

MTDATA and the Prediction of Phase Equilibria in Oxide Systems: 30 Years of Industrial Collaboration



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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, sulfide, and fluoride systems of industrial interest. The database, MTOX, has been developed over a period of thirty years based upon modeling work at NPL and funded by industrial partners in a project co-ordinated by Mineral Industry Research Organisation. Applications drawn from the fields of modern copper scrap smelting, high-temperature behavior of basic oxygen steelmaking slags, flash smelting of nickel, electric furnace smelting of ilmenite, and production of pure TiO_2 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 realize the SI unit of temperature, the kelvin.

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I. 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, sulfide, and fluoride systems (MTOX) to underpin such calculations. The bulk of this database development work, using the *Calphad* approach,^[1] has been undertaken at NPL (National Physical Laboratory, UK) using the software MTDATA.^[2] 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.

II. MTDATA

The principles of the calculation of chemical and phase equilibria, as described in the review of Bale and Eriksson^[3] 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^[4] 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

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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.

III. MTOX DATABASE FOR OXIDE, SULFIDE, AND FLUORIDE SYSTEMS

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

Crystalline phases have been modeled using the compound energy (sublattice) model^[5] and the liquid phases (alloys, mattes, slags) based upon non-ideally interacting species, either simple elemental, sulfide, and oxide species or associates containing more than one cation, for example CaSiO_3 . The use of the simple, but flexible, associate model has proved to be particularly successful in that easy extension to enable the calculation of thermophysical properties such as viscosity^[6] and electrical conductivity^[7] of slags has been possible.

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

IV. MODERN COPPER SCRAP SMELTING

Waste electric electronic equipment (WEEE) smelting is an efficient way to recover, along with the major metals copper and nickel, also rare and expensive trace elements from end-of-life computers and cell phones. As WEEE feedstock is low in calorific value and consumes often unknown amounts of combustion air, it is commonly smelted in converter-type vessels such as Kaldo or top submerged lance (TSL) furnaces.^[11] The valuable metals are collected by a suitable metal bath, such as copper or lead,^[12] and typically iron and aluminum are oxidized to slag. The slags produced differ from conventional copper smelting and refining

slags in one essential feature: they contain significant fractions of alumina^[13] due to incomplete liberation of aluminum parts from the other metal components in the man-made materials.

Alumina-bearing copper smelting slags with an iron-silicate basis formed during smelting may contain up to 10 to 20 wt pct Al_2O_3 which modifies not only their physical properties, such as viscosity and surface energies, but also the thermodynamics of their oxide constituents and thus metal value distributions. The first critical issue in these WEEE slags for their industrial use is the domain of fully molten slag and the processing window it allows in terms of the prevailing oxygen pressure. This can be studied computationally using the MTOX database, either in copper-free conditions or in equilibrium with oxygen-bearing crude copper. The key question is how and in which direction alumina concentrations of 10 to 20 wt pct modify the common iron-silicate slag at typical copper refining temperatures.

For initial scouting purposes, the $\text{Fe-O-Al}_2\text{O}_3\text{-SiO}_2$ system was studied in order to find suitable slag composition domains for the smelting and refining steps of WEEE treatment with copper as the collector metal. For clarity, the role of dissolving copper in the slag chemistry was left to be considered at a later stage, but the calculations incorporated conditions corresponding to the reduction of metallic iron from the slag. The slag-metal-gas system was defined using Al_2O_3 , FeO , SiO_2 , and O_2 as components, and the retrieved system from MTOX (version 8.1) contained 15 phases competing for stability at equilibrium. The liquid oxide and liquid alloy phases were modeled in terms of non-ideally interacting species, including pure metals, oxides, and associates. The solid solution phases spinel, corundum, FCC_A1, BCC_A2, mullite, $\alpha\text{-C}_2\text{S}$, and halite were described using the compound energy model. All remaining solid phases were stoichiometric substances. The gas phase was modeled ideally. Liquid oxide, liquid alloy, spinel, and corundum exhibited the potential for immiscibility at certain compositions.

