Role of Research in Non-ferrous Metallurgy Development—Peter Hayes' Contributions to Modern Pyrometallurgy

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Abstract A whole new group of non-ferrous pyrometallurgical processes with the ability to utilize tonnage oxygen and capture sulphur dioxide were developed and commercialized over the period 1940s–1980s. Many of these earlier process developments were undertaken with limited knowledge of the process chemistry and influence of key process variables; in many cases, piloting helped provide much new physico-chemical data, but gaps remained. The second generation versions of these technologies of today provide all the primary copper, nickel and lead produced worldwide by pyro-metallurgical smelting. Further, process development has continued and a new generation of copper and lead smelting technologies have also been developed in China since the 1990s. The older reverberatory and blast furnaces have been progressively replaced by the newer technologies—a good example being the introduction in 1992 of the copper IsaSmelt technology at the Mt. Isa smelter in Australia where the former fluid bed roaster and reverberatory furnaces were replaced by a single new smelting unit, together with an acid plant for sulphur dioxide collection. The development of these new technologies was made possible by investment in fundamental and applied research. The lesson for the future is, in order to sustain these improvements, continued investment in research and development capability is required—to do otherwise is to risk obsolescence and lack of competiveness in the world market. Dr. Peter Hayes at The University of Queensland is one of the many researchers and process engineers who have contributed to the fundamental understanding of metallurgical processes over this period of rapid change in technologies. The present paper briefly outlines some of the many contributions Peter Hayes has made to the understanding of kinetics, mechanisms and phase equilibria in metallurgical systems, and metallurgical process development.

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Introduction

The availability of metallurgical chemical and physico-chemical data often in the past has lagged behind new process technology developments. The classic cases include Bessemer's development of the pneumatic converter for steelmaking unveiled in 1856 before understanding of the control of phosphorus levels in steel was mastered, or some decades later, commercialization of the Manhes copper converter in France in 1880 occurred before data were available on copper levels in oxidized converter slags. In other words, often a process was typically developed independently of underlying knowledge.

Closer to the present era, this was the situation regarding a number of the new copper, lead and nickel smelting processes developed over the period 1940s–1970s before theoretical and experimental physico-chemical data applicable to the new processes were available. In many cases, the new metallurgical systems and their control were not only different but were considerably more complex than those of the older processes. For example, when the Outokumpu flash furnace was first piloted in Finland in 1947, much physico chemical data were lacking—in effect, original data were generated as piloting progressed. Understanding the phases present in the Noranda Process in the 1970s represented a stretch of known metallurgy that had largely focused on the fuel-fired reverberatory furnace—the workhorse technology of the industry for over a century. The Mitsubishi process, commercialized in 1974, utilized a new slag system for nonferrous metallurgy referred to as a "calcium ferrite" slag based on the $CaO–FeO–Fe_2O_3$ system. While generally known in the iron and steelmaking literature at that time, it still needed considerable work for application to the conditions of the new copper smelting system. The system was the subject of significant test work in Japan in the 1960s–1970s. It is noted that the late Professor Akira Yazawa and colleagues at Tohoko University in Japan and the late Professor Reinhardt Schuhmann of MIT and later Purdue University, USA had both pioneered improved understanding of the thermodynamics of the then conventional copper smelting systems from about the 1950s.

Thus, initially there were gaps in the literature or large variations in applicable thermodynamic data ranging from information on the free energy of formation of oxides for example, to activity data of certain solutes in liquid metal or slag phases. Peter Hayes is considered as one of the trail blazers in both developing and employing techniques for experimentally identifying reaction mechanisms and measuring chemical equilibria in pyrometallurgical systems, and expanding metallurgical knowledge in these areas. This paper explores Dr. Hayes' contribution to this story of metallurgical development. It is noted that Peter Hayes' work extended

into many aspects of ferrous and non-ferrous metallurgy for both primary and secondary production of metals, however the present paper deals with one corner of Peter Hayes' work—nonferrous smelting of copper, lead and nickel. Dr. Hayes work in other systems is acknowledged and a full list of his published papers is included in a separate paper by the present authors in this Symposium volume.

Non-ferrous Process Developments

During the period before the 1940s up to about the 1980s, most of the world's primary copper, nickel and lead was produced using reverberatory and/or blast furnace technologies plus the Peirce-Smith converter.

A case in point was the Mt. Isa smelter in Australia which used the reverberatory furnace up until 1992, or the present Glencore smelter in Sudbury, Ontario, Canada, which used the nickel blast furnace up until about 1980.

