TECHNICAL ARTICLE

Predicting iron ore sinter strength through partial least square regression (PLSR) analysis of X-ray diffraction patterns

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The decrease in quality of Australian iron ore, coupled with the demand for more efficient energy use, means that closer monitoring and optimisation of process conditions for iron ore sinter production is required. Here, the suitability of using partial least-squares regression analysis of powder X-ray diffraction data, collected for iron ore sinter samples, for the prediction of iron ore sinter strength has been further assessed. In addition, a preliminary assessment of the effect of 2θ range on the quality of prediction has been made. For the purposes of process control, the level of correlation between predicted strength and actual sinter strength would inform an operator whether or not the process was operating within the acceptable limits, or whether there was a potential problem requiring further investigation or rapid intervention. Reducing the 2θ range was found to reduce the level of correlation between predicted and actual strength, to a point where the particular analysis may no longer be suitable for process control.
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Key words: iron ore sinter, tumble index, powder XRD, partial least square regression, physical property prediction

I. INTRODUCTION

Powder X-ray diffraction (XRD) is widely used for quantitative phase analysis (QPA) of ores and processed material in the iron ore industry. Indeed, Raven and Birch (2017) have recently coordinated an international Round Robin on the QPA of iron ores. Iron ore sinter is a complex composite material of ~40–70 wt% iron oxides (hematite, Fe_2O_3, and magnetite, Fe_3O_4), 20–50 wt% Ca-rich ferrite phases, up to 10 wt% glasses, and up to 10 wt% calcium silicates of which larnite, Ca_2SiO_4, is the most common (Patrick and Lovel, 2001). Most of the Ca-rich ferrite phases contain some silica and are known collectively by the acronym SFCA (i.e. silico-ferrite of calcium and aluminium). There are two main types of SFCA discussed in the scientific literature – SFCA and SFCA-I – each having a distinct crystal structure (Mumme *et al.*, 1998) and, therefore a distinct diffraction pattern which has been exploited in *in situ* diffraction-based investigations of the formation mechanisms of SFCA and SFCA-I phases (Webster *et al.*, 2017a, and references therein). SFCA and SFCA-I are considered to be important phases which impact on physical properties of iron ore sinter such as sinter strength, reduction degradation, and reducibility. They are, however, difficult to quantify, especially *via* image analysis but also by XRD since the inadequacy of the available crystal structure models for the SFCA phases can make Rietveld refinement-based QPA, especially by non-specialist operators, of materials containing these phases problematic.

Partial least-squares regression (PLSR) analysis has been shown by König *et al.* (2014) and König and Norberg (2015) to enable prediction of sinter basicity ($CaO:SiO_2$ ratio) and Fe^{2+} content – the latter in particular being a key marker of sinter quality and used for process control – from powder XRD data without the need for rigorous mineralogical analysis by the operator. As well, the traditional wet chemical method for Fe^{2+} determination can take several hours to complete, and more rapid feedback for the purpose of process control is desirable. The PLSR approach first derives a function that links observed values of the variable of interest (e.g. Fe^{2+} content) to observed values of other independent variables (e.g. XRD data). This function is then used to predict observed values when only the independent variables are available.

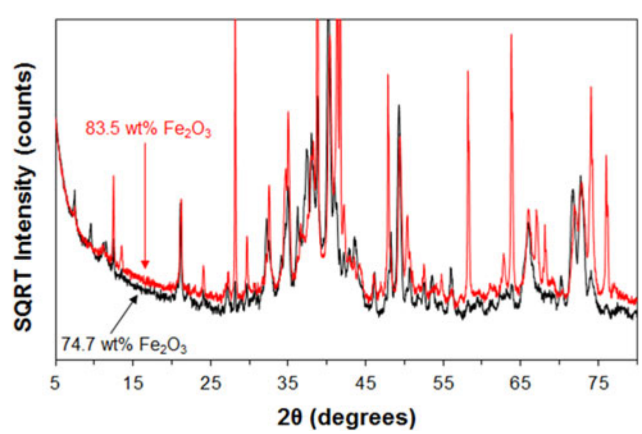

Figure 1. (Color online) XRD patterns collected for sinter samples prepared from iron ore samples with varying bulk composition, with total Fe content expressed as wt% Fe_2O_3.

