Chemical- and Micro-Analytical Techniques for Molten Slags, Mattes, Speisses and Alloys

J. Chen[1], *P. Hayes*[2] *and E. Jak*[3]

1. Theme Leader – Analytical Methods, PYROSEARCH, University of Queensland, Brisbane, QLD, 4072. Email: Jeff Chen <j.chen5@uq.edu.au>
2. Emeritus Professor, PYROSEARCH, University of Queensland, Brisbane, QLD, 4072. Email: p.hayes@uq.edu.au
3. Professor, Centre Director, PYROSEARCH, University of Queensland, Brisbane, QLD, 4072. Email: e.jak@uq.edu.au

Keywords: Analytical techniques, microanalysis, laser ablation, slag, matte, speiss, alloy

ABSTRACT

The paper provides an overview of the various analytical and microanalytical techniques currently in use to characterise the outcomes of pyrometallurgical processes, examining the advantages and limitations of these approaches. Specific focus with be given to quantitative microanalysis techniques including electron probe microanalysis and laser ablation, covering general principles, capabilities and limitations and recent development to address specific challenges associated with analysing molten slag, matte, and alloys, highlighting the necessity of embracing the application of these and other innovative analytical methodologies.

INTRODUCTION

In the field of pyrometallurgy, obtaining accurate analyses of metallurgical materials, particularly slag, matte, speiss and alloys, is imperative for advancing our understanding, and for developing quantitative descriptions, of metallurgical processes. The complex nature of these materials necessitates the application of analytical techniques capable of characterising their chemical compositions, structural properties, mineralogy/phase assemblages, and where appropriate, elemental speciation.

At industrial pyrometallurgical plants, a range of analytical methods are commonly used to facilitate both quality assurance/quality control (QA/QC) processes and assist research and development (R&D). For instance, X-ray fluorescence (XRF), Inductively coupled plasma in conjunction with optical emission spectroscopy (ICP-OES), or inductively coupled plasma in conjunction with mass spectroscopy (ICP-MS) are routinely applied for the bulk chemical analysis of intermediate and final products (e.g., Cu matte and blister), as well as byproducts and waste materials (e.g., slag). These bulk analyses in practice are used to ensure that these materials meet specified quality standards, and the data can be used for overall elemental mass balances across processes and process operations.

To provide a deeper and more complete understanding of these processes it is necessary to utilise more advanced and more specific analytical techniques capable of identifying the phases that are present in the materials and the distribution of elements within these phases. For example, slags are not necessarily homogeneous molten materials, they can contain solids and entrained liquid phases. Detailed analysis of molten materials quenched from the operating temperatures in reactor enable these important details to be identified and accurately characterised and their impacts on, for example, elemental distribution and slag viscosity to be understood and quantified.

The necessity for abundant and accurate experimental data for the development of advanced thermodynamic modelling tools also hinges directly on the availability of suitable analytical techniques. The adaptation of quantitative microanalytical methods such as Electron Probe Micro Analysis (EPMA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) have notably expanded the range of measurable conditions and enhanced data accuracy for phase equilibrium studies. These techniques have proven vital for characterising heterogeneous processes, meeting emerging demands and opening avenues for refining industrial systems. These techniques enable detailed microstructural analysis and accurate composition measurement, detecting elements at minimum levels of ~300 ppm and ppb, with spatial resolutions ranging from sub- to hundreds of microns. Microanalysis of quenched industrial samples also presents a unique opportunity to understand reactor processes, offering insights into kinetic reactions and facilitating the integration of thermodynamic models into real industrial operations.

SAMPLING AND INITIAL INSPECTION

Before embarking on extensive and time-consuming examination of samples it is critically important to ensure that the proposed procedures and practices for obtaining samples for analysis are consistent with the aim of the study. This is especially important at the outset of a new study.

If this is an equilibrium study, then the chemical and physical properties, the chemical composition and proportion of phases of all samples taken from the reaction system should be identical. If there are potentially variations in the reaction or process conditions at the time of sampling, these should be recognised and documented by sampling at appropriate times and positions within the reactor.

Obtaining accurate online chemical and analytical measurements in pyrometallurgical systems is extremely difficult in practice. The approach taken in most studies is to take representative samples and remove them from the reactor and cooling to room temperature, preserving them in a form that reflects their condition at the process temperature. Two typical methods are used to sample slag and other melts.

1. Water-quenching method

A preheated steel spoon can be used to collect molten slag samples at tapping, small aliquots of which are then quickly poured into cold water. This method allows effective quenching of the samples to preserve the phase assemblage at high temperature. However, caution should be taken when quenching samples reactive (sometimes aggressively enough to cause explosion) to water such as slag with high alkaline concentration, and those containing matte, molten salt or molten alloy. Modification to the quenching media is often needed to safely quench these materials.

2. Dip-bar method

A cold metal bar (steel or copper) is quickly submerged and removed into the molten bath, the molten sample in contact with the surface of the metal bar is quenched immediately and the high temperature phase assemblage is preserved. This method allows the sampling conducted in a safe manner. However, typically only tens to hundreds of micrometres of sample next to the sample-metal bar interface are effectively quenched, requiring careful microanalysis of the sample for characterisation. An example is show as in FIG 1.

