Wavelength-dispersive X-ray fluorescence spectrometer **ZSX PrimusIII+**



1. Introduction

The newly-released sequential general-purpose wavelength-dispersive X-ray fluorescence spectrometer, ZSX PrimusIII+ is the latest member of the ZSX Primus series. The ZSX PrimusIII+ with tube-above optics, a design based on the high-end ZSX PrimusII system, has selected functions focused on daily routine analysis. The advantages of the ZSX PrimusIII+ are as follows:

- Optimized for powder analysis with features such as tube-above optics
- High-precision analysis of major components in alloys and oxides
- Improvement in trace element analysis
- Easy operation using "EZ Analysis" window
- Software support for advanced analysis methods
- Advanced software—new SQX program
- Energy- and space-saving design

2. Specifications

The standard analyzing crystals on the ZSX PrimusIII+ are LiF (200), PET and RX25, making it capable of analyzing elements down to O. A wide variety of optional analyzing crystals is available, including high-sensitivity analyzing crystals and synthetic multi-layer analyzers. Up to 10 crystals can be mounted.

The ZSX PrimusIII+ is equipped with 2 slits standard and high resolution. Optionally, a slit for ultralight elements can be added.

The specifications of the ZSX PrimusIII+ are summarized in Table 1.

X-ray	X-ray tube	End-window Rh target 3kW	
generation	Generator	High frequency generator 3kW, 60kV-100mA	
	Sample size(max)	51mm (diameter), 40mm (H)	
	Primary beam filter	4 positions	
Spec- trometer	Diaphragm	4 positions (35.30.20.10mm)	
	Crystal	10 crystal changer Standard crystals: LiF(200),PET,RX25 [O-U]	
		Heavy elements: SC (scintillation counter)	
Counting	Detector	Light elements: F-PC (gas-flow proportional counter)	

Table 1. Specifications of the ZSX PrimusIII+.

3. Hardware

3.1. Optimized for powder sample analysis

For powder sample analysis, tube-below spectrometers generally require powders to be pressed into rigid pellets with a binder to prevent the sample from falling and contaminating the inside of the chamber during measurement, and to protect the vacuum pump and magnetic valves from fine particles scattered from specimens.

The ZSX PrimusIII+ features tube-above optics, which are optimal for powder sample analysis. This geometry, along with a programmable vacuum speed and a powder trap, enables secure analysis of powder samples without the use of binder, thereby simplifying sample preparation and reducing analysis cost. Reducing the risk of sample contamination also decreases the frequency of system maintenance. The sample chamber on the ZSX PrimusIII+ can be easily pulled out, simplifying routine maintenance.

3.2. Special optical design to reduce analysis error caused by curved sample surface for high precision analysis

The variation in distance between the sample surface and the X-ray tube significantly affects X-ray intensities observed during measurement. The ZSX series spectrometers, including the ZSX PrimusIII+, employ special optics that minimize this effect and, therefore, enable highly stable measurement (Fig. 1).

For example, fused bead specimens sometimes have curved analysis surfaces. The curvature, which depends on the condition of the bottom surface of platinum-alloy molds, results in variation of X-ray intensities. Even when the sample surface is not flat, it is possible to measure fused bead specimens with minimal error on the ZSX PrimusIII+.

3.3. High-precision sample positioning mechanism

The high-precision sample-positioning mechanism employed on the ZSX PrimusIII+ (Fig. 2) reduces analytical errors caused by sample holders such as those due to variation in their heights. This mechanism keeps the distance between the sample surface and the X-ray tube constant. Therefore, the ZSX PrimusIII+ is suitable for high-precision analysis, such as for steel and alloys.



Fig. 1. Unevenness and X-ray intensity.

(a) Schematic diagram around the sample position(b) Variation in X-ray intensity depending on the distance between the sample and the X-ray tube.

3.4. Temperature stabilizer

The power supply for the temperature stabilizer is separated from the main power supply for the spectrometer; therefore, the temperature inside the spectrometer is kept stable even while the instrument is off. Accordingly, it takes only a short time to stabilize the temperature when starting up the spectrometer.