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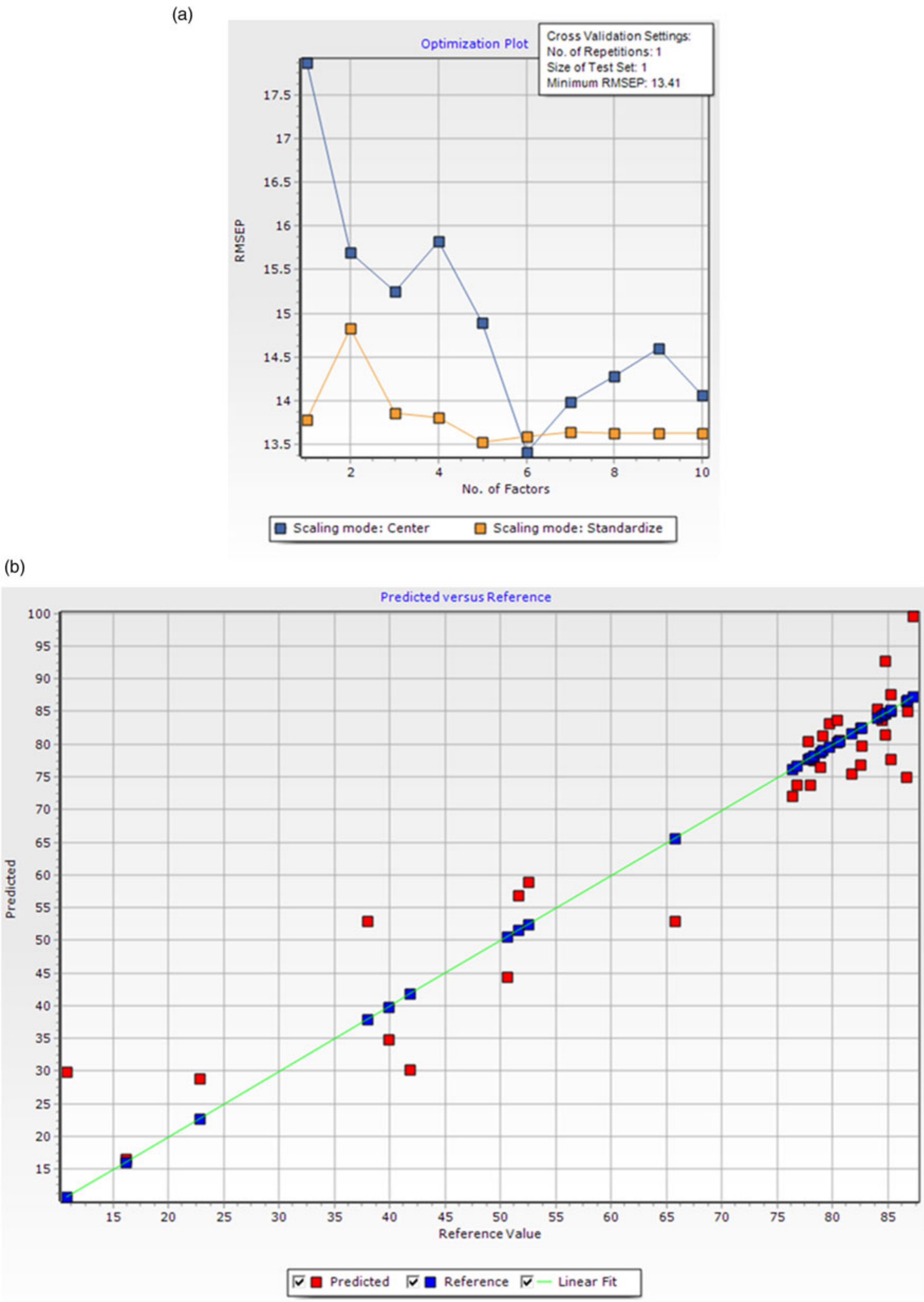

Figure 2. (Color online) (a) Optimisation plot in HighScore Plus showing two tested scaling modes, the number of factors used and the RMSEP (root-mean-square error of prediction) for a calibration set of compact sinter samples/XRD patterns, and (b) the PLSR fit to the calibration data.

High reducibility, high mechanical strength, and low reduction degradation are direct indicators of sinter quality; the ability to determine sinter strength, for example, rapidly through XRD and without the need for time-consuming physical property testing could be a powerful capability suitable for process control. The pot-grate tumble index (TI) is the industry standard method for assessing iron ore sinter strength (Ware *et al.*, 2013), and we recently reported a preliminary assessment of the potential for PLSR to be used as a method for prediction of TI from powder XRD data (Webster *et al.*, 2017b). Here we further assess the suitability of PLSR for the prediction of sinter TI through a new set of samples, as well as make a preliminary assessment of the effect of 2θ range on the analysis which will influence how rapid the XRD data collections can be performed.