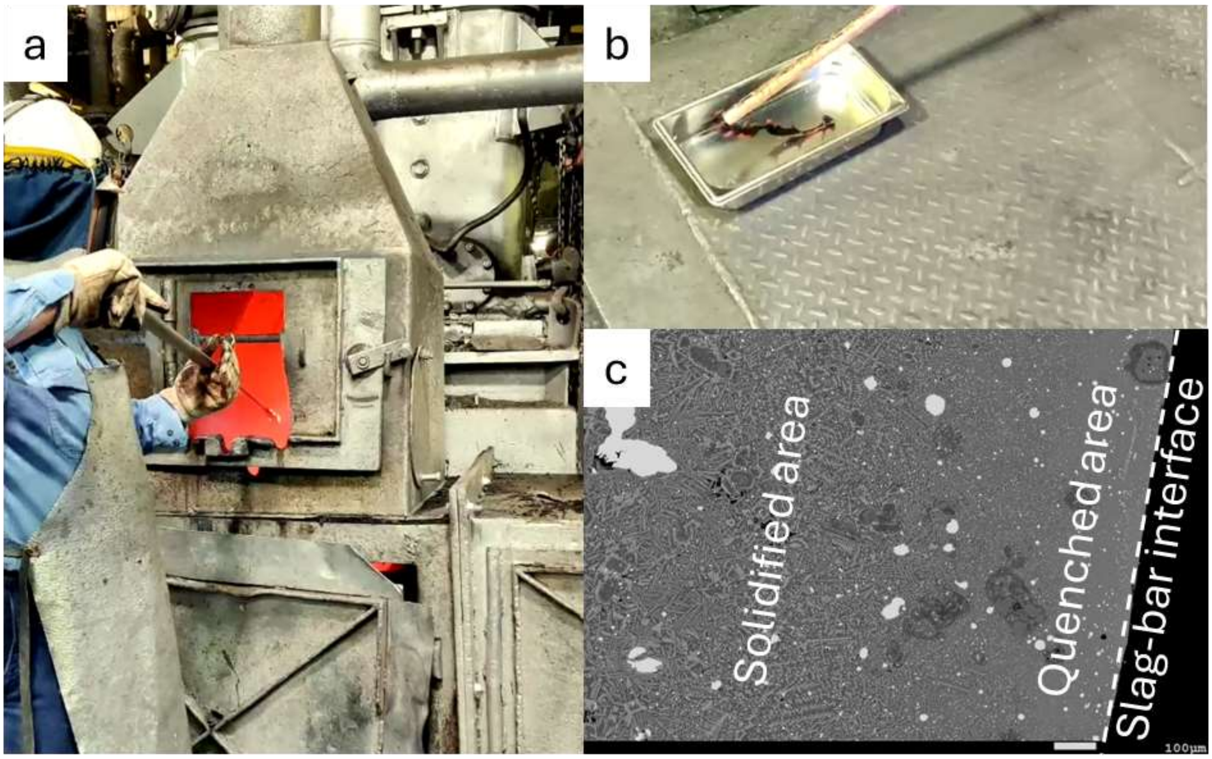

FIG 1 - a) and b) Slag sampling by dip-bar– sampling procedure; c) microstructure of the sample taken showing the fully quenched area, representative of the sample at temperature, in the region immediately adjacent to the quench bar.

An important check to undertake when a sample has been obtained is to first examine polished section under the metallurgical optical microscope. This immediately provides a checkpoint to establish the characteristics of the sample, to establish whether the sample is a single phase and uniform in appearance. If the sample appears uniform at this scale it may be sufficient to rely on bulk property measurements described in the following section to characterise the sample. If more than one phase is identified at this stage when only one phase is anticipated then further review of process conditions, sampling and preparation procedures should be undertaken to avoid the formation or presence these artefacts. In some cases, microscopic changes in sample structure can take place during the sampling procedure, particularly during cooling of samples from the process temperature;

more detailed examination is recommended in all cases to fully characterise the samples. The use of advanced high-resolution techniques is discussed in a later section below.

CLASSIFICATION OF ANALYTICAL TECHNIQUES

Bulk Chemical (Elemental) Analysis

Bulk chemical analysis is a process used to determine the mean elemental composition of a sample. It involves identifying and quantifying the concentrations selected elements present in a material or substance. This can be done through various well-established techniques, including wet chemical, spectroscopy, chromatography, and mass spectrometry.

A table summarising the underlying principles and capabilities of these various techniques is provided in TABLE1, with reference to appropriate texts addressing this topic.

Bonding structural/speciation analysis

Bonding/structural/speciation analysis techniques are used to study the types of bonds at an atomic level, molecular structures, and chemical species present in materials. Typical techniques include Fourier Transform Infrared (FTIR) Spectroscopy, Raman Spectroscopy, Nuclear Magnetic Resonance (NMR) Spectroscopy and X-ray Absorption Near Edge Spectroscopy (XANES). References and applications of these techniques are also provided in Table 1.

