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# MTDATA AND THE PREDICTION OF PHASE EQUILIBRIA IN OXIDE SYSTEMS: THIRTY YEARS OF INDUSTRIAL COLLABORATION.

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## Abstract

This paper gives an introduction to MTDATA, Phase Equilibrium Software from the National Physical Laboratory (NPL), and describes the latest advances in the development of a comprehensive database of thermodynamic parameters to underpin calculations of phase equilibria in large oxide, sulphide and fluoride systems of industrial interest. The database, MTOX, has been developed over a period of thirty years based upon modelling work at NPL and funded by industrial partners in a project co-ordinated by Mineral Industry Research Organisation (MIRO). Applications drawn from the fields of modern copper scrap smelting, high temperature behaviour of BOS (Basic Oxygen Steelmaking) slags, flash smelting of nickel, electric furnace smelting of ilmenite and production of pure TiO<sub>2</sub> via a low temperature molten salt route are discussed along with calculations to assess the impact of impurities on the uncertainty of fixed points used to realise the SI unit of temperature, the kelvin.

## Introduction

In the late 1980s a group of companies interested in making use of predictive phase equilibrium calculations to design, improve and troubleshoot their own diverse industrial processes came together through MIRO (Mineral Industry Research Organisation) to sponsor the development of a comprehensive thermodynamic database for oxide, sulphide and fluoride systems (MTOX) to underpin such calculations. The bulk of this database development work, using the *Calphad* approach<sup>[1]</sup>, has been undertaken at NPL (National Physical Laboratory, UK) using the software MTDATA<sup>[2]</sup>. The project is currently entering its ninth phase with a growing group of sponsors whose valuable guidance ensures its quality and relevance.

This paper gives a brief introduction to the MTDATA software and the MTOX database, then describes some practical applications of the phase equilibrium calculations which, together, they make possible.

## MTDATA

The principles of the calculation of chemical and phase equilibria, as described in the review of Bale and Eriksson<sup>[3]</sup> have been implemented in a number of computer programs over the years, many requiring initial estimates of the equilibrium state to be provided in order to achieve convergence. In the 1980s NPL developed a new equilibrium calculation engine providing true Gibbs energy minimization<sup>[4]</sup> through the solution of a non-linear optimization problem with linear constraints. No initial guess as to the nature of the equilibrium state was required. With significant development through the intervening years, for example to allow the reliable calculation of equilibria involving miscibility gaps, this reliable calculation engine remains at the core of MTDATA, NPL's software for the calculation of thermodynamic properties and phase equilibria.

MTDATA calculations can be set up through a user-friendly graphical interface (Figure 1), a character based interface for finer control and more traceability, particularly in complex calculations, or a programming interface allowing MTDATA functionality to be accessed from within other software. Results are typically displayed in the form of unary, binary or ternary phase diagrams, isothermal or temperature-composition sections through high order systems, phase fraction or phase composition diagrams and predominance area or Pourbaix diagrams. MTDATA also features a data assessment facility, allowing model parameters to be developed to fit target experimental phase equilibrium, thermodynamic or structural (site occupancy) data. This has been used extensively in developing the MTOX database.

## MTOX Database for Oxide, Sulphide and Fluoride Systems

The MTOX database has been developed in a series of projects, coordinated by and funded through MIRO, with the aim of building and continuously expanding a high quality, internally consistent and comprehensive thermodynamic database for oxide, fluoride and sulphide

62 containing systems of industrial importance. Industrial consortia comprising twenty-two different organisations in total have defined and  
63 steered the work, used the results in predictive calculations specific to their own process conditions and materials, and fed their experiences  
64 back to the database developers as a basis for improvements where necessary. The sharing of development costs, data and know-how, has  
65 proved extremely valuable to each industrial partner.

66  
67 Crystalline phases have been modelled using the compound energy (sublattice) model<sup>[5]</sup> and the liquid phases (alloys, mattes, slags) based  
68 upon non-ideally interacting species, either simple elemental, sulphide and oxide species or associates containing more than one cation, for  
69 example CaSiO<sub>3</sub>. The use of the simple, but flexible, associate model has proved to be particularly successful in that easy extension to  
70 enable the calculation of thermophysical properties such as viscosity<sup>[6]</sup> and electrical conductivity<sup>[7]</sup> of slags has been possible.