It is not a coincidence therefore that much of the early experimental work on phase equilibria and thermodynamics pertaining to copper smelting explored matte and slag systems common to reverberatory/Peirce-Smith converter systems. Examples are seen in the early work by Schuhmann et al. [1], Korakas [2] and Taylor et al. [3] to just name three (although the latter two studies extended measurements to the range of oxygen potential also applicable now to high-grade matte smelting and continuous converting operations). It was known, for example, that CaO in reverberatory furnace slag gave lower copper losses, however the exact mechanism and relationships were not known (for example, slag at the Gaspe smelter in Canada with 7% CaO (and 39% SiO_2) assayed about 0.27% Cu (for 33% Cu matte). This result at the Gaspe smelter was the lowest copper level in slag out of 26 smelters [4]).

At the time of the original development of the Noranda Process (for example the period mid-1960s to mid-1970s), there were insufficient physico-chemical data available to fully describe the new slag-matte-metal system involved; laboratory and pilot plant data thus provided much of the early information. One of the present authors (PJM) recalls that both Ruddle's classic text [5], first published in 1953, and the text, "Phase Diagrams for Ceramists" published in 1964 [6] were constant reference books at Noranda. The FeO–Fe_2O_3–SiO_2 phase diagram (Fig. 1) provided important liquidus data at the time [6]; however, the impact of oxides such as Al_2O_3, CaO, MgO or ZnO at Fe_3O_4 saturation was not well known and had to be extrapolated from available diagrams in Ref. [6]—which were in fact typically based on experimental work under conditions of iron-saturation and hence not readily applicable. Published information on the behaviour of minor elements in copper smelting at that time was not generally available. In one study of the behaviour of minor elements in the Noranda Process [7], engineers were forced to turn to early distribution data from publications in Transactions of the AIME dating to the 1900s!
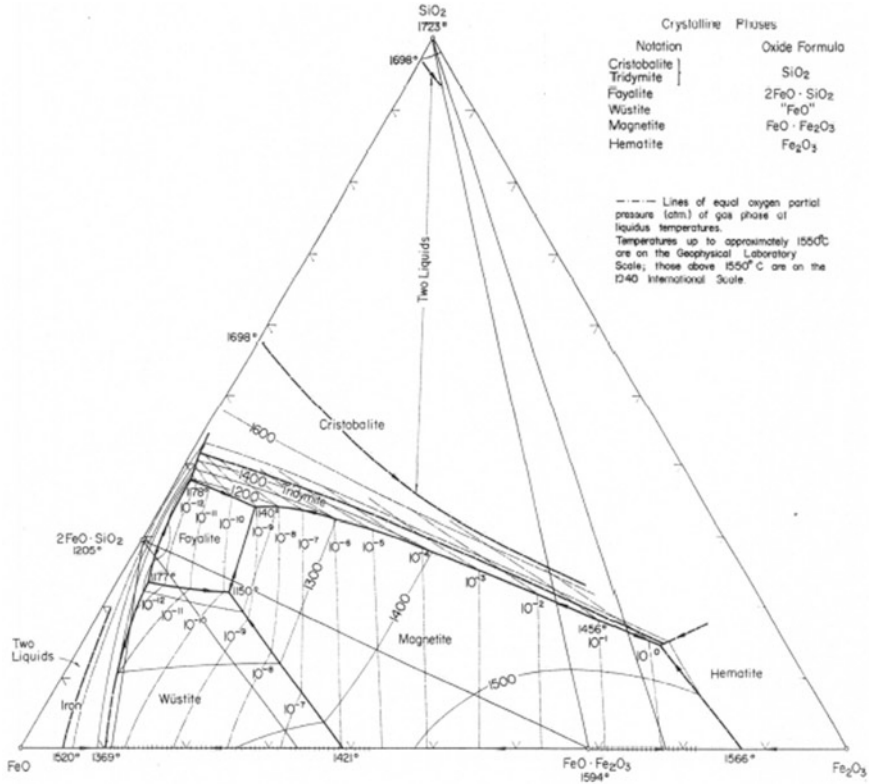
FIG. 82.—System FeO–Fe₂O₃–SiO₂; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 6, Published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

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Fig. 1 The FeO–Fe₂O₃–SiO₂ system [6]. This diagram was important in early development work on copper smelting processes before details of the impact of other oxides were known, such as those provided by Peter Hayes and co-workers

Gradually the picture changed with a large body of research work published on the emerging new copper smelting processes by the 1980s–1990s (for example refer Ref. [4]).