Both FTIR and Raman Spectroscopy have been used to study the chemical bonding in silicate melts. Different types of chemical bonds (e.g., Si-O-Si, Si-O-Al) have characteristic spectra, which can be used to identify the types of bonds present and their relative proportions. These data can be used to identify and better understand the slag structure and its relation to physico-chemical properties, such as, viscosity for different bulk compositions and process conditions.

XANES is a technique used to identify the speciation of multivalent metal cations in the solid materials. To date, it’s application has been largely limited to the characterisation of crystalline geological materials.

Deriving quantitative information from these techniques is not a straightforward process and the accuracy heavily relies on

1. The use of matrix-matching standards to establish reliable calibration curve.
2. The reliability of reference spectra in the handbook of the respective techniques
3. Peak fitting and spectra deconvolution process used, which introduce additional assumptions in the quantification of these phenomena.

TABLE 1 – Summary of bulk analytical techniques used for metallurgical materials and references for further reading

			Elements can be measured	Detection limit	Spatial Resolution	Sample preparation	Quantitative/Qualitative	Example of application
Bulk analysis techniques	Elemental	XRF (Beckhoff et al., 2007)	Na - U	10ppm	N/A	pressed pellet/fused glass	Typically quantitative; fused glass gives more accurate results	Slag, matte, speiss, alloy bulk assay
		ICP-OES (Olesik, 1991)	All except C, H, O, N and halogens	high ppbs		aqueous digestion	Quantitative	Slag, matte, speiss, alloy bulk assay
		ICP-MS (Olesik, 1991)	All except H, O, N, F and noble gas element	down to ppt		aqueous digestion	Quantitative	Trace elements
		AAS (Christian and Epstein, 1980)	All metal elements	low ppbs		aqueous digestion	Quantitative	Trace Au and Ag in slag
	Phase/ mineralogy	XRD (Epp, 2016)		1 wt%		grinding to make fine powder	Qualitative but can be quantitative	type and proportion of solids in molten slag
	Structural / speciation	Mossbauer Spectroscopy (May, 2012)	Fe, Sn, Sb, Te, I, Au, Ni, Ru, Ir, W, REEs	1 wt%		grinding to make fine powder	Qualitative but can be quantitative	Fe speciation in silicate melt/slag
		EXAFS/XANES (Teo, 2012)	Multivalent elements	0.1wt%		fine powder or bulk solid	Qualitative but can be quantitative	Ionic structure information of molten slag and salt
		NMR (Stebbins, 1995)	molecular structure	100 µmol/g		fine powder	Qualitative but can be quantitative	
	Surface	XPS (Stevie and Donley, 2020)	All except H and He	0.1-1 at%		fine powder or bulk solid	Qualitative but can be quantitative	surface elemental characterisation of slag, matte and metal/Transition metal speciation in silicate melt/slag

QUANTITATIVE MICROANALYSIS TECHNIQUES

Quantitative microanalysis techniques stand apart from bulk analysis methods by allowing the characterisation of small samples, typically at the micrometer or even nanometer scale. They excel in examining individual phases and features within complex samples where distinct phases cannot be feasibly separated for bulk chemical analysis. TABLE 2 offers a compilation of references and applications highlighting the utility of these microanalytical methods.

TABLE 2 – Summary of micro-analytical techniques used for metallurgical materials and references for further reading

			Elements can be measured	Detection limit	Spatial Resolution	Sample preparation	Quantitative/Qualitative	Example of application
Micro-analysis techniques	Elemental	SEM/EDS (Goldstein et al., 2017)	All except H, He, Li*	0.1-1wt%	1-5um	any vacuum-stable solid/powder	Semi-quantitative but can be quantitative	composition analysis of microscale phase in slag, matte, speiss, alloy
		SEM/WDS (Goldstein, 1969)	All except H, He, Li**	100-300 ppm	1-5um	mounted and polished solid	Quantitative	composition analysis of microscale phases in slag, matte, speiss, alloy
		u-XRF (Beckhoff et al., 2007, Papadopoulou et al., 2006)	Na - U	20ppm	30um	any solid/powder	Semi-quantitative but can be quantitative	elemental mapping of large areas
		LA-ICP-MS (Walsh, 2002)	All except H, O, N, F and noble gas element	low ppbs	10s to 100s um	any solid/powder	Quantitative for oxide slags, qualitative for other phases	trace elements measurement of microscale phase in slag, matte, speiss, alloy
		LIBS (Singh and Thakur, 2020)	All elements	down to ppm	10s to 100s um	any solid/powder	Qualitative but can be quantitative	Hydration of slags
	Phase/ mineralogy	Optical Microscopy (Geels et al., 2007)	N/A		down to 1um	mounted and polished solid sample	Qualitative but can be quantitative	Initial fast microstructural examination of slag, matte, alloy samples
		u-XRD (Flemming, 2007)	N/A	1 wt%	10s um	mounted and polished solid sample	Qualitative but can be quantitative	identification of SFCA in iron ore sinters
		QEMSCAN/MLA /TIMA (Sutherland and Gottlieb, 1991)	All except H, He, Li*	5wt%	1-5um	mounted and polished solid sample	Quantitative	quantitative analysis of phases in slags
	Structural /speciation	RAMAN (Long, 1977)	N/A	ppm	down to 1um	mounted and polished solid sample	Qualitative but can be quantitative	structural information of silicate slag
		FTIR (Berthomieu and Hienerwadel, 2009)	Si-O, Me-Si-O, O-Si-O groups	1-5 wt%	down to 1um	mounted and polished solid sample	Qualitative but can be quantitative	structural information of silicate slag
	Surface	TOF-SIMS (Fearn, 2015)	All elements	down to 1ppm	down to 0.1um	mounted and polished solid sample	Qualitative	surface elemental characterisation of slag, matte and metal

