PAPER from 11th International Colloquium Fuels Conventional and Future Energy for automobiles

June 27th-29th Technische Akademie Esslingen in Stuttgart/Ostfildern.

Internal Injector Deposits (IDID)

Jim Barker
Innospec Ellesmere Port UK.

Jacqueline Reid
Innospec Ellesmere Port UK.

Sarah Angel Smith,
University of Nottingham Nottingham, UK.

Colin Snape
University of Nottingham Nottingham, UK

David Scurr
University of Nottingham Nottingham, UK

Matthew Piggott
University of Nottingham Nottingham, UK

Michael Fay
University of Nottingham Nottingham, UK

Andrew Davies
University of Nottingham Nottingham, UK

Christopher Parmenter
University of Nottingham Nottingham, UK

Nicola Weston
University of Nottingham Nottingham, UK

Summary
Fuel is constantly changing to meet increasing legislative drives. The result of this has been the change in solubilising power of a fuel and its ability to “carry” material from whatever source in the fuel system. This coupled with the introduction of high pressure common rail injection systems with ever increasing pressures and temperatures and designed with exceptionally tight tolerances between the moving parts, in order to meet exacting emission standards, has resulted in injector failures because of push rod or needle sticking because of internal injector deposits (IDID). Recent publications have shown the deposits to be layered and this work will describe the gateway technique of Focused-Ion Beam Transmission Electron Microscopy (FIB-TEM), which has enabled these layers to be explored. The data will be used to describe a possible IDID layer formation mechanism rather than a simulacrum of theories based on the assumption that IDID are single layers.

1. Introduction

The current industry interest in injector internal deposits [IDID] has seen a number of papers on the subject [1-33]. Initially, the deposits were described as discreet entities and of single chemical motifs, and different work has identified different motifs:

- Carbonaceous: carbon based [15]
- Metal Salt: e.g. sodium chloride [17]
- Aged Fuel: associated with biodiesel [21]
- Metal Carboxylate: metal “soaps” [25]
- Lacquers: thought to be carbonaceous precursors [7].

This initial identification of chemical motifs used laboratory tests [10], rig tests [2], engine tests [22] or a mixture of all three and top layer surface techniques such as Fourier transform Infra-red (FTIR) Spectroscopy to compare model motifs with those found in problem injectors from the field. However, recent work has shown that IDID samples obtained from in field comprise of layers of material deposited at various times [1, 15, 23, and 24]. These deposits are difficult to analyse in situ, but in a recent publication [24] the technique of Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) was described which, for the first time, allowed the removal of the multilayer deposit from the internal injector needle surface which was then subjected to further analysis. In this paper, the technique has been applied to a push rod deposit and transmission electron microscopy (TEM) has been employed to study these layers in detail.

2. The Technique

The technique was described in detail in a previous paper [24], is well known in the semiconductor industry, and authoritive general references are available [34] as well as illustrative on-line videos [35]. The technique will only be described briefly here. Using FIB-SEM (Figures 1-3), a trench of deposit is cut from the surface using an ion beam. This process is continued until a central section is left intact which can then be thinned down. Nano machining at low currents generates a cross sectional slice of deposit which is then subjected to TEM. Analysis may be carried out at various times by subsequent application of nano machining allowing structural assessment to be determined throughout the layers. This is important in that it allows, for the first time, analysis of each layer without the loss of provenance or history of the layers which occurs with the use of extractive or toplayer surface analysis techniques.
FIB-SEM analysis was carried out using a FEI Quantia 200 3D with dual beam operation to combine SEM imaging with FIB milling. The accelerating voltages used were 1-5 kV. The sections were cut from resin blocks at 100, 200 and 1000 nm thickness and deposited onto copper TEM grids. The samples were mounted onto a TEM stub holder for the SEM and imaged at angles of 0-20 degrees with imaging performed using secondary electron imaging mode. High resolution TEM was carried out using a JOEL 2100F microscope at an acceleration voltage of 200 kV.

TEM uses a beam of electrons transmitted through an ultra-thin specimen, which interact with the specimen as it passes through it. An image is formed from the interaction of the electrons transmitted through the specimen which is magnified and captured on a screen.

3. Results

The sample was the deposit on a jammed field injector push rod from the United States. The injector had failed and produced a no start issue. Fuel was ULSD. The injector was dismantled in a workshop with minimal disruption to the deposit.

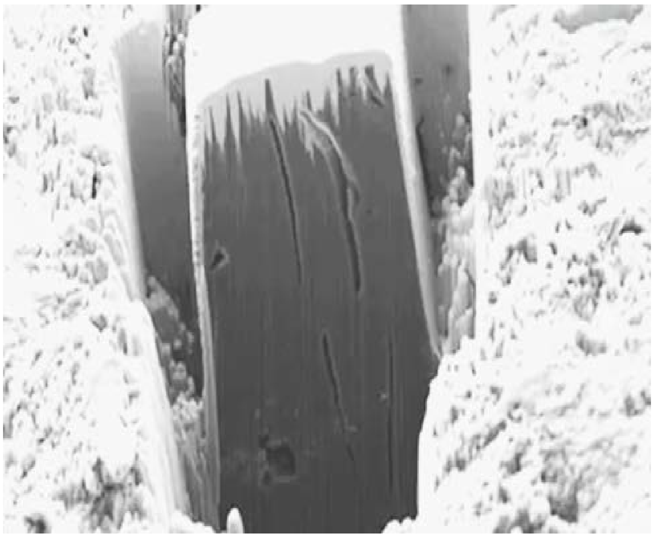

Figure 1: SEM Image of Injector deposit undergoing FIB-SEM..

