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PREDICTION OF ASH PHASE EQUILIBRIA USING FACT MODELS

RESEARCH REPORT 54

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1 EXECUTIVE SUMMARY

The behaviour of mineral matter at high temperatures in coal utilisation technologies is a major issue that influences coal value, marketing and resource utilisation. A wide variety of phenomena, such as, the formation of slagging and fouling deposits in pf combustion, agglomeration in fluidised beds, ash slag flow in IGCC and other slagging reactors, and a number of other key high temperature phenomena are directly related to the formation of liquid slag (molten oxides) and to the stabilities of solid crystalline phases. The traditional methods used to characterise the high temperature behaviour of the coal inorganic material are becoming increasingly outdated and are unable to accurately predict the behaviour of ash and slag in coals and coal blends in existing and new power generation technologies.

As a part of a strategic plan the Coperative Research Centre for Coal in Sustainable Development (CCSD) and the Australian Coal Association Research Program (ACARP) funded the development of new fundamentally-based, predictive tools for application in coal utilisation technologies. These tools involve the use of the FactSage computer program and new thermodynamic databases. FactSage is an extremely powerful tool that is used to predict thermodynamic equilibrium in these systems. This highly sophisticated tool provides information on the phases formed, their proportions and compositions, the activities of individual chemical components and the thermodynamic properties for all compositions, oxygen partial pressures and temperatures.

For accurate predictions the FactSage program requires accurate and self-consistent thermodynamic databases. The new, state-of-the-art CCSD thermodynamic database for the system Al_2O_3-CaO-FeO-Fe_2O_3-Fe_2O_3-SiO_2-MgO-K_2O-Na_2O has been completed. These are the principle chemical components present in mineral matter in coals. Development of new CCSD thermodynamic database is a significant step in modelling of coal ash /slag systems. The new database, used in conjunction with the FactSage computer package, can describe the melting behaviour of ash in coals from around the globe, making it a key tool for future coal selection and blending by coal suppliers and utilities, coal mine planning and resource optimisation. The use of the tool will assist to make major reductions in the environmental impact of electricity generation from coal through assisting the development of new more energy efficient technologies. The FactSage program and the use of the new databases is starting to have a significant impact on coal selection internationally (e.g. CRIEPI, ECN- Energy Research Centre of the Netherlands, EERC- North Dakota Energy & Environmental Research Center, Hongik University in South Korea, Chubu University Japan). FactSage is already being used in the design of step-change technologies in the evaluation and selection of coals for entrained flow coal gasification and blast furnace iron making by research teams in Japan and Korea (CRIEPI, Japan; Ishii Project, Japan; Posco, South Korea). These technologies represent the next generation of energy efficient processes with targets to greatly reduce greenhouse gas emissions and significantly improve energy efficiencies.

The phase equilibrium predictions are now also being used to solve longstanding problems in relation to the physical properties of complex oxide melts in coal ash systems. In particular, it is now possible to interpret and systematically analyse slag viscosity data, and the new thermodynamic models have been used in new advanced viscosity models enabling the viscosities of fully liquid and partially crystallised slags to be predicted.

The CCSD research team has also demonstrated how these advanced tools can be packaged in the form of customised computer software. The software retains accuracy over a wide range of compositions and was developed to provide assistance to coal marketing, sales and mine planning applications. The report describes

- Important ash characteristics that can be predicted using FactSage,
- The new CCSD database, and
- Real and potential applications of the database to problems in coal utilisation.

2 INTRODUCTION

2.1 GENERAL DESCRIPTION

The melting behaviour of coal mineral matter at high temperatures plays a key role in coal utilisation processes. The coal mineral matter in industrial processes is present in the form of complex phase assemblages, which can include liquid slag (molten oxides) and different stoichiometric compounds and solid solutions. To fully understand, interpret and predict the variety of processes occurring at high temperatures during coal power generation it is essential to know the presence, proportion, compositions and physicochemical properties of the liquid slag and the solid phases as a function of the mineral matter composition and operational parameters, such as temperature and atmosphere (reducing/oxidising).

The FactSage thermodynamic computer package is one of the leading tools in the world for the calculation of chemical equlibria in complex oxide slag systems. This work describes the thermodynamic databases that have been developed for the oxide systems relevant to coal ashes. Used in conjunction with FactSage these databases can provide knowledge to support the optimisation of current coal power generation technologies, coal marketing and the development of the technologies of the future.