3.5. Easy-to-use automatic sample changer (ASC)

The ergonomic design of the ASC's drawer and the height of the sample trays provide easy access for placing and replacing samples on the ASC trays. The ZSX PrimusIII+ includes a tray for 12 sample positions as standard. Optionally, 24 positions (2 trays), 36 positions (3 trays), and 48 positions (4 trays) are available (Fig. 3).

3.6. High throughput using a dual chamber system

The ZSX PrimusIII+ employs a "Dual Chamber System", which has the pre-evacuation chamber separated from the sample chamber. During measurement, the next sample is loaded into the preevacuation chamber, which reduces the time needed to switch samples. In addition, the sample transportation



Fig. 2. High-precision sample positioning mechanism.



Fig. 3. Automatic sample changer (ASC) of the ZSX PrimusIII+.



Fig. 4. Dual chamber system.

and vacuum system are optimized to improve the sample throughput dramatically (Fig. 4).

4. Software

The software installed on the ZSX PrimusIII+, based on the ZSX series software, was designed with intuitive operation and superior user-friendliness in mind.

4.1. User-friendly operation display

All operations can be started from a single main window. The screen has user-friendly features, such as simple menu buttons and the Flowbar.

4.2. EZ Analysis (new function)

"EZ Analysis" mode, in which all routine operations are integrated, has been added to the main menu. The intuitive user interface, with graphical displays in the "EZ Analysis" mode, enables easy daily operation from a single window (Fig. 5).

4.3. EZ Scan (advanced)

"EZ Scan", which has earned a strong reputation, enables simple dialog settings for SQX (Scan Quant X), a semi-quantitative analysis program. Information input for individual samples is used to automatically set up the calculation condition, which can provide accurate analysis results by the ZSX PrimusIII+ (Fig. 6).

4.4. Application Templates

Application Templates, in which measurement conditions, sample preparation information and quantitative methods are stored for many applications, make it easy to take advantage of Rigaku's unparalleled expertise in XRF analysis. Even inexperienced users can easily create new applications for a wide range of sample types.



Fig. 5. EZ Analysis window.

4.5. Application packages

Rigaku provides application packages that include analytical parameters and samples necessary to set up quantitative analysis for various kinds of materials.

Calibration curves are automatically stored by running standard samples included in these packages after loading parameters from an installation CD.

These application packages consist of reference standard samples, drift-correction samples, parameters such as measurement condition and correction coefficients, and an instruction manual. Years of experience accumulated by Rigaku for various applications is reflected in the contents of the packages.

4.6. SQX analysis—applicable to various types of samples

"SQX (Scan Quant X)" is a standardless, semiquantitative analysis program. With this program, a qualitative scan is run and the detected elements are then quantified by the fundamental parameter (FP) method without the use of reference standard samples.

Even for samples with complicated matrices, the program provides accurate analysis results with automatic correction for spectral overlap and absorption/enhancement effects of coexisting elements.

4.6.1. Fixed angle analysis

After the scan, X-ray intensities are counted at each 2θ angle of peak and background for an element line for a given time, usually much longer than the time for a step in the scan; therefore, the precision is much improved. This function is effective for trace element analysis in particular.

4.6.2. Theoretical line overlap correction

This function corrects spectral overlap using theoretical intensities of correcting lines. This function, unique to Rigaku software, enables accurate correction of spectral overlap for both thick (bulk) samples and thin film samples.

4.6.3. Correction functions

• Sample film correction

Based on a selected sample film type, intensity attenuation due to the absorption of the fluorescence X-rays by the film is automatically corrected.

• Correction of binder for the pressed powder method Based on information such as a binder type and



Fig. 6. Advanced EZ Scan.

ZSX - SQX Calcula	ation				
e Impurity Data	Window Help				
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EZ Analysis	Analysis	Data Processing	Qual Application	Quant Application	on Utility
🚔 SQX Calculati	on				
PET_Sb	Browse	Calc. Cor	ndition Calculate	Print	Mater
Sample: PET_S	ib	Date	analyzed : 2010-8-121	2:48	
Sample tune · D	olumer Compa	ant luna : Mata	l Matching libr		Sample are
Sample ope . 1	olymei Compoi	ion type . Moto	a Matching ibi	ay.	Jampio arc
Sample film corr.	Imprity	corr. :			
Component	Result Unit	El line	Analysis depth	Intensity ratio	_
CH2	70.1319 mass%	C-KA	0.0087	1.0000	
0	29.8311 mass%	0 -KA	0.0035	1.0000	
Mg	0.0048 mass%	Mg-KA	0.0174	1.0000	
AI	0.0011 mass%	AŀKA	0.0270	1.0000	
Si	0.0028 mass%	Si-KA	0.0403	1.0000	
P	0.0098 mass%	P-KA	0.0577	1.0000	
Sb	0.0185 mass%	Sb-KA	51.1422	0.4431	
Insett	Delete Change	e Add.			