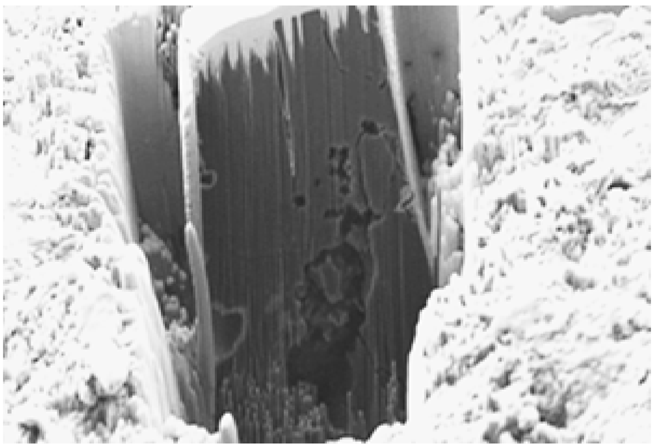

Figure 2 Example of Deposit during FIB-SEM process.

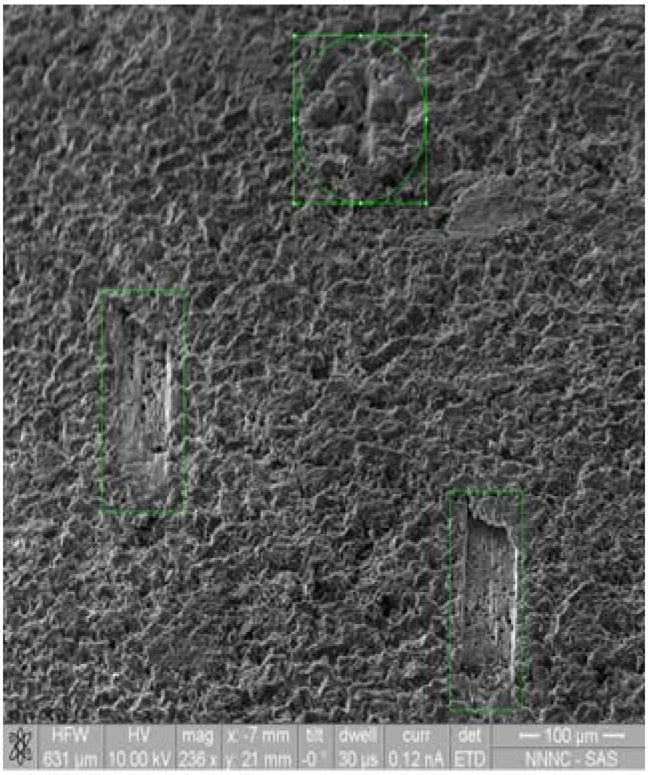

Figure 3: Example of trenches during FIB-SEM process.

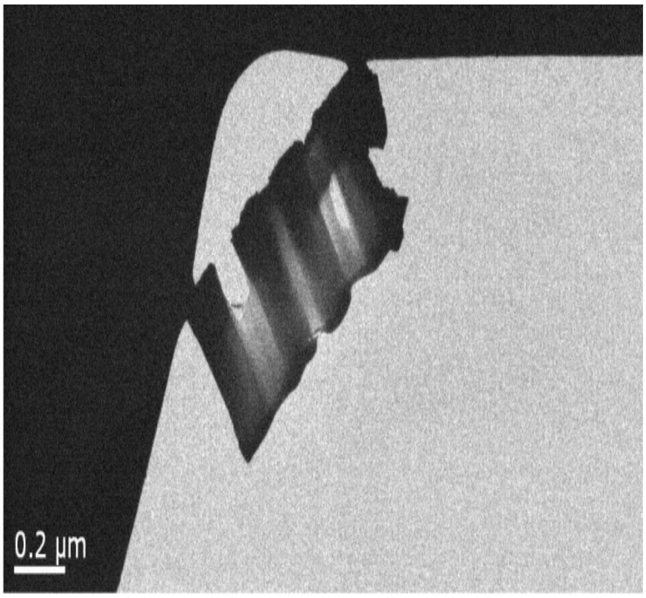

Figure 4: FIB-SEM lift out from IDID.

