, H.J., et al., *Thermal properties of polyethylene flame retarded with expandable graphite and intumescent fire retardant additives.* Fire and Materials, 2016.
5. Focke, W.W., et al., *Polyethylene flame retarded with expandable graphite and a novel intumescent additive.* Journal of Applied Polymer Science, 2014: p. n/a-n/a.
6. Kruger, H.J.F., W.W.; Mhike, W.; Taute, A.; Ofosu, O., *Cone calorimeter study of polyethylene flame retarded with expandable graphite and intumescent fire retardant additives.* 2014.
7. Focke, W.W., et al., *Characterization of commercial expandable graphite fire retardants.* Thermochimica Acta, 2014. **584**: p. 8-16.
8. Focke, W.W., et al., *Flexible PVC flame retarded with expandable graphite.* Polymer Degradation and Stability, 2014. **100**(1): p. 63-69.
9. Mhike, W., et al., *Rotomoulded antistatic and flame retarded graphite nanocomposites.* 2016.
10. Muiambo, H.F., et al., *Characterization of urea-modified Palabora vermiculite.* Applied Clay Science, 2015. **105–106**: p. 14-20.
11. Muiambo, H.F., et al., *Thermal properties of sodium-exchanged palabora vermiculite.* Applied Clay Science, 2010. **50**(1): p. 51-57.
12. Focke, W.W., N.S. Nhlapo, and E. Vuorinen, *Thermal analysis and FTIR studies of volatile corrosion inhibitor model systems.* Corrosion Science, 2013.
13. Nhlapo, N.S., W.W. Focke, and E. Vuorinen, *TGA-FTIR study of the vapors released by triethylamine-acetic acid mixtures.* Thermochimica Acta, 2012. **546**: p. 113-119.
14. Focke, W.W., R.P. Mashele, and N.S. Nhlapo, *Stabilization of low-density polyethylene films containing metal stearates as photodegradants.* Journal of Vinyl and Additive Technology, 2011. **17**(1): p. 21-27.
15. Magagula, B., N. Nhlapo, and W.W. Focke, *Mn2Al-LDH- and Co2Al-LDH-stearate as photodegradants for LDPE film.* Polymer Degradation and Stability, 2009. **94**(6): p. 947-954.
16. Focke, W.W. and W. Van Pareen, *Polypropylene-based long-life insecticide-treated mosquito netting.* Journal of Polymer Engineering, 2011. **31**(6-7): p. 521-529.
17. Merckel, R.D., et al., *Co-Intercalation of Insecticides with Hexadecyltrimethylammonium Chloride in Mozambican Bentonite.* Molecular Crystals and Liquid Crystals, 2012. **555**(1): p. 76-84.

18. Sibanda, M.M., et al., *Degradation of insecticides used for indoor spraying in malaria control and possible solutions.* Malaria Journal, 2011. **10**.
19. Kruger, T., et al., *Acceptability and effectiveness of a monofilament, polyethylene insecticide-treated wall lining for malaria control after six months in dwellings in Vhembe District, Limpopo Province, South Africa.* Malaria Journal, 2015. **14**(1).
20. Sibanda, M. and W. Focke, *Development of an insecticide impregnated polymer wall lining for malaria vector control.* Malaria Journal, 2014. **13**(1): p. P80.
21. Sibanda, M., et al., *The development of slow-release filaments to control malaria*, in *Innovate*. 2016, Graduate School of Technology Management, University of Pretoria: Pretoria, South Africa. p. 94-95.
22. Izadi, H., et al., *A promising azeotrope-like mosquito repellent blend.* Submitted for review in 2016.
23. Tichapondwa, S.M., et al., *A Comparative Study of Si-BaSO4 and Si-CaSO4 Pyrotechnic Time-Delay Compositions.* Journal of Energetic Materials, 2016. **34**(3): p. 342-356.
24. Tichapondwa, S.M., et al., *The Effect of Additives on the Burning Rate of Silicon-Calcium Sulfate Pyrotechnic Delay Compositions.* Propellants, Explosives, Pyrotechnics, 2016: p. n/a-n/a.
25. Montgomery, Y.C., et al., *Mn+Sb2O3 Thermite/Intermetallic Delay Compositions.* Propellants, Explosives, Pyrotechnics, 2016: p. n/a-n/a.
26. Tichapondwa, S.M., et al., *Calcium Sulfate as a Possible Oxidant in "Green" Silicon-based Pyrotechnic Time Delay Compositions.* Propellants, Explosives, Pyrotechnics, 2015. **40**(4): p. 518-525.
27. Ilunga, K., et al., *The effect of Si-Bi2O3 on the ignition of the Al-CuO thermite.* Powder Technology, 2011. **205**(1-3): p. 97-102.
28. Swanepoel, D., et al., *Manganese as fuel in slow-burning pyrotechnic time delay compositions.* Propellants, Explosives, Pyrotechnics, 2010. **35**(2): p. 105-113.