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The theme for this issue of the journal is modelling and its usefulness to Johnson Matthey in a wide range of research and development (R&D) areas. Modelling is one of three core competencies within Johnson Matthey, together with the ability to control materials at the atomic scale, and to characterise materials using state of the art techniques. It forms a crucial component of the company’s strategy to design and develop high performance, more resourceefficient products.

Modelling can encompass many techniques from models based on robust physical principles to those based on empirical and statistical parameter fitting. While this latter approach is widely used in the analysis of experimental data, it is the former approach that comprises the articles in this issue and the subject of this editorial. The use of physical parameter models is much more versatile than empirical fitting models as it allows the prediction of properties over a much greater parameter space than a model based on fitted parameters derived from a specific data set.

Techniques from computational chemistry (electronic structure and force field), thermodynamics and process simulation to kinetic reaction engineering form the basis of modelling based on physical principles, and all are used within Johnson Matthey in both R&D and applied contexts.

Modelling approaches have long been used in chemical engineering activities, including areas such as reactor modelling, alloy development and emissions control systems, as evidenced by the three articles by Stitt et al. (1), Heiss et al. (2, 3) and Watling et al. (4). In particular, the advent of computer based techniques such as computational fluid dynamics (CFD) and discrete element method (DEM) have revolutionised the ability to simulate complex shapes and processes with high precision and sensitivity. These methods have also benefited from the availability of inexpensive large computer resources (5).

Materials and Catalyst Design

The application of modelling to materials and catalyst design is a more recent innovation and has been in part dependent on the continued falling cost of computing power, including the appearance of relatively inexpensive local clusters of hundreds to thousands of processors, together with access by companies to a growing network of national supercomputer facilities. Johnson Matthey established an atomistic modelling group in 2004 with a single modeller and in the last eleven years this has grown to a group of nine split between Johnson Matthey Technology Centre (JMTC) facilities at Sonning Common, UK, and Pretoria, South Africa. The work from this group is tightly focused on areas where there is strong interest and collaboration with experimental R&D across the company. This allows good definition of the problem that the modelling aims to inform and continued exchange of data between modelling and experiment to better understand and apply simulation results.

Given that atomistic modelling originates within the physics community, one of the challenges has been to establish a common language to allow modelling concepts to be understood by the predominately chemistry-based experimental community within Johnson Matthey. A simple example of this is that energies calculated by atomistic modelling are usually expressed as electronvolts (eV), while chemists are used to energies in (kilo)joules (1 eV = 96 kJ mol⁻¹). One consequence of this is that although physicists may be comfortable with energies of a few eV, to a chemist this would represent energies of many hundreds of kJ which can have a significant effect on whether a material would be stable or whether a chemical reaction is favourable or not. To help overcome these possible barriers, the Johnson Matthey modelling group includes modellers with both physics and chemistry backgrounds and a strong emphasis is put on communication skills to
help experimentalists fully understand the implications of modelling results.

With the emphasis of catalysis and catalysts amongst Johnson Matthey’s products, the atomistic modelling group has focused on modelling surfaces as well as bulk structures. The ability to understand how a surface structure is different from the bulk is key in explaining and predicting reactivity. A good example is work carried out by the group on the calculation of surface compositions of metal alloy surfaces and how adsorbates change these compositions. Taking a range of Pt alloy surfaces with a range of transition metals in the absence of adsorbates, Pt tends to segregate to the surface, therefore maximising the number of possible reaction sites (for Pt specific reactions). However, in the presence of OH and O adsorbates (as would be present in an O₂ containing reaction feed such as in a cathode of a fuel cell), many other transition metals are segregated to the surface due to the greater strength of the M-O(H) bond. This has the effect of limiting reaction sites and makes these less noble metals (than Pt) susceptible to chemical leaching. Therefore, the effect of reaction conditions on the surface of catalyst materials can be predicted, further refining the prediction of moulding in terms of reactivity and stability. A forthcoming article in this journal is expected to present the work in more detail, as well as providing a more general overview of the group’s activities.

Catalysis and Collaboration

As part of developing modelling methods to be more applicable to Johnson Matthey products and processes, the company has extensive collaboration with academic groups. In general, we work with these groups in areas such as code development to overcome limitations in current commercial atomistic software. One example of this is a collaboration with the group of Dr Chris Skylaris of Southampton University, UK. Dr Skylaris is working with a linear scaling atomistic code called ONETEP which has been designed to model large molecular structures such as proteins and macromolecules. In our current collaboration we have been applying ONETEP to the modelling of large metal nanoparticles (such as Pt particles of >1000 atoms). These systems are currently beyond standard density functional theory (DFT) codes using reasonable computation resources and if the efforts continue to be successful have the potential of bridging the current modelling gap between small nanoparticle clusters and the bulk surface.

In summary, it is hoped that this issue of the Johnson Matthey Technology Review highlights some of the scope of recent developments in modelling across the chemical and chemical engineering length scales and the reasons why Johnson Matthey has invested in modelling research as a key tool in continuing to develop advanced products for demanding markets.

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References

How Good is Your Model?

“Just because the results are in colour, it doesn’t mean they are right” (1)

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Models, which underpin all chemical engineering design work, vary widely in their complexity, ranging from traditional dimensionless number correlations through to modern computer based techniques such as computational fluid dynamics (CFD) and discrete element method (DEM). Industrial users require confidence in a model under the conditions it is to be applied in order to use it for design purposes and this can be a reason for slow acceptance of new techniques. This paper explores the validity of models and their validation using a variety of examples from heat transfer, reaction kinetics as well as particle and fluid flow, considering both traditional and modern computational-based approaches.

The examples highlight that when comparing models to experimental data the mathematical form of the equations can contribute to an apparently good ‘fit’ while the actual adjustable parameter values can be poorly predicted; residuals or least squares alone are not a reliable indicator of quality of model fit or of model discrimination. When fitting models to experimental data, confidence in the adjustable parameter values is essential. A finite set of experimental data can fit many different models and often with many sets of parameter values. Not all of these models are of course useful for design.

For that purpose it needs to be founded upon the real physics of the system and the adjustable parameters represent real quantities which can be measured, computed or estimated independently. The examples show also the importance of validating a model against more than one output parameter; instances are shown where a too simplistic validation exercise can be misleading.

This paper shows therefore across a range of modelling approaches and applications that extreme care is required when validating a model. Models require validation under the conditions they are to be applied and against more than one output parameter, using appropriate data across appropriate scales and the paper encourages the practice of validating models in order to better persuade industry to adopt more advanced modelling approaches in the future.

1. Introduction

While the way engineers work has transformed massively over the last 50 years, the tools used have not progressed as much as sometimes seems apparent. Despite the extensive use of computational tools to solve the basic design equations, many of the inputs that are used in these calculations are still derived from traditional dimensionless correlations; this is especially true of heat and mass transfer coefficients. In using these correlations we should however be aware of how they represent the data.

Consider heat transfer data for fluidised beds correlated using classical dimensionless number relations. Dimensionless numbers are a critical part of chemical engineering analysis and each one holds its importance because it represents the ratio of two critical energy terms, forces or velocities. Heat transfer data analysis and correlation has classically included in Equations (i)–(iv):

\[
\begin{align*}
\text{(i)} & \quad Nusselt = 0.03 \times Re^{0.6} \times Pr^{2/3} \\
\text{(ii)} & \quad Nusselt = 0.03 \times Re^{1/2} \times Pr^{2/3} \\
\text{(iii)} & \quad Nusselt = 0.03 \times Re^{0.5} \times Pr^{2/3} \\
\text{(iv)} & \quad Nusselt = 0.03 \times Re^{0.4} \times Pr^{2/3}
\end{align*}
\]
Rowe (2) takes a heat transfer data set and plots the data on a series of log-log plots, all of which appear to represent a reasonable correlation with a few data points apparently as outliers; a selection of the correlations is shown in Figure 1. This all seems perfectly satisfactory until the raw data set is revealed as being random numbers! To explore how this can be so requires an examination of the structure of dimensionless correlations.

A typical heat transfer correlation is of the form (Equation (v)):

\[ Nu = aRe^bPr^c \]  

or expanding the dimensionless numbers in Equation (vi):

\[ \frac{hd}{K} = a \left( \frac{\rho d\nu}{\mu} \right)^b \left( \frac{C_p \mu}{K} \right)^c \]

It is noticeable that a key parameter, \( d \), the characteristic dimension, appears on both the right side and left side of the equation (as indeed does the thermal conductivity, \( K \)). This means that the correlation is in fact, generalising the variables, \( yz \) vs. \( xz \) and also plotted on log-log axes. Unless care is taken therefore this approach can be misleading.

The above should not be taken as an indictment of dimensionless correlations. They are an invaluable tool for making sense of experimental data, but care must be taken in their interpretation.

Fig. 1. Dimensionless number correlations of heat transfer data. St = Stanton number; Re = Reynolds number; Gr = Grashof number; Nu = Nusselt number (Reproduced from Rowe (2)).
method of representing data and their relationship with the key independent variables. Nor indeed should it be taken to indicate that they are the only offenders. From the world of reaction kinetics, the Langmuir-Hinshelwood expression format is frequently used to represent adsorption influenced reaction rate data in Equation (vii):

\[
r = \frac{k_rK_A p_A^n K_B p_B^m}{(1 + K_A p_A^n + K_B p_B^m + K_C p_C^n)^p}
\]  

(vii)

Generalising this equation leads to the observation (3) that this is effectively (Equations (viii) and (ix)):

\[
y = \frac{ax^p}{(1 + bx)^q}
\]  

(viii)

or rearranging \(y(1 + bx)^q = ax^p\) (ix)

As with the heat transfer example, the expression features the same variable on both sides of the equation: it is thus equivalent to Equation (x):

\[
y \propto x^c
\]  

(x)

It is hardly surprising therefore that this equation fits many data sets satisfactorily.

To re-emphasise, as with dimensionless correlations, the use of Langmuir-Hinshelwood type kinetic expressions is not wrong; they are based on a specific model of adsorption and reaction phenomena. Rather, users should be aware of the mathematical robustness that arises from the forms of these equations.

Given the typical accepted accuracy of dimensionless transport coefficient expressions, variously cited at ±20% to ±30%, engineers over the years have taken this into account by the judicious use of so-called ‘design margins’. This is what lies behind the common practice of adding 20% to the answer to provide a counterweight to the possibility of under-design due to the inaccuracy of some of the design equations or the input parameters. If this is done by three successive designers then the degree of potential overdesign is now 1.2\(^3\) = 1.75; a 75% overdesign. If a common cost scaling exponent of 0.7 is applied to this then the cost inflation of the designed plant is 1.75\(^{0.7}\) = 1.5; the plant cost is inflated by 50% (4). Use of inaccurate input data and subsequent use of design margins to account for that uncertainty has a significant impact on the final capital cost of the plant.

The approach continues to be used and trusted due to the large amount of knowledge and expertise built up over 50 years in industry. New modelling approaches need to provide us with a similar amount of confidence. That requires validation and cross referencing.

Advanced modelling techniques such as CFD are widely used across many industries (5) such as combustion (6), aerospace design (7) and environmental hydraulics (8, 9). Within the chemical and process industries, for example, it is used in furnace design (10, 11). To extend use into other and new applications requires confidence in the model results.

The industrial designer will want to use the model for scale up and design purposes. It must therefore give the correct answer where it is to be used; not just under conditions where it was derived and tested. This paper will explore the question: how valid does a model need to be and how and at what scale should it be validated?

2. Model Validation Examples in Reaction Kinetics

The accuracy of modelled or fitted kinetic parameters has been much debated due to the robust structure of kinetic expressions, as noted in Equations (viii)–(x). To demonstrate, two key, seminal papers will be reviewed below and their observations highlighted.

2.1 Effect of Adsorption Model

Corma et al. addressed the issue of the quality of the adsorption model and its impact on a kinetic model (12). They selected nineteen adsorption influenced reaction rate data sets from the literature, all of which had been previously modelled by reaction kinetics expressions incorporating a Langmuir isotherm, even where a non-ideality was known to exist. The Langmuir isotherm assumes that the adsorption energy is independent of surface coverage, viz. it is constant. The alternative adsorption isotherm models allow a reduction in adsorption energy with increasing coverage:

- Langmuir – adsorption energy independent of surface coverage,
- Temkin – linear decrease with increased coverage,
- Freundlich – logarithmic decrease with increased coverage.

It is a moot point as to whether these dependencies are real or whether they are simply a reflection of multiple adsorption sites of differing adsorption energies. That notwithstanding, the nineteen data sets were all refitted to reaction rate equations based on the three alternate adsorption models. The outcome is presented in Figure 2.
The quality of fit is surprisingly good for most cases, remembering that in all cases experimental or data error will probably exceed ±5%. Not only is the same level of fitting obtained in most cases but also few cases actually give a poor fit. This approach therefore simply does not allow model discrimination or specifically in this case discrimination of the appropriate adsorption model.

The authors observe that the effect of the distribution of site energies on the global kinetics is weak (12). Reviewing the same paper Keil observes that “the simple fitting of an [kinetic] equation hides significant features of reactions” (13). Berger et al. note that the mathematical forms of the fitting equations are too robust to enable discrimination (3).

2.2 Reactor Simulation using a Kinetic Model

Another example from reaction kinetics explores the effect of kinetic model inaccuracies or errors on the results of a consequent reactor model (14). The authors used an idealised theoretical reaction model to generate ‘experimental’ data from virtual, in silico experiments. Different kinetic models are fitted to the ‘data’ and these models are then used to simulate a reactor and the reactor model output results compared.

The selected test system was methanol synthesis (Equation (xi)), simplified by neglecting the presence of CO₂ in the reaction model.

\[ \text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \]  
\((\text{xii})\)

A mechanistic kinetic model, the ‘true’ kinetics were derived from an elementary step and thermodynamic analysis. In silico experiments using this ‘true’ kinetic model were carried out on a statistical experimental design (27 ‘experiments’) with flow, temp, total and partial pressures as prime variables and included outlier experiments. A 5% random error was applied to the results. Nineteen different kinetic models were fitted to these data and all gave a high quality fit based on residual least squares (R² values all in excess of 95%, many exceeding 99%). These kinetic models were then used in the same reactor design simulation: a steam raising converter with a specified shell side pressure (hence shell side temperature: 210°C). The results were compared using the predicted methanol production rate (Figure 3) and temperature profiles (Figure 4).

The predicted methanol production rates show a wide divergence; the reactor simulation based on the ‘true’ kinetics gave a production rate of 35.5 te h⁻¹. The explanation comes from Figure 4(a), which shows also a wide disparity in the predicted temperature profiles. Figure 4(b) shows that some of the kinetic models in fact predicted a runaway. It should be noted that the shell side temperature was set uncomfortably close to
the temperature at which the true kinetics predicted runaway (≈212ºC) which makes the results especially sensitive to minor differences in the kinetic model and rate predictions. Looking at this from a different viewing point, were the shell side temperature slightly higher a number of kinetic models with a high quality statistical fit (R^2 ≈ 99%) would fail to predict a thermal runaway.

2.3 Discussion
Quality of fit (residual squares: R^2) is a poor criterion for model discrimination. The best predictive model in this study was in fact far from best in terms of fit. That is, R^2 alone is inadequate and inaccuracies not highlighted by this simple quality of fit criterion may lead to gross misrepresentation of reactor behaviour. Residual squares values indicating accuracies that exceed the experimental data confidence are meaningless statistically; more on this later.

It has long been accepted and is well documented in the reaction engineering literature that a kinetic model must be tested thoroughly before reactor design is fixed and traditionally that has required independent data, measured on a different type of laboratory reactor or pilot unit (15). This is true in other fields as well.

Considering specifically the statistical model fitting exercise, a key issue is that simple univariate model validation is not adequate. In many cases the inherent parameter estimation is an ill-posed mathematical problem: there are more parameters than there are independent plus measured variables. The evaluation of quality of fit should extend to consideration of the statistical quality of the parameter estimates and a check for parameter cross correlation.

More generally, arising also from the ill-posedness of the mathematical problem, fitting a model against one objective function can lead to a poor model. It does not validate the entire model and it does not support other model outputs. Different aspects of a model therefore require independent validation parameterisation.

3. Assessing Parameter Estimate Quality
Fundamentally, fitted model parameters should act as estimates of physically meaningful values. To achieve this, it is of critical importance that the fitted parameters are statistically significant. A common approach is to assess uncertainty in parameter estimates using a 95% confidence interval. The value of this is influenced by correlation between observations, noise in the data and degrees of freedom in the estimation process (16). When a confidence interval is greater than the estimated value, the fitting parameter can be seen as indiscriminate from zero and discounted.

The field of reaction kinetics has utilised more systematic and robust assessment processes. Parameter sensitivity on a local and global basis can be analysed via the Jacobian matrix (i.e. the impact parameter value perturbations have on model responses). Low sensitivity parameters can be systematically discounted from the fitting process (17–19). The significance of this with respect to model responses is then checked by the statistical F-test. Cross correlation between parameters is also assessed with these methods, the presence of which impedes reliable parameter estimates.

Principal component analysis (PCA) can also be applied to the sensitivity values of the fitted parameters.
PCA provides a ranked series of eigenvalues which contain contributions from the fitting parameters. The most important parameters will have a strong contribution to the largest eigenvalues. Early examples include application to formaldehyde oxidation kinetics (20) and more recently there has been application in micro-kinetic (21) and molecular models (22). Elsewhere, methods to understand parameter range validity (23) and the impact of noise (24) have been incorporated into these approaches.

3.1 Case Study – Paste Extrusion Modelling using the Benbow-Bridgwater Equation

This example, from non-reaction kinetics, will exemplify the importance of considering parameter estimate quality in equation fitting. The Benbow-Bridgwater equation to predict extrusion pressure drop \( P, \text{ MPa} \) is described in Figure 5 (25) and contains five input variables \( (V_{\text{ext}}, D_0, D, N \text{ and } L) \) and six fitting parameters \( (\sigma_0, \alpha, m, \tau_0, \beta \text{ and } n) \). As fitting parameters outnumber input variables the problem may be ill-conditioned. While not necessarily ill-posed (where, strictly, the fitted parameters outnumber the quantity of data) this is clearly a situation that requires good structuring of the data set, relevance of the parameters and attention to the independence of the fitted parameters. As an illustration, with a well-designed data set a good fit of a univariate polynomial or other multi-parameter \( f(x) \) can be achieved. By contrast with data inadequacy even a simple linear or power law fit can yield significant cross correlation and thus poor confidence intervals of the two fitting parameters. The original version of the Benbow-Bridgwater equation features four parameters, each of which has a distinct physical relevance. The additional parameters, exponents \( m \) and \( n \), have however often been used for so-called ‘enhancement of fit’.

To assess the six-parameter model, a 20 point ceramic extrusion dataset featuring five extrusion velocities \( (V_{\text{ext}}) \) at four different die lengths \( (D) \) is utilised. All observations are repeated twice. Fitting the six-parameter model produced a high \( R^2 (0.997) \), however, as Table I shows, the parameter estimates are not satisfactory. A large confidence interval is seen in \( \beta; \alpha \) could not be estimated and \( \beta \) and \( n \) were strongly cross-correlated with one another. Additional sum-of-squares (model vs. experimental error residual) analysis revealed that the presence of a fifth and sixth parameter in the model simply described experimental errors between the repeats. A t-test of \( m \) and \( n \) with reference to a value of 1 as the null hypothesis showed both to be insignificant as fitting parameters. Table I reveals that fixing \( m \) and \( n \) greatly improves the estimation quality of the other parameters, with minimal compromise to fit \( (R^2 = 0.996) \). A final note on this topic comes from the original authors, “This six parameter fit to data is very frequently inappropriate or not warranted in view of the reliability of the primary data or the accuracy of the prediction required” (26). This important caveat is frequently overlooked.

![Fig. 5. Schematic of paste extrusion and the associated Benbow-Bridgwater equation](image)

### Table I Parameter Estimates and Confidence Intervals for Four- and Six-parameter Models

<table>
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<tr>
<th>Parameter</th>
<th>Six fitting parameters</th>
<th>Four fitting parameters</th>
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<tbody>
<tr>
<td>( \sigma_0 )</td>
<td>0.41 ± 0.043</td>
<td>0.44 ± 0.047</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>87 (?) Indeterminate</td>
<td>12 ± 5.7</td>
</tr>
<tr>
<td>( m )</td>
<td>0.72 ± 0.056</td>
<td>1.0 FIXED</td>
</tr>
<tr>
<td>( \tau_0 )</td>
<td>0.0060 ± 0.0020</td>
<td>0.0090 ± 0.0010</td>
</tr>
<tr>
<td>( \beta )</td>
<td>8.8 ± 6.9</td>
<td>1.8 ± 0.10</td>
</tr>
<tr>
<td>( n )</td>
<td>0.78 ± 0.11</td>
<td>1.0 FIXED</td>
</tr>
</tbody>
</table>

*aParameter estimation carried out using Athena Visual Studio v.14.2, Stewart and Associates Engineering Software, Inc*
4. Simulation of Catalyst Loading

How catalyst pellets load into a reactor is critical to the subsequent performance of the reactor. This is especially true of tubular reactors with low tube to particle diameter ratios, typical of steam reforming, oxidation and hydrogenation reactors. To study this experimentally is difficult as it requires forming of the pellets and different pellet shapes if that is a parameter of the study, as well as the characterisation of the bed structure. The latter tends to need advanced and expensive measurement techniques, such as magnetic resonance imaging (MRI) (27) or X-ray microtomography (XMT) (28). In view of these difficulties the potential to do this computationally was explored. At the time DEM codes were not sufficiently well developed for them to cope with complex particle shape so an alternative approach was used.

DigiPac® is a particle packing algorithm developed at the University of Leeds, UK, (29, 30) and appeared promising for the simulation of tube loading. In the code, space is discretised (Cartesian basis) and particles are represented by a coherent collection of voxels. The key components are a particle contact detection algorithm with particle behaviour on contact based on a Monte Carlo algorithm which itself has three parameters (rebounding, falling, rotating) which are assigned median values (0–1) on an empirical basis to fit measured validation data.

Preliminary attempts to validate this code against experimental MRI data indicated that although visually the results appeared comparable, it badly underpredicted packing density (31). Constraining the range of the Monte Carlo random inputs led to satisfactory prediction of packing density. Detailed consideration of the actual bed structure, using pellet orientation data, indicated however that the detailed structure predicted was far from correct.

Further improvements to the model included the incorporation of a Hertz-Mindlin contact model – allowing the inclusion of friction into the overall particle contact considerations. Re-validation of the model versions against XMT data showed that this final version not only predicted the packing density correctly but also gave a good representation of the bed structure (characterised again using pellet orientation distributions), Figure 6 (32). Both poured and tapped bed densities and structures were adequately represented.

Summarising, had validation been based only on packing density then that validation would have been false. Only by carrying out a model validation using adequate and sufficient objectives was model verification achieved.

5. Parameterisation and Validation of Discrete Element Method Particle Flow Models

Particle flow simulation using DEM is becoming more popular and more frequently used due to advances in both commercial and open-source codes coupled to the rapid advances in computing power. One of the issues impeding its implementation for industrial design is the selection of the key particle properties to be used as input parameters. Traditionally powder properties have been measured on bulk powders, whereas the DEM code is specifically based on single particles.

5.1 Discrete Element Method Input Parameters

There are many parameters for a standard Hertz-Mindlin-type contact model: shape, size, density, coefficients of static and rolling friction (particle-particle, particle-wall), coefficient of restitution, Poisson ratio, Young’s and shear moduli. There are two primary schools of thought on how they should be selected:

(a) Use results of bulk experiments and ‘fit’ parameters to achieve the correct results using, for example the “sandpile” test (33), discharge from a flat bottomed hopper (33, 34), a shear tester (34) or a powder rheometer (35).

(b) Measure the parameters directly using single particles, for example the direct measurement of sliding friction (36), rolling friction (37) and coefficient of restitution (38, 39).

How best these values should be measured, estimated or ‘calibrated’ is a matter of much debate within the DEM community and on which the present authors have recently presented a much broader discussion elsewhere (40).

In the example to be presented here the input parameters were based as far as possible on directly measured values, some of which were taken from the literature.

5.2 Discrete Element Method Simulation and Validation

The Turbula® Mixer is a commercial bench scale powder blender commonly used in the pharmaceutical industry in formulation development. It has a complex motion including rotational, gyrational and axial motion.
This complex motion was successfully imported into the commercial EDEM DEM code available from DEM Solutions Ltd, UK, and the representation assured by comparison with positron emission particle tracking (PEPT) data (41). Qualitative comparison with MRI based measurements for powder blending also looked promising (42). A more detailed, quantitative validation is however required.

A detailed comparison of DEM predicted velocity distributions and those measured using PEPT was carried out. A global summary of the results is presented in Figure 7 (43). The overall comparison is reasonable, although a systematic under-prediction of the velocities by about 10% is observed. It is noted that a remarkably similar systematic error in velocity prediction against PEPT data is obtained in an independent study of a paddle mixer (44). These studies appear therefore to validate the DEM model to within a tolerance that is generally acceptable. Does this infer though that predictions of powder blending will also be correct?

Axial and radial dispersion coefficients were calculated from the raw velocity data for both DEM and PEPT (43). The comparison of the model and experimental dispersion coefficient values as a function of the Turbula speed is shown in Figure 8 (note that the $y$-axis scales are different on the axial and radial coefficient plots). DEM was found to over-predict dispersion coefficients by a factor of approximately two.

While comfort may be drawn from the fact that DEM correctly predicts the regime change at approximately 46 rpm, it should be noted that this can be predicted also using simple dimensionless number (Froude number) based analysis (45). Despite significant sensitivity work on the DEM input parameters, it is still not clear why the error in prediction of mixing related parameters such as dispersion coefficient is so poor (46).
It is tempting to blame the offset on the experimental method. However a detailed comparison of PEPT data with results from the well-established and cross-validated particle imaging velocimetry (PIV) method has been reported for studies in turbulent liquid mixing (47). These studies have indicated an excellent agreement overall, but noted a discrepancy at the impeller tip where the highest velocities and rapid direction changes prevail. The origin of these errors is the data averaging techniques used in the reconstruction algorithm that have subsequently been refined (48). The conclusion is that while at the higher Turbula speeds the PEPT may misrepresent the full trajectory of the particles, that under-prediction is smaller than the error observed in the dispersion coefficient prediction. It also would not explain why the error is almost independent of drum speed.

In the context of this communication it is simply important to note that while validation based on a simple velocity analysis indicates that the model could be used predictively, albeit with the caveat that average velocities appear to be over-estimated by around 10%, it does not accurately predict mixer performance. The validation of DEM models needs to be against data that are closely related to the final application.