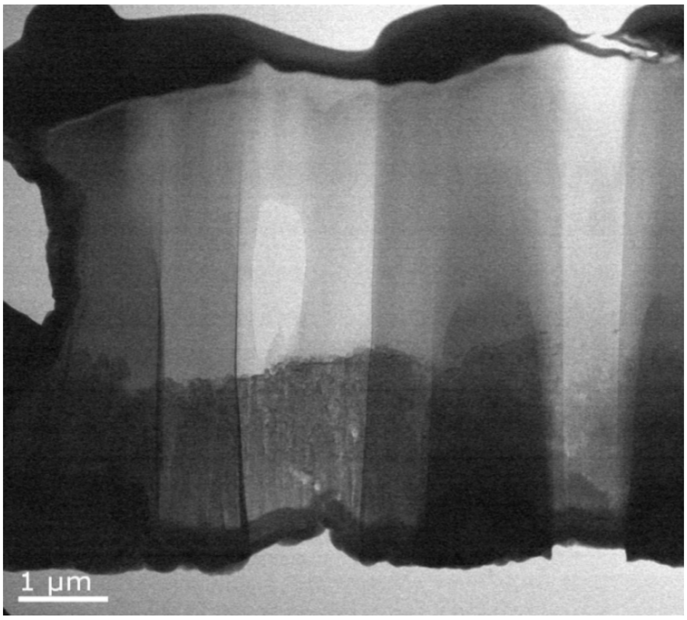

Figure 5: TEM showing deposit layers

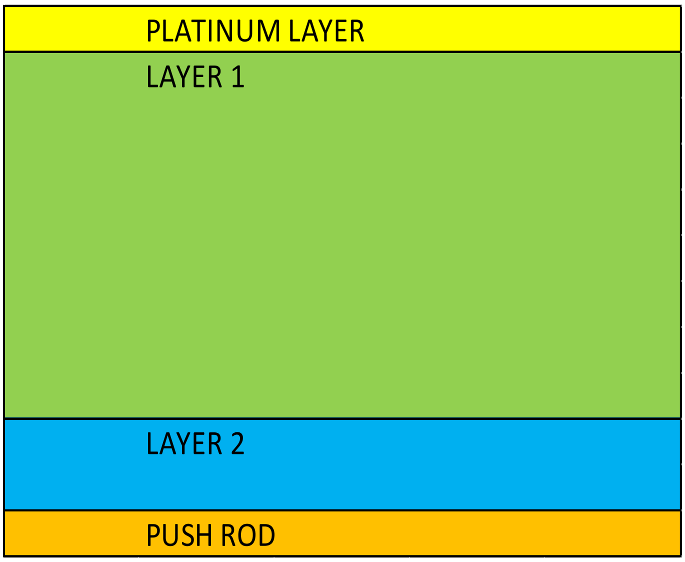

Figure 6 Schematic of Deposit Layers

The layers are best shown in the TEM micrograph in Figure 5 where at least four distinct layers (three for the sample and one for the platinum surface) can be seen and described in the schematic Figure 6. These will be viewed in more detail using the milling technique and TEM.

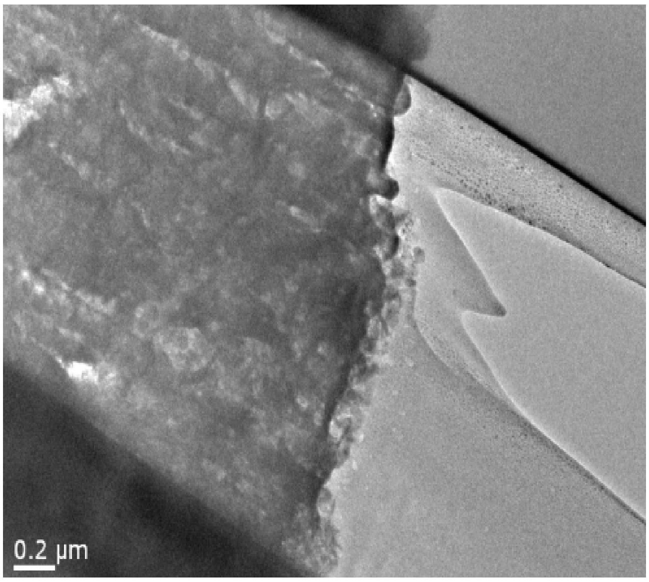

Figure 7: TEM image of layers

The layers are shown distinctly in Figure 7 and in subsequent micrographs we shall look at each layer in more detail.

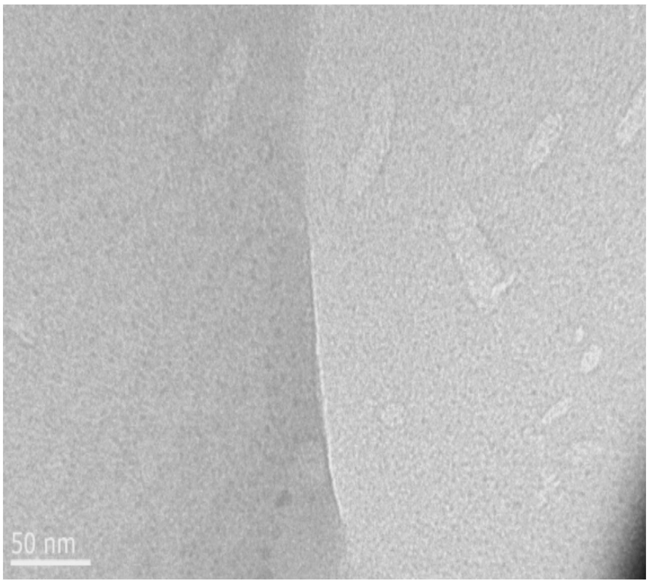

Figure 8: TEM image of layer near surface.

The image in Figure 8 is homogenous in appearance which is not unexpected. The deposit will have been in a liquid state under the injector temperature and pressure. Then when the injection temperature and pressure drop precipitously the material will solidify but maintain its liquid like appearance [36].