2.2 IMPORTANT COAL ASH CHARACTERISTICS

When coal is used in power generation or metallurgical applications the carbon and hydrocarbons react and are removed into the gaseous phase. The mineral matter present in the coal is, in the main, left behind as condensed phases. The importance of the behaviour of this mineral matter is universally accepted as it is routine to report the proportion of mineral matter present in the coal, the composition and the behaviour of these ashes in industry developed empirical tests known as Ash Fusion Temperatures (AFT's). This information provides the user with a broad appreciation of the behaviour of the coal ash under specified oxidising and reducing conditions.

It is now possible through a more fundamental understanding of the underlying chemistry and physicochemical properties to identify additional characteristics of the system, which more accurately define coal ash behaviour as functions of bulk ash composition, temperature and gas composition. These characteristics include:

- Phases present at equilibrium;
- Proportion of each phase;
- Compositions of each of these phases;
- Liquidus - conditions when the system is completely liquid;
- Solidus – conditions when all phases are present as solids;
- Vapour pressures of each species;
- Chemical and thermodynamic properties of each of the chemical species;
- Viscosities of fully liquid and partly crystallised melts.

A more detailed explanation of these properties and their significance is given in Appendix B. Information on all of these properties can be obtained with the use of FactSage computer program which predicts the chemical equilibrium for defined process conditions. In order to undertake these calculations it is necessary to develop a thermodynamic database describing all the chemical components and all possible phases that may be formed in the system. This is the basis of current research. The chemical components which have been selected for inclusion in the database in this work are Al_2O_3-CaO-FeO-Fe_2O_3-Fe_2O_3-SiO_2-MgO-K_2O-Na_2O. These components represent over 97 % of the components that are found in mineral matter in bituminous and anthracitic coals.

3 THERMODYNAMIC DATABASE DEVELOPMENT

This section provides a summary of the thermodynamic database development undertaken. The details of the thermodynamic optimisations are given in the APPENDIX A.

The FactSage program is a powerful and sophisticated software package used in the calculation of chemical equilibria. The program requires the specification of chemical species present in the system and additional conditions such as temperature and pressure in order to obtain unique solution.

The operation of the program relies on the availability of thermodynamic descriptions (Gibbs free energies) of all of the chemical species and phases that may be formed in a particular system as a function of the process variables. These descriptions are collectively referred to as “thermodynamic databases”.

The equilibrium calculations are performed by determining the minimum of Gibbs free energy of the system. A software program, called a Gibbs free energy minimiser, operates with Gibbs free energies of all phases including gas, liquid and solids. The Gibbs Free energies of the phases are combined and stored in the thermodynamic databases. The FactSage software package therefore consists of the following main components:

- DATABASES – stoichiometric species; solid, liquid, gas solutions; public and user;
- Gibbs Free Energy Minimisation software;
- Input – output software;
- DATABASE maintenance software.

A comprehensive literature review has been performed to collect all available information on the system Al-Ca-Fe-O-Si + Mg-K-Na. A review of the standard hard copy reference collections (Phase Diagrams for Ceramists, Levin, 1964 - ; Slag Atlas, 1995, and Report submitted to “Phase Diagrams for Ceramists” by Pelton in 1994) was followed by the computer search of most important electronic databases. The **Chemical Abstracts** were searched on-line using special searching procedures developed for this study. The result of the on-line search of the Chemical Abstracts was a set of abstracts in electronic form containing information on several thousand papers. The potentially useful papers were selected and originals of those papers were acquired. Approximately 6000 papers were collected this way. A preliminary review of all of these papers was undertaken to ensure that all useful information currently available was obtained. The papers were sorted and the special “library” – collection of the relevant papers – has been carefully maintained. A computer database has been developed to organise storage and access to the collection of the papers. The papers then were sorted out by sub-systems and by the type of information used for optimisations (eg equilibria between liquid and gas phases, three phase equilibria, special thermodynamic data etc.).

The thermodynamic models used in the preparation of the databases are described in more detail in APPENDIX A.