6. Validation of Computational Fluid Dynamics Models

CFD is now widely used in many fields, including reaction engineering. There has been a steady growth in its application to the 'high fidelity' modelling of flow, heat transfer and reaction in packed beds where the packing shapes are fully represented and meshed in detail (49–54), for example Figure 9, as opposed to a simplified 'porous media' type representation.

First validations of detailed CFD were made against packed tube heat transfer data (55). Simulations of heat transfer for an idealised \( \frac{D_T}{d_P} = 2 \) structured bed of 44 packed spheres compared favourably with experimental radial temperature profiles. Single-parameter validation work in the literature includes: measured pressure drop data (54, 56, 57), heat transfer correlations (58) and classic reaction engineering (pseudo-homogeneous 1D) model results (59). All of these examples attempt to validate the model against a single model output parameter. They thus allow us to state only that the simulation matches the given interrogated output.

The particle processing simulation examples above suggest that one simulation output which matches experimental data cannot be taken to imply that all other results are correct or indeed that the model components are adequate. Full validation of a CFD model requires detailed and multi-objective interrogation of model components. These are detailed below.

![Fig. 7. Comparison of PEPT and DEM velocity data (Based on data in (46))](image)

![Fig. 8. Comparison of PEPT and DEM dispersion coefficients (Redrawn based on data in (43))](image)
6.1 Fluid Flow Fields and Turbulence Model

The published packed bed simulations predominantly use the k-ε turbulence closure model. Given the large specific surface area, extent of flow curvature and high particle Reynolds numbers (Re_p) it is questionable whether the inherent assumption of isotropic turbulence is valid. A number of studies have compared MRI flow fields with both CFD (60, 61) and with Lattice Boltzmann direct numerical simulation (DNS) simulations (62–64). This is however for liquid (aqueous) laminar (or at best transitional) flow and does not help validate the selection of the turbulence closure. The impact of different turbulence closures has been evaluated by comparing the predicted heat transfer with established heat transfer correlations (65, 66), concluding that under their conditions of low Re_p (transitional flow) there is no benefit in a more complex model over a single equation form such as that of Spalart Almaras. Gas-surface contact and (momentum and heat) transfer is a critical aspect of packed tube reactor simulation. To evaluate how best to model this requires a reversion to basics. Comparative Reynolds-averaged Navier-Stokes (RANS) CFD and
fundamental DNS based on employing large eddy simulations (LES) of gas flow over a single ‘sphere in a box’ at high Re have recently been carried out to ascertain the correct turbulence model (67) and the results checked against published experimental data. The results show that flow and transport can be accurately calculated using a RANS method with shear-stress transport (SST) k–ω closure provided that the mesh at the particle surface is fine enough and covers most of the boundary layer.

6.2 Particle Contact Points

There are a large number of particle-particle and particle-wall contact points in a packed bed. This is especially a problem where a spherical packing is used. These glancing contact points lead to intractable meshing problems and it is thus necessary to ‘modify’ them to avoid a near-zero contact angle. Contact point representation is vital to different aspects of packed column simulation. It affects packing voidage (hence pressure drop), particle contact area (so conductive heat transfer) and particle spacing (so near surface flows).

A number of strategies are used in the literature:
• Shrink particles slightly (gap) (55)
• Expand particles slightly (overlap) (65)
• Expanded contact (bridge) (68, 69)
• Flatten the touching curved surfaces (caps) (70)

Dixon, Nijemeisland and Stitt classify and compare the four alternative approaches as shown in Figure 10 (71). They report and compare RANS simulation results for all four approaches and note that all approaches have a significant effect on the simulation results. The effects differ however from one strategy to another. Global approaches significantly affect voidage and thus pressure drop. The removal of the contact point (gaps and caps) distorts particle-particle conductive heat transfer. Overall, bridges appear the best overall solution – but not always. This has been confirmed, but a sensitivity to the diameter of the bridge also noted (72).

6.3 Heat Transfer Validation

Packed bed heat transfer includes convective heat transfer from wall-to-particles via the gas and conductive heat transfer via particle contact points.

Initially, the conduction model in the CFD was validated against a fundamental analysis based on well-established literature methods (73, 74). The ‘zero flow’ CFD results, incorporating only solid phase conduction, showed good correspondence with the theoretical analysis for a range of input particle thermal conductivities (75) inferring that the conduction model is correct.

In the knowledge that conduction is correctly represented, validation of the heat transfer was made by comparison of experimental heat transfer results with analogous CFD simulations. Heat transfer experiments were carried out in a 98 mm diameter by 0.6 m packed tube at 2200<ReP<27,000 with a heating jacket. The experimental data and comparative CFD results are shown in Figure 11 for the tube packed with ceramic spheres (N = DT/dP = 7.44). The simulation results are in reasonable agreement with the experimental data (76). Given that all other elements of the model have been independently validated, this demonstrates the validity of the convection heat transfer model. Alternatively the convective aspect of gas-particle transfer has been validated by comparison with theoretical or empirical models for heat (77) and mass transfer respectively (78).

6.4 Including Intra-pellet Diffusion and the Reaction

Guardo et al. have validated an intra-particle diffusion and reaction model against experimental data for different sized catalyst particles (79). For the steam reforming case, the above sections report the successive validation of key elements of the overall CFD model for flow and heat transfer. Attention can now therefore turn to assessing the inclusion of intra-particle diffusion and reaction terms in an overall reaction model (80).
Intraparticle diffusion was modelled assuming a uniform porosity and Fickian effective diffusivity evaluated based on the dusty gas model assuming pressure variation in the pellet is small compared to total external pressure (81) and user defined scalars for the species balances. The reaction rate terms were input by user-defined code based on the steam reforming kinetics of Hou and Hughes (82).

For validation of this last model component a more structured pellet arrangement was used (83). The set up used for the experiments and simulation is shown in Figure 12 and used a ‘string’ of commercial pellets (Johnson Matthey Mini-Q 57-4). The reaction zone was six catalyst pellets, with a further six inert pellets in the feed and exit zone. The holes in the pellets were used effectively as thermo-wells and thus flow was only on the quasi-annular exterior.

Temperature profile measurements of a pellet string under methane steam reforming reaction conditions are shown in Figure 13. The simulation results are in reasonable agreement with the experiments, with an error in the order of only 2ºC–5ºC for the temperature predictions. Given that there are no adjustable parameters in this model other than those in the kinetic expression this seems to be a remarkably good result. This is a result, of course, of the fact that individual model components have been independently modified and validated and that in this final step only the diffusion and reaction terms represent any uncertainty.

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**Figure 11.** Comparison of CFD and experimental heat transfer data (Reproduced from Dixon et al. (76))

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**Figure 12.** Validation of CFD model including reaction and diffusion: (a) experimental set up; (b) graphical results from CFD (Reproduced from (83) by permission of Elsevier)
7. Conclusions

Advanced modelling techniques such as CFD and DEM are transforming the way chemical engineers carry out process and equipment research and evaluation. They provide massively enhanced levels of information and understanding on many complex process operations. In order for them to achieve widespread use as primary design tools it is essential to achieve the same levels of confidence that exist in traditional design methods and approaches.

This paper has addressed the level and scope of validation required for models, considering some traditional modelling approaches as well as modern computationally intensive models. In considering kinetic and rheology models, the examples have highlighted that when fitting models to experimental data, confidence in the adjustable parameter values is essential if that constituent model is to be reliable when applied to a design. Reliance on residuals (least squares) alone will not reliably parameterise or validate a model.

In developing or fitting a model one should also bear in mind the sagacious words of the physicist and statistician George Box (84). Often recalled only for the aphorism “All models are wrong; some are useful”, the extended version reminds us that we cannot always improve a model by the addition of parameters and terms: “Since all models are wrong the scientist cannot obtain a “correct” one by excessive elaboration. On the contrary following William of Occam he should seek an economical description of natural phenomena. Just as the ability to devise simple but evocative models is the signature of the great scientist so over-elaboration and over-parameterization is often the mark of mediocrity.”

In the specific context of this paper it is noted that a finite set of experimental data can fit many different models and often with many sets of adjustable parameter values. Not all of these models will be useful for design. A model derived from the real physics of the system, where the parameters represent real quantities which can potentially be measured, computed or estimated independently from the data set, is much more likely to be useful for design. Furthermore, in accordance with Box’s observations above, the addition of parameters with limited physical meaning to achieve an enhancement of fit is not beneficial to the predictive quality of the model or indeed to the estimation of the true physical fitting parameters.

The above observations are even more important for models of increased complexity, typified by discrete particle and CFD models. Two examples of particle flow modelling were presented, demonstrating that although the respective models matched well the initial data set more detailed consideration showed that other facets or model outputs were very poorly predicted.
Single-objective validation is not enough. It is necessary to evaluate the veracity of the underpinning model components and closures. Detailed validation of detailed models can be carried out using appropriate data and at appropriate scales and this is to be encouraged if the industry is to adopt successful modelling approaches in future.

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14th Ulm Electrochemical Talks

Towards next generation technologies for a sustainable electric future

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The Ulm Electrochemical Talks are held annually in Ulm, Germany. The 14th meeting, held from 23rd–26th June, 2014, focused on the topic of “Next Generation Electrochemical Energy Technologies”. Fuel cells and batteries are described as the dominant technologies to deliver the e-mobility vision within the next few decades. This selective review will focus on battery technologies and supercapacitors; although there was also plenty of material on the equally important topic of fuel cells which is not covered here.

Next Generation Materials for Lithium Ion Batteries

Andreas Fischer (BASF, Germany) talked through BASF’s battery material portfolio that includes mainly cathode materials and electrolytes, although some work on next generation silicon and tin-based material was also discussed in regards to dynamical formation and dissolution of the solid electrolyte interphase (SEI) during cycling. For high energy applications layered oxide and high voltage spinel materials are preferred, nickel cobalt manganese (NCM) for high power and lithium iron phosphate (LFP) for plug-in hybrid electric vehicles (PHEV) and grid storage. The talk was geared towards tailoring particle size and morphology and layer porosity to meet power requirements. By varying the experimental conditions different shaped NCM particles can be obtained as for example in Figure 1 (1).

In terms of electrodes, as a general rule, smooth layers are preferred for electric vehicles (EV) and porous layers for hybrid electric vehicles (HEV) as this directly affects diffusion paths. Also, a narrow particle size distribution results in decreased cycle life and poor rate capabilities. The drop in voltage at 10 C was used as a measure of lithium diffusion. On the electrolyte side, the aim was to find a suitable solvent that decomposes in the initial stages of cycling to form a protective surface on the cathode side, to stop manganese migration to the anode at high operating voltages.

Fig. 1. Morphology of NCM materials synthesised with flux fired with alkali chlorides at various temperatures (Reprinted with permission from (1). Copyright (2013) American Chemical Society)
Maria Assunta Navarra (Sapienza University, Italy) pointed out that production of large scale cells for energy storage and vehicle applications requires replacement of graphite and of lithium cobalt oxide with alternative, higher energy density, lower cost anode and cathode materials, but also replacement of the organic carbonate liquid solutions with safer and more reliable electrolyte systems. A 3 V cell comprised of tin/carbon composite as anode and LFP as cathode in a reliable electrolyte systems. A 3 V cell comprised of tin/organic carbonate liquid solutions with safer and more and cathode materials, but also replacement of the alternative, higher energy density, lower cost anode replacement of graphite and of lithium cobalt oxide with energy storage and vehicle applications requires pointed out that production of large scale cells for electric vehicles by Gallagher et al. (3) was referenced. It identifies the reversible lithium-metal negative electrode as a common, critical high-risk technology needed for batteries to reach long-term automotive objectives. Other developments required include shallow cycling (50 cycles up to 200 μA cm−2) and suitable catalysts to reduce the

Beyond Lithium Ion Batteries

Bruno Scrosati (Helmholtz-Institute Ulm, Germany) discussed possible chemistries beyond lithium-ion: lithium-sulfur, lithium-air, sodium-ion and graphene. Challenges facing one of the two most researched conversion chemistry systems, Li-S, include low cathode conductivity, solubility of LiS and use of lithium metal as anode. Li-O2 on the other hand suffers from irreversibility of the oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) (slow kinetics, high overvoltages), electrolyte instability, carbon corrosion and also problems associated with the use of lithium metal as anode. Due to sodium's higher abundance, this system also receives a lot of attention. Graphene brings high conductivity and high surface area, however the view is that this material will play no significant role in batteries, but should be considered for supercapacitors.

A good paper quantifying the promise of Li-O2 batteries for electric vehicles by Gallagher et al. (3) was referenced. It identifies the reversible lithium-metal negative electrode as a common, critical high-risk technology needed for batteries to reach long-term automotive objectives. Other developments required include shallow cycling (50 cycles up to 200 μA cm−2) and suitable catalysts to reduce the
overpotentials. Na-oxygen batteries show much smaller overvoltages compared to their lithium counterparts. Although the highest theoretical energy is obtained from Li$_2$O and Na$_2$O, only Li$_2$O$_2$ and Na$_2$O$_2$ showed some reversibility (4).

Stefano Passerini (Helmholtz-Institute Ulm, Germany) presented a flowing electrolyte cell (Figure 2) which was designed and built during the EU Lithium-Air Batteries with split Oxygen Harvesting and Redox processes (LABOHR) Project. An O$_2$-saturated electrolyte is circulating in and out of the cell resulting in improvements in the redox reaction (5). Another paper in press to look out for is Elia et al. in Nano Letters (6) showing only 600 mV gap between discharge and charge voltages using an uncatalysed electrode.

Margret Wohlfahrt-Mehrens (Centre for Solar Energy and Hydrogen Research (ZSW), Germany) discussed new electrode materials for batteries and capacitors. Three materials were discussed in particular: lithium manganese phosphate (LMP) and lithium manganese nickel phosphate (LMNO) as high voltage cathode materials for batteries and Li$_2$V$_2$(PO$_4$)$_3$ for supercapacitors. The position of the redox potential can be tuned by partial substitution of other metals into the LiCo$_{(1-x)}$M$_x$PO$_4$ matrix, where M can be Ni, Mg or Fe. LMNO obtained by a continuous coprecipitation method results in low surface area material, ideal for good transport inside the particle. Effects of particle size, shape, morphology and stoichiometry were discussed.

### Unusual Electrochemical Energy Technologies

Chemistries discussed by Jürgen Garche (ZSW, Germany) include: (a) lead-acid, which have an electrode distance of about 1–3 mm, compared to LIBs’ 15–35 μm, therefore have less tough requirements; (b) Li metal polymer, used by Autolib’ (France) to provide a 250 km range and charge at C/4 with operation temperature in excess of 70ºC; (c) liquid metal batteries, on which a good American Chemical Society review paper by H. Kim et al. (7) was presented; (d) aqueous hybrid ion, a 1.7 kWh, 48 V system patented by Aquion Energy (USA) (8); (e) electric double-layer capacitors, which offer dual use as they can both store energy and withstand static and dynamic mechanical stresses (9); (f) self-charging Li-ion cells, using polyvinylidene fluoride (PVDF) with piezoelectric properties and could be for example sandwiched between LTO and lithium cobalt oxide (LCO) and used in shoes.

Maximilian Fichtner (Helmholtz-Institute Ulm, Germany) talked about secondary batteries based on alternative anionic and cationic shuttles in order to obtain higher volumetric efficiencies. An example of an anionic shuttle system is the fluoride-ion battery using BaF$_2$ doped LaF$_3$ obtained by mechanical milling. Liquid electrolytes have
the potential to increase the efficiencies of fluoride ion batteries (10). Another member of the rechargeable family, the chloride ion battery is based on the metal chloride/metal electrochemical couple and an electrolyte composed of binary ionic liquids that allows chloride ion transfer at room temperature (11).

For cationic shuttle systems, magnesium has the advantage that it does not form dendrites during cycling, however suitable electrolytes for Mg\(^{2+}\) are harder to find than the lithium equivalent. Magnesium electrolytes may also be compatible with a sulfur cathode to produce a Mg/S battery, as discussed by H. S. Kim (12).

Peter Notten (Eindhoven University of Technology, the Netherlands) introduced the concept of an all solid-state battery for medical applications such as drug-delivery. An in situ method based on neutron depth profiling was used to probe lithium transport in all-solid-state Li-ion batteries in collaboration with Delft University of Technology, the Netherlands. Preliminary experiments have shown a linear decrease/increase in lithium concentration during cycling (13). Future experiments will include diffusion concentration monitoring in all parts of the battery: anode, electrolyte and cathode.

**Aqueous Systems and Redox Flow Batteries for Energy Storage**

The main advantages of aqueous electrolytes are safety and cost. Battery systems currently using aqueous electrolytes include lead-acid batteries, redox flow batteries and alkaline batteries such as NiMH used in automotive applications (for example in the Toyota Prius). Lead-acid batteries have the disadvantage of slow charge, low specific energy and contain a toxic active material.

Redox flow batteries with their low energy and low specific density find use in large scale electricity storage. Huamin Zhang (Dalian Rongke Power Co, Ltd, China) discussed three redox flow battery technologies for stationary applications: vanadium flow batteries, Zn-Ni hybrid flow and Li(Zn) bromine hybrid flow batteries. Oliver Osters (Next Energy, Germany) talked about degradation in bipolar plates of redox flow batteries due to V\(^{5+}\)/V\(^{4+}\) which is corrosive. Ageing effects were analysed using electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry combined with micro-computed tomography (CT).

David Ensling (Varta Microbattery GmbH, Germany) presented his company’s portfolio of hybrid energy storage systems with aqueous electrolytes. This included: (a) symmetric supercapacitors based on activated carbon (AC)/carbon; (b) asymmetric supercapacitors based on Ni(OH)\(_2\)/AC; and (c) ultra high power (UHP) NiMH. Varta’s hybrid supercapacitors are under further development.

**Battery Systems**

Oliver Weinmann (Vattenfall Europe AG, Germany) presented the idea of using second life LIBs for stationary applications. Vattenfall buys off used BMW batteries that no longer meet the requirements for automotive use and finds new applications such as acting as a buffer between grid usage and demand or storing photovoltaic (PV) energy.

Kent Snyder (Ford Motor Company, USA) presented an extensive study of various types of cells (cylindrical, pouch, prismatic) and their use in the automotive industry (light duty) with the aim of devising a standardised matrix. For example, Ford uses a laminated pouch for EVs and a metal can prismatic unit for PHEV and HEV. Although some trends are observed, the conclusion is that cell selection is based on independent criteria and timing needs, therefore at this point standardisation is not possible.

Marc Sämann (ads-tec GmbH, Germany) discussed two lithium-polymer cell technologies used for battery modules: (a) LTO-based, 2–4 kWh with up to 1500 cycles; and (b) NMC-based, 4.2–8.3 kWh and up to 7000 cycles.

**Conclusions**

This review covers some interesting talks on a wide range of electrochemical energy technologies, from state-of-the-art Li-ion, next generation and beyond to energy storage materials and systems and unusual electrochemical energy storage technologies. This comes in the context of rapid increases in the number of electric cars on the road and at the same time the beginning of major interest in electrical energy storage technologies in combination with renewable energy. Therefore there is a need for next generation technologies for a sustainable market growth beyond the first generation products now commercially available.
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The Reviewer

Carmen Salcianu obtained her PhD degree from Cambridge University, UK, in 2009 and since then has been working at Johnson Matthey Technology Centre in Sonning Common, UK. Her research spans topics from energy efficient light emitting diodes and photovoltaics to energy storage. She is now working on fabrication and electrochemical characterisation of carbon-based anodes for lithium-ion batteries and cathodes for lithium-air batteries.
Platinum Investment Casting, Part I: Simulation and Experimental Study of the Casting Process

Developing a materials database for the casting simulation of platinum alloys

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This paper summarises the results of collaborative research on investment casting of widely used platinum alloys (platinum with 5 wt% ruthenium (Pt-5Ru) and platinum with 5 wt% cobalt (Pt-5Co)) for jewellery purposes. To enable the simulation of the casting process, a materials database was developed as a first step. Casting simulation tools based on computational fluid dynamics (CFD) were used to optimise the casting process parameters and develop an improved understanding of their role. Selected casting trials were conducted using industrial tilt and centrifugal casting machines and the casting process was monitored in detail. Dedicated tree setups for the different machines were optimised using the casting simulation tools. The form-filling, surface quality and microstructure and porosity of the cast items were analysed to investigate the role of different casting parameters and geometrical conditions in the different casting setups. The casting simulation results led to a deeper understanding of the experimental casting results.

1. Introduction

The investment casting of platinum alloys has been empirically investigated by various groups. The aim of these investigations was a better understanding of the casting process and its optimisation. The studies vary in terms of the applied casting methods, the alloy compositions and the tree setup used (1–4). However, due to the high material costs and the limited distribution of platinum jewellery fewer studies have been conducted on platinum than on gold or silver alloys. Simulation of the casting process by fluid dynamics (in this paper referred to as ‘casting simulation’) has proven to be a valuable tool in gold and silver investment casting (5, 6), complementary to conventional empirical casting studies. The combination of casting simulation, casting experiments and characterisation of the resulting cast parts results in a better understanding of the casting process and hence better (quality) control.

Casting simulation of platinum alloys is expected to have huge potential for the optimisation of process parameters and hence the reduction of costs. However, no studies have yet been published in the open literature and there have also been no systematic correlations between process parameters and casting quality. Some general knowledge can be inferred from gold and silver casting, but there are many different material parameters to take into account when dealing with platinum.

The aim of this work is to address this deficit. Specifically, it strives to understand and optimise the influences of process parameters on the quality of Pt-5Ru and Pt-5Co casts with the aid of casting simulation. This paper records the results of a collaborative research project, which aimed to develop a materials database enabling the casting simulation (form-filling and solidification) of platinum alloys. Simulations were carried out and the results validated by selected casting trials including detailed process monitoring. The work was focused on controlling the melt temperature during
casting and observations of the metal cooling inside the flask. The simulation was calibrated and used to simulate the casting process in order to understand the role of parameters on casting quality. The casting trials were carried out with different process parameters employing two different alloys and several crucibles and investment materials.

This is the first of two papers on platinum investment casting. The second paper will deal with the optimisation of alloy composition using thermodynamic simulations (7). The results described in these two papers were presented in an oral presentation at the 28th Santa Fe Symposium® on Jewelry Manufacturing Technology in 2014 and will be published in 2015.

2. Experimental

CFD can be applied to simulate the complex flow of the melt during casting and the temperature distribution as a function of time. The methods used in this work are described elsewhere (5, 6). The simulation was conducted in two steps. Form-filling during casting was simulated with the software FLOW-3D (Version 10.0.3, Flow Science, USA), while Poligon software (Version 12.1, PoligonSoft, Russia) was applied to predict solidification shrinkage and investment heating.

FLOW-3D uses the finite difference model, a method which discretises the spatial domain into small cells to form a volume mesh (or grid); the software has its own internal multi-block meshing system, which allows the level of detail on specified areas of geometry to be increased, then adopts a ‘control volume’ approach to solve the Navier-Stokes equations. For the examples presented here a grid with 600,000–1,500,000 cells (depending on the model) was adopted, with a cell size between 0.005 mm and 0.0015 mm. To simulate the tilting and centrifugal processes, the corresponding physical models were activated (‘moving and deforming objects’).

Poligon uses instead the finite element method and requires the grid to be fitted on the geometries (both cast and mould) and then to be processed by the software HyperMesh (Version 11, Altair Engineering, Germany), in order to obtain a tetrahedral solid mesh of the model that can be used for the computational step. The models adopted here have approximately 25,000–27,000 nodes and 90,000–100,000 elements, in sizes between 0.5 mm and 1 mm.

The temperature distribution after complete form-filling in FLOW-3D was transferred to Poligon by measuring the predicted temperatures of four or five points in the cast part and then assigning these values to the corresponding nodes in the tetrahedral solid mesh. The Poligon software then interpolated the values, creating a temperature distribution in the part.

Evaluating the results of the form-filling simulations allowed the optimum placement of parts, inclination of sprues and main sprue diameter to be determined. It should be noted that FLOW-3D was not used to predict incomplete filling of the form: the different tree geometries were compared based on the turbulence shown while metal flowed into the mould, paying attention that the parts were sequentially filled (avoiding the premature splashing of cold droplets in the cavities).

Using the above described criteria, five different proposed tree designs (8) (Figure 1) were tested for suitability with the FLOW-3D software (9). The trees B and D in Figure 1 were chosen and optimised for tilt and centrifugal casting experiments, respectively (Figure 2).

In order to set up the simulation of the casting process, materials data for both metals and investment materials are required. Relevant data are the viscosity, melting range, fraction of solid, thermal conductivity, density and

Fig. 1. Simulated tree designs for tilt and centrifugal casting
specific heat of the alloys as a function of temperature. The melting ranges of the alloys were taken from their binary phase diagrams. However experimental data are very limited for platinum alloys (10–12). If alloy data were not available, data for pure platinum were used. An example of temperature dependent properties for the alloys can be seen in Figure 3.

Material data for investment materials are even more difficult to determine. The thermal expansion, melting range and gas permeability were determined experimentally for three selected investment materials, while their thermal conductivity could not be determined. Therefore experimental measurements were conducted and the values obtained were used to calibrate the simulation. The output was adjusted by manipulating the internal fit parameters in the Poligon software; the same was done for the heat transfer coefficient between metal and investment.

In order to calibrate the simulation, cooling curves of the metal inside the flask were measured using Type B (Pt-30Rh-Pt-6Rh) thermocouples. Figure 4(a) shows the thermocouples mounted on the wax tree. The thermocouples were inserted in ceramic tubes and connected to a data logger inside the casting machine (Figure 4(b)). The two casting machines required a specific adaptation of the thermocouples that took into account the movement of the flask during casting (tilting, rotation). The exact position of the thermocouples was controlled by X-ray imaging the flasks after casting in order to determine the distance of the thermocouples from the tree. This distance was taken into account when comparing the calculated and measured cooling curves (Figure 4(c)). The experimental cooling curves allowed the casting simulation to be calibrated for the two different casting machines used in the project. More details on the experimental setup are given in a previous report (9).

A number of casting experiments were carried out in order to evaluate the influence of the casting parameters on the cast parts. The selection of casting tree design for tilt and centrifugal casting was made based on the form-filling simulation of different tree design variations (Figure 2). Each tree contains eight typical jewellery pieces and one grid for the determination of form-filling. Two pieces of four different rings were used on the tree, in
particular ‘solitaire ring 1’ for a larger stone, ‘solitaire ring 2’ for a smaller stone, a ‘single-gate’ ring with one sprue at the ring shank and a ‘double-gate’ ring with two sprues at the heavy sections. The two selected trees had a casting weight of ~100 g and ~125 g for tilt and centrifugal casting, respectively. The casting trials were carried out in purified synthetic air. The tilt casting machine model was a VTC100VTi (Indutherm, Germany). The centrifugal casting machine models were a TCE10 (TopCast, Italy) and a Platincast600 (Linn, Germany). The metal temperature during heating and melting was monitored using a pyrometer and a thermal imaging camera. The experimental setup was slightly different during centrifugal and tilt casting depending on the setup of the machines. The detailed experimental setup is described elsewhere (9).