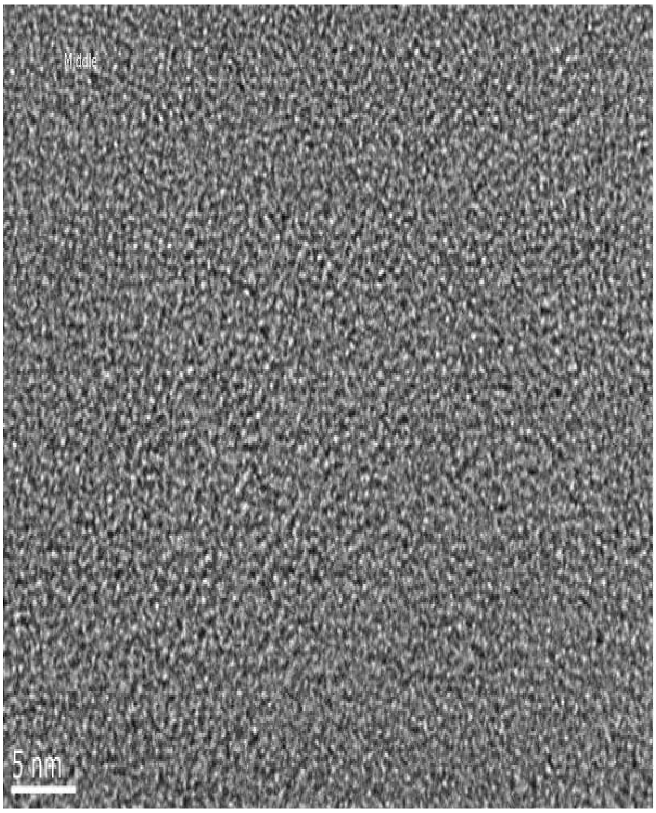

Figure 9: TEM image of middle layer

The TEM of the middle fraction of the deposit (Figure 9) shows the nano structure of the IDID with a mixture of nanosized carbon crystals and carbon in amorphous form. On either side the presence of possible aligned graphitic layers (Figures 11 and 12) and the direct steel to amorphous carbon interface (Figure 13) can be seen. The graphitic layers are less evident in the case of the push rod than found in the case of the injector needle [24] (Figure 10), which is probably because of the different temperature regimes experienced by each part.

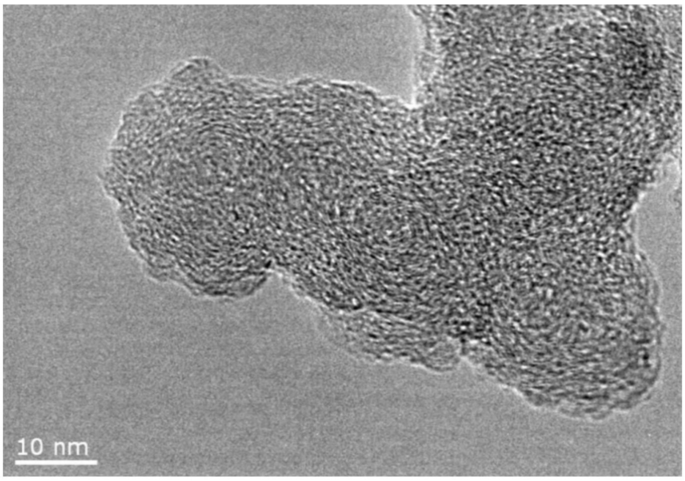

Figure 10: TEM injector needle lift out [24]