Pyrometallurgy continues to play the dominant role in primary metal production from copper, lead, nickel and complex bulk lead/zinc sulphide concentrates, and also nickel from laterites. Increasingly, however, secondary (recycled) copper and industrial waste materials are being incorporated into existing primary metal

operations and in addition, new dedicated pyrometallurgical reprocessing facilities are being designed and implemented.

The industry faces ongoing challenges as the characteristics of these waste and recycled materials have changed with time. Lead-containing cathode ray tubes, once a major hazardous waste, are no longer used in televisions and stocks of used appliances of this type are dwindling, replaced by liquid crystal and plasma display devices. Lead acid starter batteries in vehicles will be increasingly replaced in the future with batteries having very different components for use in powering electric cars. Copper wire telephone landlines are being replaced by mobile phones, increased quantities of waste electric and electronic equipment (referred to as WEEE) containing a wide range of valuable metallic elements are being collected and treated.

These technological changes cannot be efficiently and effectively undertaken without corresponding advances in fundamental understanding of the underlying process metallurgy and the development of tools to assist in quantifying the impacts of process changes. These tools and devices we now take for granted, but perhaps we do not appreciate that they were not always there as further discussed below.

Recent Advances in Metallurgical Research Capabilities

There have been major advances in our knowledge and understanding of process fundamentals, and research capabilities over the past 50 years, from a time before the digital age and the use of modern computer tools.

- Thermodynamic calculations have progressed in capability from regular solution models to the sophisticated, multi-component, multi-phase computer-based predictive platforms of today. These enable routine calculation and prediction of the outcomes of chemical reactions, replacing simpler approaches, using software packages such as Factsage.
- Thermodynamic data have been extended from phase diagrams in binary, and selected ternary and higher order systems, to complex, multi-component systems in alloys, slags, mattes and solid solutions. Laboratory data on elemental distributions between phases have also been extended to more complex systems, approaching those encountered in industrial plants.
- Heat and mass transfer calculations are no longer confined to analytical mathematical solutions of thermally activated processes, describing mass and thermal diffusion-limited processes for simple geometries. The experimental characterisation of fluid flow phenomena by using cold physical models as analogues for high temperature systems has been largely superseded by the use of computational fluid dynamic (CFD) tools, enabling decreased design and development costs, and the optimisation of reactor geometries; still, however, measurements such as tracer tests have a place in verifying model work.

- Bulk chemical analysis and optical metallographic techniques can now be supplemented with detailed examination of sample microstructures using electron microscopy (scanning electron microscopy or SEM). Accurate measurement of the compositions of individual phases is now possible using electron microanalysis techniques, such as, energy dispersive (EDS) and wavelength dispersive spectrometers (EPMA). The presence of defects in crystal lattices and even the positions of individual atoms can now be resolved using high resolution transmission electron microscopy (TEM) techniques. This enables the forensic analysis of samples to be undertaken, providing invaluable insights into the conditions present in commercial furnaces—conditions that could not previously be characterised or measured.
- Spectrometric techniques provide identification and quantification of ionisation states of elemental species in solutions.
- Online measurement of solution composition, the effective oxygen potentials in metallurgical phases and gas analysis can assist in process control.
- Older batch processes are being progressively replaced by continuous process technologies, e.g. new flash and bath continuous converting technologies, or continuous lead and tin refining techniques, providing increased energy efficiencies and reduced environmental impact.
- Computational tools enable mass and energy balances to be undertaken on complex process flowsheets enabling improved design, reduced capital costs and process optimisation.

Where did these advances, along with necessary support for the industry, come from?

These outcomes are largely the result of fundamental and applied research undertaken in our Universities, government sponsored research laboratories and selected companies. Fundamental and applied research has contributed in a number of ways.

Clearly, this research has resulted in the building of fundamental knowledge and the measurement of phase property data, and the development of theoretical models and research and development tools. These activities also provided the opportunities to generate develop and incubate new process ideas and concepts, step change/disruptive technologies. This research has not only provided deeper and broader scientific understanding, but also research training, and the opportunities to transfer specialist knowledge and skills to the bright minds needed by industry today.

The reality is then that industry today has benefited from the investment of time, effort and resources made by previous generations. We are all aware it takes time, years and in some cases decades, to develop new process concepts and translate these ideas into industrial practice. Strategic thinking and commitment is required to ensure that the pipeline of ideas and technical improvement does not dry up due to lack of investment in people and ideas. We need to invest in the future in order to survive in the competitive and changing world that is the metallurgical industry.

We need to continue to ensure that we, as an industry, support such efforts, and we have access to and fully utilise the research capabilities needed to both continue efficient operations and to support change.