The temperature/time profile in selected areas was recorded for every single casting trial. The ‘casting temperature’ was the temperature of the melt at the moment when it left the crucible. The casting temperatures were 1850ºC–2040ºC depending on alloy and casting machine (Table I and Table II). The flask temperature was varied between 550ºC and 950ºC. The alloys used were Pt-5Co and Pt-5Ru. In the second part of the work modified alloy compositions were tested (7).

Eight different investment materials were tested and three were chosen for the casting trials. Pro-HT Platinum (Gold Star Powders, UK), referred to as ‘EBM7’ is a one-part jewellery investment material for platinum alloys. Ransom & Randolph (R&R®) Platinum Binder & Investment (Dentsply, USA), referred to as ‘EBM8’ is a two-part jewellery investment material.
Table I: Casting Parameters for the Experiments in the Tilt Machine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pt-5Co</th>
<th>Pt-5Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting temperature, °C</td>
<td>1850 ± 20</td>
<td>1950 ± 20</td>
</tr>
<tr>
<td></td>
<td>1950 ± 20</td>
<td>2040 ± 20</td>
</tr>
<tr>
<td>Flask temperature, °C</td>
<td>850</td>
<td>850</td>
</tr>
<tr>
<td>Investment material</td>
<td>EBM5; EBM7;</td>
<td>EBM5; EBM7;</td>
</tr>
<tr>
<td></td>
<td>EBM8</td>
<td>EBM8</td>
</tr>
</tbody>
</table>

Table II: Casting Parameters for the Experiments in the Centrifugal Machine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pt-5Co</th>
<th>Pt-5Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting temperature, °C</td>
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<td>1850 ± 20</td>
</tr>
<tr>
<td></td>
<td>1950 ± 20</td>
<td>2040 ± 20</td>
</tr>
<tr>
<td>Flask temperature, °C</td>
<td>550</td>
<td>850</td>
</tr>
<tr>
<td>Investment material</td>
<td>EBM5; EBM7;</td>
<td>EBM5; EBM7;</td>
</tr>
<tr>
<td></td>
<td>EBM8</td>
<td>EBM8</td>
</tr>
</tbody>
</table>

for platinum alloys. SHERAFINA® 2000 (SHERA Werkstoff-Technologie GmbH & Co KG, Germany), referred to as ‘EBM5’, is a dental investment.

After casting the tree was water-blasted. In order to evaluate the surface quality its surface was inspected by optical microscopy and scanning electron microscopy (SEM). The form-filling was assessed by the filling of a grid. In order to identify shrinkage porosity and other casting defects X-ray computed tomography (CT) and metallographic investigation were carried out.

3. Casting Results

3.1 Form-filling

The form-filling ability was judged by assessing the percentage of fully intact grid parts (Figure 2) and strongly depends on the alloy composition. In previous studies with a ‘diabolo-type’ tree, Pt-5Co showed superior form-filling in comparison to Pt-5Ru (1). This was confirmed for the more conventional trees employed during the present study (Figure 5). Centrifugal casting of Pt-5Co allowed complete form-filling at melt and flask temperatures exceeding 1850°C and 550°C, respectively. Pt-5Ru required a casting temperature approximately 100°C higher. Tilt casting generally required higher casting temperatures for complete form-filling compared to centrifugal casting. For Pt-5Co, it was sufficient to increase the casting temperature by approximately 100°C. For Pt-5Ru both the casting temperature and the flask temperature had to be increased by 100°C each. The reasons for the poorer form-filling ability of Pt-5Ru are explained in detail in Part II (7).

3.2 Surface Quality

The surface quality depends primarily on the alloy but is also affected by the investment material. For Pt-5Ru significant differences were also observed between the thin and thick sections of the same cast part. Figures 6–8 show the casting results obtained by two investment materials (EBM7 and EBM8). For the Pt-5Ru alloy EBM7 produced a very poor surface quality with a glassy layer visible at higher magnification in the thick sections of the ring (Figure 6(a)). In the thin sections of the ring the surface quality was acceptable. Surface quality deteriorated with increasing casting and flask temperatures for every investment material tested; however the extent to which this effect occurred was different for each. EBM8 showed only a slight deterioration of the surface even at high casting and flask temperatures (Figure 6(b)).

The SEM investigation of the ring cast with EBM7 (Figure 7(a)) revealed dimples on the surface formed by gas bubbles at the interface of metal and investment (Figure 7(c)). The investment material was molten in contact with the metal during casting and the gas bubbles were presumed to form due to the coagulation of the investment porosity. The molten area appeared to be covered by a transparent and shiny surface layer similar to the appearance of silica glass, about 500 μm thick. X-ray diffraction (XRD) measurement of the molten investment at the interface (Figure 7(d)) revealed an amorphous structure, confirming its glassy nature. Prior to the casting experiment, the investment material consisted of hexagonal α-quartz, tetragonal β-cristobalite, orthogonal tridymite and trimagnesium diphosphate (Mg₃(PO₄)₂). It may be concluded that the melting point of EBM7 is too low to withstand the high temperatures of the Pt-5Ru melt.

By contrast the interface produced by EBM8 for the complete double-gate ring was smooth (Figures 6(b) and 7(b)). No gas pores were observed at the interface and the investment was not molten during casting (Figure 7(b)). A molten surface layer was not observed, only a ~30 μm sintered layer. The initial crystalline structure of pure hexagonal α-quartz was found to be intact (Figure 8(b)).

The dental investment EBM5 showed similar characteristics to EBM7, but produced a slightly better surface quality of the as-cast platinum rings. In an
isothermal melting test (10 min) none of the investments melted at 1675°C (the solidification temperature of Pt-5Co). At 1725°C EBM5 and EBM7 partially melted, while EBM8 did not melt. At 1775°C (the solidification temperature of Pt-5Ru) all investments melted. It appears that EBM8 has the highest temperature stability enabling it to withstand melting when subjected to short term heating during casting. For Pt-5Co, the casting and flask temperatures had very little influence on the surface quality. With all three investment materials a blue layer of cobalt silicate formed, but the surface was generally smooth.

3.3 Porosity

The casting simulation predicted decreasing shrinkage porosity with increasing casting and flask temperatures (Figures 9 and 10). Metallographic investigations confirmed this prediction for both casting machines used, in agreement with earlier studies (1). In general, high shrinkage porosity could be avoided by the correct sprue design, as in the case of the double-gate ring, allowing defect-free castings to be achieved with Pt-5Co. Only very small (<1 μm) and scattered gas pores and oxide inclusions were found, which do not deteriorate casting quality. Pt-5Ru on the other hand, showed a pronounced tendency to form micro-shrinkage porosity, even with properly designed sprues. An explanation of this effect is given in Part II (7). One way to close micro-shrinkage pores would be hot isostatic pressing as described elsewhere (13).

In tilt casting the tendency for micro-shrinkage porosity was less pronounced. However, very high casting (2040°C) and flask temperatures (950°C) were required for complete form-filling of the filigree item. As described above, very temperature resistant investment materials are required for good surface quality. Generally, the investment material has a rather small influence on the porosity formation, although EBM8 showed slightly better results compared to EBM5 and EBM7.
Fig. 7. Influence of investment material on surface quality of Pt-5Ru, $T_{\text{melt}} = 1850^\circ\text{C}/T_{\text{flash}} = 850^\circ\text{C}$. SEM image of the metal-investment interface in the thick section: (a) EBM7; (b) EBM8; and SEM surface image of the thick section: (c) EBM7; (d) EBM8

Fig 8. XRD measurement of the investment at the interface: (a) EBM7; (b) EBM8
Porosity

(a) 4.9% (b) 4.4% (c) 3.9% (d) 3.4% (e) 3.0% (f) 2.5% (g) 2.0% (h) 1.5% (i) 1.0%

Fig. 9. Simulation of calculated porosity for tilt casting of Pt-5Co. Flask temperature of 850°C and casting temperature of: (a) 1850°C; (b) 1950°C

Fig. 10. Metallographic investigation showing porosity for tilt casting of Pt-5Co. Flask temperature of 850°C and casting temperature of: (a) 1850°C; (b) 1950°C

In centrifugal casting, the tree design plays a much more important role for form-filling and solidification than in tilt casting. The tree orientation with respect to the centrifugal direction (leading and trailing side) and ring inclination with respect to the main sprue (for example 45° or 90°) have to be considered. The trees used in this study are shown in Figure 1. The tree for centrifugal casting consisted of a thin main sprue with two rows of four parts. Most of the parts were mounted at an angle of 90°±5° and some were mounted at 45°±5° to investigate the influence of the mounting angle (Figure 11). In centrifugal casting, the rings are usually mounted at 90° to the main sprue, because this causes less turbulence during form-filling as shown in Figure 12. The centrifugal machine rotated clockwise, i.e. the parts shown on the tree in Figure 11 were...
mounted on the leading side. Other parts were mounted on the trailing side. Different variations were simulated and then experimentally tested.

An example of improper sprueing is the single-gate ring (Figure 1). This way of mounting resulted in dimples on the thick section of the ring, which faced towards the crucible (Figure 13(a)). Although the ring showed no major porosity (Figures 14(a) and 15(a)) it had to be discarded, because the dimples could not be removed or repaired. It is assumed that the thick section was isolated during solidification and the one-sided dimple formed because the melt was forced by centrifugal acceleration to the outer side of the flask. If instead the ring was mounted at 45º no surface dimples were observed (Figure 13(b)). However, the X-ray CT investigation (Figure 14(b)) showed large shrinkage pores in the ring shank. Metallography revealed centreline porosity along the ring shank (Figure 15(b)), while the thick section showed only micro-shrinkage (Figure 13(b)). The ring shank acted as a feeder for the thick section and formed the centreline pores. The centreline pores did not appear during polishing and the ring would pass quality control. However, the position of the pores is random. In this case the pores were not visible, while in other cases they will be closer to the surface and would appear during polishing. Some manufacturers use hot isostatic pressing to close internal porosity. That works well with gas pores or microshrinkage. However larger pores, such as centreline pores, would leave dimples at the surface and the part would be rejected. In order to be safe proper sprueing should be used.

The metallographic investigation of the double-gate rings mounted at 45º and 90º showed no such inhomogenities in porosity distribution nor any surface dimples. Therefore this sprue design would be preferred for reliable production. Leading and trailing sides showed no significant difference in terms of filling and porosity.

4. Discussion

Casting simulation enables a deeper understanding of possible defects, for example, the formation of shrinkage porosity (Figures 9 and 10) or the deterioration of surface quality by investment breakdown (Figures 6–8 and 16). Casting can be understood as a two-step process. The first step is filling. During this step the forces acting on the melt control its flow into the flask. In tilt casting the major acting force is gravity. Therefore the flow speed of the melt is relatively low,
Fig. 13. Centrifugal casting of the single-gate ring in Pt-5Ru. Metallographic cross-section at the thick section, the angle of the ring mounted to the main sprue at: (a) 90º; (b) 45º

Fig. 14. CT images of the ring mounted to the main sprue: (a) 90º; (b) 45º

Fig. 15. Metallographic cross-section at the ring shank. The angle of the ring mounted to the main sprue: (a) 90º; (b) 45º
resulting in a comparatively long form-filling time and promoting significant cooling during form-filling. For the chosen tree design the temperature of the melt significantly deviated along the tree axis resulting in a temperature gradient from the main sprue to the tree tip. The temperature difference between the melt entering the first layer of parts in the sprue and that entering the second layer was about 40ºC (Figure 12(a)). The complete filling of the tree took about 0.6 s. The tree geometry was optimised based on the filling simulation. The main sprue diameter was reduced from 10 mm to 5 mm, because the filling speed increased with a smaller main sprue. In addition, this saved about 50% of the tree weight – an important amount of otherwise ineffectively used precious metal.

In centrifugal casting, the main acting force is ‘centrifugal’ force. The way the tree filled was found to depend strongly on the way in which the pieces were mounted on the main sprue. If the parts were mounted on the leading side of rotation, inertia caused an acceleration of the melt to the trailing side of the main sprue. Parts mounted at an angle of 90º to the main sprue were then successively filled from the tip of the main sprue towards the in-gate. This situation is illustrated in Figure 12(b) for the upper row of parts. If the parts were mounted on the trailing side of the tree, the momentum of inertia of the melt caused all parts to be filled simultaneously. The simulation indicated that such simultaneous filling might cause cold shuts. This effect was, however, in practice substantially smaller because the acting forces were small. The filling time was approximately 50% shorter for centrifugal casting compared to tilt casting although the tree was ~25% heavier. The shorter filling time resulted in a higher residual melt temperature, which explains the better filling ability of centrifugal casting at low casting and flask temperatures.

The lower row of parts in Figure 12(b) were mounted at an angle of 45º to the main sprue. This resulted in a gradient in centrifugal force $F_c$ (as in $F_c = m\omega^2 r$ with the mass $m$, the angular velocity $\omega$ and the radius of curvature $r$) and in hydrostatic pressure, which resulted in an inhomogeneous filling of the parts. Figure 11 shows the pressure distribution after complete filling. There is a significant gradient in the centrifugal force along the tree. This suggests that filigree items should be mounted on the tip of the tree, where the pressure is high and which fills first during casting. The parts mounted at 90º to the main sprue showed a small internal pressure gradient. However, even this small gradient could cause casting defects, as shown for the single-gate ring (Figures 13–15 and 17). The pressure gradient in the parts mounted at 45º was quite high. As described above, this caused inhomogeneous filling that might be detrimental. However, the pressure gradient also allowed feeding in the semi-solid state and helped avoid shrinkage porosity at critical positions.

Fig. 16. Temperature distribution in the investment after centrifugal casting of Pt-5Co obtained by Poligon at a flask temperature of: (a) 550ºC; (b) 850ºC
in some parts. This was also demonstrated for the single-gate ring in Figures 13–15.

The second casting step, solidification, was simulated using the Poligon software that allowed the solidification shrinkage and therefore local shrinkage porosity in the parts to be simulated (Figure 17). The red areas indicate high shrinkage porosity. At the tip of the tree almost no porosity would be expected in the cast parts according to the simulation. The single-gate appeared to be most prone to shrinkage porosity, especially at its thick section which was probably isolated from the melt in the main sprue due to premature solidification in the narrower parts of the sprue. In this case, feeding with fresh melt was interrupted. The pressure gradient inside the part forced the remaining melt towards the tip of the tree. Finally, a dimple formed on the ring side facing towards the in-gate. This explains the experimental findings in Figures 13–15.

The heating of the investment was also simulated using Poligon. Figure 16 shows the temperature distribution in the investment for the double-gate. Along the thin ring shank the temperatures were relatively low. Critical positions were the thick sections of the ring. A hot spot was found where the heavy sprues were connected to the ring. With increasing casting and flask temperatures local overheating increased significantly. Figures 6(b) and 7(b) show the investment reactions at the thick sections. The locally very high temperature caused the breakdown of some less stable investment materials, which resulted in poor surface quality. The breakdown of the investment materials was promoted by high amounts of magnesium phosphate used as a sintering additive, which reduces the melting range of the investment (14). Such additives can be a significant restriction for the investment material. In order to avoid investment breakdown more stable investment materials must be used or the solidification temperature of the alloy might be modified as described in Part II (7).

5. Summary

Pt-5Co has good form-filling characteristics compared to Pt-5Ru independently of flask and casting temperatures. For the machines used during this study, form-filling was better in centrifugal casting compared to tilt casting, because the acting forces are four times higher. Hence, centrifugal casting had faster filling and higher melt temperatures during filling. In tilt casting higher overheating was needed to obtain the same results.

An improvement of the form-filling with Pt-5Ru could be achieved with increased casting and flask temperatures. However, very stable investment materials had to be used in order to avoid investment breakdown. Locally, very high investment temperatures could occur and this was demonstrated by simulation. Local melting or sintering of less stable investment materials resulted in poor surface quality of the product. The most stable investment material in this study contained high amounts of hexagonal α-quartz and low amounts of sintering additives.

As predicted by casting simulation, the shrinkage porosity decreases with increasing casting and flask temperatures. This was particularly true for Pt-5Co, which only showed very small gas pores and oxide inclusions under optimum conditions. Pt-5Ru showed a
pronounced tendency to form micro-shrinkage that was difficult to avoid in centrifugal casting. In tilt casting, the micro-shrinkage was less pronounced due to slower cooling in the specific machine employed in this work.

Important and helpful indications about tree design, positioning or inclination of the parts on the tree and the temperature distribution of the investment could be concluded from the casting simulation. Particularly in the case of centrifugal casting (where the acting forces are more complex), casting simulation helped to gain an understanding of observed casting defects and find suitable solutions.

Lastly, the project showed the limits of conventional jewellery alloys (Pt-5Ru and Pt-5Co). Further alloy optimisation appears necessary (7).

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References

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Annihilation of Extremely Halophilic Archaea in Hide Preservation Salt Using Alternating Electric Current

Electrochemical disinfection of hide brine liquors for use in the leather industry

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Salt contains extremely halophilic archaea and these microorganisms degrade leather quality. The aim of this study is to find an effective treatment system to kill these microorganisms in salt used in hide brine curing. Ten salt samples were obtained from Tuz Lake, Turkey, and the total cell counts of extremely halophilic archaea, proteolytic and lipolytic extremely halophilic archaea were determined. Two sets of experiments were designed to detect the inactivation impact of alternating electric current on extremely halophilic archaea. In the first experiment, 2 A alternating electric current was applied for 25 min to the salt samples dissolved in liquid medium. In the second experiment, 2 A alternating electric current was applied for 25 min to the isolates of proteolytic extremely halophilic archaea, lipolytic extremely halophilic archaea, both proteolytic and lipolytic extremely halophilic archaea, and a mixed culture of these isolates. The extremely halophilic archaea in salt (10²–10⁴ colony forming units (CFU) g⁻¹) was annihilated in 1 min via alternating electric current and a 5 min treatment with the current was enough to destroy extremely halophilic archaeal isolates (10⁶ CFU ml⁻¹) obtained from salt samples. This electric treatment was found fairly effective to kill proteolytic and lipolytic extremely halophilic archaea in salt used for preservation of hide.

1. Introduction

The leather industry is an important sector in the world economy. Almost 23 billion square feet of leather is produced annually (1, 2) and the total value of this is estimated to be more than US$100 billion (3). Most of the global earnings are accrued from footwear sales. This sector represents 60% of the industry's total income, with annual production of 13 million pairs of shoes (4, 5). Because many consumers can perceive when leather products are manufactured from an inferior hide grade, producers are perforce obliged to dispose of damaged hides. Ignorance of effective preservation techniques therefore causes important economic losses in the industry.
Studies have shown that hides contain extensive populations of Gram-positive and Gram-negative bacteria which may be either resident or transient bacteria. As soon as the animal is slaughtered, these bacteria can grow on the raw hides and degrade the hide quality (6–8). A mixture of salt and boric acid is commonly used to prevent the growth of these microorganisms and preserve the hides. If hides are preserved with only crude solar salt, they can be contaminated by different species of extremely halophilic archaea (9–12). These microorganisms are easily detected on hides as they are revealed by red to orange pigments. Extremely halophilic archaea produce red, orange and pink coloured colonies because of the presence of C50 carotenoids (9–12). Red discolorations on the salted hides, caused by microorganisms, have been scrutinised by researchers since 1929; even at that early date, proteolytic activity of halophilic microorganisms was recognised (13). In addition, occurrence of red colouration produced by extreme halophiles has been noted in the Great Salt Lake (14), Dead Sea (15), Lake Magadi (16) and Tuz Lake (11). Salt lakes and solar saltern crystalliser ponds contain 10^7–10^8 CFU of extremely halophilic archaea per ml (9). In previous studies, salt samples which were obtained from Tuz Lake in Turkey contained 10^4–10^7 CFU g^-1 extremely halophilic archaea (11). In another study, the viable cell number of extremely halophilic archaea in water samples collected from Tuz Lake was found to be 1.38 × 10^7 CFU ml^-1 (17).

Salt collected from Tuz Lake, located in Central Anatolia, Turkey, is used to preserve hides in the Turkish leather industry. If the salt obtained from Tuz Lake is directly used in hide preservation, it may contaminate hides with halophiles. During long storage or overseas transportation of the salted hides, viable cell numbers of extremely halophilic archaea on the hides can multiply excessively. In an earlier study, extremely halophilic archaea were observed in considerably high numbers (10^3–10^8 CFU g^-1) on 36 salt-pack cured hides. Extremely halophilic archaeal counts were fairly high in 72% of the hides (10^5–10^7 CFU g^-1) as a consequence of inadequate salt-pack curing method. 94% and 81% of the samples contained proteolytic extremely halophilic archaea (10^2–10^5 CFU g^-1) and lipolytic extremely halophilic archaea (10^2–10^6 CFU g^-1), respectively (18). These findings were consistent with previous studies’ reports of the extremely halophilic archaeal counts (10^5–10^6 CFU g^-1) on the brine cured hides (19, 20).

The destructive effect of extremely halophilic archaea on salted hides has been observed. It was detected that proteolytic extremely halophilic archaea, originating in unprocessed solar salt, digested the grain surface of the hide and caused a complete disruption of collagen fibers (21). Furthermore, it was noted that proteolytic and lipolytic extremely halophilic archaea produced sponge-like vesicles within the hide and light stains on the suede surface of finished double-face leathers (22, 23). Therefore, inadequately preserved hides and skins may adversely affect final leather quality.

Due to these destructive effects of extremely halophilic archaea on the salted hides, an effective, easy and inexpensive method should be applied to eradicate these archaea in salt. Thus, using sterile salt in hide preservation will increase leather quality and prevent substantial economical losses in the leather industry.

1.1 Use of Electric Current

Electric current application is one of these methods. This treatment system has been used by several researchers to inactivate different types of microorganisms found in synthetic urine (24), water (25), fresh orange juice (26), activated sludge and biofilms (27), effluent seawater (28), soak liquors (29), brine solution (30, 31), on beef surfaces (32) and chicken legs (33). In those experiments, scientists usually used direct electric current to eliminate diverse bacterial populations.

In addition to direct electric current, alternating electric current was also used to inactivate bacteria in phosphate buffer solution (34), seawater (35) and natural waters (36). Researchers mentioned that alternating electric current treatment has advantages over direct electric current (35). The investigators found that application of 1 A direct electric current or 1 A alternating electric current for 100 ms were sufficient to kill *Vibrio parahaemolyticus* in seawater. They concluded that 1 A alternating electric current application at 5 Hz generated less chlorine concentration (<5 mg l^-1) in seawater than when the seawater was treated with direct electric current (approximately 35 mg l^-1). It was revealed that this reduced production of chlorine was due to the bidirectional flow of alternating current, resulting in less electrolysis of the test medium. It was also emphasised that chlorine gas produced in direct electric current treatment may cause serious health problems in humans (35). To overcome this adverse effect of chlorine gas, the researchers suggested using alternating electric current to
kill bacteria in natural waters (36) and industrial applications (35).

The mechanism of bacterial inactivation by alternating electric current has been explained as a byproduct of chlorine (36, 37) and hydrogen peroxide (34, 35, 38) produced during electrolysis. Previous experiments demonstrated that electric field and current caused cell membrane damage in the form of pores that opened on the membrane following electrical treatment (39, 40). Chloride and hydrogen peroxide, produced during electrolysis, may enter easily through these pores, thus hastening the inactivation process (39, 40). In addition, researchers observed that application of alternating electric current on Escherichia coli cells damaged their cell membranes, thereby causing the leakage of intracellular components, DNA-related materials and ninhydrin-positive materials from the cell (41). Moreover, alternating electric current affected E. coli cells by increasing the negative charge at the surface and decreasing their respiratory rate (42). Furthermore, the amount of phosphatidylethanolamine in the cell membrane of E. coli was reduced by electric current treatment (43).

Although studies indicate that direct electric current can annihilate different species of microorganisms in diverse industries (24–33), the inactivation effect of alternating electric current on extremely halophilic archaea in hide curing salt has not yet been evaluated. The alternating current disinfection method was used in the present study precisely because it was proven to release only a low chlorine concentration (35). Therefore, the experiments were designed to evaluate the following: the inactivation impact of 2 A alternating electric current, which produces less chlorine than direct current treatment (35), on extremely halophilic archaea in salt; the inactivation effect of 2 A alternating electric current on the isolates of proteolytic extremely halophilic archaea, lipolytic extremely halophilic archaea, both proteolytic and lipolytic extremely halophilic archaea and a mixed culture of these isolates. The total extremely halophilic archaeal counts, total proteolytic extremely halophilic archaeal counts and total lipolytic extremely halophilic archaeal counts in salt samples were also determined.

2. Experimental procedures

2.1 Determination of the Total Counts of Extremely Halophilic Archaea

Ten salt samples were collected from Tuz Lake in Turkey. A total of 20 g of salt sample was separately placed into an electrolysis cell containing a final volume of 200 ml of 25% NaCl solution in water. Then, this mixture was placed into a shaker incubator (100 rpm) for 4 h at room temperature. A total of 100 μl of the test medium was removed from each electrolysis cell before commencing the experiments. This was diluted to 10-fold (10⁻¹) dilution, 100-fold (10⁻²) dilution and 1000-fold (10⁻³) dilution with sterile 25% NaCl solution. The viable extremely halophilic archaeal cell numbers in these samples were determined by the plate count method. To detect the total extremely halophilic, proteolytic and lipolytic extremely halophilic archaeal cell numbers in the salt samples, the direct and the diluted solutions were spread over complex agar medium, gelatin agar and Tween® 80 agar media, respectively, and incubated at 39°C for 30 days. After the incubation period, the colonies on the complex agar surface were counted. To determine protease positive isolates, the colonies on the gelatin agar medium were flooded with Frazier solution. Then, the colonies with clear zones were considered as protease positive, and these colonies were counted (44, 45). The colonies with opaque zones on Tween® 80 agar were considered as lipase positive and were counted (44). Later, viable cell numbers of these archaeal isolates in 1 ml were calculated. Protease and lipase positive colonies with different colours and morphology were selected and streaked out several times to obtain pure cultures on complex agar medium by the streak plate technique.

2.2 The Electrochemical Disinfection System

An electrochemical cell was constructed of a glass beaker containing two internally attached platinum wire electrodes (1 mm in diameter, 80 mm long) submerged in 25% NaCl solution. The distance separating the two electrodes was 40 mm. These electrodes were attached to a regulated alternating current source (Ruhstrat GmbH, Germany) (input = 220 V, frequency = 50 Hz, power = 2250 VA), which had an automatic variable output voltage range of 0–220 V and user-selectable current range of 0–9 A (35, 46).