71  
72 The MTOX database has been used for applications as diverse as the analysis of severe accidents in nuclear reactors<sup>[8]</sup>, understanding  
73 cement clinkering reactions<sup>[9]</sup> and examining the effect of the quality of sand used as a fluxing addition in copper converting on slag  
74 formation<sup>[10]</sup>. Its current coverage in terms of major and minor elemental additions is illustrated in Figure 2 and several recent applications  
75 are discussed below.

## 76 77 **Modern Copper Scrap Smelting**

78  
79 WEEE (waste electric, electronic equipment) smelting is an efficient way to recover, along with the major metals copper and nickel, also  
80 rare and expensive trace elements from end-of-life computers and cell phones. As WEEE feedstock is low in calorific value and consumes  
81 often unknown amounts of combustion air, it is commonly smelted in converter type vessels such as Kaldo or TSL (Top Submerged Lance)  
82 furnaces<sup>[11]</sup>. The valuable metals are collected by a suitable metal bath, such as copper or lead<sup>[12]</sup>, and typically iron and aluminium are  
83 oxidized to slag. The slags produced differ from conventional copper smelting and refining slags in one essential feature: they contain  
84 significant fractions of alumina<sup>[13]</sup> due to incomplete liberation of aluminium parts from the other metal components in the man-made  
85 materials.

86  
87 Alumina-bearing copper smelting slags with an iron-silicate basis formed during smelting may contain up to 10-20 wt% Al<sub>2</sub>O<sub>3</sub> which  
88 modifies their physical properties, such as viscosity and surface energies, but also the thermodynamics of their oxide constituents and thus  
89 metal value distributions. The first critical issue in these WEEE slags for their industrial use is the domain of fully molten slag and the  
90 processing window it allows in terms of the prevailing oxygen pressure. This can be studied computationally using the MTOX database,  
91 either in copper-free conditions or in equilibrium with oxygen-bearing crude copper. The key question is how and in which direction  
92 alumina concentrations of 10-20 wt% modify the common iron silicate slag at typical copper refining temperatures.

93  
94 For initial scouting purposes, the Fe-O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system was studied in order to find suitable slag composition domains for the smelting  
95 and refining steps of WEEE treatment with copper as the collector metal. For clarity, the role of dissolving copper in the slag chemistry  
96 was left to be considered at a later stage, but the calculations incorporated conditions corresponding to the reduction of metallic iron from  
97 the slag. The slag-metal-gas system was defined using Al<sub>2</sub>O<sub>3</sub>, FeO, SiO<sub>2</sub> and O<sub>2</sub> as components, and the retrieved system from MTOX  
98 (version 8.1) contained 15 phases competing for stability at equilibrium. The liquid oxide and liquid alloy phases were modelled in terms of  
99 non-ideally interacting species, including pure metals, oxides and associates. The solid solution phases spinel, corundum, FCC\_A1,  
100 BCC\_A2, mullite, α'-C<sub>2</sub>S and halite were described using the compound energy model. All remaining solid phases were stoichiometric  
101 substances. The gas phase was modelled ideally. Liquid oxide, liquid alloy, spinel and corundum exhibited the potential for immiscibility at  
102 certain compositions.

103  
104 The development of the molten slag domain in the refining stage was estimated from the liquidus surface diagram constructed for a  
105 constant oxygen pressure of 0.1 Pa ( $9.869 \times 10^{-7}$  atm) with Al<sub>2</sub>O<sub>3</sub>, FeO<sub>x</sub> and SiO<sub>2</sub> as the corner compositions. Univariant equilibria between  
106 the liquid oxide phase and pairs of solid phases are shown as red lines in Figure 3. The diagram shows that the lowest temperature allowed  
107 by high alumina iron silicate slags is below 1523.15 K (1250 °C). The actual calculated eutectic temperature is, in fact, 1501.1 K  
108 (1227.95 °C) at a composition with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> mass fractions of 0.168 and 0.442 respectively. The most probable saturation phase of  
109 the molten slag at smelting and refining temperatures is indicated to be mullite, not pure alumina (or corundum).