Peter Hayes' Contributions to Metallurgical Research and Support for Metallurgical Process Development

As pointed out in the introduction, Peter Hayes and his colleagues at The University of Queensland have developed and employed new experimental techniques for the characterisation of pyrometallurgical systems, extending the knowledge of process metallurgy fundamentals.

Peter Hayes' research on the mechanisms and kinetics of heterogeneous solid/ solid, gas/solid and liquid/solid reactions started with studies on heterogeneous reactions taking place during the nitriding of steels. As part of this work, experiments were devised to provide the first direct evidence for diffusion limited and chemical reaction interface control of precipitate growth in solids through the use of in situ transmission electron microscopy [8].

This interest in heterogeneous reaction mechanisms and the use of electron microscopy as a key tool to examine metallurgical systems was later extended to detailed studies of the mechanisms of gaseous reduction of iron oxides. Figures 2a–d illustrate examples of some the different interface structures that have been identified to date in solid-gas systems [9–11]. Peter Hayes has demonstrated that these heterogeneous gas/solid reaction systems are part of a broader class of analogous fluid/solid reaction systems, including the solidification of melts systems, whose behaviour are governed by instability criteria at moving interfaces [12]. These criteria determine the transition from planar to cellular and dendritic product morphologies [13].

These were not just academic studies—their application extended to practical systems. The example shown in Fig. 3 is the first known reported observation of nano-sized Ni–Fe alloy particles formed as a result of gaseous reduction of nickel-containing saprolite ore in the Caron nickel production process, in use at the former Queensland Nickel operation in Queensland. Traditionally the Caron process was used on limonitic ores, this investigation explored extending this to saprolitic laterite ores. Counterintuitively the overall recovery of nickel in subsequent ammonia leaching was observed to decrease on increasing the reduction temperature. This was shown [14, 15] to be the result of the encapsulation of the alloy particles in a recrystallized olivine matrix (a known but little understood phenomena), which was impermeable to the ammonia leach solution.

As told to the present authors, it was during a summer sabbatical at the laboratories of CSIRO in Melbourne, Victoria, Australia in the mid-1980s that Peter Hayes recognised the gap in fundamental slag equilibria data needed to understand and optimise the operation of the new technologies. Dr. Hayes was working
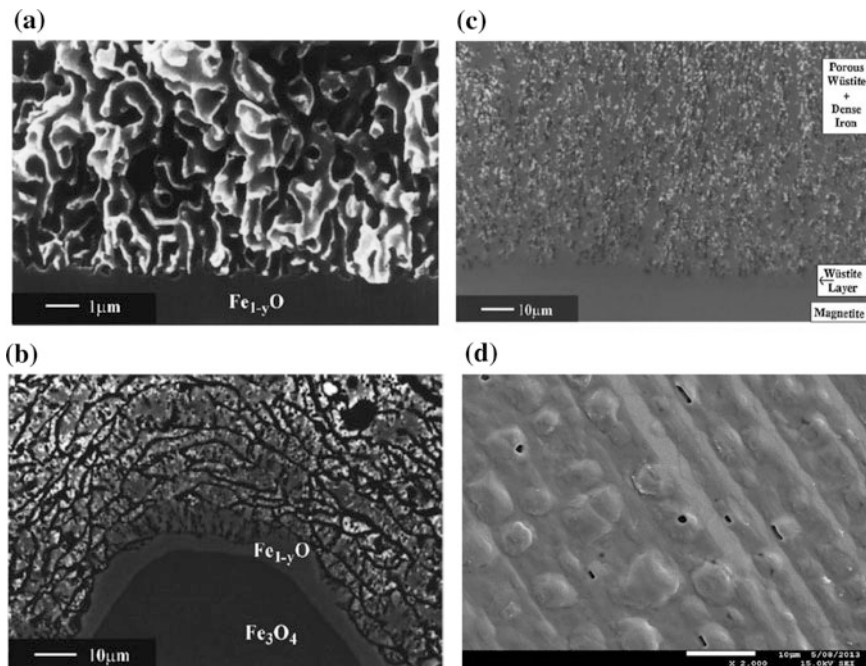
Fig. 2 **a–d**—Examples of different interface structures formed during gaseous reduction of metal oxides in H_2/H_2O gas mixtures, **a** Continuous coupled growth of gas pores and iron metal, **b** Instability formation in wustite resulting in periodic splitting of the wustite product layer and discontinuous growth, **c** Continuous growth of gas pores covered with dense iron, **d** Bursting of dense nickel layers on NiO leading to discontinuous growth [9–11]

alongside Dr. W. T (Bill) Denholm who was carrying out test work on the then new Sirosmelt process for lead and copper smelting, pioneered earlier by Dr. John Floyd of CSIRO [16].