SEM-based X-ray Microanalysis

General principles and capabilities

Electron microscope-based microanalysis is a non-destructive technique based on the interaction between a focused electron beam and a solid sample. As the electrons collide with atoms in the sample, characteristic X-rays are emitted due to inner-shell electron transitions. EPMA typically employs Wavelength Dispersive Spectrometry (WDS), crystal monochromators for high resolution wavelength separation of incoming X-rays so that the intensity of the radiation from each element can be measured and quantified. An alternative approach to the measurement of X-rays emitted is the use of Energy Dispersion Spectrometer (EDS) in which characteristic X-rays from all elements present in the sample are simultaneously captured for rapid elemental analysis. EDS can be used in scanning electron microscopy (SEM) mode or transmission electron microscopy (TEM) mode.

Both WDS and EDS offer qualitative and quantitative analysis at high spatial resolution (typically 1-3um), making it suitable for examining small features. For quantitative analysis, the measured X-ray intensities of unknown samples are compared to that of known standards applied with a well-established matrix correction algorithm (e.g. atomic number, absorption, fluorescence (ZAF)) to determine the concentration of the element of interest. Sample preparation involves mounting solid samples in epoxy resin, exposing cross-sections through grinding and polishing. A thin carbon layer (20 nm) is often applied to samples before analysis to avoid charging of the sample. TABLE 3 shows the comparison of analytical capabilities between WDS and EDS.

TABLE 3 - Comparison of the analytical capabilities between WDS and EDS measurement techniques.

	EDS	**WDS**
Spatial resolution	Down to 0.5 um	
Energy resolution	~125 ev	~ 5-10ev
Elements can be measured	Be to U	
Typical Detection limit	0.1wt%	0.01wt%
DATA Acquisition	All elements at same time (Rapid)	One element per spectrometer at a time (Slow)
Calibration	Every 3-12 months	Every 24-48 hours

Applications

EPMA typically finds applications in determining high temperature phase equilibria and chemical compositions of individual phases in multi-phased pyrometallurgical materials. The EPMA analysis is typically navigated by high resolution back scattered electron imaging, which makes the investigation of elemental process taking place during the metallurgical process highly efficient.

Challenges and development

- Measurement of trace elements

Notwithstanding its superior spatial resolution, EPMA has often been perceived as reliable only for major elements (>1 wt.%). In fact, recent advances in EPMA instrumentation such as the field-emission electron gun, large-size diffraction crystals, and the automation of aggregated intensities from multiple spectrometers (Donovan et al., 2016) have made it feasible to use EPMA to measure at least the more abundant trace elements (> 100 ppm) on a regular basis. Reviews on trace element measurement using EPMA are readily available in literature typically for geological materials (Batanova et al., 2018, Donovan et al., 2016, Jercinovic et al., 2012). The principles are normally applicable to metallurgical materials. Over the years, authors have developed analytical protocols to measure minor/trace elements in chemically complex phases, such as industry slag samples (Chen et al., 2022). These protocols address major issues associated with trace element analysis by EPMA, such as Minimal Detection Limit (MDL), spectral interferences, beam damage and background corrections to ensure the accuracies of the measurements.

- Measurement of light elements

Metallurgical research has long sought accurate determination of light elements, such as oxygen (O), fluorine (F), and boron (B) in for example, matte, mould flux, and slag. However, the available analysis techniques for these elements using electron microscope techniques are quite limited. Quantitative measurement of elements with atomic numbers less than or equal to 9 (e.g., fluorine) has been a persistent challenge for X-ray-based microanalysis (Bastin and Heijligers, 1992). This is due to several factors, including low X-ray emission, high sensitivity to surface contamination, poorly established mass absorption coefficients for matrix correction, and bonding-dependent peak shift of characteristic X-rays.

Protocols been proposed to measure light elements, such as fluorine (F), oxygen (O), nitrogen (N), carbon (C), boron (B), and beryllium (Be) in geological materials (Newbury and Ritchie, 2015, Zhang et al., 2016, Nash, 1992, Fonseca et al., 2008, Cheng et al., 2019, Wu et al., 2022). However, there is limited information available regarding how these challenges have been addressed and how the accuracy of the analysis has been evaluated.