The development of the molten slag domain in the refining stage was estimated from the liquidus surface diagram constructed for a constant oxygen pressure of 0.1 Pa (9.869×10^{-7} atm) with Al_2O_3 , FeO , and SiO_2 as the corner compositions. Univariant equilibria between 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 by high alumina iron-silicate slags is below 1523.15 K (1250 °C). The actual calculated eutectic temperature is, in fact, 1501.1 K (1227.95 °C) at a composition with Al_2O_3 and SiO_2 mass fractions of 0.168 and 0.442, respectively. The most probable saturation phase of the molten slag at smelting and refining temperatures is indicated to be mullite, not pure alumina (or corundum).

The effect of oxygen partial pressure on the molten slag domain at 1573.15 K (1300 °C) was demonstrated in a more complicated case, with CaO fluxing (Figure 4). The diagram has constant alumina and lime concentrations of 10 wt pct throughout the composition triangle, and its corner compositions are FeO , Fe_2O_3 , and SiO_2 ,

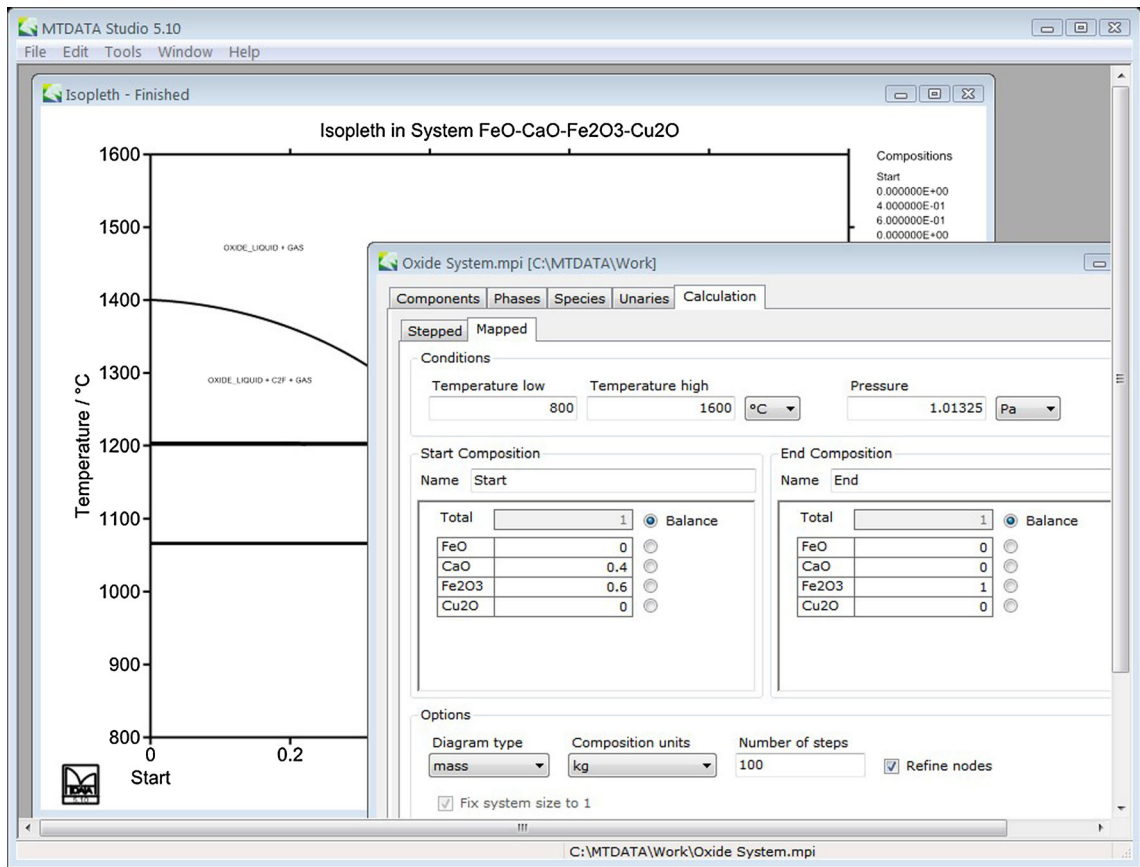


Fig. 1—Screenshot of MTDATA calculating a temperature-composition section in the FeO-CaO-Fe₂O₃-Cu₂O system.

H																	He
Li	Be	Base oxide and / or matte system										B	C	N	O	F	Ne
		Major addition to base system															
		Binary systems only or trace addition										Al	Si	P	S	Cl	Ar
Na	Mg	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
K	Ca	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Rb	Sr	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Cs	Ba	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
Fr	Ra	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Fig. 2—Current MTOX database coverage in terms of major elements (dark shading) and partial additions (lighter shading).

each with 10 pct Al₂O₃ and 10 pct CaO. The red lines are isoactivity contours of gaseous oxygen (as O₂(g)) superimposed on the isothermal section. The phase diagram shows that the slag remains homogeneous up to relatively high oxygen activities of 10⁻³ to 10⁻² at

1573.15 K (1300 °C). This allows complete oxidation of impurities from the crude copper without jeopardizing the fluidity of the slag. Fluidity will generally be higher for a single-phase liquid as opposed to a liquid containing particles of a crystalline phase.