This realisation prompted the start of pioneering work on the development of new techniques for phase equilibria characterisation and the start of a long-standing research partnership with Evgueni Jak in the early 1990s, which continues today.

New techniques for studying gas-slag-solids and gas-slag-matte-solids equilibria were developed using electron microprobe X-ray microanalysis with Wavelength Dispersive Detectors enabling accurate measurement of the individual phases present in the samples to be made rather than relying on the bulk mixture composition and X-ray powder diffraction to characterise the system [17, 18].

Examples of this research include, the first descriptions of the liquidus of lead IsaSmelt and other high lead/zinc smelting slags by the pseudo-ternary system ZnO–"Fe_2O_3"–($PbO+CaO+SiO_2$) in air, as illustrated in Fig. 4 [19, 20]. This was followed by systematic studies of the liquidus of ZnO–Fe_2O_3–($CaO+SiO_2$) slags at iron metal saturation [20], relevant to zinc fuming, and closely related to lead and zinc blast furnace slags. The liquidus and isotherms in the Cu_2O–Fe_2O_3–SiO_2
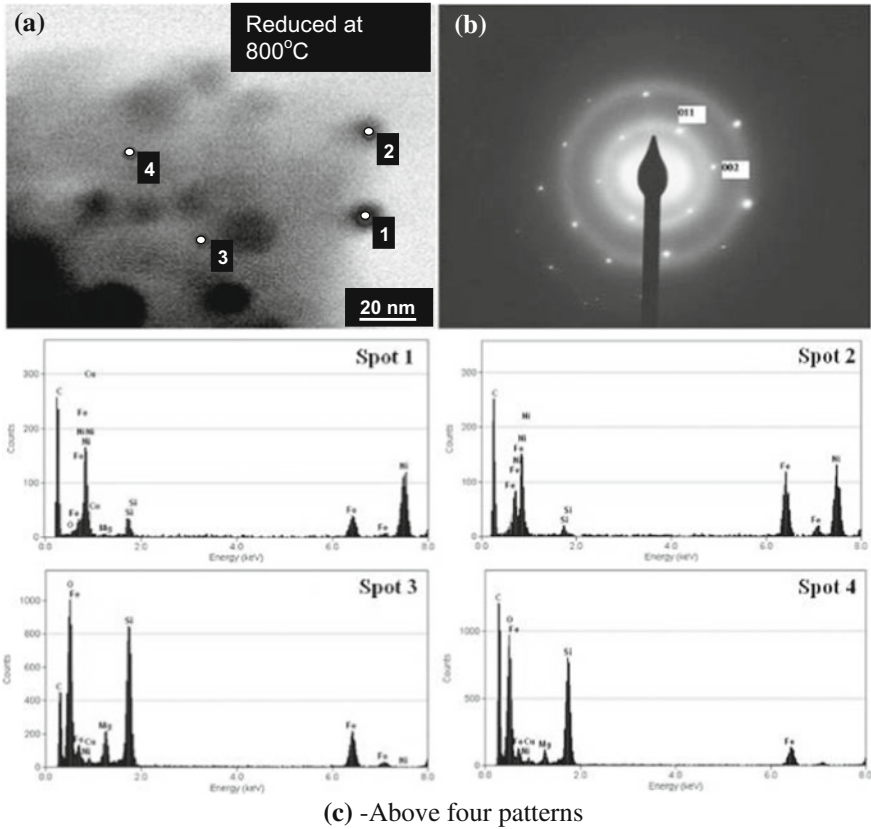
(c) -Above four patterns

Fig. 3 a TEM image of nano-sized Ni–Fe alloy particles formed in nickel-containing serpentine reduced in $15\%H_2/N_2$ for 30 min at 800 °C; **b** Selected area diffraction (SAD) pattern ((010) FCC) of Ni–Fe alloy; **c** Energy dispersive spectrometer (EDS) spectra of points shown in Fig. 2a [7, 8]