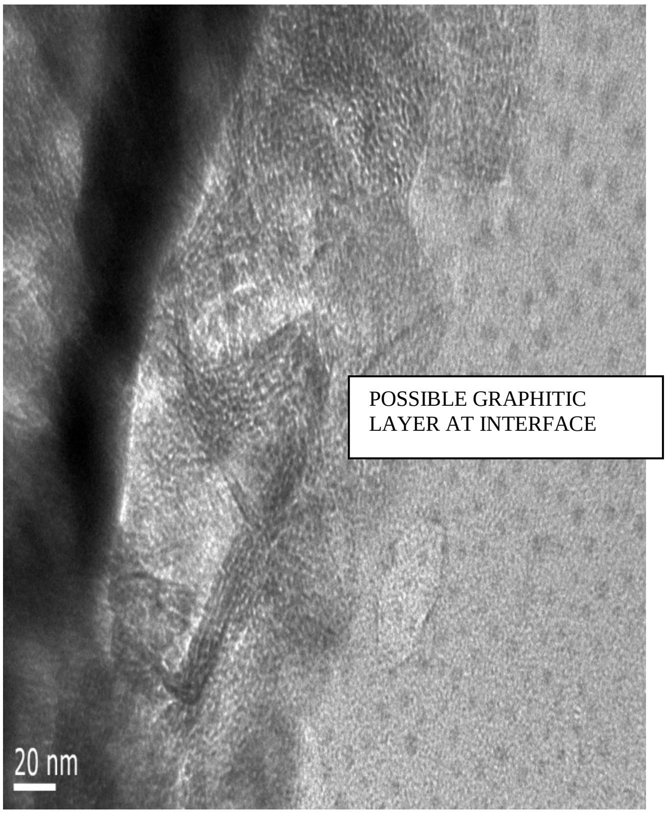

Figure 11: TEM Image of layers

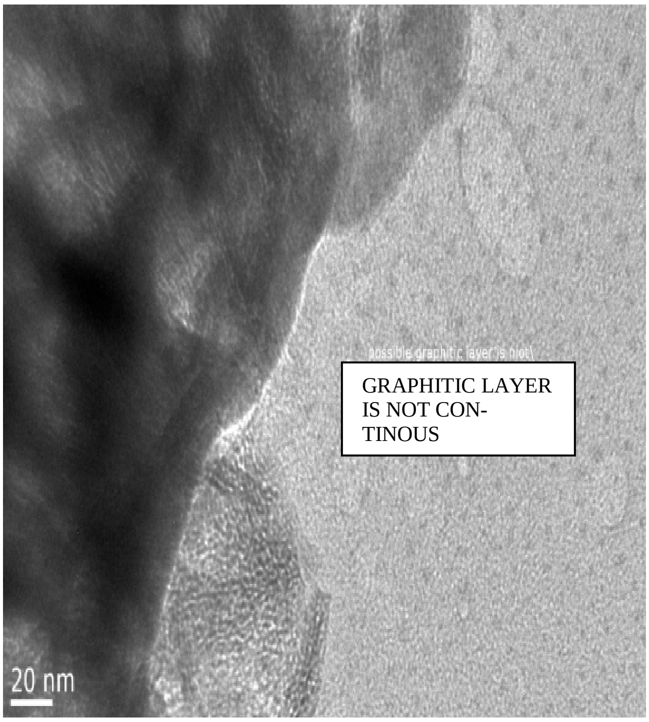

Figure 12: TEM image of layers

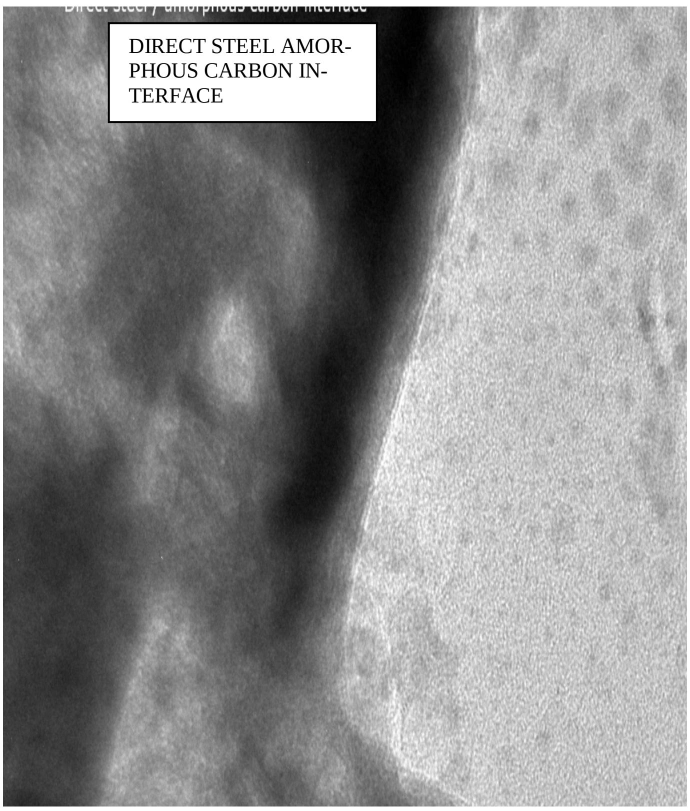

Figure 13: TEM image of layers

The uppermost layer from the injector body has a some microscopic cracks and holes (Figure 14) and is not a smooth surface, which confirms previously published Atomic Force microscopy (AFM) data which indicated IDID have a rough surface. [24].

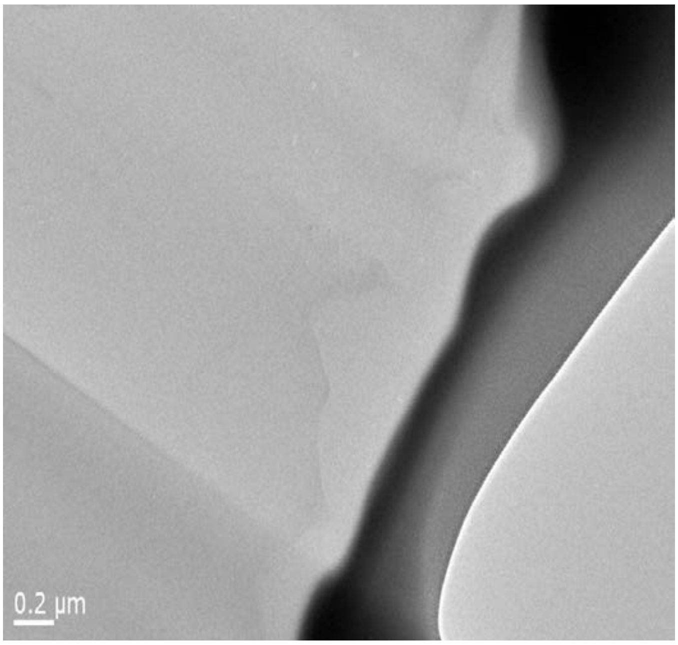

Figure 14: TEM image of uppermost layers

4. Discussion

Herein as part of ongoing studies we have described the TEM results for a FIB-SEM injector lift out. We have seen again IDID layers which have been described previously [15,21,23]. All have been different in their composition and complexity. There are two ways in which these layers could form. The first involves reaction at the metal surface with the surface itself acting as a possible catalyst, or the formation of insoluble particles which the fuel is unable to retain in solution. The first was described by Stavinoha [36] and looked at the influence of different metals on deposit formation. Grant Jones et al [37] showed that the rate of deposit formation slows if a deposit layer covers the surface. Though both or a mixture are possible given the characteristics of ULSD a second hypothesis is more probable comprising a thin film process [40] involving the solubilizing ability of the fuel and its stability under the extreme conditions of the common rail injector environment (350°C and 3000 bar are more likely). The injector needle and push rod move within very tight tolerances, as clearly illustrated by x-ray tomography data of the injector (Figure 15).

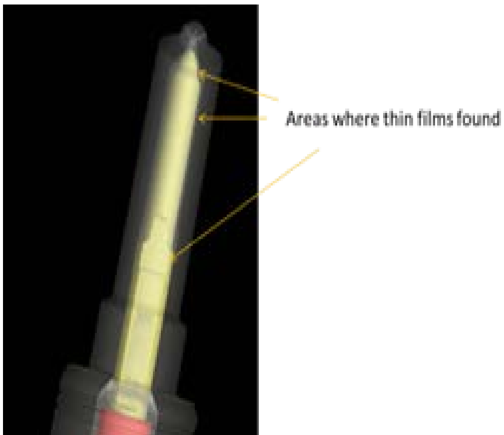

Figure 15: X-Ray Tomography Image of needle in Injector [42]

As it moves back after firing, a thin layer of fuel remains on the needle, rod surfaces and the wall of the holder. This thin film of fuel which will have already experienced significant thermal and pressure load in the high pressure fuel injection system which could have resulted in loss by evaporation or reaction of chemical species present which will affect the fuels ability to solubilize deposits and their precursors. As the cycle begins again the thin layer will be washed by fresh fuel. This fresh fuel will contain some fuel returned from the injector system, where is has been subject to the high temperatures and pressures of the common rail system and will be richer in deposit precursors and in addition any deposit precursors (Figure 18) which were already present in the fuel tank. As the injector cycle continues the thin film will be washed, removed and added to until deposition occurs. If the temperatures and pressures this thin film are subjected to cause deposition then the ability of the fuel to solubilise the depositing species is a key parameter. This may be thought of as an analogous mechanism to geological deposition, where material is unable to be transported in a liquid and deposits in a stratum (as illustrated schematically in Figure 16). The solubilizing power of the fuel is no longer able to overcome the forces of the deposition mechanism.