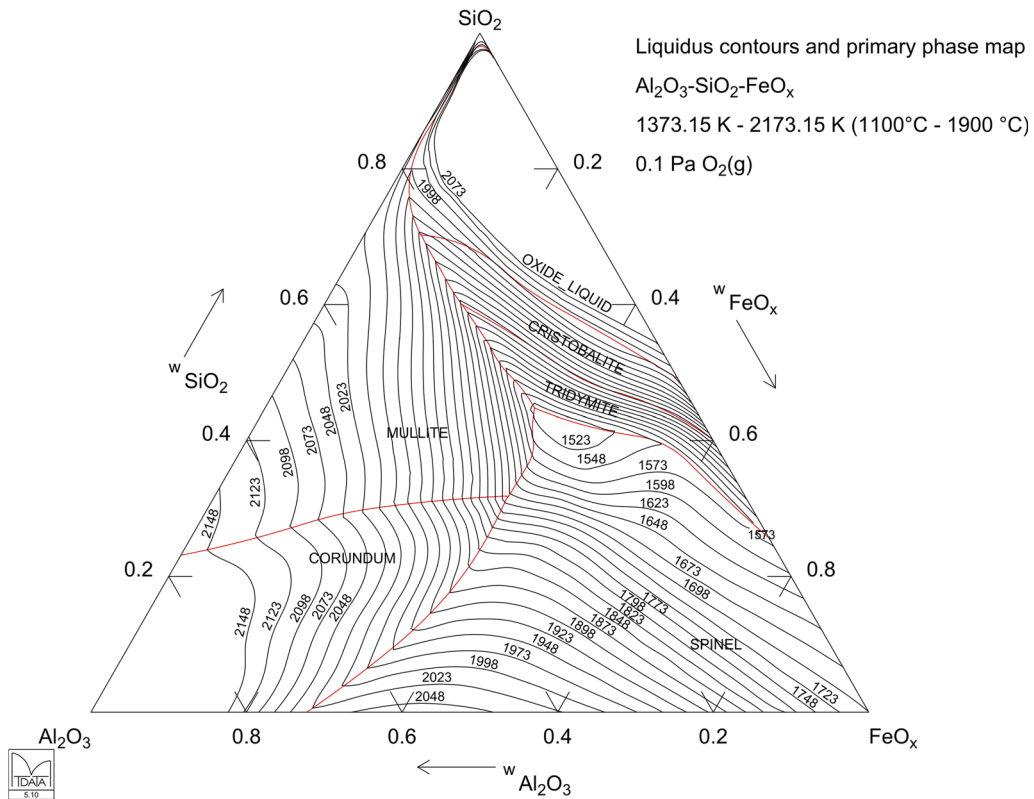


Fig. 3—Calculated liquidus contours for the Fe-O- Al_2O_3 - SiO_2 system at a constant oxygen pressure of 0.1 Pa; the red lines show the boundaries between different primary phases (spinel, corundum, mullite, cristobalite, tridymite).

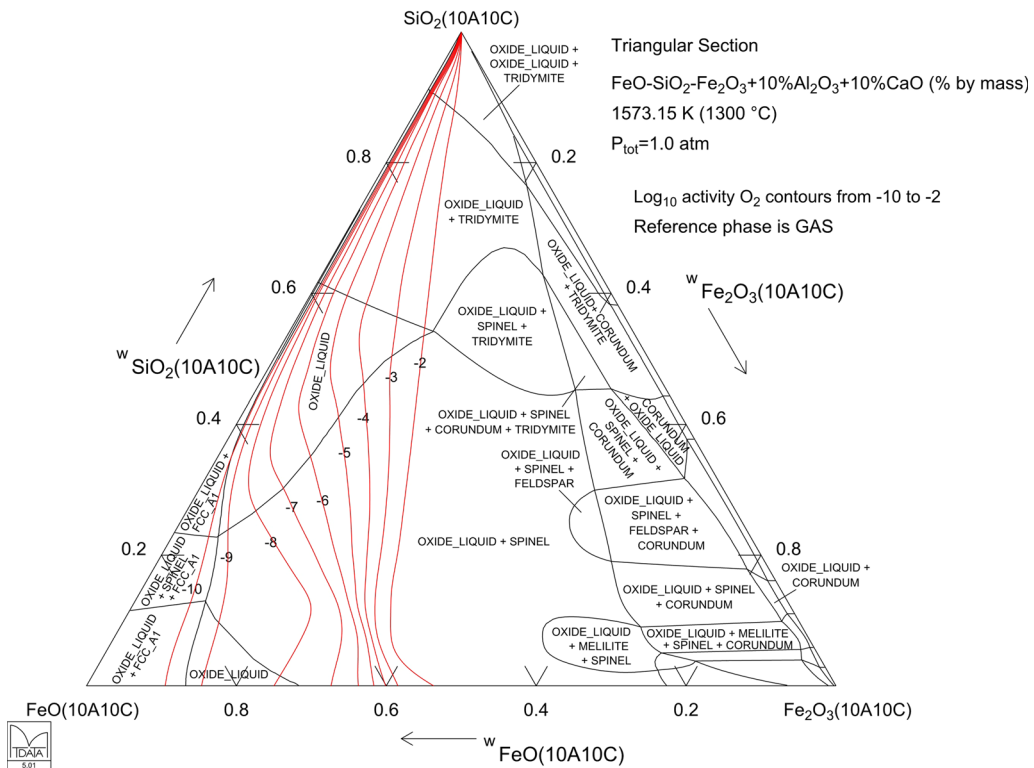


Fig. 4—Calculated isothermal section of the Fe-O-CaO- Al_2O_3 - SiO_2 system at 1573.15 K (1300 °C) and constant CaO and Al_2O_3 concentrations of 10 pct by mass; oxygen isoactivity contours are shown as red lines with gaseous O_2 as standard state.

V. CALCULATION OF SLAG LIQUIDUS TEMPERATURE IN THE OUTOTEC® ON-LINE PROCESS ADVISOR^[14]

The Outotec® On-line Process Advisor enables online and easy dynamic mass and heat balance modeling and control for pyrometallurgical furnaces, for example, the Outotec® Flash Smelting/Converting Furnace and Electric Furnaces. It calculates new operating parameters from the current operating data for the furnace and transfers information between the process control model, the process control system, and the laboratory, online. It has an easy-to-use user interface and offers an online process flow sheet view including history browsing.