system in equilibrium with metallic copper at high copper oxide concentrations is shown in Fig. 5 [21, 22]—directly relevant to direct-to-blister copper smelting and conventional copper converting, including continuous converting. Of interest, data from Ruddle et al. [3] noted above were seen to be favourably shown in the figure. The effect of the ratio SiO_2/Fe and the ratio CaO/SiO_2 on the measured liquidus temperature at fixed oxygen pressure is illustrated in Fig. 6 for the ferrous calcium silicate slag system; liquidus measurements on the same system at copper metal saturation have also been undertaken [23, 24]. The application of the techniques has been extended to non-silicate slags systems, such as the liquidus of the Cu_2O–FeO– Fe_2O_3–CaO system at copper metal saturation relevant to Mitsubishi converter, KUCC flash converter and IsaConvert TSL copper converting technologies using Ca fluxing [25]. Slags systems describing the ferronickel smelting of nickel laterites have also been characterised through experimentally measured liquidus isotherms in a high MgO slags in the system MgO–FeO–SiO_2–Al_2O_3 [26].
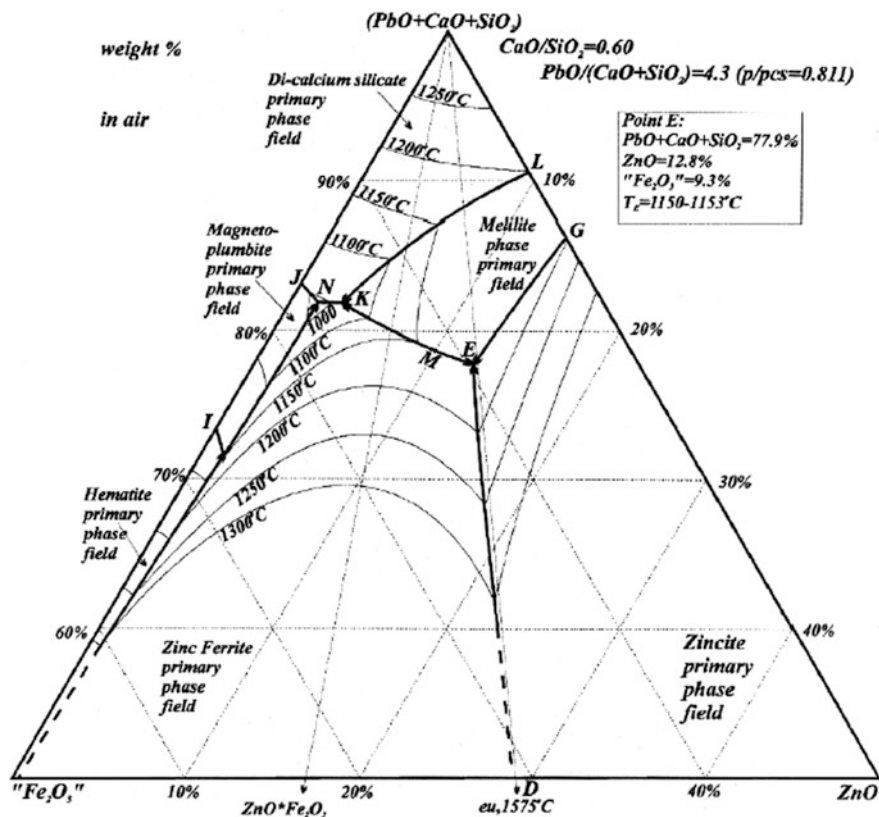
Fig. 4 Experimentally determined liquidus in the system ZnO–"Fe_2O_3"–($PbO+CaO+SiO_2$) system in air; $CaO/SiO_2 = 0.6$, $PbO/(CaO/SiO_2) = 4.3$) [19]

Important work has been carried out on providing a clearer understanding of the formation of protective freeze linings on furnace walls that have externally-mounted copper coolers [27].

In recent years the techniques have been further improved and it is now possible to accurately measure chemical equilibria in multi-component, multi-phase systems extending the range of compositions to non-oxide systems, for example gas/slag/matte/metal/speiss/solid systems [28]. Minor element distributions between these phases can also be measured. Examples of these latest developments are to be found in the present volume [29].