Recent work [24] using Atomic Force Microscopy (AFM) has shown that deposits on a surface contain adhesively attractive areas which also will play a part in a deposition process (Figure 17).

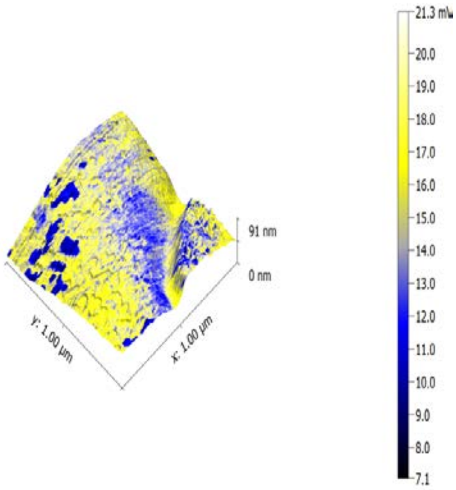

Figure 17 AFM Adhesion Areas on Surface of Injector.

A number of mechanisms have been put forward to explain the process of formation of these insoluble deposits involving condensation, auotoxidation, acid base and esterification reactions [9, 34,35]. A theory for the formation of carboxylate type IDID on injector needles resulting from micelle formation and then the breakdown of these micelles has also been proposed by Trobaugh et al [28]. Another possibility would be premiceller association [41] and then breakdown of premicelles. Alternatively, simply water solvated ions from water ingress. In the field, all or some of these mechanisms may come into play.

Each layer will be formed from precursors in a tank of fuel. That tank may be fed with these from a variety of sources within the fuel supply chain. Fuel washing may remove or reduce the deposit.

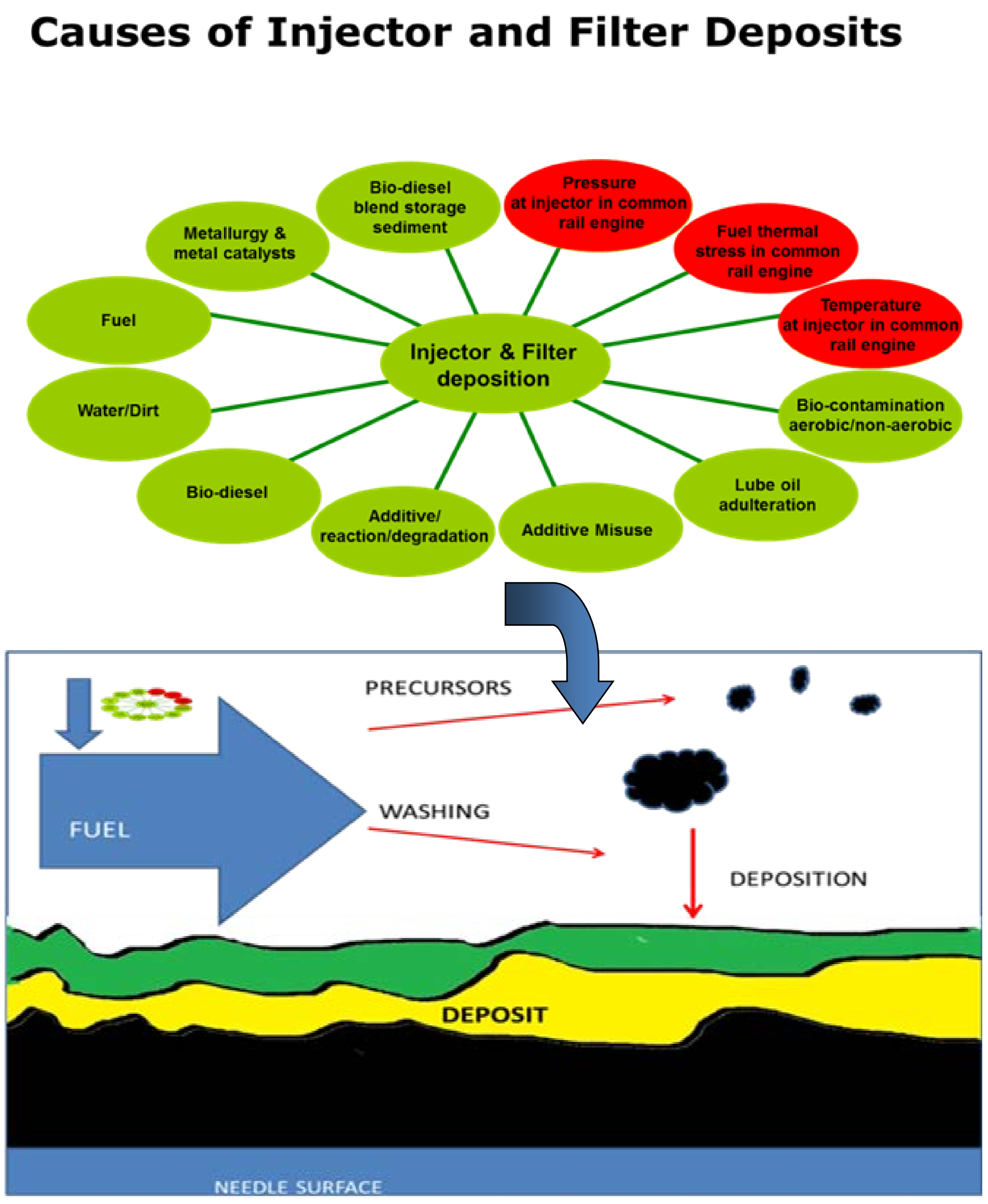

Figure 16: Causes of injector deposits and Mechanism and close up of Thin Film

The fuel may solubilize parts of the deposit or physically cause it to break off by flow induced attrition, resulting in a roughened surface. Deposit control additives (DCAs) have their part to play in the process in blocking such deposit forming processes and in the process of removing any deposits from critical areas within the injector. Figure 16 shows a number of possible sources of deposits which under an insoluble material regime will form IDID layers on the injector parts. The number of layers and type of layer will be dictated by the fuels seen by the injector system during its lifetime.