In the present study, 2 A alternating electric current treatment was applied to two experimental sets. In the first experimental set, consisting of ten tests, 2 A alternating electric current was applied to salt samples mixed separately into 25% NaCl solutions. In the second experimental set, consisting of four tests, 2 A alternating electric current was applied to a mixed culture of proteolytic extremely halophilic archaea, a mixed culture of lipolytic extremely halophilic archaea,
a mixed culture of both proteolytic and lipolytic extremely halophilic archaea, plus a mixed culture of these isolates added to 25% NaCl solutions.

2.3 Inactivation of Extremely Halophilic Archaea

As explained above, for the first experimental set, an electrolysis cell containing 200 ml of liquid test medium, 25% NaCl and separate salt samples was used in this experiment. 2 A alternating electric current was applied to the electrolysis cell for 25 min. Aliquots of 100 μl were removed from this medium at intervals of 1, 5, 10, 15, 20 and 25 min during the alternating current treatment. Then, the aliquots were diluted to 10-fold (10−1) dilution, 100-fold (10−2) dilution and 1000-fold (10−3) dilution in sterile physiological saline solution. 100 μl of the direct and diluted solutions were spread over complex agar medium and incubated at 39ºC for 30 days. Then, the colonies on the agar surface were counted. The detection limit of this experiment was 10 CFU ml−1.

2.4 Inactivation of Proteolytic and Lipolytic Extremely Halophilic Archaea

For the second experimental set, protease and lipase positive extremely halophilic archaea were isolated from the salt samples obtained from Tuz Lake. Two isolates of protease positive (TLPI1 and TLPI2), two isolates of lipase positive (TLLI1 and TLLI2) and a mixed culture of these extremely halophilic isolates (TLP11, TLP12, TLI1, TLI2, TLP11 and TLP12) were selected as test isolates to use in alternating electric current treatment experiments. Each of these isolates was cultivated for 15 days at 39ºC in a shaker incubator (Edmund Bühler, Germany) at 100 rpm in a liquid complex medium. After the incubation period, each of these extremely halophilic archaeal isolates was diluted in 25% NaCl solution in a final population density of 107 CFU ml−1. Next, the aforementioned isolates were prepared. 20 ml of protease positive (TLP11 and TLP12), lipase positive (TLLI1 and TLLI2), both protease and lipase positive (TLP11 and TLP12) and the mixed culture (TLP11, TLP12, TLI1, TLI2, TLP11 and TLP12) were separately placed into an electrolysis cell containing 180 ml of 25% NaCl solution. Later, 2 A alternating electric current was applied to each electrolysis cell for 25 min. A 100 μl quantity of the test medium was removed from the electrolysis cell at intervals of 1, 5, 10, 15, 20 and 25 min. Each of the test media was plated onto complex agar medium both directly and after serial dilutions, then incubated for 30 days at 39ºC. After the incubation period, colonies on the agar surface were counted and CFU of extremely halophilic archaea in 1 ml was calculated. The detection limit of this experiment was 10 CFU ml−1.

The log10 reduction factor (RF) for each treatment time was calculated according to the following formula:

$$RF = \log_{10} n_b - \log_{10} n_a$$

where nb is the initial number of viable cells (CFU ml−1) in the inoculum of the first experiment (salt samples dissolved in 200 ml of liquid medium containing 25% NaCl) or in the inoculum of the second experiment (test isolates found in 200 ml of liquid medium containing 25% NaCl); and na is the number of viable cells (CFU ml−1) in the inoculum (salt samples or test isolates) after treatment with 2 A alternating electric current.

The pH and temperature of all samples were measured at each of the aforementioned intervals using a pH meter (Professional Meter PP-50, Sartorius AG, Germany). The temperatures of all test media were adjusted to 25ºC before application of alternating electric current treatment.

3. Results and Discussion

Extremely halophilic archaea, proteolytic and lipolytic extremely halophilic archaea were detected in all salt samples (Table I). Although salt samples mostly contained between 103 and 104 CFU of extremely halophilic archaea per gram, proteolytic and lipolytic extremely halophilic archaeal numbers were between 101 and 103 CFU g−1 in salt samples (Table I). These findings were consistent with previous experiments (18, 30). In those studies, 80 salt samples used in hide preservation were examined for extremely halophilic archaea. It was found that all salt samples contained 102–105 CFU g−1 of extremely halophilic archaea (18, 30). Moreover, all salt samples contained proteolytic and lipolytic extremely halophilic archaea (102–104 CFU g−1) (18, 30).

In this study, two sets of experiments were conducted to examine the inactivation effect of alternating electric current on extremely halophilic archaea. In the first experiment, extremely halophilic archaea, proteolytic and lipolytic extremely halophilic archaea in salt samples were killed in 1 min via 2 A alternating electric current treatment. There was a sharp decrease in the
<table>
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<th>Salt sample</th>
<th>Exposure time, min</th>
<th>Log10 Number, CFU ml⁻¹</th>
<th>Reduction factor</th>
<th>Log10 Log10 values</th>
<th>Reduction factor</th>
<th>Log10 Reduction factor</th>
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<td></td>
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<td></td>
<td>1.4 × 10³</td>
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<td>&gt;3.1</td>
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<td>&gt;2.1</td>
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<td>&lt;1</td>
<td>&gt;2.9</td>
<td>&lt;1</td>
<td>&gt;1.5</td>
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</table>

*The number was not detected because it was under the detection limit*
numbers of extremely halophilic archaea, proteolytic and lipolytic extremely halophilic archaea in the salt samples after 1 min of 2 A alternating electric current treatment (Table I).

Temperature values of the test media did not change when the extremely halophilic archaea in the salt samples were killed. The temperature of all test media containing salt samples was 25°C before the experiment and remained the same after 1 min of electric treatment. At the end of experiment (after 25 min), the temperature of these media reached 35°C. The pH of the test media did not change during the experiment. Voltage levels of the test media containing the salt samples varied according to the samples and the duration of electric current treatment. However, all voltage levels decreased at the end of these experiments (Table II).

The inactivation effect of alternating electric current on Gram-negative bacteria has been examined in previous studies (34–36, 47, 48). E. coli cells in the test medium containing nutrient broth, peptone and NaCl were killed by 110 mA alternating electric current in 10 s (36). E. coli cells suspended in a phosphate buffer solution were also killed by 300 mA cm⁻² alternating electric current (34). V. parahaemolyticus in effluent seawater was killed by 3 A alternating electric current treatment in 30 ms (35). In an earlier study, both E. coli ATCC 25922 (resistant to ampicillin (10 μg ml⁻¹) and amoxicillin-clavulanic acid (30 μg ml⁻¹)) and fecal E. coli MAAG 1405 (resistant to ampicillin (10 μg ml⁻¹) and amoxicillin-clavulanic acid (30 μg ml⁻¹), imipenem (10 μg ml⁻¹), cefuroxime (30 μg ml⁻¹), cefotaxime (30 μg ml⁻¹)) were killed within 1–3 min in media containing marine waters (1 A), 5–10 min in Ayamama River water (1 A), 5 min in Sarisu River water (0.5 A) and 20–35 min in lauryl sulfate broth (1 A) by applying alternating electric current. Log₁₀ reduction factors of E. coli ATCC 25922 and fecal E. coli MAAG 1405 were between 3.47 and 3.99 in the different water samples when these bacteria were completely inactivated. The pH of all water samples was between 6 and 7 and remained constant during alternating current treatment (47). Furthermore, in another study 1.5 A alternating electric current was used to kill Enterobacter cloacae, Pseudomonas luteola and Vibrio fluvialis, as well as a mixed population of these Gram-negative bacteria isolated from hides. 15 min exposure to 1.5 A alternating electric current inactivated Enterobacter cloacae, Pseudomonas luteola and Vibrio fluvialis in the brine solution containing 25% NaCl. Moreover, exposure to 1.5 A alternating electric current for 15 min followed by 1.5 A direct current for 1 min inactivated the mixed population of these bacteria in the brine solution. The maximum temperature rise was 6°C (48).

In the second experiment, the mixed culture of protease positive isolates (TLPI1 and TLPI2), mixed culture of lipase positive isolates (TLLI1 and TLLI2), mixed culture of both proteolytic and lipolytic isolates (TLPLI1 and TLPLI2) and mixed culture of all test isolates (TLPI1, TLPI2, TLLI1, TLLI2, TLPLI1 and TLPLI2) were prepared as four different treatment groups. In our previous study we detected proteolytic and lipolytic extremely halophilic archaea between 10²–10⁶ CFU g⁻¹ in 36 salted hides (18). Hence, high populations of proteolytic and lipolytic extremely halophilic archael isolates (10⁶ CFU ml⁻¹) were used to examine the inactivation effect of alternating electric current. 2 A alternating electric current was applied to the mixed cultures of these isolates in the test media containing 25% NaCl for 1, 5, 10, 15, 20 and 25 minutes. As indicated in Table III, the archael cell counts in all test media also decreased during the electric treatments. The mixed culture of protease positive isolates dramatically decreased during 1 min of electric treatment. Likewise, lipase positive isolates, both proteolytic and lipolytic isolates, and the mixed culture of all isolates also decreased sharply. After 1 min alternating electric current treatment, the numbers of protease positive isolates, the numbers of lipase positive isolates, the numbers of both proteolytic and lipolytic isolates, and the mixed culture of all isolates decreased sharply. After 1 min alternating electric current treatment, all archaeal cells were annihilated in each treatment (Table III).

In the second experiment set, temperature values of the test media increased slightly when the test isolates were inactivated. All voltage levels decreased slightly when the test isolates were inactivated. At the end of the experiment, temperature values and voltage levels of the test media were measured respectively at 35°C and between 4.6–5.1 V (Table III).

4. Recommendations

The authors of this study highly recommend this easy, effective, economical, fast, broad-spectrum activity system to prevent archael damage on brine cured hides. Although there are a few studies which explain the mechanism of bacterial inactivation by alternating
Table II  Values of Temperature, Voltage and pH in the Liquid Test Media Containing Salt Samples Treated by 2 A Alternating Electric Current Over 25 min

<table>
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<th>Salt sample</th>
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<th>V</th>
<th>pH</th>
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<th>V</th>
<th>pH</th>
<th>3 °C</th>
<th>V</th>
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\(^b\) Temperature, \(^c\) Voltage

Table II  Continued

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### Table III Values of Temperature, Voltage and pH, Total Counts, Log_{10} Values and Reduction Factors of the Test Isolates in the Brine Media Treated by 2 A Alternating Electric Current Over 25 min

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<th>Exposure time, min</th>
<th>Mixed culture of proteolytic extremely halophilic isolates (TLPI1 and TLPI2)</th>
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### Table III Continued

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<thead>
<tr>
<th>Exposure time, min</th>
<th>Mixed culture of extremely halophilic both proteolytic and lipolytic isolates (TLPLI1 and TLPLI2)</th>
<th>Mixed culture of all extremely halophilic archaeal isolates (TLPI1, TLPI2, TLLI1, TLLI2, TLPLI1 and TLPLI2)</th>
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electric current (34–38, 41–43), to our knowledge there is no study of the mechanism of haloarchaeal inactivation by alternating electric current. The mechanism of haloarchaeal inactivation by alternating electric current requires elucidation. This will necessitate additional studies for determination of disinfection byproducts arising after alternating electric current treatment. Also, the morphological and physiological effects of the treatment on the cells should be examined in order to clarify the inactivation mechanism of this process. With improved understanding of the uses of alternating electric treatment for haloarchaeal inactivation, this cheap and practical application is expected to prove itself useful as science and as a boon to the leather industry. The knowledge gap will be reduced further as the mechanisms of haloarchaeal inactivation by alternating electric current are analysed in forthcoming experiments.

5. Conclusions

The experimental results of this study proved that using 2 A alternating current may effectively kill extremely halophilic archaea, proteolytic extremely halophilic archaea and lipolytic extremely halophilic archaea in a time period between 1 min and 5 min. The extremely halophilic archaeal population in salt samples was killed in 1 min, and the extremely halophilic archaeal isolates were killed in 5 min. This alternating current treatment was found to be fairly effective in killing extremely halophilic archaea in salt. In conclusion, this cheaper and simpler inactivation treatment system compared to antimicrobial agent applications may be used in hide brine solutions to destroy proteolytic and lipolytic extremely halophilic archaea.

Acknowledgements

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Sema Anik graduated from the Departments of Biology and Chemistry, Faculty of Arts and Sciences, Marmara University, in 2010. She received her MSc degree in Biology in 2014 from the Institute for Graduate Studies in Pure and Applied Science, Marmara University. She then worked as a researcher in a clinical microbiology laboratory. She has also worked as a biology teacher in a private high school. Her research experience is in controlling the growth of extremely halophilic archaea using electric current applications. She has presented two poster presentations in international congresses.

Meral Birbir received a bachelor's degree in Biology Education in 1985, MS and PhD degrees in 1987 and 1991, respectively from the Department of Biology, Marmara University. She has been working in the Biology Department of Marmara University since 1985. She was a visiting research scientist at the Department of Pathology and Microbiology, Veterinary Medical School, Purdue University, USA, in 1990. She was a research scientist in the Hides and Leather Department of the United States Department of Agriculture (USDA) from 1992 to 1993. Her research interests are in halophilic bacteria, hide microbiology, food microbiology, antimicrobial agents, electric current application and microbiology of hypersaline environments. Professor Birbir especially focuses on halophilic and non-halophilic bacteria that live on salted hides and their control with antimicrobials or electric current. She has published 61 research articles and graduated 32 masters and one doctoral student. She has presented 50 oral and poster presentations in national and international congresses and has completed 25 scientific projects.

Pinar Caglayan graduated from the Department of Biology, Ataturk Faculty of Education, Marmara University, in 2007. She received her MSc degree in Biology in 2010 from the Institute of Pure and Applied Sciences, Marmara University. She was an Erasmus student in the Department of Microbiology and Parasitology, Faculty of Pharmacy, Sevilla University, Spain, from 2008 to 2009. Pinar Caglayan is currently a graduate student (PhD) at Marmara University, Department of Biology. She has been working as a research and teaching assistant at the Division of Plant Diseases and Microbiology, Department of Biology, Faculty of Science and Letters, Marmara University since 2011. Her research interests are moderately halophilic bacteria, extremely halophilic archaea, antimicrobial agents, electric currents and hide microbiology. She has published five research articles and presented 17 poster presentations at international congresses.
Diego J. Ramón is a Professor in the Department of Organic Chemistry at the University of Alicante, Spain. His research focuses on the development of catalysts based on transition metal oxides impregnated on the surface of magnetite and their application to different reactions of general interest in Organic Chemistry. He has published over 100 papers.

About the Research

The particle size of active material in heterogeneous catalysts has a great impact on selectivity, efficiency and specificity. In fact, nano-catalysts have properties different from the macroscopic systems due not only to different specific area but also to the presence of electric charges over them, and above all to the presence of extremely distorted bonds.

Metallic oxides, including magnesia, alumina, silica, zirconium oxide and cerium oxide, are supports commonly used in the preparation of nano-metal catalysts. Although magnetite (Fe₃O₄), like any other metal oxide, could be used as a suitable support, as has been demonstrated in other areas including medicine, biology and materials science, its use in organic chemistry has been minimal, due to the axiomatic idea that magnetite is unstable. As a support, magnetite has a unique advantage due to the superparamagnetic behaviour of its nanoparticles that allows its recovery and confinement by using a simple magnet or electromagnetic field. This property should make magnetite an ideal support material.

Ramón's group has designed a simple, robust and inexpensive methodology for the impregnation of different transition metal oxides on the surface of magnetite. The impregnation protocol allows all active nano-metallic species to be on the surface of the catalyst, and therefore increases their activity. The group has prepared catalysts derived from cobalt, copper,
ruthenium, palladium, osmium, iridium and platinum (Figure 1). These versatile catalysts have been used to carry out several transformations of general interest in organic chemistry (Figure 2), among others Suzuki-Miyaura cross-coupling, the multicomponent reductive amination of aldehydes, hydrosilylation of alkynes, borylation of olefins, benzo-furans and indole synthesis, and the alkylation of amines through a borrowing hydrogen strategy. Moreover it has been possible to achieve the first practical cross-alkylation of primary alcohols using iridium impregnated on magnetite.

When an external magnetic field is applied, the superparamagnetic particles of the magnetite acquire magnetisation, but it is lost when the magnetic field is retired. So, magnetite nanoparticles can be isolated easily from the reaction media using an external magnet (Figure 3) after the reaction. In many cases, the catalyst could be recovered by the simple use of a magnet and recycled in successive cycles with the same initial activity. Figure 4 shows the yields obtained with the different catalysts in ten successive reaction cycles.

![Figure 1. Transmission electron microscopy (TEM) images of magnetite-derived catalysts: (a) copper; (b) ruthenium; (c) palladium; and (d) iridium](image1)

![Figure 2. Application of magnetite and transition metal oxides impregnated on magnetite to different organic synthesis reactions](image2)
Fig. 3. Easy recovery of the catalyst after reaction by using a magnet

Fig. 4. Obtained yields in selected reactions after recycling different catalysts

Selected Publications

J. M. Pérez, R. Cano and D. J. Ramón, *RSC Adv.*, 2014, **4**, (46), 23943
R. Cano, M. Yus and D. J. Ramón, *Tetrahedron*, 2013, **69**, (34), 7056
J. M. Pérez, R. Cano, M. Yus and D. J. Ramón, *Synthesis*, 2013, **45**, (10), 1373
R. Cano, M. Yus and D. J. Ramón, *ACS Catal.*, 2012, **2**, (6), 1070
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R. Cano, D. J. Ramón and M. Yus, *Synlett*, 2011, (14), 2017
“Metal-Organic Frameworks: A New Class of Crystalline Porous Materials”

By B. Seyyedi (University of Maragheh, Iran), edited by S. Bordiga (University of Torino, Italy), Lambert Academic Publishing, an imprint of VDM Publishing, Saarbrücken, Germany, 2014, ISBN: 978-3-659-52782-1, £39.00, €55.90

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“Metal-Organic Frameworks: A New Class of Crystalline Porous Materials” published by Lambert Academic Publishing, 2014, is a book written by Dr Behnam Seyyedi on the emerging porous materials of metal-organic frameworks (MOFs). The term MOF was coined by Omar Yaghi in 1995 (1). MOFs consist of both organic and inorganic building entities, where the organic ligands, i.e. spacers, are coordinated to the metal ion clusters, i.e. nodes, to create extended frameworks. In some cases, the frameworks are rigid enough to form internal voids after solvent removal, forming structures with high porosity and surface areas (up to ~ 7000 m² g⁻¹). MOFs have shown potential applications in a wide range of fields, such as gas separation and storage, catalysis, sensing and drug delivery.

Focus on Spectral Features

The reviewed book focuses on spectral features (particularly ultraviolet-visible (UV-vis)) of metal phosphonate and carboxylate MOFs, rather than presenting a general picture of MOFs synthesis, structures and applications. UV-vis is a powerful tool for studying the phosphorescence properties of MOFs, but it is not a common characterisation method since it cannot provide definitive structural information.

The book is organised into six chapters. The first two chapters provide a background introduction to the field of MOFs, while the later four chapters cover spectroscopic studies of four types of MOFs. Lastly, the conclusions summarise the use of spectroscopic techniques to study MOF structure evolution during activation and gas sorption.

Chapter 1 provides a brief overview of the history and development of MOFs. This covers aspects such as the inception of MOF reticular chemistry inspired by the classic sol-gel processes, the similarity between MOFs and the inorganic microporous materials of zeolites and zeotypes, and the recent applications of the modular building strategy to covalent-organic frameworks. A few potential applications of MOFs such as catalysis, gas purification and storage are also discussed.

Chapter 2 offers an introduction to the common analytical methods used for MOF characterisation, like X-ray diffraction (XRD), electron microscopy, atomic force microscopy, UV-vis and infra-red (IR) spectroscopy, and gas sorption measurements. The fundamental principles behind these techniques are provided to facilitate better understanding and choice of applications for the reader. Specifically, IR and Raman spectroscopy provides complementary information about the functional groups and local...
Chapter 3 discusses the UV-vis and IR spectra of metal phosphonate MOFs. These MOFs consist of two-dimensional infinite metal-oxygen layers pillared by organophosphorus ligands. The metal phosphonate MOFs exhibit varying dehydration behaviours depending on the metal coordination centre: for example, cobalt phosphonates exhibit good thermal stability during solvent removal but this is not the case for manganese or iron phosphonates. By using UV-vis spectroscopy, it is shown that the Co coordination environment changes from octahedral to a combination of square-pyramidal and tetrahedral during dehydration. Meanwhile, IR characterisation illustrates the framework closure and loss of water molecules upon solvent removal, whereas Raman spectroscopy shows only slight perturbations in the vibrational mode.

Chapter 4 covers the metal carboxylate MOFs and their spectroscopic features. Metal carboxylate MOFs incorporate linear carboxylic acids as the ligands, especially the terephthalate analogues, which have the capacity to form extended large functional pore networks. MIL-53 (MIL: Materials of Institute Lavoisier) and MIL-68 are two prominent examples from this MOF family. Their topologies are made up of infinite chains of oxo-metal clusters linked through the terephthalate ligands. The free ligands and solvent molecules trapped inside these MOFs are difficult to remove to obtain an open structure, even upon prolonged thermal treatment in high vacuum. Ageing is another issue that may cause problems in reproducing results. Nevertheless, the presence of uncoordinated amine functionality in NH$_2$-MIL-53 helps to increase the absorption energy and capacity of certain gas molecules, like CO$_2$ and methane, due to increased enthalpies of absorption. Ab initio calculations show that there is a slight electrostatic potential variance along the MOF framework, with the oxygens from the carboxylate group being the most negatively charged (Figure 1(c)). The FT-IR spectrum (Figure 2) shows a blue shift of CO stretching vibration in CPO-27-Mn compared to

![Fig. 1](http://dx.doi.org/10.1595/205651315X687425)
the free gas molecules, implying strong electrostatic bonding with CO. A separate study on CO$_2$ adsorption shows that magnesium coordinated CPO-27 MOF has a higher sorption capacity than other coordination metals, due to the higher heat of absorption and the lighter weight of metal.

Conclusions

Overall, the reviewed book offers a primer for people interested in the vibrational spectroscopic aspects of carboxylate and phosphonate MOFs. The more advanced reader might like to consider publications such as “Metal-Organic Frameworks: Applications from Catalysis to Gas Storage” published by Wiley (2), or review articles like ‘Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites’ published in Chemical Reviews (3), which cover the topic in much more breadth and depth. Lastly, this book possibly needs more editing work to offer an improved reading experience.

References


The Reviewer

Dr Shuai Cao is a research scientist at Johnson Matthey Technology Centre, Sonning Common, UK. His current work focuses on the industrial production of MOFs for clean energy applications. He received a PhD (2014) in materials science from Trinity College, University of Cambridge, UK, with Professor Tony Cheetham FRS. He was a Cambridge Overseas Trust Scholar (2010–2013) and winner of the Dow Sustainable Innovation Student Challenge (2013) and Outstanding Overseas Chinese Students Award (2014).
“Handbook of Advanced Methods and Processes in Oxidation Catalysis: From Laboratory to Industry”

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“Handbook of Advanced Methods and Processes in Oxidation Catalysis”, edited by Daniel Duprez and Fabrizio Cavani, aims to give an overview of catalytic oxidation methods. It is divided in two parts, covering total and selective oxidation, and draws on the experience of a number of academic and industrial scientists. It is a broad and generally useful book which fulfils its aims, being intended for the technical parts of the chemical industry as well as the academic community. This book is particularly interesting in that it clearly describes the very diverse applications and importance of oxidation catalysis within the chemical industry. These applications are manifested in the production of speciality chemicals as well as large bulk chemical processes. It also shows the rapid growth and development of oxidation catalysis in recent years.

The first ten chapters on total oxidation regard hydrocarbon oxidation, soot, liquid phase techniques and five chapters on volatile organic compounds (VOCs) including plasma processes and chlorinated VOCs. The remaining 18 chapters regard selective oxidations and include industrial perspectives of varying degrees of interest as well as reactor technologies and experimental tools and techniques. This breadth of scope makes it a great resource but also ensures that the reader will only be interested in the detail of some parts of the book.

Only the parts of the book which are mainly concerned with platinum group metal (pgm) catalysts have been reviewed as these are of most interest.

Total Oxidation

Chapter 1 regards the oxidation of carbon monoxide and hydrocarbons in exhaust gas treatments and is authored by Jacques Barbier Jr and Daniel Duprez (University of Poitiers). This is a fairly detailed and informative chapter with 83 references and describes the kinetics and mechanisms around three-way catalysts using platinum, palladium and rhodium; however, the science is relevant to oxidation promoters in fluid catalytic cracking (FCC).

Chapter 8 is authored by Unni Olsbye (University of Oslo, Norway) and regards the catalytic combustion and partial oxidation of hydrocarbons to syngas. The author starts from the basics and thermodynamics of these transformations, then moves on to partial oxidation reactions catalysed by base and noble metals. Nickel is active, cheap and abundant but easy to oxidise.
and the presence of metal oxide leads to combustion. Coke formation is a problem that can be mitigated by the use of rare earth metals or basic oxides, as well as the use of noble metals; an interesting observation was that pgms can operate under conditions that are thermodynamically favourable for the formation of graphite. The final part of the chapter regards catalytic combustion, in which the relative ease of combustion of hydrocarbons, the ignition temperature for each metal and the impact of particle size on the combustion is discussed. It appears that there is an optimum particle size in which Pt is present both as an oxide and as metal. Chemical looping is also briefly discussed, but with very little detail.

**Selective Oxidation**

Chapter 11 by Edouard Mamedov and Khalid Karim (Saudi Basic Industries Corporation (SABIC) Technology & Innovation Center, Saudi Arabia) discusses the selective oxidation of ethane to acetic acid and of ethylene to vinyl acetate monomer (VAM). For the former, they describe the development of a Pd-doped mixed oxide and for the latter they describe the use of palladium-gold on silica including references to three patents. They also discuss mixed metal oxides for oxidative dehydrogenation of propane. The impression was that they used a complex empirical approach, but no incisive fundamental insights were developed.

Chapter 12 by Gerhard Mestl (Clariant R&D, Germany) deals with the development of selective oxidation catalysts at Clariant. The theme is a reliance on high-throughput testing to identify leads and an interesting insight was how they use catalyst particulates in their high-throughput screening. Hardly any formulations are described, which detracts from the interest.

Chapter 16 by Paul L. Alsters (DSM Innovative Synthesis BV, The Netherlands) *et al.* is a wide-ranging contribution that describes the use of oxidation catalysis in the synthesis of a number of products such as vitamin C and quinones from various phenols and the cobalt-catalysed toluene side-chain oxidation.