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

The On-line Process Advisor shows the current composition of the slag as a red point on the closest isothermal diagram corresponding to that composition. It calculates the liquidus temperature of the current slag composition based on all diagrams available in the program for the process in question. Diagrams have already been calculated for a number of different Outotec technologies Flash Smelting of Copper, Direct-to-Blister Flash Smelting of Copper, Flash Converting of Copper Matte (Calcium ferrite slag), Flash Smelting of Nickel, and Electric Furnace Smelting of Ilmenite (TiO₂ slag). The underlying liquidus isotherms in the On-line Process Advisor have been calculated using MTDATA with the MTOX database used as the source of thermodynamic data for the different slag systems.

The slag system for Flash Smelting of Nickel was defined using Al₂O₃, CaO, Cu₂O, FeO, Fe₂O₃, MgO, NiO, and SiO₂ as components in MTDATA. The system retrieved from MTOX (version 8.0) contained 13 phases among which liquid oxide, spinel, melilite, clinopyroxene, olivine, and halite featured miscibility gaps. The solid solution phases spinel, melilite, clinopyroxene, olivine, halite, wollastonite, α' -C₂S, α -C₂S, and pseudowollastonite were described by sublattice models, and the rest, merwinite, quartz, and tridymite, were stoichiometric substances. Figure 5 is an example of a liquidus isotherm diagram for Flash Smelting of Nickel.

The slag system for Electric Furnace Smelting of Ilmenite was defined using Al₂O₃, CaO, FeTiO₃, MgO, SiO₂, Ti₂O₃, and TiO₂ as components. The system retrieved from MTOX (version 8.0) contained 7 phases among which liquid oxide, pseudobrookite, Ti₂O₃, and quartz featured miscibility gaps. The solid solution phases pseudobrookite, rutile, Ti₈O₁₅, Ti₂O₃, and quartz

were described by sublattice models, and Ti₂₀O₃₉ was a stoichiometric substance. Figure 6 is an example of a liquidus isotherm diagram for Electric Furnace Smelting of Ilmenite.

VI. IN SITU NEUTRON DIFFRACTION STUDY OF BOS SLAGS

A key challenge in the basic oxygen steelmaking (BOS) process, currently the dominant steelmaking process, is to efficiently remove the impurity phosphorus from hot metal to the BOS slag at low cost. An understanding of the high-temperature behavior of the BOS slag is therefore very important.

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

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

Three synthetic BOS-type slags were studied using a specially designed experimental setup at ISIS GEM.^[15] Their compositions were CaO-SiO₂0Fe_xO-2P₂O₅-1.5Al₂O₃-3MnO-6MgO (pct by mass) with CaO/SiO₂ mass ratios of 1.0, 2.0, and 2.5. Analyses of the collected neutron diffraction data generated relative phase fractions and structure parameters of the phases as a function of composition and temperature.

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

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

VII. PURIFICATION OF TiO₂ BY PROCESSING IN MOLTEN SALTS

A new process for refining rutile slag (95 pct TiO₂) by means of complete dissolution in a molten salt (alkali metal chloride-fluoride) at 1023.15 K (750 °C) to permit electro-separation of transition metal impurities has been described.^[16] Transition metals give the mineral