Gibbs Free Energies of stoichiometric compounds in the FactSage databases are defined through the standard enthalpy ($\underline{H}^0_{298}$) , standard entropy (S_{298}) and heat capacity ($\underline{C}_P$) expressed as a function of temperature. In some cases a $\underline{C}_P$ expression was split into a few temperature ranges to describe more accurately the experimental data. Each polymorph (crystal of the same chemical composition and different crystal structure) has its own Gibbs Free energy expressions as a function of temperature.

The mathematical description of the Gibbs Free Energy of a solution as a function of temperature and composition is called a solution model. Various solution models were used to describe Gibbs Free Energies of solutions as a function of temperature and composition.

The ideal solution is the result of random mixing of chemical species. The Gibbs Free Energy of the gas phase was described by the ideal solution model.

The thermodynamic properties of solid solutions with one sub-lattice were described by the *polynomial solution model*.

Most crystals have very complex internal structures with a number of sub-lattices. Metal cations have certain preferences to occupy different sub-lattices depending of their size and charge. This internal arrangement results in specific changes of the thermodynamic properties of the crystalline phases as a function of temperature and composition that have to be taken into account. The *compound energy model* developed by M.Hillert was used to describe complex thermodynamic function of the crystal solutions with a number of sub-lattices.

The slag (oxide melt) liquid solution can have an internal order – some components of the slag may not mix randomly but have certain preferential internal arrangement. To reflect the internal structure of the slag, structurally based thermodynamic models are used. One of the most successful for the slag phase is *quasi-chemical solution model* developed by M.Blander and A.Pelton and used in the FactSage package.

The *modified quasichemical model* has been further developed and improved in the course of the present study. A number of essential modifications have been introduced into the system are discussed below.

Charge Compensation

In silicate melts containing alumina charge compensation phenomenon occurs in presence of alkali or alkaline earth metal oxides. Liquid silicates possess a significant short-range order. The thermodynamics and other physicochemical properties of slags are controlled principally by this internal structure. Silicate slags can be considered to be made up of silica tetrahedrons SiO_4^{4-} linked with each other into three-dimensional networks by strong bonds (Si – O – Si). Al^{3+} can replace Si^{4+} in tetrahedrally coordination positions if the excess negative charge for Al^{3+} is compensated by the presence of alkali or alkaline earth cations, thus keeping the silicate network structure instead of breaking it. As a result, associates of the form $Me^{+}AlO_2$ or $Me^{2+}Al_2O_4$ are formed in the melt. This is commonly referred to as the “charge compensation effect”. This effect introduces particular changes into the thermodynamic and other properties of the slag phase that are especially significant in the silica-alumina-alkali-containing systems and have to be taken into account to describe phase equilibria in these systems. Previous quasi-chemical models did not describe the charge compensation effect. The charge compensation effect was described in this study through the introducation of the associates $NaAlO_2$ and $KAlO_2$ as separate species. This important modification was introduced for the first time in the course of the present study.

Ternary Grouping

An important feature of the quasi-chemical thermodynamic model is the method used for the extrapolation of the binary parameters into ternary and higher order systems. The rules of extrapolation are selected based on the chemical nature of the components in terms of acid / basic behaviour. In previous quasi-chemcial models all oxides were separated into two groups – acid and basic. The problem appears when a certain component is amphoteric and behaves as basic in presence of acid components and as acid in presence of the basic components. The previous quasi-chemical model did not have required flexibility to select the way in which binary parameters could be extrapolated causing significant problems in description of the thermodynamic properties of the slag. To resolve this limitation, the quasi-chemical model was further developed, and the software was modified by the FactSage team. The method of extrapolation of the binary parameters in each ternary system can now be individually selected. This "grouping" approach has enabled the thermodynamic properties of the liquid slag to be described much more accurately.

GUTS Parameters

A significant further modification of the slag thermodynamic model has been the development and implementation of the GUTS model (General Unified Thermodynamic Solution Model). This model enables the binary parameters to be much more flexibly expressed and also enables the binary systems described with different thermodynamic models to be unified into one thermodynamic model of a multi-component system. These modifications enabled the description of the slag thermodynamics to be significantly improved.

Thermodynamic Optimisations

The database development is carried out through **thermodynamic optimisations**. Thermodynamic optimisations involve the thermodynamic model selection / development and then fitting the parameters of the model to ensure all available experimental data are described within experimental errors. In the thermodynamic "optimisation" of a system, all available thermodynamic and phase equilibrium data for the system are evaluated simultaneously to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties.