110  
111 The effect of oxygen partial pressure on the molten slag domain at 1573.15 K (1300 °C) was demonstrated in a more complicated case,  
112 with CaO fluxing (Figure 4). The diagram has constant alumina and lime concentrations of 10 wt% throughout the composition triangle,  
113 and its corner compositions are FeO, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, each with 10% Al<sub>2</sub>O<sub>3</sub> and 10% CaO. The red lines are isoactivity contours of gaseous  
114 oxygen (as O<sub>2</sub>(g)) superimposed on the isothermal section. The phase diagram shows that the slag remains homogeneous up to relatively  
115 high oxygen activities of 10<sup>-3</sup> to 10<sup>-2</sup> at 1573.15 K (1300 °C). This allows complete oxidation of impurities from the crude copper without  
116 jeopardizing the fluidity of the slag. Fluidity will generally be higher for a single phase liquid as opposed to a liquid containing particles of  
117 a crystalline phase.

## 118 119 **Calculation of slag liquidus temperature in the Outotec® On-line Process Advisor<sup>[14]</sup>**

120  
121 The Outotec® On-line Process Advisor enables on-line and easy dynamic mass and heat balance modelling and control for  
122 pyrometallurgical furnaces, for example the Outotec® Flash Smelting/Converting Furnace and Electric Furnaces. It calculates new  
123 operating parameters from the current operating data for the furnace and transfers information between the process control model, the

124 process control system and the laboratory, on-line. It has an easy-to-use user interface and offers an on-line process flow sheet view  
125 including history browsing.

126  
127 Part of the On-line Process Advisor is an on-line tool for the calculation of slag liquidus temperature, including history browsing, which  
128 helps the furnace operator to adjust the operating temperature of the furnace to a correct level. The calculation of slag liquidus temperature  
129 is based on pre-calculated liquidus isotherms in which the major components of the slag are taken into account. These isotherms represent  
130 systems with more than three components, some having constant concentration throughout the diagram. The compositions are based on  
131 either calculated data or real data from analyses of smelting slags.

132  
133 The On-line Process Advisor shows the current composition of the slag as a red point on the closest isothermal diagram corresponding to  
134 that composition. It calculates the liquidus temperature of the current slag composition based on all diagrams available in the program for  
135 the process in question. Diagrams have already been calculated for a number of different Outotec technologies: Flash Smelting of Copper,  
136 Direct-to-Blister Flash Smelting of Copper, Flash Converting of Copper Matte (Calcium ferrite slag), Flash Smelting of Nickel and Electric  
137 Furnace Smelting of Ilmenite ( $\text{TiO}_2$  slag). The underlying liquidus isotherms in the On-line Process Advisor have been calculated using  
138 MTDATA with the MTOX database used as the source of thermodynamic data for the different slag systems.

139  
140 The slag system for Flash Smelting of Nickel was defined using  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{NiO}$  and  $\text{SiO}_2$  as components in  
141 MTDATA. The system retrieved from MTOX (version 8.0) contained 13 phases among which liquid oxide, spinel, melilite, clinopyroxene,  
142 olivine and halite featured miscibility gaps. The solid solution phases spinel, melilite, clinopyroxene, olivine, halite, wollastonite,  $\alpha'$ - $\text{C}_2\text{S}$ ,  
143  $\alpha$ - $\text{C}_2\text{S}$  and pseudowollastonite were described by sublattice models, and the rest, merwinite, quartz and tridymite, were stoichiometric  
144 substances. Figure 5 is an example of a liquidus isotherm diagram for Flash Smelting of Nickel.