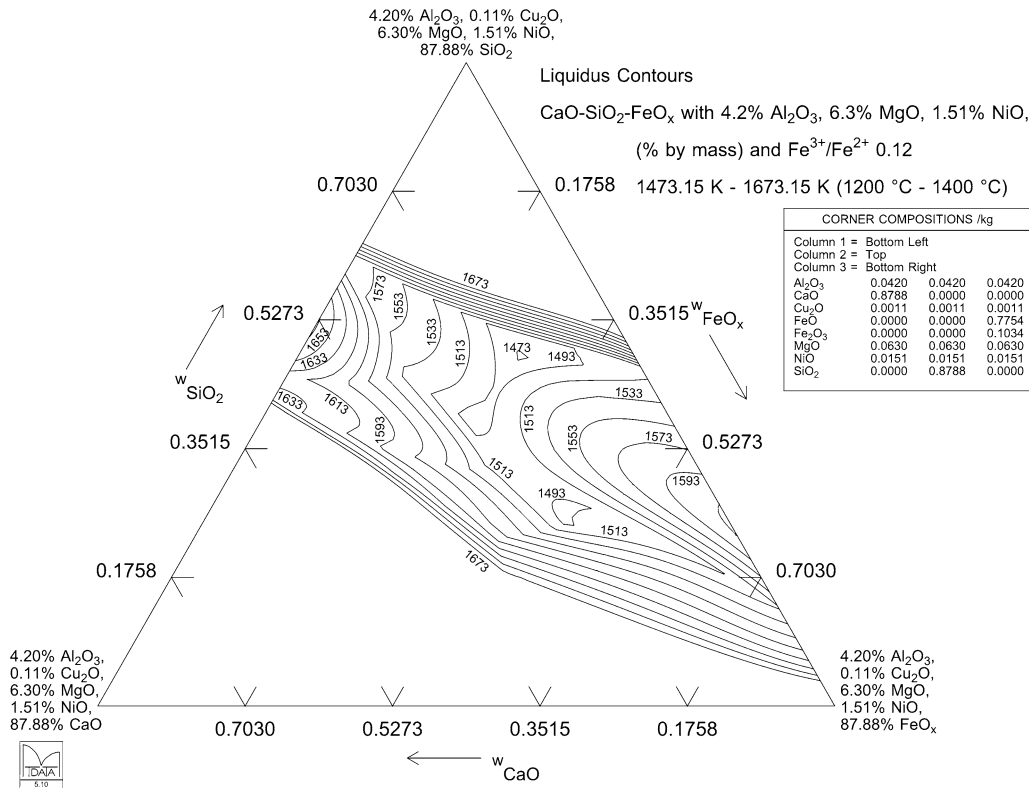


Fig. 5—Example of a liquidus isotherm diagram for a slag system for Flash Smelting of Nickel.