- Measurement of beam sensitive materials

Analysing beam-sensitive materials, such as alkaline-rich slags and halogen-bearing minerals, with SEM-based X-ray microanalysis technique requires careful consideration of several principles to ensure accurate results without damaging the sample. These principles have been discussed and measures taken to minimize the uncertainty due to beam damage have been extensively discussed in the literature (Willich and Bethke, 1996, Chen et al., 2020, Henderson, 2011, Chen et al., 2022). In general, the following analytical conditions are preferred: low beam voltage and current, short analysis time and avoiding high magnification for navigation. Modern software like Probe for EPMA (http://www.probesoftware.com/) has allowed the monitoring and the correction of time dependent intensity if required.

- Measurement of melt with microcrystalline precipitation

In the process of sampling molten materials, not all phases can be effectively quenched and retained as a homogeneous glassy phase. Ionic liquids, including calcium ferrite slag, matte, speiss, alloy, and molten salt, crystallize much more rapidly than silicate melt, leading to a microcrystalline textured phase upon quenching.

To determine the composition of phases that exhibit micron/submicron-scale heterogeneity, some researchers have used a defocused electron beam with a fixed beam diameter during measurement. However, this approach has been controversial due to the matrix correction procedure of EPMA analysis, which assumes the sampling volume of the analysis area to be homogeneous. A previous study (Barkman et al., 2013) adopting this approach observed errors of up to 6% in obtaining the average composition of a heterogeneous material. Conversely, other studies have shown that analysis accuracy is not affected by this approach. Fallah et al.(Fallah-Mehrjardi et al., 2017) analysed the copper concentration in slag samples containing finely precipitated Cu-rich particles from gas/slag/matte/tridymite phase equilibrium experiments using EPMA with varying beam sizes. The authors observed improved analysis precision with no significant impact on analysis accuracy when employing larger beam sizes. Similarly, Chen et al.(Chen et al., 2022) measured the industry copper-converting slag with quench precipitations using a defocused beam. The authors evaluated the extent of potential error by measuring the areas of the slag phase with different extents of quench crystallization. No systematic difference was observed between measurement results from different areas, suggesting that the potential error in minor element concentration measurement in the slag phase due to heterogeneity within the sampling volume is negligible.

In practice, the potential error in the measurement results due to heterogeneity within the sampling volume should be evaluated on a case-by-case basis. We suggest two possible ways to evaluate this potential error:

1. Measure the areas of the same phase with different extents of heterogeneity and compare the results. The smaller the difference in the results, the less uncertainty due to the sample heterogeneity.

2. Use alternative methods, such as LA-ICP-MS, to verify the measurement results by EPMA.

Systematic errors could be observed in certain cases and should be documented and included when reporting the analytical results.

- Dealing with boundary secondary fluorescence

The Boundary Secondary Fluorescence effect (BSF) is a known phenomenon in electron-induced X-ray microanalysis in SEM-EDS/WDS and is well recognized in materials and geoscience research (Borisova et al., 2018). The primary X-rays generated by electron-material interaction can travel within the sample and further produce characteristic X-rays of lower energies, extending the range of secondary X-ray fluorescence beyond that of primary X-ray generation. While the impact of secondary fluorescence is generally corrected for during matrix correction in X-ray microanalysis, there's uncertainty near phase boundaries. When analysing a phase close to a boundary with another phase containing a significantly higher level of the same element, the element of interest is often measured at a higher level than the true value. This is because some primary X-rays generated within Phase A travel across the phase boundary and excite secondary X-rays of lower energies inside Phase B. Some of these emitted secondary X-rays, characteristic of Element α from Phase B, are collected by the X-ray detector, leading to an apparent higher concentration of Element α in Phase A than its actual concentration. A schematic description of the BSF effect is shown as FIG 2.

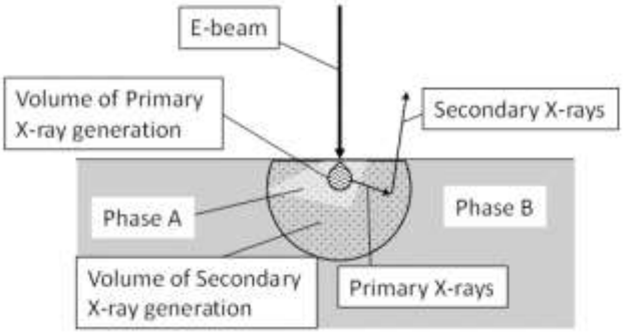

FIG 2 Schematic description of the Boundary Secondary Fluorescence effect

Despite numerous proposed methods to mitigate this issue, existing approaches have inherent limitations and lack of universal efficacy. Many methods assess boundary secondary fluorescence (BSF) through computer or experimental simulations. These methods rely heavily on precise knowledge of the geometrical and dimensional characteristics of the phase under analysis and its surrounding matrix, which is extremely challenging to obtain itself in real-world scenarios. Other methods exhibit effectiveness only for specific elements.