The large number of important modifications and improvements in the thermodynamic model of the slag phase have been introduced since the previous version of the database for this five-component system Al_2O_3–CaO-FeO-Fe_2O_3-SiO_2 was developed in 1999. It was important therefore to re-optimise this five-component system Al_2O_3–CaO-FeO-Fe_2O_3-SiO_2 to incorporate the latest advances in the thermodynamic theory (see described above). In addition, this re-optimisation was a necessary step to ensure consistency with the new databases of MgO-containing systems.

All binary, ternary and quaternary sub-systems and finally the five-component system Al_2O_3-CaO-FeO-Fe_2O_3-SiO_2 have been completely re-optimised. This re-optimisation has enabled the FactSage database for this system to be significantly improved and prepared a more accurate and robust basis for extention to the Mg-, Na- and K-containing systems.

All binary and higher order sub-systems in the higher-order systems Al-Ca-Fe-O-Si-Mg, Al-Ca-Fe-O-Si-Na and Al-Ca-Fe-O-Si-K have been optimised. Necessary solid solutions were modified or incorporated. The best possible agreement was achieved between predictions and existing experimental data.

The new database introduces significant improvement in accuracy and reliability of the predictions. In addition, in a number of systems calculations were previously not possible at all. For example, predictions in the system K_2O-Al_2O_3-SiO_2 that corresponds to the decomposed compound illite $K_yAl_4(Si_{8-y}Al_y)O_{20}(OH)_4$ became possible only with the new database (predictions with previous old database gave erroneous results). The predictions with the new database were crosschecked with all available experimental information and the best possible fit was found in the course of the database development. The new database now is the leading database available in the world.

The details of the optimisation of sub-systems and demonstrations of the agreement with experimental data are given in APPENDIX A.

4 REAL AND POTENTIAL APPLICATIONS OF FACTSAGE WITH CCSD DATABASES

The principal motivations for the development of the FactSage thermodynamic databases are the improved utilisation and marketing of coal resourses, and assistance of the development of new step change coal utilisation technologies. Current work continues to demonstrate how the FactSage program and the new CCSD databases may be used by industry. In the following sections selected examples are provided showing how the new database can describe the behaviour of coal ashes from around the globe, not just Australian coals. This brings particular advantage to the Australian coal marketing companies to be able to promote Australian coals compared to other coals with poor quality, and to be able to suggest blending to increase the use of the Australian resources. This makes FactSage potentially a key tool for future coal selection and blending by coal suppliers and utilities, in coal mine planning and resource optimisation, and in the development of new utilisaiton processes.

The database and models are valid for a wide range of chemical compositions and process conditions from oxidising to reducing atmospheres and enable the selection of coal for particular uses to be made on the basis of the properties of the ash and/or slags. These applications may be in conventional pulverised fuel (pf) combustion, fluidised bed combustion or gasification, or in emerging technologies, such as, entrained flow slagging gasifiers.

The examples given in the present report have been prepared over the period of the project and are available in the open scientific literature. The real and potential industry applications that have been addressed to date are summarised in the report, the issues are listed in Table 1. Brief descriptions of these real and potential applications are given in Appendix B.

Table 1 Real and potential applications of the CCSD databases and scientific papers dealing with these issues

Application	Paper No.
Ash fusion temperatures (AFTs)	J35, J24
Ash Adhesion	J12
Coal Blending	J35, J8, J24, J12, J3
Coal Resource Optimisation / Mine Planning	J35, J8, J24, J12
Coal Fluxing	J35, J8, J21, J3
Custom Designed Software Packages	J35
Operability Diagrams	J33
Mineral Matter Reactions	J24
Slag Deposit Formation / Flow	C54
Slag Viscosity Prediction	C54, J33, J23 J21, J35
Slagging – Melting (liquidus)	J35, J33, J3, J21, J12
Slagging – Crystallisation	J35, J8, J3, C54, J33, J21
Slagging – Oxygen pressure effect	J35, J3, C54
Trace elements	C27

* List of papers is provided at the end of this section.