II. EXPERIMENTAL

Laboratory-based compact sinter tests were carried out using the method described by Clout and Manuel (2003). The <1 mm size fraction of five natural iron ores were fluxed to 2.4 basicity using limestone, then compacted into Ni pots using a press to form 4 g tablets. Samples were heated in a tube furnace in a $pO_2 = 5 \times 10^{-3}$ atm under a standard heating profile, held at the desired set point (in the range 1200–1320 °C) for 3 min before being rapidly cooled in nitrogen to produce fired compacts. The fired compacts were then tumbled in a modified bond abrasion tester for 8 min, sieved and the compact TI recorded as the percentage of material retained above 2 mm.

Tumbled compact samples were then crushed using a percussion mortar to <500 µm, and micronised in ethanol for 4 min g^{-1}. Powder XRD data were collected over the range $5° \leq 2\theta \leq 80°$ on micronised samples using a PANalytical MPD fitted with Co tube, post-diffraction graphite monochromator, and an X'Celerator detector used in one-dimensional mode (active length of 2.122° 2θ). PLSR analysis was carried out using PANalytical HighScore Plus V4.1. The calibration model was 'trained' using 32 samples/datasets, and tested on 22 different samples/datasets. Background subtraction was applied to account for minor background variation with ore composition, with increasing background with Fe content (Figure 1) consistent with the study of Fransen (2004). Similar to the approach described by König and Norberg (2015), an optimal regression model was found automatically using the PLSR tool in the HighScore Plus software. The optimal number of PLSR factors was found to be 6 with the scaling mode 'Center', and the root-mean-square error of prediction (RMSEP) was 13.41 [Figure 2(a)]. Figure 2(b) shows the PLSR fit to the calibration data.

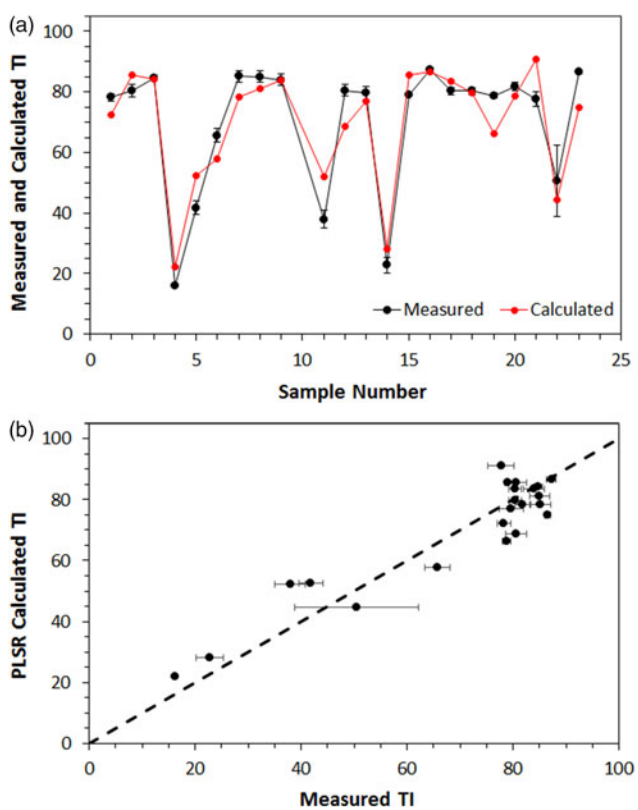

Figure 3. (Color online) Plots of calculated vs. measured tumble index (TI) values for a series of compact sinter test samples. In (b) correlation coefficient (R^2) = 0.87. The dashed line in (b) is not a line of best fit, it is simply a line showing where prediction = correlation. The error bars on the measured TI values show ± standard deviation of repeat measurements.

III. RESULTS AND DISCUSSION

Figure 3 summarises the outcomes of the PLSR analysis applied to the 22 test samples/datasets. Trends in measured TI variation are followed by the calculated TI values. This is despite significant variations in mineralogy even for samples with similar measured TI values (Figure 4). The peaks attributed to Ca-Al-Silicate in Figure 4 have previously been observed in the study of Pownceby *et al*. (2015, 2016). The other phases observed – magnetite, hematite, larnite, SFCA, and SFCA-I – are the typical iron ore sinter phases which have been widely reported.