Fig. 7. "Analysis depth" output in SQX.

A depth of 50 mm is required to reach infinite thickness for Sb-K α in this example. Deviations from the infinite thickness can be corrected by inputting a sample diameter and a weight.



Fig. 8. Applications where the SQX Scattering FP Method could be used.

weights of sample and binder, an FP calculation is performed to take into account absorption by the binder.

4.6.4. Analysis depth calculation (new function)

Based on SQX analysis results, "analysis depth (critical depth)" and "intensity ratio to infinite thickness" can be output for each element. Analysis results can be evaluated with respect to sample thickness by examining the analysis depth information (Fig. 7).

4.6.5. SQX Scattering FP Method

The "SQX Scattering FP Method" estimates the effect of elements that are not measured, typically from H to O, using X-ray intensities of the scattering lines from the X-ray tube. This method is effective for samples whose base matrices are unknown, such as sludge, plants or polymers. Fig. 8 shows applications where the SQX Scattering FP Method can be used. Table 2 shows an example of analysis results by SQX using the Scattering FP method and the conventional FP method. In the latter case, the correct material has to be assigned for the balance component in analysis of organic materials. The analysis results show that the Scattering FP method enables accurate analysis by SQX without specifying the balance component.

Table 2.	SQX analysis result by the Scattering FP method and
	the conventional FP method.

(unit: mass%)					
Met	hod	Scattering FP	FP	FP	
Balance component		Estimated	C (carbon)	O (oxygen)	
Element	Standard value	Analysis value	Analysis value	Analysis value	
Mg	0.145	0.143	0.094	0.195	
Р	0.236	0.236	0.163	0.359	
S	0.316	0.363	0.231	0.517	
Са	0.64	0.735	0.461	1.06	
Zn	0.0032	0.0032	0.0019	0.0045	

Sample: a plant (dried)

4.7. Various functions to support high-precision analysis

4.7.1. Search function for overlap lines

This function searches potential overlap lines (including higher-order lines) to the element lines of analytes based on representative sample compositions and the wavelength database of fluorescence X-rays. It is possible to select a true overlap line from the list of potential overlap lines.

4.7.2. Automatic selection of correction model in theoretical matrix correction coefficients (new function)

Matrix correction coefficients can be obtained easily from the ZSX PrimusIII+ software.

Matrix correction, a correction for absorption from and enhancement by coexisting elements in the empirical calibration method, has been used widely in applications such as steel and alloys, refractories and lubricating oils.

Matrix correction coefficients are obtained by one of the following methods. To obtain matrix correction coefficients empirically, it is necessary to prepare a large number of standard samples and carry out multiple regression calculations. Alternately, the coefficients may be calculated from theoretical X-ray intensities by the FP method without using any standards.

There are several models for matrix corrections with theoretical matrix correction coefficients (theoretical alphas); which model to use depends on the particular applications. Therefore, knowledge of applications and correction models is required to select the best one for calculation of theoretical matrix correction coefficients.

The ZSX PrimusIII+ software automatically selects the proper correction model for each analyte based on sample information and compositions of standard samples, and then calculates theoretical matrix correction coefficients. This function makes it easy to apply matrix corrections for calibration.

4.7.3. Fusion bead correction (advanced)

In the fusion method, there are several factors that cause analysis errors; loss on ignition (LOI), gain on ignition (GOI), variation of dilution ratio from weighing error of sample and flux, and evaporation of flux during



Fig. 9. Sample preparation information for the fusion bead correction.

- (1) Flux compound, flux and sample weight
- (2) LOI correction
- (3) Oxidizer information
- (4) Correction for dilution ratio



Fig. 10. MgO calibration curve using fused beads with different dilution ratios.

fusion. All of these error factors can be corrected efficiently using the unique fusion bead correction functions. Analysis parameters for the fusion bead correction can be set up by entering simple sample information (Fig. 9). Figure 10 shows an example of a MgO calibration curve using fused beads having different dilution ratios with the fusion bead correction applied. The correction works well and the calibration curve shows a good fit.