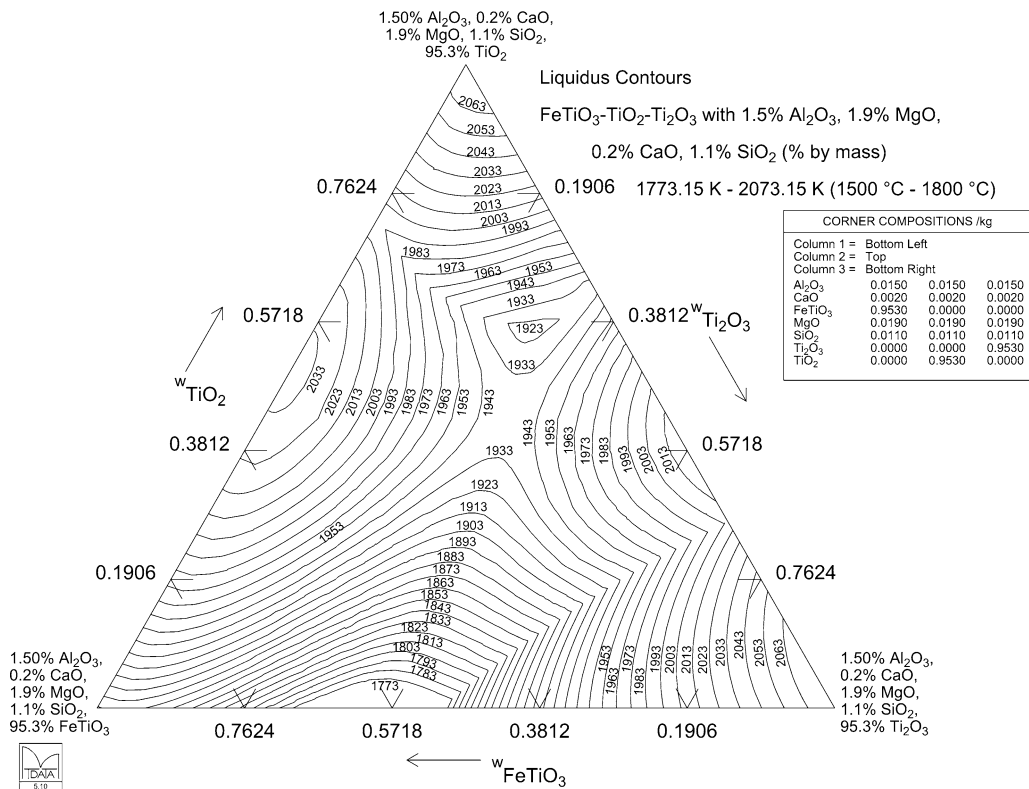


Fig. 6—Example of a liquidus isotherm diagram for a slag system for Electric Furnace Smelting of Ilmenite.

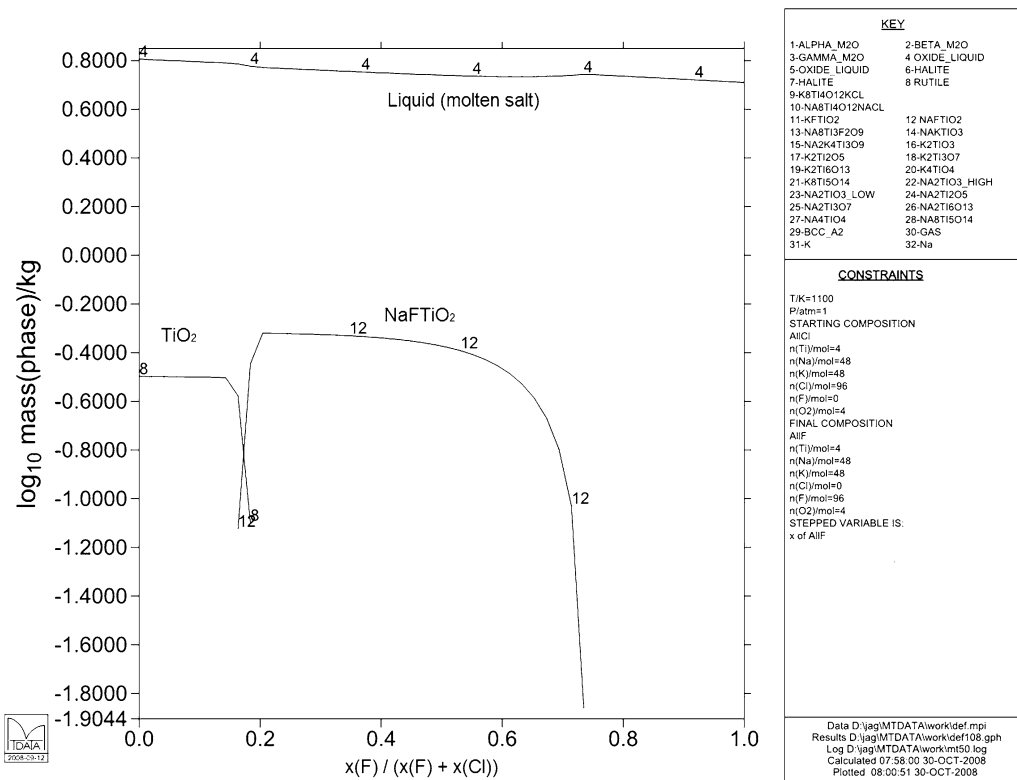


Fig. 7—Masses of phases formed (logarithmic scale) as molten (Na,K) chloride is replaced by molten (Na,K) fluoride dissolving TiO₂ at 1100.15 K (827 °C).