Chapter 22 by Nikolaos Dimitratos and Graham Hutchings (Cardiff University, UK) and Jose A. Lopez-Sanchez (The University of Liverpool, UK) deals with supported metal nanoparticles in liquid-phase oxidation reactions. This is a topic which is likely to be of increasing importance in the future and this particular contribution is very welcome. The first topic covered is ruthenium for the oxidation of benzyl alcohol to benzaldehyde in solution and this is very interesting not because of the transformation, which is just a probe reaction, but for the discussion on the nature of the active catalytic species. The authors then describe Pd based catalysts for similar transformations, which appear to be structure sensitive since decarbonylations tend to occur on (111) planes whilst hydrogenations occur on all of the crystal faces. This type of insight should be behind any rational design of catalysts. The authors then discuss size-controlled Au catalysts, Pt catalysts and bimetallic catalysts.

Chapter 24 by Francisco Ivars and José M. López Nieto (Universidad Politécnica de Valencia, Spain) deals with the oxidation of light alkanes and begins with an interesting comparison of the feed required to produce one ton of ethylene: 3.3 tons of naphtha compared to 1.7 tons of ethane. The only industrially established oxidation of alkanes is butane to maleic anhydride which is, surprisingly, easier with butane than with 1-butene. Most of the examples given are based on mixed oxide catalysts, whilst the application of pgms is limited to the partial oxidation of methane to syngas.

Chapter 27 by Miguel Menéndez (University of Zaragoza, Spain) discusses membrane technologies for catalytic oxidations and is a useful addition to the book. These are mainly mixed oxide but the application of pgms may be advantageous in these systems.

Finally Chapter 28 by Gianpiero Groppi, Alessandra Beretta and Enrico Tronconi (Politecnico di Milano, Italy) discusses the use of structured catalytic reactors for selective oxidations. One of the key points made in this chapter is that there is a significant gas-phase component to reactions occurring above 500°C which indicates that catalyst design becomes less important at these temperatures. It is a lengthy chapter of 45 pages and 141 references, which would be a useful resource for those with an interest in the field since it starts from the basics and includes engineering concepts.

**Concluding Remarks**

Perhaps a downside of various (industrially written) chapters is that they describe their own companies’ technologies, but do not make much reference to, or comparison with, competing or alternative technologies and so, in many instances a true comparison and evaluation is difficult to make. In general most of the
technologies and processes described are up to date and relevant; there are some instances where dated information is used. Overall it is a useful and detailed reference book. It also contains a large number of references which readily enables the reader to find more detailed and in-depth information on specific topics he/she may require.

Acknowledgement

The reviewer would like to thank Dr Peter Johnston (Johnson Matthey, Royston, UK) for his comments.

The Reviewer

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Platinum Investment Casting, Part II: Alloy Optimisation by Thermodynamic Simulation and Experimental Verification

Improved casting results found with addition of cobalt to platinum-ruthenium alloys

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Two widely used jewellery investment casting alloys (platinum with 5 wt% ruthenium (Pt-5Ru) and platinum with 5 wt% cobalt (Pt-5Co)) suffer from poor castability and other drawbacks. In this work thermodynamic calculations of alloy properties were employed to optimise the alloy compositions. Segregation behaviour appeared to be important for the melting range. Scheil simulations were used to simulate segregation under typical casting conditions. Based on these simulation results, small additions of Co were found to significantly improve the castability of PtRu. Casting trials proved that ternary Pt-Co-Ru alloys show superior casting properties, in particular better form-filling and surface quality and reduced grain size and porosity compared to binary alloys. In order to replace Co, further work on other ternary systems appears necessary to study their melting range experimentally.

1. Introduction

The investment casting of platinum alloys is challenging due to their high melting temperatures and other physical properties (1), which promote crucible and investment reactions and limit the form-filling ability of the alloys. Platinum investment casting has been reviewed in the literature (2). Fryé et al. (3) studied the casting performance of the binary alloys Pt-5Ru and Pt-5Co. Pt-5Ru is the preferred alloy of many jewellery manufacturers, because it contains 100% platinum group metal (pgm), is non-magnetic and can be cast in air without oxidation. However, due to its high melting point, this alloy is very difficult to cast into filigree shapes. In addition it has a pronounced tendency to form micro-shrinkage porosity. Hot isostatic pressing (HIP) has been successfully used to reduce the residual porosity (4). Pt-5Co is a superior casting alloy for filigree items. The drawbacks of this alloy are its ferromagnetism, the potential oxidation of Co in air and the possibility that Co might be allergenic (5). Different platinum alloys have been studied for jewellery use (6), but alternatives to these simple binary alloys are currently limited.

The present study was carried out at the Research Institute for Precious Metals and Metals Chemistry (FEM), Germany, in collaboration with a group of German companies to better understand the investment casting of platinum alloys. The casting process was simulated using computational fluid dynamics (CFD) to help understand and optimise the relevant process parameters. The simulation was based on material parameters of the alloys, investment and crucible materials which were determined in advance. Selected casting trials were undertaken with optimised casting parameters. Based on sophisticated process control, the relevant process parameters were determined and
controlled in order to achieve reproducible casting conditions.

The present paper is divided into two parts. The first part (7) dealt with the evaluation of material properties, the casting simulation and the effect of process parameters on the casting result, in particular form-filling, surface quality and porosity of the cast parts. This paper presents the second part of the study. It describes the use of thermodynamic simulation for the optimisation of platinum alloys for investment casting. Based on equilibrium and non-equilibrium phase diagram simulations, the behaviour of the binary alloys was investigated and related to the casting process. Variations of the alloy composition resulted in a change of the thermodynamic properties such as melting range, segregation behaviour or energy release during solidification. By using and interpreting such information, alloy compositions with optimised casting properties were obtained and successfully tested in casting experiments. The potential of thermodynamic simulations has been demonstrated for gold and silver casting (8). Other industries have been using such simulation techniques successfully for many years (9). Elaborate thermodynamic databases have been developed for steels, aluminium, magnesium, titanium and nickel alloys (10). Due to the high material costs of precious metals the use of such simulation would help to develop new and superior alloys more cost effectively.

2. Experimental

Thermodynamic calculations were performed using the software Thermo-Calc V4.0 (Thermo-Calc, Sweden) and the software database SNOB3 (Scientific Group Thermodata Europe (SGTE) and Thermo-Calc, Sweden) which is dedicated to noble metal alloys (11). The software allows the calculation of multicomponent equilibrium phase diagrams based on assessed binary and ternary systems. The principle of thermodynamic simulation is the minimisation of the Gibbs free energy of the system as a function of temperature, pressure, composition and other selected variables. The CALPHAD methodology (CALculation of PHAse Diagrams) was introduced by Kaufman and Berstein in 1970 (12). It is based on a critical assessment of all available data (for example phase diagram, thermochemical data and ab initio data) of an alloy system (13). Each phase is described by a model that allows the calculation of its Gibbs free energy. This function contains several interaction parameters determined by least squares fitting to the data and depends mainly on crystal structure, composition and temperature. Such assessment is usually done for binary and ternary systems. The idea is to obtain a comprehensive and consistent description of all phases, allowing the properties of multicomponent systems to be predicted. An example of a thermodynamic database for platinum-rich alloys is available in the literature (14).

The database SNOB3 that was used in this study was developed by the SGTE. It contains a description of the binary systems Pt-Co and Pt-Ru (Figure 1) and is recommended for calculations of platinum-rich alloys with small amounts of alloying elements. Very few ternary interaction parameters are available in the database. Therefore, the calculation of the ternary Pt-Co-Ru system was based only on binary interaction parameters. However, as binary systems are simple and do not have intermetallic compounds, this approach was deemed suitable.

Casting trials by centrifugal and tilt casting were made in order to demonstrate whether Co additions to Pt-5Ru improve the casting behaviour. Details of the experimental procedure, the casting parameters and the tree setup are given elsewhere (7). Evaluation criteria to assess the performance of the alloys were the form-filling of filigree items, the surface quality and the microstructure and porosity of the as-cast part. Vickers hardness measurements on as-cast samples were carried out according to a standard procedure (15) with a load of 1 kg (HV1). At least three measurements on at least two samples per composition were made. The values and uncertainty ranges (standard deviation) given in Table I are the average of at least six measurements per composition.

3. Thermodynamic Simulation Results

Figure 1 shows the Pt-rich side of the binary systems Pt-Co and Pt-Ru, which are the basis for the most common jewellery alloys Pt-5Co and Pt-5Ru. The Pt-Co system shows complete solubility in the solid and liquid phases and a minimum melting temperature at about 50% Pt (16). The addition of Co to Pt results in a significant reduction of the melting point, about 100°C for 5 wt% Co. The melting range at 5 wt% Co is relatively small and only about 15°C (Figure 1). The binary Pt-Ru system shows a peritectic reaction on the Ru-rich side involving the hexagonal (Ru) phase. Ru increases the melting point by about 50°C for 5 wt% of Ru. The melting
range of ~15°C is similar to that of Pt-5Co. It should be noted that the original data on the Pt-Ru system are limited to the melting points of the pure elements and the solidus and liquidus temperature of two binary alloy compositions (17). Hence, the solidus and liquidus line (16) are given as dashed lines. The thermodynamic calculations fit reasonably to the experimental data, but further experimental investigations are required for the binary Pt-Ru system.

The calculation of the ternary Pt-Co-Ru system was based on extrapolation from the binary systems. No experimental data of the ternary system were found in the literature.

Fig. 2(a) provides the calculated liquidus (red lines) and solidus surface (blue lines) in the Pt-rich corner. For alloys with a Pt content of 95%, a vertical section has been calculated (Figure 2(b)). With increasing Co content, liquidus and solidus temperatures are lowered. The solidus and liquidus lines are nearly parallel, i.e. the melting range of alloys with the composition Pt$_{95}$Co$_{5-x}$Ru$_{5-x}$ is nearly constant.

The thermodynamic simulations presented so far are valid for the equilibrium condition, however this is not applicable to investment casting processes. Usually segregation of the lower melting component occurs into the interdendritic regions during cooling, resulting in a depletion of the component with higher melting temperature and hence a reduction of the solidus temperature. McCloskey and Aithal (18) investigated the segregation in Pt-5Ru and Pt-5Co and compared experimental results with thermodynamic simulations. The melting point of pure Pt is lower than that of Pt-Ru and this limits possible segregation, because segregation beyond pure Pt cannot occur. Therefore, the experimentally observed non-equilibrium melting range of Pt-5Ru was only 30°C, while it was ~175°C for Pt-5Co under similar casting conditions. The higher non-equilibrium melting range is supposed to be the reason for the better casting characteristics of Pt-5Co.

The green tie lines in Figure 2(a) connect the solid and liquid phases in thermodynamic equilibrium during solidification. If Ru is replaced by Co in alloys with 95% Pt, the orientation of the tie lines, i.e. the direction of segregation, changes. The composition of the melt moves towards pure Pt since at a given temperature, the Pt-rich side of the solid-liquid two-phase region is still liquid while the Ru-rich side solidifies. Small
additions of Co change the direction of segregation in the ternary system, i.e. the melting interval is increased by segregation and is no longer limited by the melting point of pure Pt.

The extent of segregation under real casting conditions can be simulated by the Thermo-Calc software in the so-called Scheil module. The Scheil calculations in Figure 3, which are taken into account for the segregation, show the non-equilibrium melting range of some binary and ternary alloys. The replacement of Ru by Co results in a significant increase of the melting range of the ternary Pt-RuCo alloys compared to binary Pt-5Ru. The melting range of the ternary alloys under non-equilibrium solidification is approximately constant for the different calculated Co contents shown in Figure 3(a). Associated with the segregation is a non-uniform/inhomogeneous composition of the cast product. Figure 3(b) shows the composition of the solid phase precipitate at a certain temperature. According to the orientation of the tie lines, Pt segregates to the liquid phase in Pt-5Ru. Therefore, the primarily solidifying dendrite cores have a low Pt concentration, which increases towards the surface of the dendrites. The Pt content in the dendrite varies between 93% at the onset of solidification and 98% at the end of solidification.
For the ternary alloys, a gradual change in segregation behaviour occurs as Ru is replaced by Co, as described by the tie line orientation in Figure 2(a). As a consequence, the composition of the as-cast microstructure supposedly becomes more homogenous for ternary alloys. Alloys with 2% Co and 3% Ru show a nearly constant dendrite composition of 94–95% Pt throughout the solidification (Figure 3(b)). At higher Co content the segregation direction changes, i.e. Pt shows no segregation to the dendrites. Hence, Pt is enriched in the dendrite cores and depleted in the interdendritic areas. For Pt-5Co, the concentrations of Pt are 96% and 91% at the beginning and at the end of solidification, respectively.

Qualitative energy-dispersive X-ray (EDX) spectroscopy mappings of the platinum distribution for three selected alloys (Pt-5Ru, Pt3.5Co-1.5Ru and Pt-5Co) are shown in Figure 4. The brightness level of the image is proportional to the platinum content, which is high in the bright areas and low in the dark areas. The segregation is most pronounced for Pt-5Ru. Platinum-poor dendrite cores are clearly visible in the elemental map. Pt-5Co shows platinum-rich dendrites that are larger than those seen in Pt-5Ru. Therefore the concentration gradients are less steep in the dendrite cores. The ternary alloy Pt-3.5Co-1.5Ru shows no pronounced segregation of platinum. A good correlation between the non-equilibrium Scheil simulation in Figure 3(b) and the experimental findings was observed.

4. Casting Results

4.1 Form-filling

Standard grid patterns were mounted at the tip of a casting tree with ~150 g metal weight. The dimensions of the grid were 29 × 23 mm (length × width). The mesh had a rectangular cross section of 0.8 × 1.0 mm (Figures 5 and 6). As expected from previous studies (2) Pt-5Co showed much better form-filling than Pt-5Ru. Complete grid-filling was obtained by both casting methods for Pt-5Co, while the grid was only ~20% filled for Pt-5Ru. Tilt casting resulted in slightly less form-filling compared to centrifugal casting. If Ru was partially substituted by Co, the form-filling increased significantly. In centrifugal casting, minor substitutions resulted in significant improvement in form-filling as can be observed in Figure 5(b) for 0.7% Co. When the Co content exceeded 1.5%, complete grid-filling could be achieved by centrifugal casting. Tilt casting, on the other hand, only resulted in complete form-filling at a Co content of at least 3.5%.

Fig. 4. SEM-EDX elemental maps of the distribution of platinum in the as-cast condition for three different alloys: (a) Pt-5Co; (b) Pt-3.5Co-1.5Ru; (c) Pt-5Ru

Fig. 5. Form-filling of a test grid in centrifugal casting as a function of alloy composition: (a) Pt-5Ru; (b) Pt-0.7Co-4.3Ru; (c) Pt-1.5Co-3.5Ru; and (d) Pt-5Co
4.2 Surface Quality

The surface quality was evaluated for a given phosphate bonded investment and a standard ring pattern with thin and thick cross-section areas. The available investments produce fairly significant differences in surface quality (7). Especially heavy sections are prone to cause investment breakdown for some commercially available materials. For the present study, an investment was chosen that provided good surface quality for Pt-5Co, but showed investment breakdown in heavy sections for Pt-5Ru. The mechanism of investment breakdown is explained in detail in Part I (7). Figures 7(a)–(c) show macroscopic images of the selected rings. Detailed scanning electron microscopy (SEM) images were taken from the surface of the thick, flat section close to the sprues (Figures 8(a)–(c)). At this position, the surface was very rough for the Pt-5Ru part, while a smooth surface was obtained in the thin sections of the ring. Pt-5Co showed a smooth surface over the entire ring. The substitution of Ru by Co improved the surface of the ring in its thick sections. With 1.5% Co a surface quality nearly as good as that of Pt-5Co was obtained. Higher Co contents resulted in further improvement. Similar surface quality results were obtained for both casting methods.

4.3 Microstructure and Porosity

Metallographic samples were prepared by standard metallographic techniques. Grinding was done by...
successively employing silicon carbide paper down to 1200 grit followed by polishing with diamond suspension of 6 μm and 3 μm. The standard preparation leaves a thin deformed surface layer which is impossible to avoid during grinding and polishing of relatively soft metals like Pt. Therefore, a final polishing step was performed by ion beam milling using two argon ion guns at an angle of 1.5º. The sample was rotated to achieve homogenous polishing. Such ion polishing removes the deformed surface layer and reveals micro-porosity, which is usually obscured by the surface deformation when using conventional sample preparation. Finally, the polished samples were investigated without further etching by SEM using back-scattered electrons. The electron channelling contrast in backscatter SEM-imaging shows different grain orientations at different brightnesses.

The microstructure of the prepared samples is shown in Figure 9. The metallographic sections were made in the ring plane. The area shown in Figure 9 was observed in the thick section of the ring, which was most prone to shrinkage porosity. The Pt-5Ru ring had many small pores of up to 10 μm in size. The shape and interdendritic position of the pores indicate that such pores were formed at the very end of solidification when further feeding was no longer possible. Micro-shrinkage pores and small grain size are typical for Pt-5Ru in the as-cast condition (3). Additional sprues were not sufficient to avoid micro-shrinkage. The effect of casting conditions, heat treatment and HIP on microstructure and porosity of the most common binary Pt alloys is described in detail elsewhere (4, 7). Pt-5Co showed no such micro-shrinkage, but had a much larger grain size compared to Pt-5Ru. Therefore neither alloy shows an ideal microstructure, which would be fine grained and free of porosity.

In the present study the substitution of Ru by small amounts of Co helped to avoid micro-shrinkage. Even small additions of 0.7% Co were sufficient to significantly reduce the porosity, while the grain size remained comparable to Pt-5Ru. ~1.5% Co was necessary to fully avoid micro-shrinkage (Figure 9(b)). With increasing Co content, the grain size gradually increased. Typical hardness values for some binary and ternary alloys are given in Table I. No significant difference in hardness was observed.

5. Discussion

The replacement of 1–3% Ru in Pt-5Ru by Co resulted in a significant improvement of form-filling, surface quality and microstructure during investment casting. The better form-filling could be explained by a lowering of the solidus and liquidus temperatures of the ternary alloys. However, the melting range of the binary and ternary alloys was very similar. Taking into account segregation during non-equilibrium solidification provided a better understanding of the improved form-filling. The direction of segregation changed even for very small additions of Co, i.e. the melting point of pure Pt was no longer a limitation for the end of solidification. This gave more time for the flow of the semi-solid metal during casting. With increasing Co content the castability of the ternary alloys became similar to Pt-5Co. Depending on the casting process 1.5% Co (centrifugal casting) or 3.5% Co (tilt casting) were required for complete form-filling under the chosen casting conditions.

Fig. 9. SEM-BSE images showing the microstructure and porosity of 95% platinum alloys: (a) Pt-5Ru; (b) Pt-1.5Co-3.5Ru; (c) Pt-5Co
An important drawback of Pt-5Ru was the formation of micro-shrinkage pores throughout the entire cast piece. Small Co additions reduced this effect significantly. As described above, Co increased the solidification interval and thereby enabled feeding for a longer time. Figure 10 also shows that in Co containing alloys more heat was released towards the end of the solidification over a relatively broad temperature range, which should keep the alloy longer in the semi-solid state and thereby improve feeding at this critical step of forming. The cooling rate during casting was also found to be critical for the occurrence of micro-shrinkage. In a comparative study of tilt and centrifugal casting, the cooling speed was slower for tilt casting. This was not so much a factor of the casting method, but of the construction of the particular machines. Slower cooling in the tilt casting machine made it possible to avoid micro-shrinkage even for Pt-5Ru (7).

6. Summary and Conclusions

Ternary Pt-Co-Ru alloys are currently not available on the market. In view of the drawbacks of Co, including its magnetism and the suspicion that Co could be allergenic, further alloy development, and especially the experimental investigation of melting ranges, is required. Very little and sometimes contradictory thermophysical data are available in the literature, even for pure platinum (19) and this deficiency needs to be addressed, in order to investigate whether Co could be completely replaced by other alloying elements.

Thermodynamic simulations were used in order to better understand the behaviour of the widely used jewellery casting alloys Pt-5Ru and Pt-5Co and to develop alloys with improved castability. The addition of Co to Pt-5Ru lowered the equilibrium solidus and liquidus temperatures meaning that lower casting temperatures were required. Non-equilibrium calculation showed a change of the segregation direction and thereby a significant increase of the melting interval. The improved casting performance of the ternary alloys could be explained by the alloy thermodynamics, i.e. the heat release as a function of temperature during solidification.

Casting trials demonstrated that small additions (1–2%) of Co to Pt-5Ru significantly improved forming and surface quality. Micro-shrinkage could be avoided while small grain size was maintained. The chemical homogeneity of the ternary alloys was
improved compared to the binary alloys. The hardness was not altered by the Co addition. The required Co content to obtain optimised form-filling depended on the casting method and was about 1.5% and 3.5% for centrifugal and tilt casting, respectively.

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SAE 2014 Heavy-Duty Diesel Emissions Control Symposium

Improving air quality while reducing the emission of greenhouse gases

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1. Introduction

The Society of Automotive Engineers (SAE) 2014 Heavy-Duty Diesel Emission Control Symposium was, like its predecessors, hosted in Gothenburg, Sweden. This biennial two-day event attracted around 160 delegates. Most of the delegates (>95%) came from catalyst system and component suppliers as well as original equipment manufacturers (OEMs). A few delegates came from academia, government organisations, media and consultancies. Most delegates came from Europe (>80%) with the remainder from the USA, Japan, China, India and Brazil. The conference was set up to provide attendees with the latest in upcoming regulatory actions, state-of-the-art technical information and first-hand experience relating to heavy-duty diesel (HDD) emission control strategies, engine and aftertreatment systems integration and the future direction of the industry.

This review aims to capture the key messages of the presentations given and to identify common views and differences between the presentations given in each session. The keynote lectures will be looked at individually. The other presentations will be summarised under their session headlines, with special attention given to the impact on catalytic emission control.

2. Keynote Lectures

2.1 Emissions and Environment for Bus Systems

Both conference days began with keynote lectures. On day one Edward Jobson (Volvo Bus Corporation, Sweden) gave an insight into an OEM’s view on ‘Emissions and Environment for Bus Systems’. He explained that Volvo places its commitment to hybrid city buses in line with its commitment to seat belts in 1959 and three-way catalysts (TWCs) in 1976. Pure diesel buses are now only available for regional and line-haul routes. Volvo city buses are now hybrids, plug-in hybrids or entirely electric. Utilising braking energy offers not only environmental benefits from lower emissions but also lower operational costs. Additional benefits are the options of utilising quiet emission free electrical driving for emission free and quiet city zones.

2.2 Improving Air Quality in Gothenburg

The second keynote lecture was given by Anders Roth (Gothenburg City), titled ‘Improving Air Quality in Gothenburg – From Bans of Dirty Vehicles to Behaviour Change – The Role and Possibilities of Local Authorities’. Roth gave an insight into what the City of Gothenburg has done to improve its air quality. The early introduction of an environmental zone banning the most polluting buses and trucks from the city centre reduced particulate matter (PM) levels by 30% and nitrogen oxides (NOx) levels by 10%. A legal ban of studded tyres reduced the PM levels further. Procuring low emission vehicles (LEV) for the city’s vehicle fleet and...
aiming for a 90% reduction of fossil fuel use from 2010 to 2020 will minimise the emissions of the city’s own vehicles. Currently the city of Gothenburg expresses a clear preference for gasoline over diesel vehicles. Other measures include utilising biofuels (especially biogas) to reduce CO₂ emissions, incentivising the use of modern (low emission) construction machines, introducing congestion charging, investing in public transport and minimising truck traffic to and from the harbour by utilising a harbour railway system. Mandatory car sharing for business trips, a free bicycle service and bus cards in compensation for no free parking as well as payments per avoided tonne of CO₂ emissions have been introduced for city authority employees with the aim of changing their travelling behaviour. Improving the air quality in the City of Gothenburg makes the central area around the river a more attractive place to live and increases its value dramatically. Being a coastal city, concerns about sea level rises through global warming make the City of Gothenburg very committed to minimising its greenhouse gas (GHG) emissions.

2.3 Exhaust Emissions and Carbon Dioxide Regulations

On day two Jürgen Stein (Daimler AG, Germany) gave a keynote talk titled ‘Exhaust Emissions and CO₂ Regulations for Heavy Duty and Non-road Engines – An Outlook Beyond Euro VI and Stage IV’. Stein took the audience through the issues with a focus on the triad markets (EU, USA and Japan). The emissions limits are similar to those for on-road applications allowing the introduction of a global base technology. For non-road applications harmonisation (with minor differences in the timeline) has largely been achieved since 2000 and the use of a global base technology is already established. Emission testing against the World Harmonised Test Cycles aims to enable technology harmonisation but differences in details may lead to diversification. The introduction of particulate number (PN) limits for Euro VI forced the introduction of diesel particulate filters (DPFs). The Euro VI package ensures the lowest in-use emissions of any current legislation. While limits between heavy-duty and non-road are converging, the difference in PM/PN limits is decisive for the aftertreatment technology.

In-service conformity requirements vary between the EU and the USA. In Europe there are currently no activities towards a HDD Euro VII standard. However, it seems likely that NOx emission values might become aligned with the Environmental Protection Agency (EPA) 10 value of 0.27 g (kW h)⁻¹. Limiting nitrogen dioxide (NO₂) emissions to 50% of the NOx seems likely as well. Further work on portable emissions measurement systems (PEMS) might also find its way into a future Euro VII regulation. In the USA there are currently no EPA activities on further emissions reductions, but the California Air Resources Board (CARB) will introduce optional low NOx limit values in 2015. However, Stein reckons that further tightening of Euro VI or EPA 2010 limit values will have no significant effect on air quality. Instead an efficient in-use scheme such as that in the EU is key to low in-use emissions.

For non-road applications the EU will introduce non-road mobile machinery (NRMM) Stage V by 2019/2020. The introduction of a PN limit value will force DPF technology for most applications. NRMM PEMS provisions derived from Euro VI are expected for Stage V (reporting only as a first step). Daimler would welcome the USA to harmonise with Stage V. Stein also reported on a recently completed test procedure for heavy-duty hybrid vehicles. In view of emerging regulations regarding CO₂ emissions in Europe and the USA Stein sees the key challenge for the next year in the reduction of CO₂ emissions and fuel consumption and demands that contrary to criteria pollutants a CO₂ regulation must be a whole-vehicle approach for heavy-duty vehicles and NRMM.