5. Conclusions

The FIBSEM lift out technique has successfully facilitated ex-situ TEM analysis without the loss of IDID history or provenance.
The TEM data show the layers present within the deposit and the presence of amorphous and aligned pseudo-graphitic carbon, though less graphitic carbon is observed in this push rod sample than seen previously on a needle.
A hypothesis based upon thin films and fuel solubilising capacity is proposed as the mechanism by which these layers are formed.
As part of an ongoing study this work further reinforces the presence of layered IDID in field failure injectors.
No evidence of inorganic layers was noted in this case.

6. References

[1] Crusius S., Lange R., Junk R. and Schumann U.: Using of SEM and EDS for Analysis of Internal Diesel Injector Deposits TAE 10th International Colloquium Fuels Conventional and Future Energy for Automobiles Jan 20th-22nd (2015) 299.
[2].Ullmann, J., Geduldig, M., Stutzenberger, H., Caprotti, R. et al.:Investigation into the Formation and Prevention of Internal Diesel Injector Deposits, SAE Technical Paper 2008-01-0926, (2008)
[3].Quigley, R., Barbour, R., Fahey, E., Arters, D.C., Wetzel, W. and Ray, J.: A Study of the Internal Diesel Injector Deposit Phenomenon In TAE Fuels 7th Annual Colloquium, (2009).
[4].Schwab, S., Bennett, J., Dell, S., Galante-Fox, J. et al. : Internal Injector Deposits in High-Pressure Common Rail Diesel Engines, SAE Int. J. Fuels Lubr. 3(2):865-878,(2010)
[5].Caprotti, R., Bhatti, N., and Balfour, G., : Deposit Control in Modern Diesel Fuel Injection Systems, SAE Int. J. Fuels Lubr. 3(2):901-915, (2010)
[6].Cardenas Almena, M., Lucio Esperilla, O., Martin Manzanero, F., Murillo Duarte, Y. et al. : Internal Diesel Injector Deposits: Sodium Carboxylates of C12 Succinic Acids and C16 and C18 Fatty Acids, SAE Technical Paper 2012-01-1689, (2012)
[7].Arondel, M., Rodeschini, H., Lopes, M., and Dequenne, B.: Fuel Additives for Reduction of Internal Diesel Injectors Deposits (IDID, “lacquering”): A Critical and Priority Route, SAE Technical Paper 2012-01-1687, (2012).
[8].Lacey, P., Gail, S., Kientz, J., Milovanovic, N. et al.: Internal Fuel Injector Deposits," SAE Int. J. Fuels Lubr. 5(1):132-145, (2012)
[9].Lacey, P., Gail, S., Kientz, J., Benoist, G. et al.,"Fuel Quality and Diesel Injector Deposits, SAE Int. J. Fuels Lubr. 5(3):1187-1198, (2012)
[10].Painsi, M. and Grafl, A. :Understanding Internal Diesel Injector Deposits: New Insights from Laboratory Experiments TAE 9th International Colloquium,121-139, (2013)
[11].Tanaka, A., Yamada, K., Omori, T., Bunne, S. et al. :Inner Diesel Injector Deposit Formation Mechanism,SAE Int. J. Fuels Lubr. 6(3):755-761, 2013
[12].Reid, J. and Barker, J.: Understanding Polyisobutylene Succinimides (PIBSI) and Internal Diesel Injector Deposits, SAE Technical Paper 2013-01-2682, (2013)
[13].Żak, G., Ziemiański, L., Stępień, Z. and Wojtasik, M:. Engine testing of novel diesel fuel detergent–dispersant additives Fuel, 122, pp.12-20, (2014).
[14].Singer, P. and Rühe, J. :On the mechanism of deposit formation during thermal oxidation of mineral diesel and diesel/biodiesel blends under accelerated conditions” Fuel, 133, pp.245-252, (2014)
[15].Barker, J., Snape, C., and Scurr, D., : Information on the Aromatic Structure of Internal Diesel Injector Deposits From Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), SAE Technical Paper 2014-01-1387,(2014)
[16].Dallanegra, R. and Caprotti, R. : Chemical Composition of Ashless Polymeric Internal Diesel Injector Deposits," SAE Technical Paper 2014-01-2728, (2014)
[17].Reid, J., Cook, S., and Barker, J.:Internal Injector Deposits From Sodium Sources, SAE Int. J. Fuels Lubr. 7(2):436-444, (2014).
[18].Barker, J., Reid, J., Snape, C., Scurr, D. et al.: Spectroscopic Studies of Internal Injector Deposits (IDID) Resulting from the Use of Non-Commercial Low Molecular Weight Polyisobutylenesuccinimide (PIBSI), SAE Int. J. Fuels Lubr. 7(3):762-770,(2014)
[19].Lau, K., Junk, R., Klingbeil, S., Schümann, U. and Streibel, T..: Analysis of Internal Common Rail Injector Deposits via Thermodesorption Photon Ionization Time of Flight Mass Spectrometry Energy & Fuels, 29(9), pp.5625-5632, (2015)
[20].Fink, C., Crusius, S., Schümann, U., Junk, R. and Harndorf, H. :Alteration of fuel properties at extreme conditions–Formation of deposits in common-rail injectors. In 15. Internationales Stuttgarter Symposium 1021-1032. Springer Fachmedien Wiesbaden, (2015).
[21].Barker J., and Reid J.: Injector and Fuel System Deposits TAE 10th International Colloquium Fuels Conventional and Future Energy for Auto-mobiles Jan 20th-22nd (2015) 263.
[22].Quigley R., Barbour R., Arters D. and Bush J.: Understanding the Spectrum of Diesel Injector Deposits TAE 9th International Colloquium Fuels Conven-