A rapid and effective method aimed to eliminate the secondary fluorescence effect at boundaries in quantitative X-ray microanalysis has recently been developed by the authors (Chen et al., 2024). Utilizing a Focused Ion Beam – Scanning Electron Microscope (FIB-SEM) dual-beam system, separate phase/features less than 10um of interest can be separated from their original matrix and remounted onto a suitable substrate for subsequent EPMA analysis as shown in FIG 3.

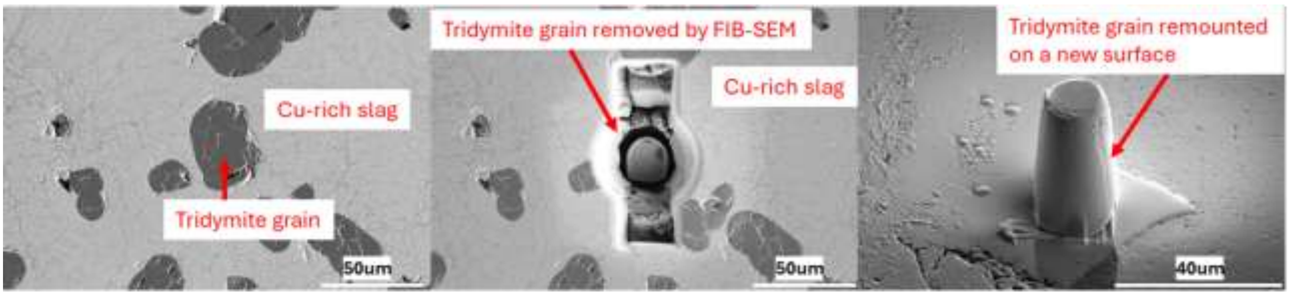

FIG 3 Demonstration of removing and remounting of targeted phase for EPMA analysis to eliminate the SBF effect.

LA-ICP-MS

General principles and capabilities

LA-ICP-MS is an analytical technique for elemental analysis of solid samples. The process begins with a focused laser beam ablating material from the sample's surface. The ablated material is then transported into an ICP as an aerosol, where it undergoes ionization at high temperatures. The resulting ions are then introduced into a mass spectrometer for precise elemental identification and quantification based on their mass-to-charge ratios. LA-ICP-MS offers significant advantages over EPMA, notably superior detection limits (down to ppb), enabling precise measurement of trace elements within targeted phases. To ablate sufficient material for ICP-MS analysis, the spot size and sampling depth of LA-ICP-MS analysis is typically in the range of tens of μm, as opposed to 1 μm to 3 μm for EPMA. Accurate quantification of the raw data often requires,

1. well-characterised standard reference materials that are generally available in the form of oxide glass or pressed-powder-pellets from National Institute of Standards and Technology and US Geological Survey and

2. separate measurement of the concentration of a major element in the sample served as internal standard – typically by EDS or WDS.

Applications

Originally developed for earth science research, LA-ICP-MS has found recent adoption within the metallurgical research community. The two groups that have been actively utilising the technique in extractive metallurgy research are thermodynamics and modelling group at Aalto University, Finland and Pyrosearch at University of Queensland, Australia since 2015 (Avarmaa et al., 2015, Chen et al., 2016) studies by these groups have showcased LA-ICP-MS's efficacy in accurately measuring trace elements in slag phases, contributing new fundamental data, and resolving discrepancies in literature regarding minor element distributions in non-ferrous melt smelting and converting processes.

Challenges and development

- Analysis of matte, speiss and alloy

While LA-ICP-MS has demonstrated excellent analysis precision and accuracy when analysing oxide phases. There has been an on-going challenge in the measurement of sulphide and metal phases with consistent accuracy. It has been well documented (Sylvester, 2008) that the ablation and mass transportation processes of sulphides and alloys are very different from oxide minerals/glasses during the analysis, thus the relative proportions of element present in the material being detected and measured can vastly differ. Therefore, the LA-ICP-MS analysis accuracy heavily relies on the use of appropriate standard reference materials. However, the availability of high-quality metal and sulphide standards for LA-ICP-MS has been very limited compared to the oxide standards. Over the years, a number of solutions have been proposed to address this issue

1. Use non-matrix matching external standards (i.e. NIST 610/612 for non-silicate materials), establish correction factor for each element and apply to the results - the method has very limited applicability and is dependent on analytical conditions and sample-standard pair
2. Development of other matrix correction methods, such as multivariate regression algorithms for using non-matrix matching external standards - this method has broader applicability, but large calibration library needed for good analysis accuracy.
3. Development and use of matrix-matching standards - the solution for the best analytical accuracy, however standard synthesis can be challenging and requires expertise to ensure the homogeneity of the standard at microscopic level is achieved.
4. Use Femtosecond-LA-ICP-MS - the femtosecond laser ablation reduces matrix effect in the ablation process, but not as widely available as nano-second laser and laser energy output stability needs to be more closely monitored throughout the analytical session.