145  
146 The slag system for Electric Furnace Smelting of Ilmenite was defined using  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{FeTiO}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$  as  
147 components. The system retrieved from MTOX (version 8.0) contained 7 phases among which liquid oxide, pseudobrookite,  $\text{Ti}_2\text{O}_3$  and  
148 quartz featured miscibility gaps. The solid solution phases pseudobrookite, rutile,  $\text{Ti}_8\text{O}_{15}$ ,  $\text{Ti}_2\text{O}_3$  and quartz were described by sublattice  
149 models and  $\text{Ti}_{20}\text{O}_{39}$  was a stoichiometric substance. Figure 6 is an example of a liquidus isotherm diagram for Electric Furnace Smelting of  
150 Ilmenite.

#### 151 152 **In-situ Neutron Diffraction Study of BOS slags**

153  
154 A key challenge in the BOS (Basic Oxygen Steelmaking) process, currently the dominant steelmaking process, is to efficiently remove the  
155 impurity phosphorus from hot metal to the BOS slag at low cost. An understanding of the high temperature behavior of the BOS slag is  
156 therefore very important.

157  
158 Previously analyses have been carried out on naturally cooled or “quenched” slags, which may not be truly representative of the phase  
159 combinations which exist at high temperatures. Alternatively phase equilibrium calculations have been made, the results obtained being  
160 predictions, which although based on firm foundations in terms of critically assessed thermodynamic data for low order systems, are  
161 unverified for the multi-component systems that BOS slags represent.

162  
163 Recently, to clarify the phases formed as a function of temperature and composition, Tata Steel have undertaken a real-time, in-situ neutron  
164 diffraction study of BOS type multi-component oxide systems at high temperatures, up to 1973.15 K (1700 °C). This, as yet unpublished  
165 work, has advanced the understanding of the phosphorus refining process and provided valuable experimental information to feed back to  
166 developers of thermodynamic databases for multicomponent oxide systems such as MTOX.

167  
168 Three synthetic BOS-type slags were studied using a specially designed experimental setup at ISIS GEM<sup>[15]</sup>. Their compositions were  
169  $\text{CaO-SiO}_2\text{-}20\text{Fe}_x\text{O-}2\text{P}_2\text{O}_5\text{-}1.5\text{Al}_2\text{O}_3\text{-}3\text{MnO-}6\text{MgO}$  (% by mass) with  $\text{CaO/SiO}_2$  mass ratios of 1.0, 2.0 and 2.5. Analyses of the collected  
170 neutron diffraction data generated relative phase fractions and structure parameters of the phases as a function of composition and  
171 temperature.

172  
173 A preliminary comparison with phase equilibria calculated based upon MTOX data showed good agreement with neutron diffraction data  
174 in terms of the main phases formed but some differences regarding minor phases. In addition calculated liquidus temperatures tended to be  
175 rather high.

176  
177 This valuable information will be analysed further to ascertain whether, for example, the formation of some crystalline phases was  
178 kinetically inhibited. This could account for the discrepancies observed.

#### 179 180 **Purification of $\text{TiO}_2$ by Processing in Molten Salts**

181  
182 A new process for refining rutile slag (95 %  $\text{TiO}_2$ ) by means of complete dissolution in a molten salt (alkali metal chloride-fluoride) at  
183 1023.15 K (750 °C) to permit electro-separation of transition metal impurities has been described<sup>[17]</sup>. Transition metals give the mineral  
184 concentrate a strong colour and must be removed in order to produce pigment grade  $\text{TiO}_2$ .

185

186 Phase equilibrium calculations based upon the MTOX database supplemented by critically assessed data for molten salts systems from the  
187 NPL SALTS database were used to troubleshoot the development of this process predicting conditions under which the TiO<sub>2</sub> yield would  
188 be optimized and calculating limits for the electrolyte composition beyond which TiO<sub>2</sub> contamination was likely to occur due to metal  
189 titanate formation.

190  
191 An example of such a calculation is shown in Figure 7. This shows the masses of phases (on a logarithmic scale) formed at 1100.15 K  
192 (827 °C) in a system containing 24% each of Na and K, 4% TiO<sub>2</sub> and 48 % Cl, (by amount) as Cl is gradually replaced by F. The abscissa  
193 is the fraction of F with respect to the total Cl + F content of the system.