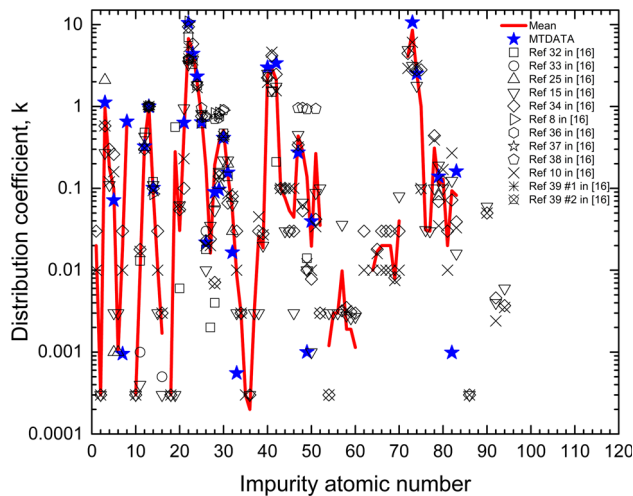


Fig. 8—Distribution coefficients (*k*) for impurity elements in Al shown as a function of impurity atomic number and compared with MTDATA calculations.

concentrate a strong color and must be removed in order to produce pigment-grade TiO₂.

Phase equilibrium calculations based upon the MTOX database supplemented by critically assessed data for molten salts systems from the NPL SALTS database were used to troubleshoot the development of this process predicting the conditions under which the TiO₂ yield would be optimized and calculating the limits for the

electrolyte composition beyond which TiO₂ contamination was likely to occur due to metal titanate formation.

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 (827 °C) in a system containing 24 pct each of Na and K, 4 pct TiO₂, and 48 pct Cl, (by amount) as Cl is gradually replaced by F. The abscissa is the fraction of F with respect to the total Cl + F content of the system.

Clearly the liquid solvent (molten salt) phase dominates the system for all compositions. If this phase is chloride rich some of the TiO₂ in the system remains undissolved. As Cl is replaced by F a mixed oxide-fluoride compound, NaFTiO₂ forms. This would cause contamination of TiO₂ produced using a solvent of the compositions indicated. Only with more than about 75 pct F (25 pct Cl) is no crystalline metal titanate calculated to form at the chosen temperature.

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

VIII. REALIZING THE INTERNATIONAL TEMPERATURE SCALE OF 1990

The International Temperature Scale of 1990 (ITS-90) is based upon a number of “fixed-point” temperatures, mostly corresponding to the defined melting temperatures of pure metallic elements. One difficulty

encountered in the practical realization of these fixed points, and in standard platinum resistance thermometer calibrations,^[17] arises from the fact that impurities dissolved in each pure metal, at the level of parts per million, often cause an elevation or depression of the melting temperature of the order of millikelvin.

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

MTDATA has been used, along with thermodynamic databases for alloys including SGTE solution database, NPL Aluminium database, and the SOLDERS database (created through the COST531 project), to calculate k values for more than 170 binary systems, covering the fixed-point metals Hg, Ga, In, Sn, Zn, Al, Au, Ag, and Cu with likely impurities.^[17] The results have been compared with experimental measurements. In Figure 8, the results for Al are shown, with k plotted as ordinate and the atomic number of impurity elements as abscissa. Variations in k with atomic number are clearly predicted using MTDATA illustrating the potential for using phase equilibrium calculations in accounting for the effects of impurities in fixed-point metals.

New work to investigate the effects of oxide impurities on the realization of fixed-point temperatures, using the MTOX database, is underway.

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