tional and Future Energy for Automobiles Jan 15th-17th (2013)
[23].Barker J., Snape C., Scurr D.: A Novel technique for Investigating the Characteristics and History of Deposits Formed Within High Pressure Fuel Injection Equipment. SAE Int. J. Fuels Lubr. 5(3) (2012) , doi:10.4271/2012-01-1685.
[24].Barker, J. Reid J. Piggott, M. Fay, M. Davies, A. Parmenter, C. Weston, C. Snape, C. Scurr, D. Angel-Smith, S. : The Characterisation of Diesel Internal Injector Deposits by Focussed Ion-Beam Scanning Electron Microscopy (FIB-SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Raman Spectroscopy SAE Technical paper 2015-01-1826. (2015).
[25]Ullmann, J., Geduldig, M., Stutzenberger, H., Caprotti, R. et al.: Effects of Fuel Impurities and Additive Interactions on the Formation of Internal Diesel Injector Deposits. TAE Fuels 7th International Colloquium, January (2009).
[26].Galante-Fox, J. and Bennett, J. : Diesel Injector Internal Deposits in High Pressure Common Rail Diesel Engines. Institution of Mechanical Engineers (IMechE), Fuel Systems for IC Engines, March (2012), pp. 157-166.
[27].Richter B, Crusius S, Schümann U, Hanrndorf H. : Characterisation of Internal Deposits in Common-Rail Injectors MTZ worldwide (2013), 74, 50-57.
[28].Trobaugh C, Burbank C, Zha Y, Whitacre S, Corsi, C and Blizzard N. :Internal Diesel Injector deposits: Theory and Investigations into Organic and Inorganic Based Deposits SAE technical paper 2013-01-2670. (2013)
[29].Barker J., Snape C., Scurr D. : Diesel Deposits TAE 9th International Colloquium Fuels Conventional and Future Energy for Automobiles January 15-17 (2013).
[30].Fink C., Schumann U.,Junk R.,Nowotny M.,: Harndorf H.: Internal Diesel Injector Deposits-Causes and Measures with the Focus on Marine Applications and Fuels. Cimac 28,(2016), 217.
[31].Banning M., Barker J., Mulqueen S.,:The Nature and Cause of Internal Diesel Injector Deposits and the Effectiveness of Fuel additives.” Cimac 28-(2016)-192.
[32].Feld H., OberenderN. : Characterisation of Damaging Biodiesel Deposits and Biodiesel Samples by Infra-red Spectroscopy (ATR-FTIR) and Mass Spectrometry (TOF-SIMS), SAE Int. J. Fuels Lubr. 9(3):717-724, (2016), doi:10.4271/2016-01-9078.
[33].Hoffman H.,Feldhoff s.,Koch W., Lucka K.:Internal Diesel Injector Deposits: Investigations with the Non-Engine Test “ENIAK”.: Ta-gung Diesel und Bezindirectteinspritzung (2016),269-280
[34]Volkert, C.A. and Minor, A.M. : Focused ion beam microscopy and micromachining MRS Bulletin, 32(5), pp.389-399, (2007).
[35].http://www.msm.cam.ac.uk/phasetrans/2005/milling.swf (2005).
[36].Stavinova L.L., Westbrook S. R., McInnis L.A., Mechanism of Deposit Formation on Hot Fuel Wetted Surfaces. Report BFLRF No. 290, DTIC, and SWRi
[37].Grant Jones E., Balster W.J, Surface Fouling: Short –versus Long Term Tests American Chemical Society Division of Fuel Chemistry Preprints (1994), 39, 952-961. Http://web.anl.gov.PCS.
[38].Venkkataraman R., Eser S.: Characterisation of Deposits Formed On Diesel Injectors in Field Test and from Thermal Oxidative Degradation of n-hexadecane in a Laboratory Reactor,. Chemistry Journal (2008), 2 , 25-35.
[39].Cook S., and Richards P.: Possible Influence of High Injection Pressure on Diesel Fuel stability: A Review and Preliminary Study. SAE paper 2009-01-1878.(2009).
[40].Zerda T.W., Yuan X., Moore S.M., and Leon C.A.,: Surface Area Pore Size Distribution and Microstructure of Combustion Engine Deposits Carbon 1199-2009, 37, (1999).
[41].Barker J., Gardiner D. J., Rasburn J. W., Raman Spectroscopic Studies and Evidence for Pre-Micellar Association in 4-Bromobutyric Acid Solution. Advances in Molecular Relaxation and Interaction Processes, (1982), 24,(1) 7-13 .
[42].Angel-Smith S., Snape C., Scurr D., Barker J.:Analysis of Diesel Engine Deposits Using Advanced Characterisation Techniques. UKSAF SAS Conference Chester England (2014).

6. Acknowledgments

The authors would like to thank Mr. D Knight Innopsec for the disassembling the injector and EPSRC for funding Sarah Angel Smith’s Engineering Doctorate through the Centre for Doctoral Training in Efficient Fossil Energy Technologies.