Realising early on the potential of this new experimental approach and the value of the new data, Peter Hayes established strong working relationships with Professors Art Pelton and Chris Bale and the Centre for Research in Computational Thermochemistry (CRCT) at Ecole Polytechnique in Montreal, Quebec, Canada. Starting from 1995, Evgueni Jak whilst working on projects related to coal ash slags, spent a year at CRCT and subsequently revised the (Al–Ca–Fe–Si–O) and
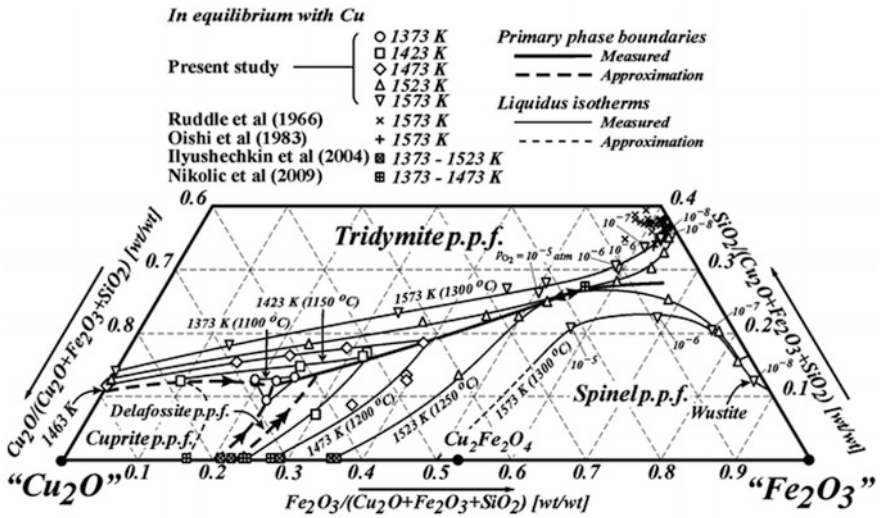
Fig. 5 Liquidus isotherms in the "Cu_2O"–"Fe_2O_3"–SiO_2 system in equilibrium with metallic copper-iron alloy (data points in the pseudo-binary "Cu_2O"–SiO_2 in equilibrium with metallic copper [21] and in the pseudo-binary "Fe_2O_3"–SiO_2 in equilibrium with metallic iron. pO_2 in atm.) [22]
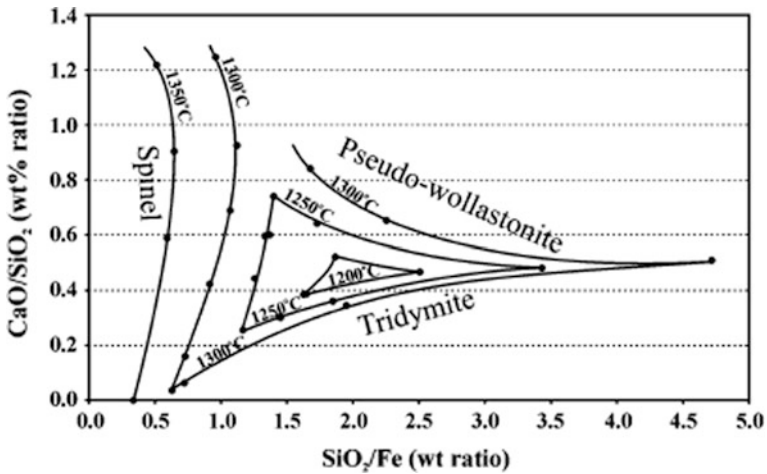

Fig. 6 Experimental measurements defining the effect of temperature on the liquidus of the "FeO"–CaO–SiO_2 system in terms of CaO/SiO_2 and SiO_2/Fe weight ratio at an oxygen partial pressure of 10^{-6} atm. [23, 24]

developed lead-zinc and coal (Al–Ca–Fe–Na–Pb–Si–O–Zn) databases for Fact-Sage. This initiative has resulted in more than a 25-year long collaboration between the research teams in PYROSEARCH and CRCT, in particular Sergei Degterov, and support of the development of FactSage thermodynamic oxide databases [30, 31].

A chronology of selected major research initiatives by Peter Hayes in relation to process developments is of interest, since his career paralleled many key industrial developments. Figure 7 illustrates the chronology of selected major research initiatives by Peter Hayes, Evgueni Jak and coworkers in copper and lead smelting as shown on the x-axis in relation to the year of commercialization of the major copper and lead smelting technologies in use today (y-axis). Each bar on the x-axis indicates a specific initiative, with the bar height denoting year of commencing the work. (Data here are approximate.). It is seen that this research was at the centre of the major developments then underway, and importantly, contributed to the process optimization activities that followed. For reference, details on the chronology of the development of the major commercial technologies in copper, lead and nickel smelting are presented in Table 1.
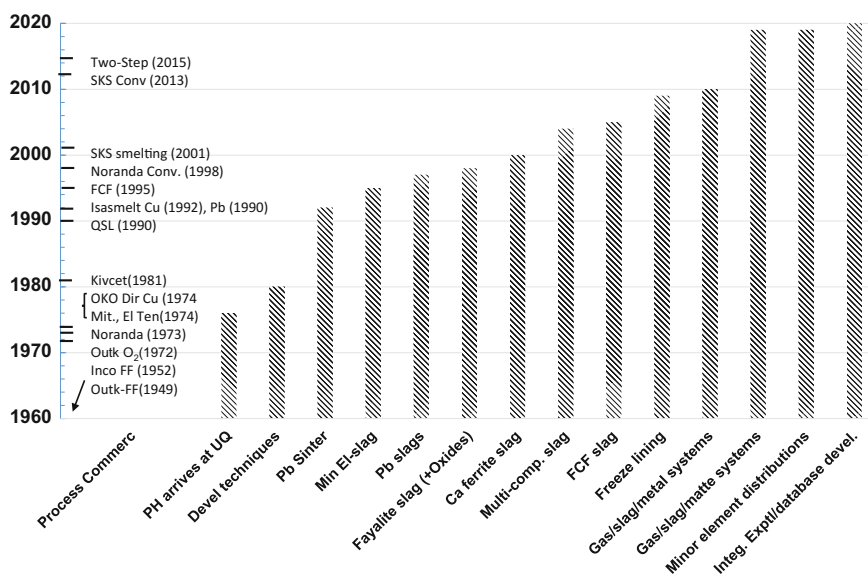