194  
195 Clearly the liquid solvent (molten salt) phase dominates the system for all compositions. If this phase is chloride rich some of the TiO<sub>2</sub> in  
196 the system remains undissolved. As Cl is replaced by F a mixed oxide-fluoride compound, NaFTiO<sub>2</sub> forms. This would cause  
197 contamination of TiO<sub>2</sub> produced using a solvent of the compositions indicated. Only with more than about 75 % F (25% Cl) is no  
198 crystalline metal titanate calculated to form at the chosen temperature.

199  
200 An upper limit for the chloride level in the molten salt solvent was fixed based upon these calculations and subsequent preparations  
201 remained free of metal titanate contamination.

## 202 203 **Realising the International Temperature Scale of 1990**

204  
205 The International Temperature Scale of 1990 (ITS-90) is based upon a number of “fixed point” temperatures, mostly corresponding to the  
206 defined melting temperatures of pure metallic elements. One difficulty encountered in the practical realisation of these fixed points, and in  
207 standard platinum resistance thermometer calibrations<sup>[16]</sup>, arises from the fact that impurities dissolved in each pure metal, at the level of  
208 parts per million, often cause an elevation or depression of the melting temperature of the order of millikelvin.

209  
210 To correct for the effect of impurities a detailed knowledge of the amount and type of impurities is required along with their distribution  
211 coefficients, that is to say the the ratio of solid solubility to liquid solubility, denoted k. The former remains a challenge at ppm levels but  
212 the latter can be addressed either by accurate doping experiments or, in principle, by MTDATA calculations.

213  
214 MTDATA has been used, along with thermodynamic databases for alloys including SGTE solution database, NPL Aluminium database  
215 and the SOLDERS database (created through the COST531 project), to calculate k values for more than 170 binary systems, covering the  
216 fixed point metals Hg, Ga, In, Sn, Zn, Al, Au, Ag and Cu with likely impurities<sup>[16]</sup>. The results have been compared with experimental  
217 measurements. In Figure 8 the results for Al are shown, with k plotted as ordinate and the atomic number of impurity elements as abscissa.  
218 Variations in k with atomic number are clearly predicted well using MTDATA illustrating the potential for using phase equilibrium  
219 calculations in accounting for the effects of impurities in fixed point metals.

220  
221 New work to investigate the effects of oxide impurities on the realisation of fixed point temperatures, using the MTOX database, is  
222 underway.

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247 **Figure Captions**

- 248
- 249 Figure 1. Screenshot of MTDATA calculating a temperature-composition section in the FeO-CaO-Fe<sub>2</sub>O<sub>3</sub>-Cu<sub>2</sub>O system
- 250
- 251 Figure 2. Current MTOX database coverage in terms of major elements (dark shading) and partial additions (lighter shading)
- 252
- 253 Figure 3. Calculated liquidus contours for the Fe-O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at a constant oxygen pressure of 0.1 Pa; the red lines show the
- 254 boundaries between different primary phases (spinel, corundum, mullite, cristobalite, tridymite).
- 255
- 256 Figure 4. Calculated isothermal section of the Fe-O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at 1573.15 K (1300°C) and constant CaO and Al<sub>2</sub>O<sub>3</sub>
- 257 concentrations of 10% by mass; oxygen isoactivity contours are shown as red lines with gaseous O<sub>2</sub> as standard state.
- 258
- 259 Figure 5. Example of a liquidus isotherm diagram for a slag system for Flash Smelting of Nickel
- 260
- 261 Figure 6. Example of a liquidus isotherm diagram for a slag system for Electric Furnace Smelting of Ilmenite.
- 262
- 263 Figure 7. Masses of phases formed (logarithmic scale) as molten (Na,K) chloride is replaced by molten (Na,K) fluoride dissolving TiO<sub>2</sub> at
- 264 1100.15 K (827°C).
- 265
- 266 Figure 8. Distribution coefficients (k) for impurity elements in Al shown as a function of impurity atomic number and compared with
- 267 MTDATA calculations.
- 268