3. Legislation and Global Trends

This session contained three presentations. Erik White (CARB, USA) presented the ‘Long Term Impact on Air Quality (ARB-2020 Initiative): California’s Comprehensive Program for Reducing Heavy Duty Diesel Emissions’. With an ozone map of the USA (Figure 1), White showed that California has a unique need for NOx reduction. CARB sees opportunities to strengthen the current standard with improved certification and durability requirements, improved durability testing and expanded warranties. Low temperature/low load NOx issues could be addressed through supplementary test cycles, expanded not-to-exceed (NTE) zones and PEMS-based compliance testing. California is interested in pushing the technical boundaries regarding NOx emissions and aims to demonstrate 0.02 g (bhp h)⁻¹ NOx emissions over the Federal Test Procedure (FTP) cycle without GHG or fuel efficiency penalties. California also pushes for a new national standard as one million interstate
trucks operate there. Current and future GHG rules are harmonised with the rest of the USA. California’s long term priorities are to continue to be a global leader in the pursuit of advanced emission control requirements; to pursue advanced technologies like zero-emission vehicles, near-zero emission vehicles and renewable fuels; and finally to implement strategies to develop, demonstrate and deploy these technologies.

A ‘Review of HD Regulations and Technology Implications’ was presented by Timothy Johnson (Corning Inc, USA). Three regulatory megatrends were highlighted:

(a) The World Health Organization (WHO) has designated air pollution as a carcinogen causing 7 million deaths worldwide (1).

(b) The PN fraction of PM$_{2.5}$ is emerging as the most harmful fraction responsible for 90% of PM toxicity (2).

(c) The United Nations (UN) Intergovernmental Panel on Climate Change (IPCC) placed a CO$_2$ limit for the atmosphere of 1 trillion tonnes cumulative. This would be exceeded in 2040 in a status quo scenario and would mean that only 17% of the feasible fossil fuels can be burned to prevent massive climate change.

Johnson then went on to present some emission control highlights, such as California’s voluntary NOx standards reaching down to 0.02 g (bhp h)$^{-1}$ NOx, for which feasibility is going to be demonstrated in a Southwest Research Institute (SwRI) programme. He also discussed the schedules for introducing Euro V and Euro VI emission levels in China and India. Figure 2 shows HDD vehicle timelines around the world.

Johnson then reported that various GHG emission regulations are being introduced in Japan, the USA, China, the EU, Canada and Mexico. There is also significant progress in improving HDD engine efficiencies. 50% brake thermal efficiency (BTE) has been demonstrated through the US Department of Energy (DOE) SuperTruck programme. A pathway to 55% BTE has been shown by Cummins. Through engine, truck and trailer modifications freight efficiency can be increased by 86%. Trailer modifications in particular offer large gains for a very small investment. Significant progress has been reported for NOx aftertreatment systems. DPF developments are focused on ash management and selective catalytic reduction (SCR) consolidation such as ‘SCR on filter’ concepts. For the success of SCR on filter systems it is important to find the optimum balance between good deNOx
performance and sufficient PN filtration efficiency on one side against an increase of backpressure on the other.

Finally Magnus Lindgren (Swedish Transport Administration, Sweden) presented ‘Euro VI vs. Transport Sector, An Environmental and Climate Success or Not?’.

Large trucks (>20 tons) and truck trailers emit higher levels of CO₂ than inland water vessels, diesel trains and especially electric trains (see Figure 3).

A similar order is found for current PM₁₀ emissions for these transport modes (Figure 4). However with the new Euro VI PM₁₀ emission limits for heavy trucks and truck trailers set between 0 and 0.01 g PM₁₀ per ton-km, and the NOx emission limits for Euro VI trucks being 10 times lower per kWh than for diesel trains and more than 20 times lower than for inland waterway vessels, trucks and truck trailers will leave diesel trains and inland water vessels behind regarding PM and NOx emissions.
To get out of this CO₂ emissions vs. pollutant emissions dilemma, Lindgren concludes that the climate impact of heavy-duty trucks must be reduced through higher energy efficiency and alternative, sustainable fuels while inland waterway vessels, diesel locomotives (and other NRMM) must be as clean as heavy-duty trucks.

4. Non-Road Strategies and Future Developments

This session contained four presentations.

‘Off-road Mobile Machinery Fuel Efficiency – A Total Systems Perspective’ was presented by M. Lou Balmer-Millar (Caterpillar Inc, USA). She showed that while there are regional differences in the cost split between depreciation, labour, fuel and maintenance costs, a more efficient, less fuel consuming machine is universally desirable. Balmer-Millar showed potential CO₂ savings for the example of non-road machine applications: the choice of fuel offers the biggest CO₂ saving potential of up to 100%. (Balmer-Millar’s presentation did not specify which fuels she had in mind, but the use of biofuels could count as CO₂ free). Components (these were not specified, but could be for example a transmission) offering 5%–10% and machine systems (these were also not specified but could be a hydraulic system) 10%–25% CO₂ saving potential. A greater CO₂ savings potential comes from the operator and job site of the application. Balmer-Millar showed that through a range of small measures, which improve engine efficiency each by 0.5%–4%, a combined improvement of 15% can be achieved. She then went on to show various examples of how system integration, hybridisation, innovative transmissions, high conversion efficiency SCR, machine control and Global Positioning System (GPS) based guidance technology can be used to significantly reduce fuel consumption, save on labour costs and complete work ahead of schedule.

Regis Vonarb (Liebherr Machines Bulle SA, Switzerland) presented ‘The Next Liebherr Aftertreatment Solution: Towards Stage V?’. Vonarb started with an overview of Liebherr Machines Bulle’s (LMB’s) NRMM product range and showed that these are meeting Stage IV/Tier 4 final emission requirements through a vanadium-based SCR-only system without exhaust gas recirculation (EGR), a diesel oxidation catalyst (DOC) or a DPF, while being spark arrestor approved. For the Swiss market and LEZs closed DPFs are mandatory. For this market LMB offers an SCR on filter system. For the same NOx conversion efficiency the SCR on filter system volume is 1.2 times the SCR system volume. Substrate and coating definitions were found to be key for achieving the PN emissions limit. The NO₂:soot ratio was found to be the key parameter for passive regeneration behaviour and is impacted by the application cycle, the DOC design and the engine calibration. A 4000 h durability test showed the SCR on filter system has very stable functionality.

‘Model Based SCR Control – Key to Meet Tier 4 Final with Lowest Calibration Effort’ was presented by Markus Iivonen (AGCO Power, Finland) and Armin Wabnig (AVL, Austria). Iivonen explained that AGCO Power’s engines, some of which have EGR, range from 50 kW to 440 kW and all have the same principle exhaust aftertreatment system containing DOC + SCR + ammonia slip catalyst (ASC). They are used in different, mainly agricultural, applications with different exhaust line layouts, therefore a model based exhaust aftertreatment strategy was chosen. Wabnig led through the model based development process and showed how the SCR control algorithms were implemented and tested. An adaptive dosing control strategy ensured the system was robust against dosing errors. AGCO was very pleased with this approach as different engine variants can be handled with reasonable calibration effort and development time can be reduced by utilising models in the software functionality and in off-line calibration.

Markus Müller (Deutz AG, Germany) concluded the non-road session by presenting ‘Deutz Emission Control Solutions for a Diversity of Applications’. He gave an overview of the Deutz engine range from 30 kW to 520 kW. The focus of his presentation was the company’s Tier 4 exhaust aftertreatment system, which contains DOC + DPF (or DPF with integrated DOC) + SCR + slip catalyst and emphasises DPF soot regeneration allowing their engines to operate under extreme conditions.

5. Emerging Markets

This session contained three presentations.

Jacob David Raj (Mahindra Trucks and Buses, India) could not be in Gothenburg to present the ‘Indian Emissions Update’ and asked Sougato Chatterjee (Johnson Matthey, USA) to present on his behalf. Raj’s presentation gave an introduction into the Indian HDD market, which is undergoing fast changes from
conventional trucks, which are often overloaded, have low power and torque, no safety norms, a single speed axle and a hard wired network, to the new generation trucks, which operate at rated load, have tubeless tyres, slightly higher power and torque, anti-lock braking system (ABS), speed limiter, twin speed axles and a controller area network (CAN). Despite new market requirements like better comfort, drivability, reliability, warranty, and reduced cost of operation, there are still challenges such as an aversion to new technology, driver shortages and the need for local truck servicing to be able to handle modern trucks. Further concerns are the skill level of mechanics and local modification of emission components. The general emission strategy in India is:

- For light commercial vehicles (LCVs): cooled EGR + oxidation catalyst + partial filter
- For medium commercial vehicles (MCVs): EGR or SCR
- For heavy commercial vehicles (HCVs): SCR is preferred (EGR option package as back-up).

Mahindra’s recipe for technology to meet emissions requirements is: to keep costs low but provide reliability, to design for abuse and servicing which can be done locally, to keep trouble shooting simple and to increase the warranty of emission control components.

Qin Li (Weichai Power Co, Ltd, China) presented ‘Challenge and Solution for Reduction of Emissions from Commercial Vehicle in Beijing’. Li started with an overview of the heavy-duty regulations in Beijing. These have been introduced up to seven years ahead of regulations for the rest of China. Beijing 1–3 limits were the same as those for Euro I–III. However, Beijing 4 and 5 show interesting additions to the European standards they are based on: Beijing 4 is Euro IV + World Harmonised Transient Cycle (WHTC) and Beijing 5 is Euro V + WHTC + PN limit. PEMS is used for in-use engine control and a heavy-duty vehicle cycle is under development. After introducing the company, which produces more HDD engines than any other company worldwide, Li presented its emission solutions, summarised in Table I.

Georg Hüthwohl (Albonair GmbH, Germany) presented ‘Introduction of the Bharat Stage (BS) 4 Emission Legislation in India’. India is ranked 155th of 178 in the Environmental Performance Index and 174th out of 178 for air quality. In 2010 commercial vehicles were responsible for 90% of NOx, 80% of sulfur dioxide (SO2), 70% of CO2 and 55% of PM10 emissions in India. He then presented the schedule for introducing the BS IV in India, which has already been introduced in major cities and will come to the north of India in 2015 and to five additional provinces in 2016 before being rolled out nationwide in 2017. Fuel changes (BS III fuel has 350 ppm S, BS IV fuel has 50 ppm S) are scheduled to match this timescale. However, the AdBlue® infrastructure is a bottleneck for the introduction of BS IV. The main reason for a very slow uptake of BS IV technologies is a loophole in the legislation which allows commercial BS III vehicles registered outside of BS IV cities to enter these cities. Therefore city buses are almost the only BS IV vehicles in BS IV cities.

### 6. Alternative Fuels and Powertrains

This session contained two presentations.

Donald Stanton (Cummins Inc, USA) was not able to be in Gothenburg to present ‘High Efficient Natural Gas Engine Technologies to Meet the New U.S. Greenhouse Gas Emissions for Commercial Vehicles’ but had submitted his presentation for publication. Stanton’s presentation explained that in the USA the natural gas vehicle market is driven by the lower cost of natural gas compared to oil. An additional benefit is the potential for nearly 25% reduction in CO2 emissions. Figure 5 shows the cost comparison of oil vs. natural gas. However, natural gas adoption in the transport market is facing several challenges, including

![Figure 5. Ratio of Brent crude oil price to Henry Hub spot natural gas price in energy equivalent terms 1990–2040.](http://dx.doi.org/10.1595/205651315X687524)
vehicle fuel storage, delivery system costs and weight; limited fuel station infrastructure; maintenance facility upgrade costs; and an inefficient component and vehicle supply chain.

Cummins has a broad natural gas product line and offers lean burn (meeting Euro V emission limits) and stoichiometric gas engines (meeting Euro VI/EPA13 emission limits). His presentation included a natural gas technology comparison discussing the pros and cons of dedicated natural gas engines vs. dual fuel engines and high pressure direct injection (HPDI) engines. While the dedicated spark Ignited natural gas engine is 10%–15% less efficient than diesel engines or the dual fuel and HPDI engines, it only requires TWC aftertreatment compared to a DOC + DPF + SCR aftertreatment system for the diesel or HPDI engines. If the deNOx capability of the TWC could be extended, it would be possible to improve the fuel economy of dedicated natural gas engines.

‘CO₂ and Energy: Challenges of Future Heavy Duty Propulsion’ was presented by Staffan H. Lundgren (Volvo (HD), Sweden). Lundgren’s presentation showed strategies for reducing fuel consumption and CO₂ emissions from heavy-duty vehicles. Starting from the energy flow chart (Figure 6), he highlighted charge air cooling, exhaust gas energy and heat to coolant losses on the engine side and air drag and rolling resistance on the vehicle side as targets for improvements.

In order to refine diesel internal combustion engines he suggested sustainable fuel, efficient engine configuration, an optimised combustion process for the selected fuel, exhaust heat and brake energy recovery and the utilisation of the engine configuration and transmission. To increase the engine’s BTE to between 55% and 60% Lundgren suggests optimisation of the thermodynamic cycle(s) through more expansion, higher peak pressure, thermal insulation and reduced friction losses and de-coupling the soot-NOx trade off. Further fuel savings can be achieved through energy recovery by either an electrical hybrid or Rankine waste heat recovery.

Lundgren suggests methane and its derivatives as energy carriers that can improve the efficiency of diesel

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**Table I Some Proposed Commercial Vehicle Emission Control Solutions for Beijing 4 to 6 Standards**

<table>
<thead>
<tr>
<th>Standard</th>
<th>Application</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing 4</td>
<td>HDD</td>
<td>Euro IV engine with SCR and optional thermal management</td>
</tr>
<tr>
<td></td>
<td>Heavy-duty gas</td>
<td>Euro IV lean burn gas engine</td>
</tr>
<tr>
<td>Beijing 5</td>
<td>HDD</td>
<td>Euro VI engine, without EGR system and with new DPF calibration</td>
</tr>
<tr>
<td></td>
<td>Heavy-duty gas</td>
<td>Euro V lean burn gas engine</td>
</tr>
<tr>
<td>Beijing 6</td>
<td>HDD</td>
<td>Euro VI engine</td>
</tr>
<tr>
<td></td>
<td>Heavy-duty gas</td>
<td>Euro VI gas engine</td>
</tr>
</tbody>
</table>

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**Fig. 6. Current energy flow from fuel to wheels for a Swedish heavy-duty truck (Reproduced with kind permission from Staffan Lundgren, Volvo (HD))**
internal combustion independently of whether they are derived from fossil or renewable sources.

He then compared the CO₂ emissions of comparable energy carriers from fossil sources vs. renewable sources. While fossil fuel based diesel, natural gas and dimethyl ether (DME) cause between 85 kg and 95 kg CO₂ emissions per 100 km, biodiesel causes less than 60 kg CO₂ emissions per 100 km, biogas around 25 kg CO₂ emissions per 100 km and DME from wood less than 10 kg CO₂ emissions per 100 km. Vehicle based measures are to use the correct engine size (operate near peak efficiency), improve vehicle aerodynamics and reduce rolling resistance. Lundgren reckons that product improvements could provide ca. 25%–30% fuel savings with reasonable added costs and complexity.

7. Engine Developments

This session contained four presentations.

Chris Such (Ricardo UK, Ltd) presented ‘Developments to Reduce CO₂ Emissions from Heavy Duty Engines’. The first part of the presentation was a report about the European CO₂ Reduction (CO₂RE) Project, which addresses the reduction of CO₂ emissions from HDD engines for long distance transport through conventional methods. The four-year CO₂RE project, which is run by 16 partners and coordinated by Volvo, started in 2012. So far, design analysis and rig testing has been carried out. Multi-cylinder testing is on its way. Waste heat recovery is covered by another project. The project aim is a 15% fuel consumption reduction compared to Euro V while being Euro VI compliant. These improvements will be achieved by addressing the engine platform, hybridisation, friction reduction and exhaust aftertreatment. The technologies investigated for the engine platform are down speeding, variable valve actuation, increased peak and cylinder pressures and high efficiency turbocharging. For friction reduction revised pistons and rings and lower viscosity lubricants were investigated. For exhaust aftertreatment optimisation low flow resistance DPFs and higher SCR efficiency at low exhaust temperatures were studied.

The second part of Such’s presentation started with the question: “Is there an alternative to evolutionary development of current technologies?” He introduced the concept of a split cycle engine in which the compression and combustion/expansion processes are separated in different cylinders (Figure 7). A split cycle isothermal compression engine has already demonstrated >55% thermal efficiency in diesel generator set applications in 2002. Concept simulation work at Ricardo indicates that >60% thermal efficiency could be achieved. This work will be taken forward in the Innovate UK project ‘CryoPower’. Such suggested investigating this engine concept within the EU project framework Horizon 2020.

Martin Tunér (Lund University, Sweden) presented ‘The Journey from direct injection (DI)-diesel via HCCI to Partially Pre-mixed Combustion with Very High Thermal Efficiency’. The advantages of the homogenous charge compression ignition (HCCI) combustion process are high efficiency, fuel flexibility and ultra-low NOx and soot emissions, but the disadvantages are high hydrocarbon emissions, limited load and difficulties in control with the risk of engine destruction through misfire. Tunér then developed the concept of combining HCCI with DI diesel combustion to come to a partially premixed combustion (PPC). The advantages of PPC are that it is simple and rugged, fuel flexible, highly efficient and capable of high load operation, it has low emissions and is suitable for waste heat recovery. The challenges are idle to low load operation, transient emissions and combustion noise.

Vadim Strots (IAV GmbH, Germany) presented ‘Modelling and Simulation for the Development of the Next Generation of Aftertreatment Systems’. Strots showed that exhaust aftertreatment system modelling is an integral part of the modern system development process. The kinetic models of exhaust aftertreatment components support the early evaluation of system solutions and optimisation of the component parameters.
at the concept development stage. Modelling and simulation is further applied to check the system performance in virtual certification work as well as in-use compliance simulations. Model based calibration aids the control concept selection as well as the engine control unit (ECU) calibration itself. It allows improved system robustness and diagnostics. However, high quality models are crucial and should be validated on gas benches and engines.

Frank Peter Zimmermann (Daimler AG) presented the ‘Global Emission Strategy of the New Mercedes Benz Medium Duty Engines’. Zimmermann’s historical retrospect about Daimler’s medium duty engines since 1949 was followed by an overview on today’s Euro VI engine and a comparison of emission concepts based on EGR and non-EGR, which require a different amount of NOx reduction through an SCR system. He argued that achieving the NOx limit through a combination of EGR and SCR enables 50% lower AdBlue® consumption, a smaller SCR volume and low tailpipe NOx emissions even under low load conditions. After covering engine thermodynamics he then focused on the Euro VI exhaust aftertreatment system. He started with the effect of thermal ageing on DOC performance and how Daimler addresses this issue. He then explained why silicon carbide (SiC) has been chosen over cordierite as the filter substrate material and that Daimler applies passive and active filter regeneration. The company had considered various SCR options (Figure 8) and concluded that there is no ‘universal’ catalyst. Daimler selected iron-based SCR catalysts. It excluded V-based SCR catalysts due to the need for active regeneration at temperatures exceeding 550°C, and Cu-based SCR catalysts because of concerns about nitrous oxide (N₂O) emissions. Using an Fe-based SCR catalyst allows Daimler to meet EPA10, JP05, JP09 and Euro VI emission limits. For non-road applications Daimler can fulfil the PM certification limits without a DPF. This opens the way to use a V-based SCR catalyst.

Finally Zimmermann compared Daimler’s Euro VI and Tier 4 concepts with its previous generations Euro V and Tier 4 Interim and showed a reduction in operating costs of about 3% for the new systems.

8. Catalyst and Substrate Developments

This session contained three presentations. Adolf Schafer-Sindlinger (NGK Europe GmbH, Germany) presented ‘Cordierite and SiC Filters for On-road and Off-road Heavy Duty Applications’. He focused on two areas: catalysed soot filters and SCR on filter concepts.

![Figure 8](http://dx.doi.org/10.1595/205651315X687524)
For catalysed soot filter applications, requirements for robustness have to be balanced against the pressure of soot loaded filters. For minimum pressure drop performance thin wall technologies offer advantages over standard types. The higher sensitivity to thermal stress of thin wall filters can be compensated by new reinforced designs. Pore size and pore volume of the filter material shows a clear influence on PN emissions. With pre-conditioning, all thin wall filters in the study achieve the Euro VI PN limits. For SCR on filter applications the pore size distribution must be optimised to satisfy low pressure drop and high PN filtration efficiency requirements.

Andrew P. Walker (Johnson Matthey Plc, UK) presented ‘Future Challenges and Incoming Solutions in the Global Catalyst-based Emission Control Area’. Starting with a global regulations overview and a description of typical exhaust aftertreatment systems for on-road and non-road applications he explained the general challenges for future applications. Further fuel economy improvements will increase engine out NOx, reduce exhaust temperatures and require reductions in backpressure. Further regulatory reductions in NOx emissions will increase the system NOx conversion requirements. DPFs are expected to be used for PN compliance, for example for non-road Stage V in Europe. There will also be an increased focus on other emissions like N2O, NO2, CH4 and carbon black and a drive for further reductions in system volume.

Walker then moved on to show how extruded and high porosity substrates with increased cell density can improve SCR conversion efficiency (Figure 9) allowing potentially up to 50% volume reduction.

He gave an insight into the capabilities and challenges of the SCRF® component (which is the Johnson Matthey term for SCR on filter systems). Applying an SCR coating to the filter enables the SCR component to get hotter earlier and increases the SCR volume in the system, both of which enable increased NOx conversion. It also increases the PN filtration efficiency. However, increased competition for NO2 between PM combustion and NOx conversion require attention and good system design.

Another important incoming technology is the diesel Cold Start Concept (dCSCTM) component, which traps NOx from cold start and releases it when the downstream SCRF® component is hot enough to convert the NOx. A highly efficient SCR system can also be enabled by low temperature ammonia availability, which can be realised through converting urea to ammonia in a side stream, bypassing the DOC component and injecting ammonia directly onto the SCRF®. As increasing NOx conversion requirements lead to more aggressive urea dosing strategies, highly efficient and highly selective ASCs are required and significant improvements in selectivity have already been made.

![Fig. 9. Comparison of Cu-SCR on various substrates (HPS = high porosity substrate) (Copyright Johnson Matthey)](https://dx.doi.org/10.1595/205651315X687524)
Andreas Geisselmann (Umicore AG & Co KG, Germany) presented ‘Future Aftertreatment Concepts for Heavy Duty Application’. Geisselmann’s presentation confirmed the general view of Walker’s presentation but focused on SCR on filter systems, which are called SDPF by Umicore. He listed possible reasons why the HDD on-road sector appears to be reluctant to implement SDPF systems, while the non-road sector appears to be more open to them. In his very detailed analysis Geisselmann showed various SCR coating choices and concluded that Cu-SCR appears to be most attractive for SDPF applications. He also presented details on active and passive SDPF regenerations. He emphasised the passive regeneration challenges caused by back diffusion and missing NO2 recycling. Geisselmann anticipates that there are still challenges in this technology.

9. On-Road Strategies and Future Developments

This final session contained three presentations.

Richard Dorenkamp (Volkswagen AG, Germany) presented ‘How the European LDD Industry Cope with Incoming RDE Regulations?’ He briefly introduced some key challenges, such as the LEV III regulations in the USA with very low NOx emission limits, real world driving emissions (RDE) requirements in Europe and the requirement to meet emission standards in China under poor fuel quality conditions. Global CO2 emission reduction requirements add another challenge to the light-duty diesel (LDD) industry. Key enabling technologies are engine modifications, the ECU which links the fuel with the exhaust aftertreatment system, sensors and actuators. He gave an overview of the measures applied inside the engine starting from high level areas like weight, friction, combustion, recuperation, exhaust gas aftertreatment, temperature management, air management, energy, control and consumables before zooming in into the component level of the engine itself, the air/gas system and the exhaust aftertreatment system. A key message for the exhaust aftertreatment system was that measures to bring down CO2 emissions cause a decrease in exhaust gas temperatures. Therefore the exhaust aftertreatment system needs to be close coupled in order to reach a high enough temperature for effective operation. VW’s current LDD emission control concept combines a close coupled NOx storage component, a urea injection point and mixer, and a Cu-zeolite SCR coated DPF.

Dorenkamp summarised the requirements and concluded that the exhaust gas aftertreatment system needs to be effective in a wider temperature range, have a higher deposition rate of pollutant removal and no negative impact on the fuel consumption. Finally he highlighted the differences between LDD and HDD exhaust aftertreatment especially regarding system volume to engine size ratio.

Magnus Mackaldener (Scania AB, Sweden) presented ‘A Bumpy Road Towards Euro 6: How Scania Did it and the Experience After 2 Years in the Field’. After a brief introduction to the Euro VI challenge and the history of Scania aftertreatment development, he gave a detailed description of the modular Scania Euro VI exhaust aftertreatment system, which comprises a replaceable DOC followed by a serviceable DPF, an AdBlue® injection and twin parallel SCR/ASC units. After showing a few performance results he presented relative cost benchmarks for engine and aftertreatment systems between Euro III, Euro IV, Euro V and Euro VI technologies showing that the costs for engine plus aftertreatment have more than doubled from Euro III to Euro VI. Mackaldener then went on to show a cost analysis of engine and aftertreatment systems for Scania, Volvo, MAN, Mercedes Benz, Iveco and DAF HDD Euro VI engines concluding that Scania engines have lower relative costs and lower exhaust treatment costs per g (kW h)−1 NOx reduced. The next part of his presentation showed how the amount of fuel consumed by food distribution, taking into account both trucks and cars, could be reduced: each 25 tons of food distributed through supermarkets today requires 860 l of fuel; if this food were distributed via local stores it would require 312 l and if it were sold over the internet it would require 300 l. Finally he highlighted the differences between high and no negative impact on the fuel consumption.

Heimo Schreier (AVL) presented ‘Potentials and Challenges for Next Generation HD Diesel Engines’. After briefly describing the commercial vehicle market situation he used a Euro VI fuel efficiency roadmap for HDD engines to show that the engine efficiency BTE can be increased from 45% to 50% between 2014 and 2020, causing the brake specific fuel consumption to decrease by about 10%. This could be done through advanced turbocharging concepts,
increased compression ratio, thermal insulation, friction reduction, variable valve timing and waste heat recovery. This would require significant base engine design modifications (for example peak firing pressure (PFP) >220 bar). Further improvement could be achieved through powertrain system optimisation including smart auxiliaries, down speeding, advanced shifting strategies and predictive powertrain control.

Schreier then focused on technologies to improve the engine efficiency. He explained that turbocharging efficiency is key to further fuel consumption improvements. High turbocharging efficiency resulting in higher exhaust mass flows and lower exhaust temperatures will require alternative EGR concepts, like turbo compound and low pressure EGR. This will be an increasing challenge for exhaust aftertreatment systems. He showed the influence of compression ratio (CR) and advanced timing on fuel consumption and PFP. With higher CR improving fuel economy PFP demand will increase beyond 220 bar, requiring base engine modifications. Through model based adaptive emission control, engine settings can be optimised according to the exhaust aftertreatment status or performance level. Advanced aftertreatment systems (Figure 10) include one close coupled component (DOC or DPF) and may incorporate SCR on filter technology. The warmer location makes volume reductions of 15%–35% seem possible without loss of performance. The larger volume of SCR coated components and higher temperatures of the SCR on filter leads to higher deNOx capability for these variants.