5. Various maintenance functions

The ZSX PrimusIII+ has several maintenance functions introduced below, which makes daily maintenance easy.

5.1. Automatic pulse height adjustment

By simply designating the position of the pulse height adjustment sample and choosing one of the detectors, the system will automatically adjust the pulse height of the detector.

5.2. Automatic aging of X-ray tube

The system automatically controls tube aging speed based on the duration in which the X-ray tube is off.

5.3. Automatic center wire cleaning (ACC)

The energy resolution of the gas-flow proportional counter (F-PC) deteriorates gradually owing to the quenching gas and impurities contained in P-10 gas. The Automatic Center wire Cleaning function recovers the performance of the F-PC by a simple operation from the computer without the need to open the optical chamber or turn off the system. This function has been mounted in over 3,000 spectrometers; Rigaku has received favorable reports from users about the reliability and ease-of-use of this function.

5.4. Self-diagnostics

Operators can examine the condition of the spectrometer and each of its driving mechanisms by simple computer operations. The ZSX PrimusIII+ provides various tests, such as throughput of each driving mechanism, vacuum condition, performance and repeatability.

5.5. Maintenance check list

Maintenance items are listed with recommended maintenance intervals.

5.6. Maintenance records

The results of PHA adjustments, check analysis (QC analysis) and drift corrections are recorded and can be displayed on control charts. This enables easy review of the spectrometer condition for determining the causes of any problems.

6. Applications

6.1. Cement raw meal analysis by the pressed powder method on the ZSX PrimusIII+

Cement is one of the most important materials for construction. Various physical properties are given to cement by changing the mineral compositions of clinker; therefore, it is important to control the chemical compositions of cement raw meal.

XRF spectrometry has been used for chemical composition analysis in cement production processes owing to simple sample preparation, rapid analysis and high precision.

The ZSX PrimusIII+ can be used for quantitative analysis of cement raw meal by the pressed powder method, as demonstrated here.

6.1.1. Standard and sample preparation

A series of reference materials of cement raw meal certified by CSBTS were used for calibration.

Cement raw meal powder samples, previously pulverized, were pressed into aluminum rings at 120 kN to form pressed pellet specimens.

6.1.2. Measurement and results

Measurements were performed on the ZSX PrimusIII+ with a 3 kW Rh-target X-ray tube.

^{♦:} Dilution ratio 10, ♦: Dilution ratio 22.17

Table 3. Measurement condition.

Path atmosphere	Vacuum					
Tube condition		50	k) (and E	0 0		
rube condition		50	kv and 5	0 MA		
Analysis area		30 ו	mm in dia	meter		
Element	Si	AI	Fe	Ca	Mg	
Line	Κα	Κα	Κα	Κα	Κα	
Primary filter	Out	Out	Out	Al25	Out	
Slit	S4	S4	S2	S4	S4	
Crystal	PET	PET	LiF(200)	PET	RX25	
Detector	F-PC	F-PC	SC	F-PC	F-PC	
Counting time (s)	6	6	6	4	10	
Element	S	Na	K	Ti	CI	
Line	Κα	Κα	Κα	Κα	Κα	
Primary filter	Out	Out	Out	Out	Out	
Slit	S4	S4	S4	S4	S2	
Crystal	PET	RX25	LiF(200)	LiF(200)	PET	
Detector	F-PC	F-PC	F-PC	F-PC	F-PC	
Counting time (s)	6	10	6	6	10	

Table 4. Calibration result.

Analyte	Calibration range (mass%)	Accuracy (mass%)
SiO ₂	10.05 – 14.43	0.12
Al ₂ O ₃	2.41 – 4.27	0.039
Fe ₂ O ₃	1.96 – 4.52	0.075
CaO	39.84 - 44.84	0.11
MgO	0.69 - 2.59	0.044
SO ₃	0.06 - 0.24	0.0079
Na ₂ O	0.03 - 0.09	0.0044
K ₂ O	0.14 - 0.30	0.0039
TiO ₂	0.16 - 0.25	0.0042
CI	0.004 - 0.286	0.018

Measurement conditions are shown in Table 3. The RX25 multilayer analyzer, included in the standard configuration, has high sensitivity for Mg and Na and is capable of reducing higher-order lines such as Ca-K α -3rd, which would interfere with Mg-K α .