4.1 ASH FUSION TEMPERATURES (see paper J35)

Ash Fusion Temperatures (AFTs) of coals and coal blends at the present time are widely used by coal mining and marketing companies and power generation utilities to assess coal quality. It is important to be able to predict AFTs to assist in coal selection, blending, fluxing, and to optimise and maximise the use of coal resources. It is well known that the AFTs of coals cannot be estimated by simple averaging techniques and the AFT's do not vary linearly with coal ash composition.

It has been shown (see Paper J35) that the AFTs can be correlated with the liquidus temperatures (temperatures at which first solid just starts to precipitate on cooling of a slag – liquid oxide melt) predicted by the FactSage computer package. The strength of this approach to the prediction of AFTs using the computer-aided thermodynamic modelling is that it is based on phase equilibrium science rather than simple empirical relationships with the bulk composition. The relative stabilities of the liquid and solid phases therefore are taken into account.

The study shows that AFTs, which are empirical indicators of ash behaviour used by the industry, can be predicted form bulk ash compositions. This opens up important possibilities for use of this tool for coal mine planning and blending applications.

4.2 ASH ADHESION (see paper J12)

The inorganic material in coal is present in the form of a number of minerals having a range of compositions. Analysis of slagging and fouling deposits within pf boilers has shown that these deposits are heterogeneous and in practice only approach equilibrium at temperatures close to the liquidus temperatures of the mixtures.

Ash deposits have been collected on probes placed inside boilers and analysed using CCSEM. These measurements provide quantitative analyses of the compositions of the inorganic ash particles that are deposited, and the proportions of these particles present. This information may be used in conjunction with the thermodynamic models to predict the state of this non-equilibrium deposit. The assumption that all particles have the mean ash composition appears here to indicate a worst case scenario for a particular coal ash based on the information from the base system SiO_2-Al_2O_3-FeO-Fe_2O_3-CaO. In practice, other elements and minerals are also present in the ashes, e.g. Na, K, Mg etc. These have been now included in the CCSD databases. This form of analysis provides a quantitative basis for comparing the relative slagging and fouling behaviour of coal ashes with different mineralogy and in different areas of the boiler.

4.3 COAL BLENDING (see paper J24)

In order to meet product specifications it may be necessary to blend coals from within the same mine or from shipment from other sources. It has been shown that Ash Fusion Temperatures of coals can be correlated to the ash liquidus temperatures calculated by FactSage. This makes it possible to predict the blending ratios necessary to achieve product specifications from a range of coals which individually are "under" and "over" specification. This application has significant commercial potential for coal suppliers.

4.4 RESOURCE OPTIMISATION / MINING PLANNING (see paper J35)

The blending of coals to maximise resource utilisation, and to optimise coal properties and cost is a common practice. Blending can effectively be used to control coal ash slag melting and flow behaviour in coal slagging gasification technologies. Selection of the most effective combination of the coals and their blending proportions is a difficult task. The liquidus temperatures, proportions of liquid and solids, and viscosity of liquid and slurry are complex functions of composition and temperature. The application of the new viscosity model in conjunction with the FactSage thermodynamic computer package enables systematic analysis of the melting and flow characteristics of the coal blends to be performed and coal blending strategy to be optimised to achieve the best results.

4.5 COAL FLUXING (see paper J8)

In some cases it is not possible, or it is economically attractive, to add fluxes to change the coal ash characteristics. In the case of a slagging gasifier it may be necessary to lower the liquidus temperature or the viscosity of the slag by the addition of fluxing reagents. Although the proportion of solids can readily be derived from the phase diagram for binary systems, deriving the same information for a complex multi-component system is not possible without a complete thermodynamic model of the system. The FactSage predictive tool may be used to describe fluxing requirements in complex slags.

4.6 CUSTOM DESIGNED SOFTWARE PACKAGES (see paper J35)

The development of customised software packages enables the power of the FactSage package to be fully utilised and results to be delivered in a format that can be directly used by engineers, researchers and plant operators. The Pyrometallurgy Research Centre has developed such custom-built software packages, which predict the effects of changes to process conditions such as feed composition, temperature and atmosphere on ash properties. The customised software packages may be used by research and process development personnel without special training.

The customised software packages

i) Provide the researchers and industry engineers with fundamental information on the chemistry and physicochemical properties of slags in a simple-to-use form.

ii) Provide predictive computer models and tools in a form that may be used in plant operations by wider engineering community to improve process design, control and operational efficiencies.