Friction reduction will provide limited fuel consumption savings. However, some measures might require significant base engine modifications. Organic Rankine cycle based waste heat recovery (Figure 11), which provides a 3%–5% fuel saving in the European long haul cycle, can be expected to be in series production by model years 2018 or 2020. The integration of waste heat recovery with calibration requires system simulation. The current focus is on product cost and weight reduction.

10. Summary
The SAE 2014 Heavy-Duty Diesel Emission Control Symposium was very well attended and well organised.

Fig. 10. Advanced exhaust aftertreatment systems (TC = turbocharging, WHR = waste heat recovery, EAS = exhaust aftertreatment system) (Reproduced with kind permission from Heimo Schreier, AVL)
The sessions covered a wide range of relevant topics. Emission control and GHG regulations in many parts of the world present current and future challenges for both on-road and non-road applications, and technical solutions to many of these challenges were presented. Emerging markets largely follow the European emission legislation with a few years' delay. Legislative advances in emission control legislation mainly focus on closing the gaps between real world driving or operation and durability legislative requirements. The introduction of particulate number regulation will clean up NRMM in Europe. California continues to push the technical boundaries in emission control by working towards highly efficient NOx control. GHG regulations are emerging in a wide range of countries and attract an increasing amount of resources to meet the challenge. HDD engines are becoming more and more efficient and these efficiency improvements, together with integrated machine- or vehicle-based approaches, show tremendous potential to limit GHG emissions even further. Despite higher demands on emission control the required system volumes are only increasing moderately due to increased integration of functionalities, for example SCR on filter systems. The industry is learning lessons from each other's successes as well as from related industries like the light duty vehicle manufacturers. Overall the symposium drew an optimistic picture of exciting challenges ahead.

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The Reviewer

Dr Claus Görsmann received his PhD from the University of Würzburg in Germany. He joined Johnson Matthey in 1997 and most of his career has been in diesel emission control. Since 2012 he is Technology Strategy Manager monitoring external technology trends and influencing Johnson Matthey’s current and future activities in emission control for all mobile applications.
Computer Simulation of Automotive Emission Control Systems

Key developments in modelling of diesel emissions control components and catalysts are highlighted

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Computer simulation has become an important tool for designing automotive emission control systems. This paper highlights some of the key developments made in modelling of diesel emissions control components and catalysts by Johnson Matthey. The general methodology for model development involves determination of the reaction kinetics using laboratory reactor data, followed by validation of the resulting model against vehicle or engine data. The development of models for diesel oxidation catalysts (DOCs), ammonia selective catalytic reduction (SCR) catalysts, lean nitrogen oxides (NOx) traps (LNTs) and diesel particulate filters (DPFs), including coated filters such as the SCR coated DPF (SCRF®), is discussed.

A new methodology for developing models (or at least adapting existing models) using engine or vehicle data, which offers a faster route to a finished model, is also discussed. The use of this methodology to develop a DOC model capable of predicting the effect of platinum group metal (pgm) loading is presented; the model gives a good prediction of carbon monoxide, hydrocarbon (HC), NOx and nitrogen dioxide (NO2) over a vehicle test cycle for pgm loadings in the range 30 g ft⁻³ to 120 g ft⁻³.

1. Introduction

Catalytic exhaust gas aftertreatment has considerably reduced the emissions from automotive sources since its introduction in the late 1970s (1–5). The progress made in developing improved aftertreatment catalysts and technologies has been complemented by the development of mathematical models (6, 7), which are used for designing aftertreatment systems and for improving understanding of the way these systems function; computer simulation offers a faster and more cost effective route for the system design than a purely experimental ‘trial and error’ process. This paper gives an overview of some of the work done at Johnson Matthey on developing models for computer simulation of aftertreatment systems.

Johnson Matthey has been working on computer simulation of emission control systems for more than 25 years. The original work used computational fluid
dynamics to understand the impact on performance of flow maldistributions across the catalyst \(^{(8)}\). Subsequent work has focused on developing models for predicting the performance of aftertreatment systems using a chemical reaction engineering approach with the major effort devoted to the development of detailed reaction kinetics (rate equations) to describe the multitude of reactions occurring over the catalyst.

Earlier work has already been reviewed in a paper published in 2007 \((9)\); this paper will highlight some of the work done since then. This review only covers diesel aftertreatment, but we have also been active in modelling gasoline aftertreatment catalysts \((9, 10)\). The rest of this paper is structured as follows. Firstly, our general approach to modelling will be outlined. Next the paper covers individual aftertreatment technologies, highlighting key developments. Finally, the paper will look at a faster method of developing models.

2. Approach

A model for an aftertreatment catalyst consists of two parts, the physical model and the kinetics (chemical model). The physical model describes the heat, mass and possibly momentum balance equations for the gas and solid (catalyst) phases, while the kinetics describes how the rate of each reaction varies with the concentration of the reactants (and other species present) and the temperature, i.e. the chemistry of the system. We use one-dimensional models, i.e. models in which concentrations and temperature vary along the length of the catalyst but not in a radial direction. Such models offer a good compromise between accuracy and runtime. Our model for a flow-through monolith catalyst is discussed in more detail elsewhere \((9, 11)\); equations for our DPF model are given in \((12)\).

Generally, we use laboratory reactor data for developing kinetics, as, unlike engine or vehicle tests, they allow complete control. This allows the kinetics of individual reactions to be studied separately, unlike the real system where all reactions occur together. It also allows a wide range of conditions (such as concentration and temperature) to be explored, something which is difficult to do with an engine. Reactor data allows the kinetics of a given reaction to be studied with a simple reaction mixture, enabling the basic rate equation to be defined; further experiments with more complicated gas feeds then allow extra terms to be added to the rate equation to describe additional inhibiting effects.

Once kinetics have been developed from the reactor data, it is important to validate the model against engine or vehicle test data; these models are used to predict catalyst performance over an engine or vehicle test so it is crucial to verify that they actually give a good prediction over such tests. Model validation is important to give confidence in the predictions, to understand the limitations of the model and to know where (if) improvements need to be made. The model development process is described in more detail elsewhere \((9)\).

3. Diesel Oxidation Catalysts

A DOC serves not only to remove CO and unburnt HCs from the exhaust of diesel engines, but also to generate exotherms for active regeneration and for producing NO\(_2\) used by downstream components \((13–16)\).

Our original DOC model \((9, 17, 18)\) was for a Pt-based DOC and contained effectively just four reactions, CO oxidation, HC oxidation, nitric oxide (NO) oxidation and HC SCR (Equations (i)–(iv) in Table I). (Actually the model has more than four reactions as it contains more than one HC). While this model worked reasonably well under some conditions, demand for more accurate models has resulted in an increase in the number of reactions included in our DOC models. Our latest DOC model is for a platinum-palladium based DOC \((19)\) and contains nine reactions (Table I). The reduction of NO\(_2\) to NO by CO and HC (Equations (vii) and (viii)) was added as it is required for accurate prediction of NO\(_2\), which in turn influences the performance of downstream emission control components. HC steam reforming (Equation (v)) and H\(_2\) oxidation (Equation (vi)) were also added for use in emission control systems containing an LNT as these reactions occur during the rich conditions encountered during an LNT regeneration.

Another improvement in the Pt-Pd DOC model was the inclusion of what might be called the ‘oxide effect’ on NO oxidation \((19)\). In this effect, the active metal surface can be oxidised by NO\(_2\) to form a layer of oxide which is inactive for NO oxidation. This oxide layer can be removed by reduction with NO. This oxide effect results in suppression of NO oxidation by NO\(_2\) and leads to hysteresis when the temperature is ramped up and then down in a reactor test \((19, 20)\). This effect has been reported by other workers \((20–22)\). Its inclusion can be important for accurate prediction of NO\(_2\) production over a DOC. For example, a model for...
A heavy-duty diesel (HDD) DOC including this effect was able to give a good prediction of the NO₂:NOx ratio at the DOC outlet over a wide range of engine tests (transient and steady-state engine light-off tests, the heavy-duty Federal Test Procedure (HD-FTP) transient cycle, the World Harmonised Transient Cycle and the Non-Road Transient Cycle); we found that it was not possible to get a good NO₂ prediction over such a wide range of engine test cycles without including the oxide effect in the model (19).

The Pt-Pd DOC model using the reaction scheme in Table I was based on about 75 reactor tests. This demonstrates the amount of data required for developing an accurate model. This data was used not just for developing the model, but also for gaining important insights in the chemistry occurring over the catalyst (19). Figure 1 shows that this model is capable of giving a good prediction of CO, total hydrocarbon (THC) and NO₂ emissions over the New European Drive Cycle (NEDC) (23). This DOC model has been extended to predict the effect of Pt:Pd ratio on catalyst performance (24, 25).

### 4. Ammonia Selective Catalytic Reduction

NH₃ SCR is an important technology for removing NOx from vehicle exhaust. It works by reducing the NOx to (predominantly) N₂ by reaction with NH₃ (usually supplied in the form of an aqueous solution of urea) over a base metal catalyst (26–29).

Our original SCR model was for a vanadia-based formulation (30). Since then we have developed models for copper-zeolite (31) and iron-zeolite catalysts (32), as well as for NH₃ slip catalysts which include an SCR component (33). Since our original SCR model (30), we have considerably improved our methodology for

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**Table I Reaction Scheme for a DOC Model (19, 25)**

<table>
<thead>
<tr>
<th>Reaction Scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation:</td>
</tr>
<tr>
<td>CO + ½O₂ → CO₂</td>
</tr>
<tr>
<td>(i)</td>
</tr>
<tr>
<td>Oxidation of HC or oxygenate:</td>
</tr>
<tr>
<td>CₓHᵧOₗ + (x+y(4−z)/2)O₂ → xCO₂ + (y/2)HᵧO</td>
</tr>
<tr>
<td>(ii)</td>
</tr>
<tr>
<td>NO oxidation:</td>
</tr>
<tr>
<td>NO + ½O₂ ⇌ NO₂</td>
</tr>
<tr>
<td>(iii)</td>
</tr>
<tr>
<td>HC SCRᵃ:</td>
</tr>
<tr>
<td>(1−Sₙ₂₀/2)C₃H₆ + 9NO → 3(1−Sₙ₂₀/2)CO₂ + 3(1−Sₙ₂₀/2)H₂O + 4½Sₙ₂₀ N₂O + 4½(1−Sₙ₂₀)N₂</td>
</tr>
<tr>
<td>(iv)</td>
</tr>
<tr>
<td>Steam reformingᵇ:</td>
</tr>
<tr>
<td>CₓHᵧ + (x−N₇₅₃)H₂O + N₇₅₃ CO₂ → (x+N₇₅₃)CO + (x+y/2−N₇₅₃)H₂</td>
</tr>
<tr>
<td>(v)</td>
</tr>
<tr>
<td>H₂ oxidation:</td>
</tr>
<tr>
<td>H₂ + ½O₂ → H₂O</td>
</tr>
<tr>
<td>(vi)</td>
</tr>
<tr>
<td>NO₂ reduction by CO:</td>
</tr>
<tr>
<td>CO + NO₂ → CO₂ + NO</td>
</tr>
<tr>
<td>(vii)</td>
</tr>
<tr>
<td>NO₂ reduction by HC:</td>
</tr>
<tr>
<td>CₓHᵧ + (2x+y/2)NO₂ → xCO₂ + (y/2)H₂O + (2x+y/2)NO</td>
</tr>
<tr>
<td>(viii)</td>
</tr>
<tr>
<td>Extra reaction to explain NO₂ conversion during vehicle test:</td>
</tr>
<tr>
<td>NO₂ → ½N₂ + O₂</td>
</tr>
<tr>
<td>(ix)</td>
</tr>
</tbody>
</table>

ᵃSₙ₂₀ is the selectivity to N₂O formation;ᵇN₇₅₃ is the number of molecules (apparently) reacting by the reverse water gas shift reaction
developing SCR models. Our original model was based on reactor experiments in which the gas composition was kept constant and the temperature ramped up (30). Since then we have realised that at lower temperatures it can take a long time for the amount of adsorbed NH\textsubscript{3} and hence the rate of reaction to stabilise, particularly with metal-zeolite SCR catalysts, which store a lot more NH\textsubscript{3} than vanadia-based catalyst. For example, we observed that it took about 70 min to achieve constant activity with a Cu-zeolite catalyst at 200ºC (31). Thus, it is much better to run experiments at constant temperature in which NH\textsubscript{3} is added to the feed gas at a known time, so that the rate at which the reaction approaches steady-state can be followed. This experiment is then repeated for a series of different temperatures and gas compositions with each experiment started with the catalyst in a stored NH\textsubscript{3}-free state (31–32). The experimental procedure for studying NH\textsubscript{3} storage and desorption on the catalysts has also been improved, for example, by making measurements over a wider range of temperatures (31).

The reaction scheme for our Cu-zeolite SCR model is shown in Table II. Reaction schemes for vanadia-based and Fe-zeolite SCR catalysts are similar, but there are some differences, for example, reduction of nitrous oxide (N\textsubscript{2}O) by NH\textsubscript{3} occurs over Fe-zeolite catalysts (34, 35), but not over Cu-zeolite or vanadia catalysts. The reaction scheme in Table II is similar to that used by other workers (36, 37) with the exception of the last reaction (Equation (xviii)), the reduction of NO\textsubscript{2} to NO by NH\textsubscript{3}. This reaction was added to correct for a failure to predict the decrease in NO\textsubscript{x} conversion with increasing temperature at high temperature when the catalyst inlet NO\textsubscript{2}/NO\textsubscript{x} ratio is high, as well as the observation that most of the NO\textsubscript{x} slipped from the catalyst at high temperature is NO, even when the catalyst inlet NO\textsubscript{2}/NO\textsubscript{x} ratio is high (31). However, in a more recent model of a Cu-zeolite SCR catalyst (38) we have found that this reaction is not necessary to achieve a good prediction. This suggests that this reaction was not ‘real’, but rather served to correct for inadequacies in the kinetics of the other reactions, which became apparent at high temperature when the inlet NO\textsubscript{2}/NO\textsubscript{x} ratio was high.

The Cu-zeolite SCR model was validated against a range of engine or vehicle test data (31). As with all the SCR models we have developed, we found that the prediction of post-catalyst NO\textsubscript{x} emissions was generally good, but that the accurate prediction of NH\textsubscript{3} slip is much more challenging. Particularly disappointing was the prediction of NH\textsubscript{3} slip over the HD-FTP where the model predicted NH\textsubscript{3} slip, but the measured data apparently showed none. We subsequently discovered that there had been a problem with the NH\textsubscript{3} measurements on these tests. Hence here we present further validation of the model over the HD-FTP (39) against new data (Figure 2). These HD-FTP tests were run using a 9 l engine. Three tests were run with a 20 min soak between the first and second test and no time gap between the second and third tests. These tests are denoted as the ‘cold’, ‘warm’ and ‘hot’ tests, reflecting the increase in SCR catalyst temperature from test to test. The SCR catalysts were free of adsorbed NH\textsubscript{3} at
Table II Reaction Scheme for a Cu-zeolite SCR Catalyst Model (31)

NH\textsubscript{3} adsorption and desorption:
\[\text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_3(\text{ads})\]  
\([x]\)

NO (or standard) SCR:
\[4\text{NH}_3(\text{ads}) + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}\]  
\([xi]\)

Fast SCR:
\[2\text{NH}_3(\text{ads}) + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}\]  
\([xii]\)

NO\textsubscript{2} SCR:
\[2\text{NH}_3(\text{ads}) + 2\text{NO}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + \text{N}_2\text{O}\]  
\([xiii]\)
\[4\text{NH}_3(\text{ads}) + 3\text{NO}_2 \rightarrow 3\frac{1}{2}\text{N}_2 + 6\text{H}_2\text{O}\]  
\([xiv]\)

NH\textsubscript{3} oxidation to N\textsubscript{2}:
\[4\text{NH}_3(\text{ads}) + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}\]  
\([xv]\)

NH\textsubscript{3} oxidation to NO:
\[4\text{NH}_3(\text{ads}) + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}\]  
\([xvi]\)

NO\textsubscript{2} decomposition:
\[\text{NO}_2 \rightleftharpoons \text{NO} + \frac{1}{2}\text{O}_2\]  
\([xvii]\)

Reduction of NO\textsubscript{2} to NO by NH\textsubscript{3}:
\[2\text{NH}_3(\text{ads}) + 3\text{NO}_2 \rightarrow 3\text{NO} + \text{N}_2 + 3\text{H}_2\text{O}\]  
\([xviii]\)

Fig. 2. Comparison of measured and simulated cumulative NOx: (a) ‘cold’; (b) ‘warm’; (c) ‘hot’; and NH\textsubscript{3} slip over the HD-FTP for a Cu-zeolite SCR catalyst: (d) ‘cold’; (e) ‘warm’ and (f) ‘hot’. (System: 10.5″ × 4″ (266.7 × 101.6 mm) (diameter × length), 400/4 DOC with 40 g ft\textsuperscript{-3} pgm + 10.5″ × 12″ (266.7 × 304.8 mm), 200/12 cordierite CSF with 6 g ft\textsuperscript{-3} pgm + two 10.5″ × 6″ (266.7 × 152.4 mm), 400/4 Cu-SCR parts in series; all parts were hydrothermally aged for 100 h, the DOC and CSF at 700ºC, the SCR at 650ºC)
the start of the cold test. Other experimental details are given elsewhere (31) under ‘transient HDD tests’. The simulations of this data were run with the stored NH₃ remaining on the catalyst at the end of one test still being present on the catalyst at the start of the next test (reflecting the way the engine tests were run); both the amount of stored NH₃ and its distribution were unchanged. Note that these simulations were run using kinetics developed from reactor data without any adjustment (to improve the prediction of the engine data). The model gives a reasonable NOx prediction for all three tests (Figure 2), correctly predicting the fact that light-off occurs earlier in the warm and hot tests than in the cold test due to both the increase in catalyst temperature and the presence of stored NH₃ at the start of the test.

The model predicts the NH₃ slip to occur at the correct times in the test, although it fails to predict the magnitude of the large peak in NH₃ slip at about 730 s in the warm and hot tests. In a transient test, NH₃ slip occurs when a rise in catalyst temperature causes desorption of unreacted NH₃ which has accumulated on the catalyst during the test. Thus, the shape of the NH₃ slip curve reflects the catalyst temperature. The model correctly predicts the increase in NH₃ slip from the cold test to the warm and hot tests due to build-up of stored NH₃. While there is still room for improvement, Figure 2 represents an advance over the HD-FTP data previously presented (31).

5. Lean NOx Traps

The LNT is a commonly used technology for the removal of NOx from the exhaust of diesel and lean-burn gasoline engines (40–42). LNTs work by storing NOx during normal (lean) operating conditions in the form of nitrates of alkali or alkaline earth metals, or both. As the LNT fills up with NOx, the rate of storage falls. To maintain a sufficiently high rate of NOx removal from the exhaust, it is necessary to periodically regenerate the LNT by briefly running the engine rich; this results in the conversion of the nitrates to NOx, and the subsequent reduction of this NOx to (predominantly) N₂ (40–42).

Our original LNT model was published in 2006 (43). This model included all the main reactions occurring over the LNT during the storage and regeneration (deNOx) phases of operation. Since then we have been focusing on improving the modelling of specific aspects of the LNT. Improvements in the prediction of NOx storage over an LNT are illustrated in Figure 3 (44). This figure shows measured NOx breakthrough curves (points), together with model predictions (lines), for a wide range of temperatures (125°C–450°C). In these experiments, the LNT is first regenerated so that it is free of stored NOx. At time zero NOx is switched into the feed stream. Initially, all the NOx is stored and no NOx is seen at the reactor exit. However, as the NOx storage sites become occupied, the rate of NOx storage slows and NOx is seen at the reactor exit. Close examination of the breakthrough curves reveals that the initial part of the curves are the same irrespective of temperature, while the latter part of the breakthrough curves are temperature dependant. This suggested that there were two types of storage site, one giving rise to the temperature independent part of the curves and the other associated with the temperature dependant part of the curves; these sites were denoted ‘fast’ and ‘slow’ sites, the names reflecting the relative rates of NOx storage on the two sites.

In the paper three different models were considered for NOx storage on the slow sites (44). While there were some differences in the predictions of these models, all of the models tried gave a good prediction of the measured data. Figure 3 compares the predictions of one of these models with the measured data; the model gives a good prediction across a wide temperature
window. From this it was concluded that key requirements for an effective NOx storage model are:

- Fast storage sites, where the temperature independent storage rate and capacity are required to explain the initial part of the breakthrough curves, which is the same for all temperatures
- Slow storage sites, where the temperature dependent rate of storage and capacity is required for the later part of the breakthrough curves
- Kinetics for both sites need to account for the rate of storage decreasing faster than the number of available sites as storage sites become occupied.

Provided these basic criteria are met, there is no reason to use more complicated kinetics (for example microkinetics) for modelling NOx storage. It was also found to be crucial to use data covering a wide range of temperatures, so as to provide a sufficiently demanding test for potential models; many LNT modelling studies in the literature have used rather limited temperature ranges (44), which makes modelling the data easier, but makes it less likely that the resulting model will give a good prediction over the full range of conditions encountered in a real application.

6. Diesel Particulate Filters

DPFs serve to remove soot (particulate matter) from diesel engine exhaust. The collected soot is then burnt off by oxidation either with NO\textsubscript{2} or with O\textsubscript{2}; the former tends to dominate at lower temperatures, while the latter dominates at higher temperatures (45, 46). The functionality of a DPF can be increased by adding a catalytic coating to the DPF. Thus, addition of an oxidation catalyst coating (as would be found on a DOC), results in a catalytic soot filter, which is capable of removing (oxidising) CO and THC and oxidising NO to NO\textsubscript{2}, in addition to removing soot from the exhaust. Similarly, addition of an SCR coating to the DPF results in an SCR\textsuperscript{®}, which removes NO\textsubscript{x}, in addition to soot, from the exhaust.

Our physical model for a DPF, like that of most workers, is based on the pioneering work of Bissett (47), but with improvements. The development of DPF modelling has been reviewed by Koltsakis et al. (48).

One of the challenges of DPF modelling is that soot is a variable entity, so its reactivity will vary from engine to engine or even for the same engine operating under different conditions. We have developed a method for determining soot oxidation kinetics using engine bench tests (49), which ensures that we are studying the reaction of real diesel engine soot under realistic conditions. In these experiments, the DPF was first loaded with soot on the engine under one engine condition, followed by regeneration at constant temperature under a different engine condition. During regeneration, the DPF was periodically removed from the system and weighed, so that the regeneration could be followed by observing the change in weight of soot as a function of time. This was repeated for a series of temperatures (225ºC–450ºC). Key experimental innovations for getting good results were: (a) the use of another DPF in front of the DPF being studied, to remove soot from the engine exhaust and avoid the need to know accurately how much soot is coming from the engine during the regeneration; and (b) the use of a bypass around the DPF being studied, to allow the engine to stabilise before exhaust gas is directed over the DPF, ensuring that the gas flowing over the DPF is as consistent as possible.

The engine data collected was used to develop kinetics for soot oxidation. Measured and simulated soot loading as a function of regeneration time are compared in Figure 4. Generally, the model gives a good prediction across the full temperature range. When looking at this figure it is important to remember that these are difficult experiments to perform and, in particular, that the measurement of a relatively small change in soot mass on a heavy DPF means that the data is subject to error. Thus, there are points where the measurement shows an apparent increase in soot loading with time; clearly this is due to experimental error and the model cannot be expected to predict this. The other major discrepancy between model prediction and measured data is that the measured weight loss in the first period of regeneration is often larger than that predicted. This has been investigated in detail (49); it was found that in the first regeneration period the weight loss was much larger than expected from the NO\textsubscript{2} consumption, while in the second regeneration period there was good agreement. (At these temperatures, soot oxidation is predominantly due to reaction with NO\textsubscript{2}.) Thus it was concluded that much of the weight loss in the first regeneration period was due to a process other than soot oxidation by NO\textsubscript{2}; it is speculated that some of this weight loss could be due to evaporation of volatile components in the soot. The fact that the weight loss during the first regeneration period is often much greater than
the weight loss in subsequent regeneration periods is consistent with this idea.

When modelling coated DPFs it is important to correctly model the transport of reactants to the catalytic coating to obtain a good prediction of post-DPF emissions (50). In our original coated DPF model, reactant molecules reached the catalyst coating solely by travelling with the bulk gas flow through the filter wall and the coating. This makes no sense when one thinks of a flow-through coated monolith catalyst where the gas flows over the catalyst along the channels, so reactants must reach the coating by diffusion through the gas in the channels. Thus, it is logical that reactant molecules in a coated DPF should reach the catalytic coating by diffusion from the gas flowing along a coated channel as well as from the gas as it passes through the filter wall (and hence the catalytic coating); both transport routes are included in our current model for a coated filter (9, 50). This results in better prediction of post-DPF emissions and more plausible predicted concentration profiles along the filter compared to our original model (50).

Moving on to SCRF® modelling, we have demonstrated that with the transport model already mentioned, it is possible to obtain a good model for an SCRF® by adding SCR kinetics developed for a flow-through monolith catalyst to the model for a coated DPF. Such a model gives a good prediction of engine or vehicle data without having to make any changes to the SCR kinetics (apart from allowing for the difference in washcoat loading). This has been demonstrated for both Cu-zeolite and Fe-zeolite formulations (12).

One point of interest with SCRF®s is the interaction between the NOx reduction (SCR) and soot oxidation functionalities; NOx removal results in a reduction in the availability of NO2 for soot oxidation, while soot oxidation by NO2 lowers the NO2/NOx ratio, which is unfavourable for SCR if it moves away from the optimum value of 0.5. Therefore the SCRF® model has been applied to investigate this (12). The presence of soot on the SCRF® is predicted to have no significant impact on NOx conversion (Figure 5). Conversely, SCR activity (NOx reduction) is predicted to significantly retard the rate of soot removal at lower temperatures (200°C–400°C), where soot oxidation is predominantly by reaction with NO2, but to have little effect at higher temperatures (450°C–550°C), where soot is predominantly oxidised by O2 (Figure 6). Both predictions are in agreement with experimental results.
In fact, the model predicts that SCR activity actually enhances soot oxidation at 500ºC and 550ºC; this is due to the heat generated by the SCR reaction increasing the rate of soot oxidation with O₂.