Chen et al. (Chen et al., 2023) developed a Cu-based reference materials doped with minor elements of interest for laser ablation ICP-MS using high temperature melting/equilibration and fast quenching method. The composition and homogeneity of the sample was measured by EPMA. The standard deviation for most doped minor elements is within 5% except for Se and Pb which exsolved significantly from Cu phase during the quenching due to their low solubility in Cu. LA-ICP-MS analysis of the sample show the analysis accuracy is analytical condition dependent and could introduce over 200% error for certain elements (FIG 4) when using non-matrix matching standard (e.g. NIST610 glass)

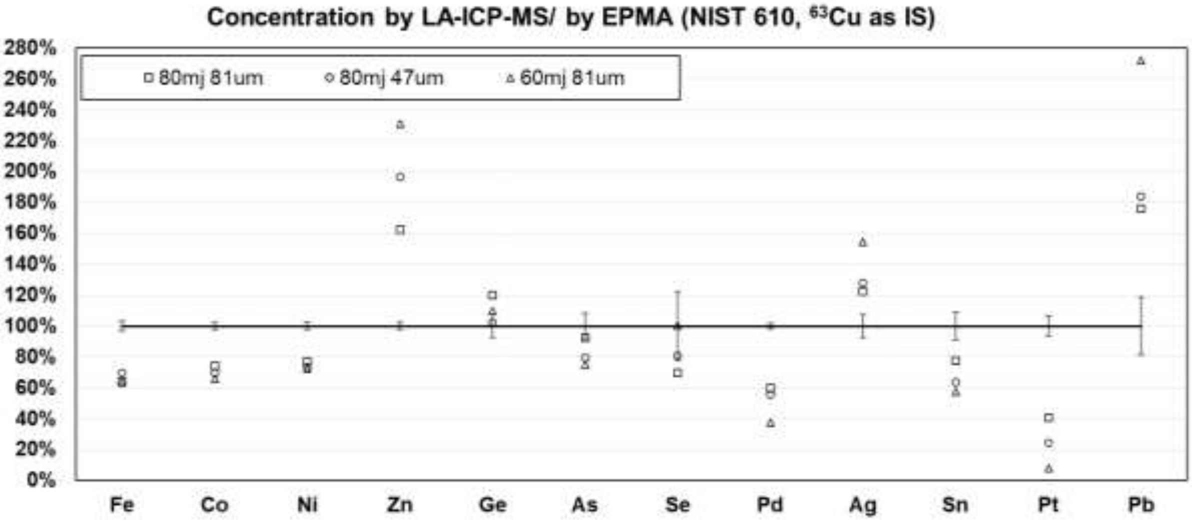

FIG 4. Analytical error of LA-ICP-MS measurement of minor elements in Cu metal when using NIST 610 as reference material (Chen et al., 2023)

- Spatial resolution

To ablate sufficient material for ICP-MS analysis, the spot size and sampling depth of LA-ICP-MS analysis is typically in the range of tens of µm, as opposed to 1 µm to 3 µm for EPMA. This adds to the possibility of error due to the increased chance of sampling inclusions of another phase beneath the sample surface (i.e. entrained matte/metal in slag phase). Typically, this type of error can be identified by examination of time-resolved ablation spectra, allowing their effects to be minimized by removing the affected time segments for these elements (as show in Figure 5).

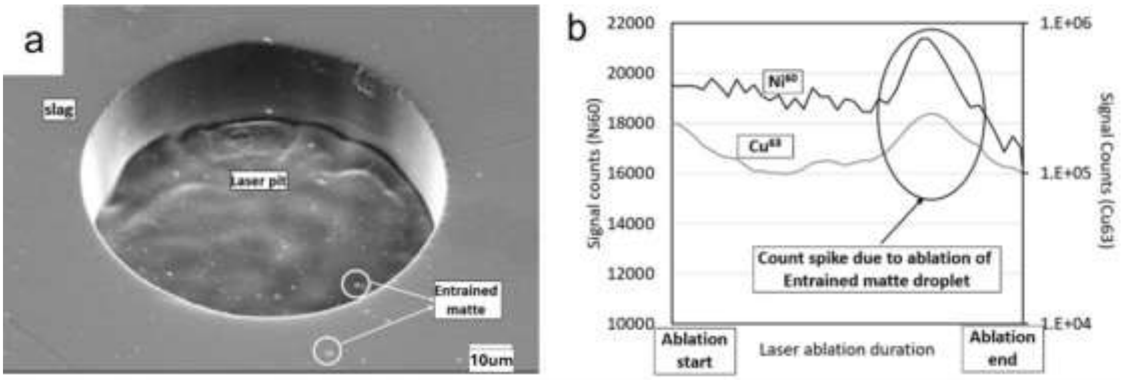

FIG 5. (a) Ablation crater in slag phase; (b) LA-ICP-MS time-resolved intensity showing count spikes for Cu63 and Ni60 (Chen et al., 2022)