The calibration results are listed in Table 4 and the calibration curves for the representative analytes are shown in Fig. 11.

6.1.3. Repeatability test

One specimen of the reference materials used for the calibration was measured 10 times consecutively to demonstrate the performance of the ZSX PrimusIII+ with regard to short-term stability. The test results, shown in Table 5, prove that it is possible to analyze pressed pellet specimens of cement raw meal with high repeatability on the ZSX PrimusIII+.

6.1.4. Summary for cement raw meal analysis

Cement raw meal samples can be routinely analyzed with high accuracy and precision on the ZSX PrimusIII+ by the pressed powder method, a simple sample preparation.

6.2. Quality and process control of iron ore products by the pressed powder method

Iron ore is the most abundant mineral resource and



Fig. 11. Representative calibration curves for cement raw meal.

Table 5. Repeatability test result.

	(ur	nt: mass%)		
Analyte	Std. value	Average	Std. dev.	RSD%
SiO ₂	12.76	12.78	0.016	0.12
AI_2O_3	3.56	3.56	0.0048	0.14
Fe ₂ O ₃	2.94	2.92	0.0047	0.16
CaO	41.74	41.70	0.012	0.029
MgO	1.87	1.85	0.0078	0.42
SO ₃	0.17	0.18	0.0016	0.86
Na ₂ O	0.07	0.07	0.0008	1.1
K ₂ O	0.24	0.24	0.0003	0.13
TiO ₂	0.22	0.21	0.0009	0.44
CI	0.179	0.205	0.0008	0.38

iron is also one of the most important materials in modern industries. Since the amount of seaborne trade and the price have been increasing in recent years, analytical requirements have become more stringent. Total iron concentration in iron ore is a focal point for trading; therefore, analysis for determination of total iron requires high accuracy.

In mining sites, laboratory analysis includes quality check of run-of-mine and products, grade check for beneficiation and blending, and also research for area exploring. Similarly, iron ore analysis is required in pelletizing plants near mining sites and in sintering plants and stock yards at steel manufacturing sites. Wet chemical analysis is a traditional analytical technique for total iron determination, but it requires analytical skill and is time-consuming. In addition to being accurate, these analyses must be fast, simple and cost effective.

For powder samples in X-ray fluorescence spectrometry, the pressed powder method is the best solution in terms of quickness and simplicity. Since iron ore has a complex matrix owing to its various mineral assemblages, suitable corrections for that matrix effect are required in XRF analysis. The conventional correction technique for total iron by XRF is a method using Compton scattering as the internal standard (the Compton scattering ratio method), but the method has not met the requirements of the iron ore industry. Rigaku has developed an improved Compton scattering method by integrating it with a theoretical alpha correction, which has improved analysis accuracy significantly.

The ZSX PrimusIII+ can be used for iron ore analysis, especially for determining total iron in iron ore and products, by the pressed powder method, as demonstrated here.

6.2.1. Standard and sample preparation

The standard samples used for calibration were six commercially available certified reference materials (CRMs) supplied by Japan Iron and Steel Federation (JISF) and Bureau of Analysed Samples Ltd (BAS). These standards are composed of hematite ore, sintered ore, pellet and pure iron oxide. The range of total iron concentration in these CRMs is wide, from 39.8 mass% to 69.8 mass%.

The well-dried (two hours at 105°C) powder samples were ground in a tungsten carbide container and the resulting powders were pressed at 250 kN using sample cups without any binder.

6.2.2. Measurement and calibration method

The ZSX PrimusIII+ with a 3 kW Rh target X-ray tube was used to measure the element lines of Fe, Si, Al, P, Mg, S, Ca, K, Ti, Mn, V and Rh-K α Compton. For the Fe-K α measurement, the attenuator was used to reduce intensity without changing the tube loading.

The calibration equation for "total iron" is as follows,

$$W_{Fe} = (AI_R^2 + BI_R + C) (1 + \sum \alpha_j W_j)$$

$$I_R = I_{Fe} / I_{remen}$$

- α_i : theoretical alpha of element j
- W_i : weight fraction of element j
- I_{Fe} : intensity of Fe-K α
- I_{Comp} : intensity of Rh-K α Compton.