7. Faster Methods for Model Development

One of the things we have been looking at recently is faster ways of developing models, ideally using data that would be routinely collected (rather than data specially collected for model development). For example, the Pt-Pd DOC model discussed in Section 3 required 75 reactor experiments to develop the kinetics. Clearly repeating this for every catalyst formulation, or indeed for a different ageing, pgm loading or Pt:Pd ratio with the same catalyst, would represent a considerable amount of effort and time. What is needed to enable model development to keep pace with the rapid development in catalyst formulation is a faster method for adapting models to different formulations/ageings/pgm loadings (rather than developing new models from scratch each time). Thus, we have developed a methodology for adjusting/optimising existing models to best match measured engine or vehicle data. Of course this is reliant on knowing the reaction scheme for the catalyst and the form of the rate equations, so it does not entirely replace reactor testing and kinetics development, but it does mean that this does not have to be done for every formulation or variation. We have previously used this method to extend the Pt-Pd DOC model described in Section 3 to be capable of predicting the effect of changing Pt:Pd ratio at a fixed total pgm loading across the full range from monometallic Pd to monometallic Pt (25). Here we discuss the application of this method to adapt the Pt-Pd DOC model described in Section 3, to a model for a different formulation and ageing, capable of predicting the effect of pgm loading on DOC performance.

The samples used for this DOC pgm loading study were of a commercial light-duty diesel (LDD) Pt-Pd DOC with five different pgm loadings (30 g ft⁻³, 50 g ft⁻³, 70 g ft⁻³, 90 g ft⁻³, 120 g ft⁻³). All samples had a uniform pgm and washcoat loading, contained zeolite as a HC storage component and contained Pt and Pd in equal amounts by weight (i.e. a Pt:Pd ratio of 1:1). The same washcoat was used for all samples. The catalysts were hydrothermally aged for 15 h at 750ºC. This ageing is correlated to the thermal exposure typically experienced inside the catalyst over 160,000 km of use on an LDD application where elevated temperatures are periodically encountered during DPF regeneration. The catalysts were coated on 5.66″ × 3.82″ (143.8 × 97.0 mm) (diameter × length), 400/4.3 (620,000 cells m⁻², 0.11 mm wall thickness), cordierite substrates.

Engine data was collected on an engine bench dynamometer using a 2.4 l, LDD engine with a common rail fuel system, EGR and an EU5 calibration. European ultra-low sulfur diesel was used. NEDC (23) tests were run according to standard procedures. In each case, a number of repeat tests were done to ensure the data were representative. During the NEDC there was no rich operation, as would be encountered during an LNT regeneration, or unusually high HC levels for exotherm
generation. Emissions were measured simultaneously before and after the DOC using standard analysers and methods. The catalyst gas inlet temperature was measured with a 1.5 mm diameter thermocouple placed 25 mm in front of the catalyst with the tip in line with the centre of the catalyst.

To be able to model the effect of pgm loading on catalytic activity, it is necessary to have a function which describes how the rate constants vary with pgm loading. In general, while catalytic activity initially increases with pgm loading, this increase in activity with pgm loading will not go on forever, but rather the increase in activity will plateau off, reflecting the tendency for the larger metal particles with lower surface area to volume ratios to form at higher loadings instead of highly dispersed small particles. We have found the following arbitrary function works well (Equation (xix)):

\[ k = \frac{k_{\text{max}} A}{1 + A x} \]  

(\text{xix})

where \( k \) is the rate constant, \( k_{\text{max}} \) is the maximum or limiting value of the rate constant at high pgm loading, \( A \) is a constant and \( x \) is the pgm loading. This equation fulfils a number of key criteria for the dependency of a rate constant on pgm loading, viz. it predicts zero activity at zero pgm loading, it is single valued, it produces a continuous smooth curve without discontinuities and it predicts the rate of increase in activity with pgm loading to tail off at high pgm loadings with the rate constant eventually reaching a plateau value at high pgm loading. Ideally we would have used a more fundamental function, which relates the activity of the catalyst to the changes in metal particle morphology and dispersion as the pgm loading is increased, but this simple equation was found to work well.

More details on the optimisation method/procedure are given elsewhere (25). In the optimisation process, rate constants for CO oxidation (Equation (i)), HC oxidation (Equation (ii)), NO oxidation (Equation (iii)) and NO\(_2\) reduction by CO and HC (Equations (vii) and (viii)) were assumed to be functions of the pgm loading. The model includes a number of HCs; the rate constants for the reaction of all HCs were assumed to scale with pgm loading in the same way, i.e. the same value of \( A \) in Equation (xix) was used for the oxidation of each HC, but the value of \( k_{\text{max}} \) was different for each HC. Similarly, the rate constants for all the NO\(_2\) reduction reactions were assumed to scale in the same way with pgm loading. The parameter optimisation was carried out for all pgm loadings at once with the parameters in Equation (xix) being optimised, rather than optimising the kinetic parameters for each pgm loading and then fitting a function to the resulting rate constants obtained for each pgm loading, as this ensures that the rate constants vary smoothly with pgm loading. The rate constants for the main NO\(_x\) reduction reaction (Equation (ix)) was also optimised, but was assumed to be independent of pgm loading as previous work suggests that the dominant NO\(_x\) reduction reaction (Equation (ix)) does not occur over the pgm; we observe that an uncoated substrate gives comparable NO\(_x\) reduction over the NEDC to a DOC (19).

In addition to optimising the constants controlling the variation of rate constants with pgm loading, the activation energies for CO oxidation, NO oxidation and NO\(_2\) reduction by HC were also optimised at the same time; (other activation energies were kept the same as in the original model). However, unlike the rate constants, the same activation energy for each reaction was used for all pgm loadings, i.e. it is assumed that changing the pgm loading changes the number of catalytic sites, but not the nature of the site. This may not be entirely true, but it results in a model capable of predicting the effect of pgm loading on catalytic activity. It was necessary to change the activation energies from the values in the original model (19), as this model was for a different formulation. The constant for inhibition of CO oxidation by CO was also included in the optimisation as we have previously shown that it is difficult to obtain a reliable value for this constant using only reactor light-off data (11); again the same value for this constant was used for all pgm loadings.

The variation in catalytic activity for the key reactions in the model with pgm loading is shown in Figure 7. Here the relative activity for each reaction is defined as the activity (or rate constant) of that reaction relative to that of the 120 g ft\(^{-3}\) sample, i.e.:

\[ \text{Relative Activity} = \frac{\text{Value of preexponential factor}}{\text{Preexponential factor for 120 g ft}^{-3}} \]  

(xx)

The variation in activity for NO\(_2\) reduction (Equations (vii) and (viii)) and NO oxidation (Equation (iii)) with pgm loading exhibits a pronounced curve, while the line for CO oxidation (Equation (i)) exhibits only slight curvature. In this model the variation in activity for HC oxidation was observed to be linear in pgm loading over the range of pgm loadings considered (Figure 7). However we would not expect this trend to continue \textit{ad infinitum} with further increase in pgm loading.
Measured and simulated DOC outlet cumulative CO, THC and NO\textsubscript{2} emissions over the NEDC for all pgm loadings are compared in Figure 8; predicted emissions are shown with a solid line, while the measured outlet is shown by a dashed line. Generally, the model is giving a good, although not always perfect, prediction of the measured data through the NEDC. Figure 9 compares the measured and simulated conversions over the whole NEDC. Again the model is giving a good prediction over the full range of pgm loadings from 30 g ft\textsuperscript{-3} to 120 g ft\textsuperscript{-3}. It is worth noting that while the simulated conversions show a smooth variation with pgm loading, the measured conversions in some cases show a more irregular trend with pgm loading presumably due to experimental error/test-to-test variability.

As expected, CO and THC conversion increase continuously with increasing pgm loading. NO\textsubscript{2} conversion, on the other hand, decreases with increasing pgm loading. This is because the NO\textsubscript{2} conversion depends on the NO\textsubscript{2} reduction reactions (which remove NO\textsubscript{2}) and NO oxidation (which produces NO\textsubscript{2}). During the urban part of the NEDC (first 800 s (23)), levels of unreacted CO and HC are high, so NO\textsubscript{2} reduction (Equations (vii) and (viii)) dominates over NO oxidation (Equation (iii)) and the net result is conversion of NO\textsubscript{2} to predominantly NO. During the extra-urban

![Fig. 7. Relative activity for the various reactions occurring over the DOC as a function of pgm loading. Relative activity for each reaction is defined as the activity of that reaction relative to that of the 120 g ft\textsuperscript{-3} sample (Equation (xx))](http://dx.doi.org/10.1595/205651315X687876)

![Fig. 8. Comparison of measured (short dashes) and simulated (solid lines) post-DOC cumulative: (a) CO; (b) THC and (c) NO\textsubscript{2} emissions for a series of DOCs with different pgm loadings over the NEDC. DOC inlet emissions for each test are also shown (long dashes)](http://dx.doi.org/10.1595/205651315X687876)

![Fig. 9. Comparison of measured and simulated: (a) CO; (b) THC and (c) NO\textsubscript{X} and NO\textsubscript{2} conversion for a series DOCs with different pgm loadings over the NEDC](http://dx.doi.org/10.1595/205651315X687876)
part of the NEDC (after 800 s (23)), temperatures are higher resulting in high CO and HC conversions which means there is little reductant available for NO₂ reduction and so NO oxidation is the dominant process. In this part of the test cumulative NO₂ increases with pgm loading, indicating that the rate of NO oxidation to NO₂ increases with pgm loading, as expected.

8. Conclusions

This review has highlighted some of the key developments in diesel aftertreatment modelling made by Johnson Matthey. Increasingly stringent emissions legislation has created a demand for more accurate models, which in turn has resulted in models with more comprehensive reaction schemes and the need for larger experimental studies to provide the data for developing kinetics.

Demand for faster model development has led to the need for a new methodology for developing models (or at least adapting existing models) using engine or vehicle. This has been used to model the effect of Pt:Pd ratio and total pgm loading on DOC performance.

Acknowledgment

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Glossary

<table>
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<tr>
<th>Term</th>
<th>Definition</th>
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<tr>
<td>ANR</td>
<td>Ammonia to NOx ratio</td>
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<td>DOC</td>
<td>Diesel oxidation catalyst</td>
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<td>DPF</td>
<td>Diesel particulate filter</td>
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<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
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<td>FTP</td>
<td>Federal test procedure</td>
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<td>HC</td>
<td>Hydrocarbon</td>
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<td>HDD</td>
<td>Heavy-duty diesel</td>
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<td>HD-FTP</td>
<td>Heavy-duty FTP transient cycle</td>
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<td>LDD</td>
<td>Light-duty diesel</td>
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<tr>
<td>LNT</td>
<td>Lean NOx trap</td>
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<tr>
<td>NEDC</td>
<td>New European drive cycle</td>
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<tr>
<td>pgm</td>
<td>Platinum group metal</td>
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<td>SCR</td>
<td>Selective catalytic reduction</td>
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<td>SCRF®</td>
<td>SCR coated DPF</td>
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<tr>
<td>THC</td>
<td>Total hydrocarbon</td>
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“Understanding Organometallic Reaction Mechanisms and Catalysis: Computational and Experimental Tools”

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This review is about the book “Understanding Organometallic Reaction Mechanisms and Catalysis: Computational and Experimental Tools” edited by Valentine P. Ananikov, a professor at the Russian Academy of Sciences who has contributed much to the field of catalysis in the past decade. His work has received international attention along with many awards and research grants. He has been working on developing new concepts in transition metal and nanoparticle catalysis, sustainable organic synthesis and mechanistic studies of complex chemical transformations, which gives him the required background and expertise to edit a book that consolidates various experimental and computational tools used by various research groups around the world.

This book is a collection of chapters written by renowned professors and researchers in this field from Russia, Italy, Denmark, Germany, the United Kingdom, Hong Kong and the United States of America. Although there are many other books on organometallic reactions focusing separately on fundamentals, experiments and computational studies, the uniqueness of this book is to highlight new horizons in studying reaction mechanisms by drawing from the first-hand experience of experts who have worked both on computational and experimental tools. The book succeeds in convincing the reader about the importance of translating the knowledge obtained from state-of-the-art theoretical methods to experimental studies and vice versa to facilitate mechanistic studies leading to better understanding and innovation in the field of catalysis.

The book consolidates studies from different groups that emphasise the benefits of integrating experimental techniques along with computational tools (mainly density functional theory (DFT)) to understand organometallic reaction mechanisms and catalysis. The book is aimed at people looking for ways to use the recent advances in experimental and computational chemistry in their research. It assumes readers have prior background in kinetics and the fundamentals of DFT.

There are some chapters in this book that deal only with case studies, presenting their results and discussion without much introduction or discussion of fundamentals. Such chapters are useful for those who are familiar with that particular area of research but will be more difficult to follow for a reader who is looking for generic information on what and why certain techniques are used. Out of the 11 chapters, this review covers Chapters 1 to 4, 8 and 9.
Chapter 1 is written by Robert Kretschmer, Maria Schlangen and Helmut Schwarz (Institut für Chemie, Germany). This chapter focuses on two gas-phase carbon-nitrogen coupling processes with metal complexes bearing carbon- and nitrogen-based ligands (Figure 1). The studies look at thermal reactions of these ligands with ammonia and hydrocarbons, elucidating the mechanisms of metal-mediated coupling reactions. This chapter launches immediately into the case study at hand without introducing the reader to any background connecting to the title of the book. This was rather disappointing as the chapter would have benefited from additional background to introduce the topic given its position within the book.

Adrian Varela-Alvarez and Djamaladdin G. Musaev (Emory University, USA) have written the second chapter on transition-metal-catalysed C–H bond alkylation by diazocarbene precursors. The chapter is well written with a nice flow of thought, starting from the electronic structure of free carbenes and discussing the nature and factors affecting the stability of the metal-carbene bond. Theoretical models and methods used (such as the polarisable continuum model) are introduced first, followed by an example to show how to use these theoretical methods to design a catalyst with a non-redox-active metal and a non-innocent ligand. Based on the theoretical predictions (there is no experimental proof), the chapter concludes that the inclusion of donor substituents to the carbene fragment makes diazocarbene decomposition more exergonic and a benzylic C–H bond alkylation catalysed by a complex containing a non-redox calcium(II)-centre and a non-innocent pyridine diimine (PDI) ligand is practically possible.

Chapter 3 is written by John M. Slattery, Jason M. Lynam (University of York, UK) and Natalie Fey (University of Bristol, UK). This is a very well written chapter keeping in mind the scope of the book. Initially the authors talk about the importance of experimental and computational techniques and how both should go hand in hand – backed by nice examples – using metal vinylidene complexes. This chapter gives an excellent overview of experimental and computational methodologies, different options in DFT calculations and pitfalls in using the functionals – a good source of information for a beginner. After discussing extensively the methodologies, the chapter proceeds to a selection of case studies. Four case studies looking at the mechanisms of: (a) Rh-mediated alkyne to vinylidene transformation, (b) ruthenium-vinylidene complex formation, (c) vinylidenes in gold catalysis, and (d) the effects of metal on alkyne/vinylidene tautomers are discussed in detail.

Chapter 4 is written by Franziska Schoenebeck (RWTH Aachen University, Germany). This is again a nice chapter that concentrates on selected mechanistic studies using both experimental and computational approaches to study reactivities derived from palladium.

Fig. 1. Simplified potential energy surface (PES) of the reaction [Pt(CH$_2$)]$^+$/NH$_3$ > [Pt(CHNH$_2$)]$^+$/H$_2$ calculated for the doublet spin surface at the B3LYP/TZP//B3LYP/DZP level. Red = Pt, grey = C, blue = N, white = H (Adapted with permission from (1). Copyright 1999 American Chemical Society)
in oxidation states (0) to (III). This led to mechanistic insights and reactivity discoveries relating to additive, ligand and solvent effects. The computational studies focus on selectivities and relative reactivities rather than the full catalytic cycle. In selectivity studies, the nature of the crucial points of the energy surface is generally quite similar and hence error cancellation will be beneficial. This chapter gives the reader a better understanding of how rational development of desired reactivities can be carried out.

Experimental and Computational Techniques

Daniel Lupp, Niels Johan Christensen and Peter Fristrup (Technical University of Denmark) contribute Chapter 8 of this book, exploring reaction mechanisms in catalysis by transition metals (Figure 2). This chapter explains kinetic isotopic effects and Hammett substituent effects which can benefit by the advancements in computational chemistry. There is a detailed section on recent developments in DFT relevant to transition metal catalysis, divided into four areas: computational efficiency, dispersion treatment, solvation treatment and effective core potentials. A very useful section for many readers searching for a direction on connecting theory to experiment (through Gibbs free energy, Boltzmann population, relative reactivity) is given in this chapter. In addition there are four case studies each targeting a specific catalyst type based on rhodium, iridium, palladium and ruthenium.

Chapter 9 is written by Sebastian Kozuch (University of North Texas, USA). This chapter is a highlight of the book. The author knows how to keep the reader engaged and presents an excellent chapter on myths and facts in the analysis of catalytic cycles. It will be a good starting point for many budding researchers in catalysis and chemistry. The author touches upon various basics in kinetics like rate constants, activation energies, kinetic graphs, turnover frequencies, Sabatier volcano and power law.

Conclusion

The book in itself is a collection of case studies on different organometallic catalyst studies. I consider this more as a collection of journal papers with slight modifications to add the flavour of a book. Based on the title, one would expect to learn in depth about the experimental and computational tools that can be used in catalysis, followed by case studies that use or implement the introduced tools. In contrast, each chapter is written by separate groups talking about the

![Fig. 2. Proposed catalytic cycle for the palladium-catalysed allylic C–H allylation (reproduced with permission of Wiley-VCH Verlag GmbH & Co KGaA)](http://dx.doi.org/10.1595/205651315X687713)
research conducted in their laboratories. In my opinion, the continuity between each chapter is missing and this has a negative effect on the smooth flow of information through the book. It could have been structured in a better way by, for example, arranging Chapters 3, 4, 8 and 9 as initial chapters. Some chapters feel more like reading a research report rather than a book.

The book does however give the reader an insight as to how systematic theoretical studies can build better understanding and innovative directions when combined with targeted experiments. Some chapters are very well written with a neat introduction, describing the analytical aspects and successfully taking the reader on a journey to connect theory and experiment. The evidence presented by the various authors to tie theory with experiment to enhance the understanding of kinetics is good and convincing. If you are looking for basics of computational and experimental tools used in organometallic catalysis, this book will give you a general overview, but it is not a one-stop place and you might have to dig into the enormous references in each chapter to find more complete answers to your questions.

**Reference**


**The Reviewer**

Balaji Sukumar obtained his PhD in Chemical Engineering from the National University of Singapore in 2007 and completed his post-doctoral studies at Carnegie Mellon University, USA, from 2007–2009. Later, he worked at Industrial Learning Systems, USA, where he designed a novel high-temperature casting process for continuous production of single crystalline silicon wafers. He currently manages the computational modelling group in the Emission Control Technologies division at Johnson Matthey Inc, USA. Dr Sukumar specialises in computational modelling, data analysis and control of process systems. His expertise includes design and advanced control of processes in exhaust aftertreatment, solar grade silicon production, silicon wafering, gasification and chemical looping combustion.
Is Reactor Light-Off Data Sufficiently Discriminating Between Kinetic Parameters to be Used for Developing Kinetic Models of Automotive Exhaust Aftertreatment Catalysts? The Effect of Hysteresis Induced by Strong Self Inhibition


Kinetic parameters used to predict CO oxidation over a diesel oxidation catalyst were found to give different results over a vehicle test cycle compared to a test reactor. This is thought to be due to two factors: dependence on the concentration of CO, since the reaction is strongly inhibited by CO; and hysteresis during temperature ramping up and down. This may be solved by using ramp down reactor data as well as ramp up reactor data; however this leads to the problems of discretising the data for ramp down into a much larger number of elements, and the fact that hysteresis does not always occur.

Model-Based Experimental Screening for DOC Parameter Estimation


A new method of estimating both kinetic and mass transport parameters was investigated for a DOC on a full-scale engine rig. Data screening by sensitivity analysis was applied, selecting different subsets using multivariate data analysis (MVDA) on a large transient data set. Principal component analysis (PCA) and D-optimal onion design were used to continuously update the data subset. The proposed method achieved a 32% lower residual sum of squares but was also less likely to converge to a local minimum. However it also took significantly more time than the alternative methods.

The Effect of Pt:Pd Ratio on Heavy-Duty Diesel Oxidation Catalyst Performance: An Experimental and Modeling Study


The effect of the Pt:Pd ratio on DOCs was investigated by both experiment and modelling. The pgm loadings were <50 g ft\(^{-3}\). Transient light-off and steady state experiments were carried out over hydrothermally aged DOCs and increasing the ratio of Pt:Pd was found to increase the oxidation of both n-decane and NO, although the oxidation of unsaturated C3 and C7 HCs levelled off at higher Pt:Pd ratios. The higher Pd catalysts exhibited better activity for CO oxidation. In addition, HCs lowered the outlet NO\(_2\):NOx ratio due to reduction of NO\(_2\) to NO.

Interstitial Modification of Palladium Nanoparticles with Boron Atoms as a Green Catalyst for Selective Hydrogenation


The modification of the Pd/CaCO\(_3\) Lindlar catalysts with lead acetate and quinoline are commonly used for the partial hydrogenation of alkynes but there are limitations because lead is toxic and there is a risk of leaching. In this study Pd was modified below the surface to produce an ultra-selective nanocatalyst. Boron atoms are located in the Pd interstitial lattice sites and are chemically and thermally stable due to a strong host-guest electronic interaction after treating supported Pd nanoparticles with a borane tetrahydofuran solution. The subsurface boron atoms alter the adsorptive properties of Pd and demonstrate ultra-selectivity in some demanding alkyne hydrogenation reactions.

Low Temperature Growth of Carbon Nanotubes on Tetrahedral Amorphous Carbon using Fe–Cu Catalyst

Carbon nanotubes are grown on tetrahedral amorphous (sp³ rich) carbon by a CVD process using a Fe-Cu catalyst at <500ºC. Cu decreases the temperature at which the reduction of Fe occurs. The catalytic activity of Fe for the nucleation of nanotubes at low temperatures is improved and at the same time its tendency to diffuse into the carbon substrate is reduced resulting in minimal damage to the support. This study shows that nanotubes can be directly grown on the carbon fibres and can, therefore, be used in composites and fuel cell electrodes.

**PROCESS TECHNOLOGIES**

**Origin of Catalytic Activity in Sponge Ni Catalysts for Hydrogenation of Carbonyl Compounds**


The activity of sponge Ni catalysts is affected by Al and other dopants. The direct reduction of acetaldehyde as a test system was investigated and a kinetic model for this reaction is constructed using density functional theory (DFT). The catalytic performance of carbonyl hydrogenation was enhanced by Al due to the increased reactivity towards O containing molecules and the affinity towards C was simultaneously decreased. In this study, the author compared this test system to acetylene hydrogenation where the activity depends on the C affinity of the catalysts. Early transition metal dopants may aid the selectivity of the hydrogenation of a carbonyl group in the presence of an alkene. The intrinsic electronic structure of the dopant was found to be responsible for the change in catalytic activity.

**Innovative Oxygen Carriers Uplifting Chemical-looping Combustion**


There is no gas separation stage required in chemical looping combustion, therefore, this removes the high energy penalty and costs associated with other carbon capture techniques. The authors investigate chemical-looping combustion with gaseous fuels rich in methane in this EU funded project, Innovative Oxygen Carriers Uplifting Chemical-Looping Combustion (INNOCUOUS). Viable alternative oxygen carriers with low or no Ni are required due to the high cost of Ni-based materials and special environmental/safety precautions. This study focuses on the preparation and testing of oxygen carrier; two oxygen carriers of CaMn$_x$Ti$_y$Mg$_{1-x-y}$O$_3$ were produced by spray-drying and an oxygen carrier of Fe$_2$O$_3$/Al$_2$O$_3$ was produced by impregnation. The Ca-based material displayed promising results in a 10 kW and 120 kW unit and complete combustion was achieved.

**Development of Mixed Matrix Membranes Containing Zeolites for Post-combustion Carbon Capture**


A solvent casting method was used to synthesise mixed matrix membranes from poly(amide-b-ethylene oxide) (PEBAX MH1657) and zeolite 13X for CO$_2$/$N_2$ separation. A constant volume–variable pressure method was used to determine the gas permeation properties of neat PEBAX membranes and 5 wt%, 10 wt% and 15 wt% of zeolite 13X loadings for pure CO$_2$ and N$_2$. An increased loading of zeolite 13X resulted in a higher CO$_2$ permeability and at the maximum loading, the CO$_2$/N$_2$ selectivity was 47.

**Direct Steam Reforming of Diesel and Diesel-Biodiesel Blends for Distributed Hydrogen Generation**


Diesel and 7 vol% biodiesel blends were directly steam reformed at different operating conditions: reformer temperature, feed mass flow rate and diesel sulfur content. A precious metal based catalyst was used. Low catalyst inlet temperatures and high feed mass flow rates adversely affect the catalyst activity. However the long term performance of the precious metal catalyst tested with a desulfurised diesel-biodiesel blend showed an improvement. A stable product gas composition close to chemical equilibrium was attained over 100 h on stream by using diesel with 1.6 parts per million weight (ppmw) sulfur at a catalyst inlet temperature of >800ºC, a steam-to-carbon ratio of 5 and a feed mass flow per open area of catalyst of 11 g h$^{-1}$ cm$^{-2}$. 

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Discrete Element Method (DEM) for Industrial Applications: Comments on Calibration and Validation for the Modelling of Cylindrical Pellets
M. Marigo and E. Hugh Stitt, *KONA Powder Particle J.*, 2015, 32, 236

DEM is increasingly being used for simulation of complex processes. In order to extend its usefulness into more industrial application areas, the present study has investigated a test case involving cylindrical pellets represented by conjoined spheres in a “sand pile test”. The input parameters were calibrated, validated and optimised along with the shape representation. Two configurations of rotating drum system were simulated, one with a single baffled and one unbaflled. The results were compared with experimental data. The qualitative results compared well, however there were significant errors in the quantitative results. Further work is needed to improve the evaluation protocols for estimating key properties of particles, and better understand the quality of fit in such models.

The Effect of Solvent and Temperature in the Synthesis of CPO-27-Ni by Reflux

A Ni-based MOF, CPO-27-Ni, was synthesised by reflux at temperatures up to 110°C using various mixtures of organic solvent (THF, 2-butanol, hexanol, n-butanol, ethylene glycol and glycerol), with water or water alone. The size and morphology of the crystal growth are affected by the choice of solvent. The same organic solvent/water mixture was tested at various temperatures and an effect on crystallisation and crystal morphology was observed. The large scale synthesis of CPO-27-Ni is feasible by the reflux method.