Better spatial resolution/smaller sampling volume may also be achieved by adopting femtosecond laser ablation ICP-MS. Femtosecond laser pulses can generate smaller ablation craters compared to conventional nanosecond pulses. This finer spatial resolution (down to 1um) allows for more precise sampling of small features within a sample, resulting in improved spatial resolution in elemental mapping and analysis (Russo et al., 2002)

MEASUREMENT OF HETEROGENOUS MATERIALS AND PHASES

PXRD

PXRD is a technique used to determine the crystal structure of a material. It is widely used to identify mineral phases present in ores, slags, and other materials. When X-rays are directed at a sample, they diffract at specific angles according to the crystal lattice structure, producing a diffraction pattern. By analysing the positions and intensities of these diffraction peaks, the crystalline phases and their relative abundances in the sample can be determined. Detection limits depend on mean atomic number but typically difficult to quantify materials containing lets than 2wt% of individual crystalline solids.

Quantification by PXRD relies on the relationship between the intensity of X-ray diffraction peaks and the concentration of crystalline phases in a sample. Generally, this process involves comparing the intensities of diffraction peaks from the sample with those of known standards of known compositions. By calibrating the instrument and using appropriate mathematical models, such as the Rietveld refinement method or the internal standard method (Epp, 2016), it's possible to quantitatively determine the relative concentrations of different crystalline phases in the sample. However, caution should be taken when trying to determine the proportion of crystalline phases (solids) in the melt cooled (even quenched) from high temperature as the technique typically is unable to distinguish between the primary phase present at temperature and crystalised phase formed on upon cooling.

Quantitative Phase Analysis by Microscopy

Optical microscopy

Optical microscopy has been widely used to examine the microstructure of metallurgical materials. It has been proven to be a fast, effective and low-cost tool for initial examination of samples particularly for quality control. Sections of the material are prepared and polished to create a flat surface for observation. By illuminating the sample with visible light, and adjusting magnification and focus, microstructural features are analysed. Modern instrument equipped with automated stage and image analysis software allows fast examination of large representative area of the sample and extracting quantitative information, such as phase size distribution, phase proportions and phase relations at high resolution (down to 1um). This is particularly of interest for evaluating metal loss in the slag in the form of entrained metal and/or matte.

Automated SEM

Automated SEM techniques are now available that combine imaging with EDS to characterize the mineralogy and texture of a sample. This technique is conventionally used for characterizing ores, tailings, and concentrate samples, but also valuable in pyrometallurgy. The technology requires the integration of the SEM measurement system and advanced software programs that store, then analyse and display the analytical data produced in useful formats. Current systems include AMICS, TIMA, Maps Min and Mineralogic. The approach is useful for several reasons:

1. Phase Identification: Automated SEMs can identify solid/mineral phases in a sample, including their abundance and size distribution as well as their chemical composition – e.g. steel inclusions

2. Phase Texture Analysis: Information can be provided on mineral textures, such as grain size, shape, and associations. This information can be crucial for optimizing the process condition for example for further recovering of Cu or Ni from smelting slag via slow cooling + crushing + flotation methods.

3. Elemental Analysis: The EDS component of SEM also allows for the elemental analysis of each mineral grains at microscopic level, providing information on the chemical composition of the phase. This is important for accurate determination of elemental partitioning information of a heterogeneous material (typically flue dust) when performing phase identification analysis.

In addition to above, the automated SEM techniques allow for high-throughput data collection. This can significantly speed up the analysis process compared to manual methods such as point and count method.

SUMMARY

A range of advanced analytical techniques have been developed for the characterisation of the chemical compositions and physico-chemical properties of materials. These tools have been primarily used to date to measure the properties of geological materials and to assist in the further development of new materials, for example ceramics and alloys. It has been shown however that these tools can be used in determining chemical equilibria in complex phase assemblages, the measurement of the kinetics of reaction processes occurring at the microscopic levels and in the characterisation of complex heterogeneous materials encountered in industrial pyrometallurgical practice. The ability to undertake accurate measurements at the microscopic and atomic levels has provided the opportunity to obtain important new fundamental information about these systems thereby increasing the potential to improve process performance in technical and economic terms. The paper has provided an overview of the analytical tools currently available, their capabilities and limitations with a view to guiding the selection of the appropriate methods and procedures when embarking on examination of phenomena taking place in high temperature molten systems.

ACKNOWLEDGEMENTS

The research funding and technical support is provided by the consortium of copper and lead producing companies: Anglo American Platinum (South Africa), Aurubis AG (Germany), BHP Billiton Olympic Dam Operation (Australia), Boliden (Sweden), Glencore Technology (Australia), Metso Oy (Finland), Peñoles (Mexico), RHI Magnesita (Austria), Rio Tinto Kennecott (USA) and Umicore NV (Belgium), as well Australian Research Council Linkage program LP190101020 “Future copper metallurgy for the age of e-mobility and the circular economy”. Present study would not be possible without the facilities and technical assistance of the staff of the Centre for Microscopy and Microanalysis in The University of Queensland.

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