Fig. 12. Calibration curve of total iron using Compton scattering ratio with theoretical alpha correction.

Table 6. Calibration results of iron ore.

Component	Concentration range (mass%)	Accuracy (mass%)
Total Fe	39.76 - 69.84	0.10
SiO ₂	1.70 – 13.69	0.11
CaO	0.039 – 17.78	0.074
Mn	0.018 – 1.07	0.0017
Al ₂ O ₃	0.38 - 6.42	0.13
TiO ₂	0.044 - 0.48	0.0076
MgO	0.018 – 1.92	0.074
Р	0.014 – 0.59	0.0027
S	0.002 - 0.115	0.0002
K ₂ O	0.007 – 0.52	0.0029
V	0.004 - 0.46	0.0053

Matrix correction coefficients (alphas) applied to the matrix correction in the calibrations were theoretically calculated by the built-in FP software. The theoretical alphas for total iron calibration were calculated in consideration of the Compton scattering ratio by the Quant Scattering FP Method, an optional program for the ZSX PrimusIII+.

6.2.3. Results

The accuracy of total iron calibration obtained in this study is excellent, as shown in Fig. 12.

The calibration accuracy for all the components analyzed in this study is listed in Table 6.

The accuracy is calculated by the following formula,

Accuracy =
$$\sqrt{\frac{\sum_{i} (C_i = \hat{C}_i)^2}{n - m}}$$

Ci: calculated value of standard sample

 \hat{C}_i : reference value of standard sample

n : number of standard samples

m: degree of freedom (2: linear, 3: quadratic).

To evaluate this correction method, two types of iron ore CRMs were analyzed. Measurements were

Table 7. Analysis result of iron ore pellet.
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(unit: mass%)						
Analyta	Chemical	Duplicate #1		Duplic	ate #2	
Analyte	Value	XRF	Diff.	XRF	Diff.	
Total Fe	65.41	65.48	0.07	65.46	0.05	
SiO ₂	2.29	2.414	0.124	2.405	0.115	
CaO	2.49	2.610	0.120	2.610	0.120	
Mn	0.039	0.040	0.001	0.040	0.001	
Al ₂ O ₃	0.54	0.539	0.001	0.547	0.007	
TiO ₂	0.14	0.143	0.003	0.142	0.002	
MgO	0.49	0.489	0.001	0.489	0.001	
Р	0.043	0.044	0.001	0.044	0.001	
S	0.003	0.003	0.000	0.003	0.000	
K ₂ O	0.098	0.094	0.004	0.094	0.004	
V	0.19	0.186	0.004	0.192	0.002	

 Table 8.
 Analysis result of sintered ore.

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(unit: mass%)						
Analyte	Chemical	Duplicate #1		Duplicate #1 Duplicate #2		
Analyte	Value	XRF	Diff.	XRF	Diff.	
Total Fe	56.16	56.06	0.10	56.16	0.00	
SiO ₂	5.41	5.232	0.178	5.237	0.173	
CaO	9.91	9.860	0.050	9.886	0.024	
Mn	0.263	0.263	0.000	0.265	0.002	
Al ₂ O ₃	2.01	1.821	0.189	1.831	0.179	
TiO ₂	0.31	0.318	0.008	0.318	0.008	
MgO	1.62	1.688	0.068	1.699	0.079	
Р	0.06	0.056	0.004	0.057	0.003	
S	0.012	0.012	0.000	0.012	0.000	
K ₂ O	0.036	0.037	0.001	0.037	0.001	
V	0.031	0.038	0.007	0.038	0.007	

performed with duplicated pressed pellet specimens. The test results are shown in Tables 7 and 8.

6.2.4. Summary of iron ore analysis

X-ray fluorescence spectrometry is a rapid, precise and accurate method to meet the requirements of the iron ore industry. It can also minimize cost and time in iron ore analysis.

The results above demonstrate that this method is applicable in practice with little dependence on mineral assemblages. They also indicate that the pressed pellet method with Rigaku's advanced correction technology is widely available to people in the iron ore industry such as suppliers, producers and steel manufacturers with high cost-efficiency and higher throughput than conventional methods.