A characteristic feature of the XRD patterns collected for the samples which exhibited low TI ($\leq 40\%$) was the presence of a significantly higher amount of SFCA compared to the samples with the high (~80%) TI values. The correlation observed in Figure 3(b) was similar to that reported by Webster *et al*. (2017b), and so this may be an indication of the limitations of the PLSR method as applied to iron ore sinter TI prediction. However, for the purposes of process control, this level of accuracy would inform an operator whether or not the process was operating within acceptable limits, or whether there was a potential problem (e.g. fuel rate or flux addition too low for the given ore feedstock) requiring further investigation or rapid intervention.

Figure 5 summarises the outcomes of the PLSR analysis when the upper 2θ angle was cropped at 55°. Clearly, the correlation between the calculated and measured TI values is lower than in Figure 3, and this is especially true for the samples which exhibited very low TI index. For the purposes of process control, this level of accuracy may no longer be sufficient to reliably inform an operator whether or not the process

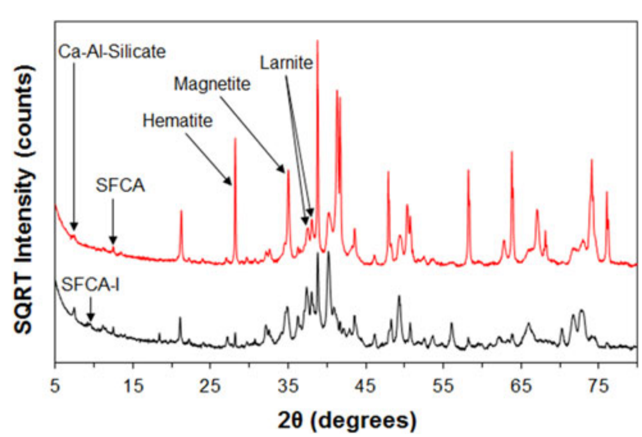

Figure 4. (Color online) XRD patterns collected for sinter samples with TI = 80.5 (lower) and 80.3 (upper). Here, patterns have been offset in the intensity axis for clarity.

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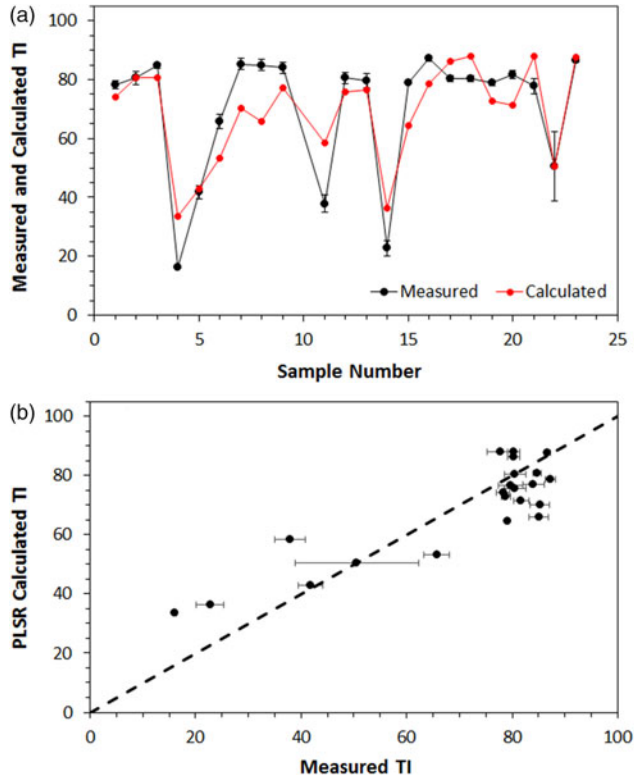

Figure 5. (Color online) Plots of calculated vs. measured tumble index (TI) values for the compact sinter test samples, with the upper 2θ angle in the XRD datasets cropped at 55°. In (b) $R^2 = 0.77$.

was operating within acceptable limits, or whether there was a potential problem.

IV. CONCLUSION

PLSR analysis shows promise as a method for rapid determination of TI from XRD data and, therefore, process control of iron ore sintering operations. Here a preliminary assessment of the effect of 2θ range was made and the reduced correlation between calculated and measured TI after cropping of the 2θ range to 5–55° has implications for how rapid the XRD data may be. Further testing is required to assess the robustness of the method as applied to pot-grate iron ore sinter samples, and to establish where improvements in the speed of analysis may actually be made (e.g. in terms of sample preparation, whether or not micronizing is required, or whether coarse grinding using a ring mill is adequate; in terms of data collection, what level of counting statistics is required). Testing is also required to assess the potential for using PLSR to predict sinter reducibility and reduction degradation properties from powder XRD data.

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