4.7 OPERABILITY DIAGRAMS (see paper J33)

Phase diagrams and physico-chemical property data are widely used in the metallurgical industry to assist in the selection of slag chemistry and operating conditions. Reading diagrams that describe the properties of ternary systems is not always straightforward, and rapidly becomes difficult for higher order systems.

With the emphasis on applications to plant practice it is suggested that the thermodynamic and physico-chemical property information can now be presented in the form pseudo-binary limiting operability diagrams (LOD’s) for slags. These LOD’s can be in the form of

1) maps defining compositions and temperatures for complete melting (Liquidus surfaces);

2) maps defining compositions and volume fractions of solids present in the slag at defined operating temperatures;

3) maps defining compositions and temperatures to denote sub-liquidus conditions where given volume fractions of solids are present in the slag;

4) maps defining compositions and temperatures to achieve defined slag viscosity conditions.

Clearly additional forms of LOD's are possible as further data and models become available to describe other important physicochemical properties.

This form of representation is particularly useful and convenient to plant engineers and operators who wish to evaluate the effect of changing coal ash composition or process conditions on the slag properties.

4.8 MINERAL MATTER REACTIONS (see paper J24)

Mineral matter is present in coals as descrete particles, which may be surrounded by organic material (included) or be present as separate grains (excluded). As the ash is heated these separate particles react, diffuse, sinter and combine to form a new different phase assemblage. FactSage thermodynamic program can provide important information on the reaction paths and the mechanisms of reaction.

4.9 SLAG DEPOSIT FORMATION / FLOW (see paper C54)

One of the common problems in coal gasification is the formation of slag deposit on the walls of a slagging gasifier; these deposits affect the overall heat balance, the temperature of the off-gases and the tappability of slag (i.e. ability of slag to flow freely from a gasifier). In extreme situations the slag tap-hole will become blocked leading to shut down of the reactor. In order to predict the rate of build up of deposits, information is required on the melting and viscosity characteristics of the slag. An example of the use of this information is given in paper C54. The development of a comprehensive slag flow predictor is proposed in CCSD project 2.5.

4.10 SLAG VISCOSITY PREDICTION (see paper J21)

The viscosity of coal ash slags is a major characteristic influencing behaviour of fully liquid and partially reacted or partially crystallised slags. Whilst a number of empirical correlations have been developed relating bulk ash composition and temperature to viscosity, these correlations are applicable to only very narrow composition ranges. The Pyrometallurgy Research Centre, UQ, has recently developed two slag viscosity models. The models are i) a modified Urbain model that can be expanded to include descriptions of additional modifiers and amphoteric components, and ii) a quasi-chemical model that is linked to the internal slag structural information provided by the FactSage thermodynamic model. These models have been shown to be accurate over a wide range of compositions, temperatures and gas conditions, for homogeneous and heterogeneous slag systems.

4.11 SLAGGING – MELTING (LIQUIDUS) (see paper J3)

An important characteristic of any slag is the temperature above which it becomes completely molten (all liquid). This is referred to as the liquidus temperature of the slag. Liquidus temperatures are particularly important to the smooth operation of step change entrained flow slagging gasifier. Liquidus temperatures can now be accurately predicted for the system

Al_2O_3-CaO-FeO-Fe_2O_3-Fe_2O_3-SiO_2-MgO-K_2O-Na_2O using the FactSage program and CCSD database.

4.12 SLAGGING – CRYSTALLISATION (see paper J3)

In practice the operational temperature of the gasifier may be lower than the liquidus, or complete fusion temperature, of the slag.

In these cases solid material will also be present in the slag. If the viscosity of the liquid/solid slurry is still low this may be acceptable practice. If not, then the reactor may experience operating problems.

The sensitivity of the system to changes in temperature may be deduced by calculating the proportions of the various phases present as a function of temperature. This information can also be combined with slag viscosity models to predict the resultant viscosity of the partially crystallised material. This type of predictive tool is essential for the smooth operation of the gasifier.

4.13 SLAGGING – OXYGEN PRESSURE EFFECT (see paper J3)

In various combustion processes the effective oxygen partial pressure can vary over a wide range, from reducing conditions in the case of gasifiers to oxidizing conditions in the case of pulverized fuel boilers. Depending on the bulk ash composition the coal ash characteristics can vary significantly with changing oxygen partial pressure. The FactSage program can be used to predict the effect of oxygen partial pressure on phase equilibrium conditions.