Fig. 7 The chronology of selected major research initiatives in lead and copper smelting by Dr. P. Hayes and co-workers shown on the x-axis in relation to the year of commercialization of the major copper and lead smelting technologies in use today. Each bar on the x-axis indicates a specific initiative, with the bar height denoting year of commencing the work. Data are approximate

Table 1 Chronology of the development of major commercial technologies in copper, lead and nickel smelting

Process	Year started		
	Laboratory tests	Pilot tests	Commercial plant
Non-ferrous electric furnace smelting	~1917	~1917	1917
Electric furnace-PGM concentrates	No lab tests	Year not known	1969
(Outokumpu) flash furnace (air)	No lab tests[a]	1947–1948	1949 (O_2 1972)
Inco flash furnace	1945–1946	1946–1949	1952
Vanuykov process (Cu, Ni)	~1950s	1950–1970s	1977
Outokumpu direct Cu	1960s	1969	1978
Fluidized bed- Electric furnace[b] (Ni)	NA	Used Coy. data	1960
RKEF Fe–Ni smelting	NA	Likely early 1950s	1955
Noranda process	1963–1968	1968–1972	1973 (O_2 1976)
El Teniente process	NA	1972–1974	1974
Mitsubishi process	1961	~Mid 1960s–1972	1974
Ausmelt process (Pb, Sn, Cu, Ni)	1971	1981–1992	1992
Isasmelt process (Pb, Cu)	1978–1979 (Pb)	1980–1985 (Pb), 1987 (Cu)	1990 (Pb), 1992 (Cu)
QSL (Pb)	Late 1970s	1981	1990
Kivcet (Pb)	~1950s	1950s	1984
Kennecott-Outokumpu flash converter	Mid-1980s	1984	1995
Noranda converter	No lab tests	1996–1997	1998
SKS/BBM smelting	NA	1990–2000	2001
SKS converter	NA	<2013	2013
Two-step Cu process	NA	<2015	2015

[a]At the time (mid 1940s), Outokumpu had developed the concept for flash smelting using a vertical cylindrical shaft positioned over a stationary rectangular hearth. It was felt by the developers that the technical information required to design a commercial scale plant could not be determined in the laboratory and they decided to move straight to a 3.1 tonne/hr pilot plant. The design capacity of the first commercial plant was 24,000 tonnes Cu/year (22.84% Cu in conc.), or ~14 tonnes conc./hr., representing a modest scale-up of 4.4 times

[b]Fluid bed roasting of sulphides was commercialized in 1949 on pyritic gold concentrates following a period of laboratory and pilot testing

NA not available

Conclusions

Peter Hayes has been part of the development of new process technologies and improvement to new industrial processes over a number of decades. Today these processes play a huge role in providing a wide range of metals for society. The metallurgical industry continues to see changes in production technologies with increased process efficiencies and reduced environmental impact. Increasingly improvements in design and operations are reliant on advanced process knowledge and predictive tools to reduce development costs and optimise production practices. Continued investment in research capability and people having advanced skills is needed to further improve and sustain metallurgical performance.

Peter Hayes has been an active researcher during this past half century and has made important contributions to our fundamental knowledge of the behaviour of metallurgical systems during this period. Peter has published extensively in the scientific literature and has developed new experimental research techniques that

have greatly extended our research capabilities, provided scientific support for a wide range of industrial processes and assisted and mentored several generations of students to graduate into the metallurgy profession. Peter Hayes has also provided leadership in establishing new interdisciplinary undergraduate and postgraduate education and research programs; he wrote and published undergraduate texts on the principles underpinning metallurgical processing. The emphasis of these contributions has been on understanding and describing process fundamentals as a means of improving problem solving, and providing solutions to metallurgical process problems.

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