4.14 TRACE ELEMENTS (see paper C27)

Development of the methods to predict the fate of the Trace Elements (TE) in coal power generation is important to address growing focus on harmful gas and fine particle emissions, especially to those species of the greatest environmental concern. The fate of TEs depends on numerous factors including TEs concentration in the coal, TEs modes of occurrences, other coal properties, type of the power generation utility and operating parameters. A number of approaches have been used to model TEs behaviour in the coal power plants. One of these approaches is the development of the extensive information computer databases in which data on the TEs behaviour for various power plants and coals is collated and can further be used for estimates and predictions. Development of the generalised emission factors is another approach. An alternative method of prediction the fate of TEs is to develop computer models describing the complex processes occurring in power generation plants. The latter approach usually uses thermodynamic modelling predictions as a basis or as a sub-module of a more complex integrated computer package. The thermodynamic calculation provides a fundamental basis for the predictions of the fate of Tes and the condensation of species from the process gases.

4.15 SELECTED SCIENTIFIC PAPERS ADDRESSING THE REAL AND POTENTIAL APPLICATIONS OF FACTSAGE TO COAL UTILISATION PROBLEMS

1. C54. E.Jak, D.Saulov, A.Kondratiev, and P.C.Hayes, “Prediction of phase equilibria and viscosity in complex coal ash slag systems”, 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004, Symp. “Ash and Slag Chemistry in Power Systems’, Am. Chem. Soc., Div. Fuel Chem. 2004, 49 (1).

2. J35. Jak E., Kondratiev A., Christie S., Vladimirov I. and Hayes P.C., " Thermodynamic Modelling To Characterise Melting And Flow Properties Of The Coal Ash Slags ", presented

at United Engineering Foundation Conf. Power Production in the 21st Century: Impacts of Fuel Quality and Operations, Utah, USA, 28Oct-2Nov 2001, submitted to Fuel Apr 2003.

3. J33. E.Jak, A.Kondratiev, S.Christie and P.C.Hayes , “The Prediction And Representation of Phase Equilibria And Physico-Chemical Properties In Complex Slag Systems”, Presented at Mills Symposium, London, UK, August 2000, Met.Trans B, 2003, vol. 34B, pp. 595-603.

4. J29. A.Kondratiev, E.Jak and P.C.Hayes, “Predicting Slag Viscosities in Metallurgical Systems”, JOM, 2002, 2002, vol. 54 (11), pp. 41-45.

5. J24 Jak E., “Prediction of coal ash fusion temperatures with the F*A*C*T thermodynamic computer package”, Fuel, 2002, vol. 81 (13), pp. 1655-1668.

6. J21. Kondratiev A. and Jak E., "Predicting coal ash slag flow characteristics (viscosity model in the Al_2O_3-CaO-"FeO"-SiO_2 system)", Fuel, 2001, vol 80(14), pp. 1989-2000.

7. J12. Jak E., Degterov S., Zhao B., Pelton A.D., Hayes P.C., "Coupled Experimental and Thermodynamic Modelling Studies for Metallurgical Smelting and Coal Combustion Slag Systems", Metal.Trans., 2000, vol. 31B, pp.621-630.

8. J8. Jak E., Degterov S., Pelton A.D., Happ J., Hayes P.C., "Thermodynamic modelling of the system Al_2O_3-SiO_2-CaO-FeO-Fe_2O_3 to characterise coal ash slags", The Impact of Mineral Impurities in Solid Fuel Combustion, edit. Gupta R.P., Wall T.F. and Baxter L., Kluwer Academic / Plenum Publishers, New York, N.Y., USA, 1999, pp. 723-734.

9. J3. Jak E., Degterov S., Hayes P.C., Pelton A.D., "Thermodynamic modelling of the system Al_2O_3-SiO_2-CaO-FeO-Fe_2O_3 to predict the flux requirements for coal ash slag", Fuel, 1998, vol 77, No 1/2, pp. 77-84.

10. C27. Jak E., "Use of thermodynamic approaches to predict trace element speciation”, Symp. Trace Elements and Fine Particle Emissions, CRC Black Coal Utilisation, Newcastle, Oct. 2000.