

CHAPTER FIVE

EXPERIMENTAL METHODS

This chapter describes the experimental systems, the method of preparation of EAF dust samples for microstructure investigation, the diagnostic leaching method for study phase analysis as well as x-ray diffraction analysis (Section 5.1). Laboratory experiments were carried out on iron-reduction distillation process. The experiments consisted of two reduction stages. The first reduction stage was carried out on the reduction of iron oxide to metallic iron (Section 5.2). The second reduction stage was carried out using nitrogen atmosphere and vacuum system for study the zinc oxide reduction by metallic iron from the first reduction stage (Section 5.3). The experimental conditions, such as effect of temperature and time as well as effect of reduction gas compositions were performed. The samples were prepared in the laboratory of the Department of Chemical and Metallurgical Engineering, the Royal Melbourne Institute of Technology. All the laboratory experiments were carried out at the G.K. Williams Cooperative Research Centre for Extractive Metallurgy at the University of Melbourne, Australia.

5.1 CHARACTERISATION OF SMORGON STEEL WORK DUST

5.1.1 Microscopic Examination

Samples of EAF dust from Smorgon Steel Works were mounted in hot mounts with bakelite powder. After cooling, the surface of the samples was prepared by grinding with silicon carbide paper with grit 60 and 400 respectively. The samples were examined under a PHILIPS XL 30¹ scanning electron microscope (SEM) equipped with a

¹ PHILIPS XL 30 is a trademark of Philips Electron Optic Ltd., Holland.

OXFORD ISIS² energy dispersive spectrometer (EDS) which was employed in obtaining the micrographs.

5.1.2 Chemical Composition and Phase Analysis

EAF dust samples were sent to Spectrometer Services PTY.LTD., Coburg, Melbourne, Australia for checking the chemical compositions by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) method.

Characterisation of phases was based on x-ray diffraction patterns (XRDPs) generated on a PHILIPS PW 1800³ x-ray diffractometer. Powdered EAF dust samples were packed into a circular steel container with a diameter of 25 millimeters and depth 1 millimeter. X-ray diffraction was carried out using a Cu-K α radiation source set on 30mA and 40kV. Each packed sample was scanned for 46.2 minutes.

The estimated concentrations of the common compounds in Smorgon Steel Works dust used in these experiments were carried out by diagnostic leaching. Sodium and potassium chloride were dissolved by a hot water leaching method. Zinc oxide phase analysis was carried out by a dilute sulphuric acid leaching method. The amount of zinc ferrite and magnetite were calculated from the remaining zinc and iron values. The outline, procedure and the calculation method of diagnostic leaching are shown in Appendix A. The residues after leaching were analysed by XRD.

² OXFORD ISSI is a trademark of Oxford Instruments Pty.Ltd., England.

³ PHILIPS PW 1800 is a trademark of Philips Electron Optic Ltd., Holland.

5.2 FIRST REDUCTION STAGE EXPERIMENTS

5.2.1 Materials

EAF dust from Smorgon Steel Works was used in the experiments. The pelletising dust was ground in a ball mill and dried at 120 °C for twelve hours, to ensure removal of moisture. The dried dust was mixed with bentonite in a 1% ratio by weight of treated dust. The powders were mechanically mixed together and formed into cylindrical briquettes by compacting the powders in a 15.00 millimeters inside diameter cylindrical mold under a standard load of 3×10^3 kilograms per square centimeter for 30 seconds. This alloy steel floating mold, with movable plungers at both ends, was used to produce uniform briquettes. A briquette mass of 5.05 (± 0.05) grams was chosen, and this produced a briquette with a length of 8.00 millimeter. All briquettes were placed in a desiccator before using in reduction process. The size, surface area, and texture of briquettes were easily reproduced. High purity carbon dioxide and carbon monoxide were used as the reactant gases.

5.2.2 Experimental Set-up

A schematic diagram of the experimental set-up is shown in Figure 5.1 . A horizontal furnace with a 4.5 centimeter diameter silica tube inside was used for the experiments. The briquette sample was weighed, placed in a silica boat and heated at definite temperatures in gas mixtures of high purity carbon dioxide and carbon monoxide. A mass flow controller, BRONKHORST HI-TEC, was used to manage the flow and mixing of gases. Prior to the experiment, the silica tube inside the furnace was flushed with carbon dioxide/carbon monoxide mixture for 20 minutes to ensure that no oxygen was presented and also to allow the equilibration of the temperature in the hot zone of the furnace.

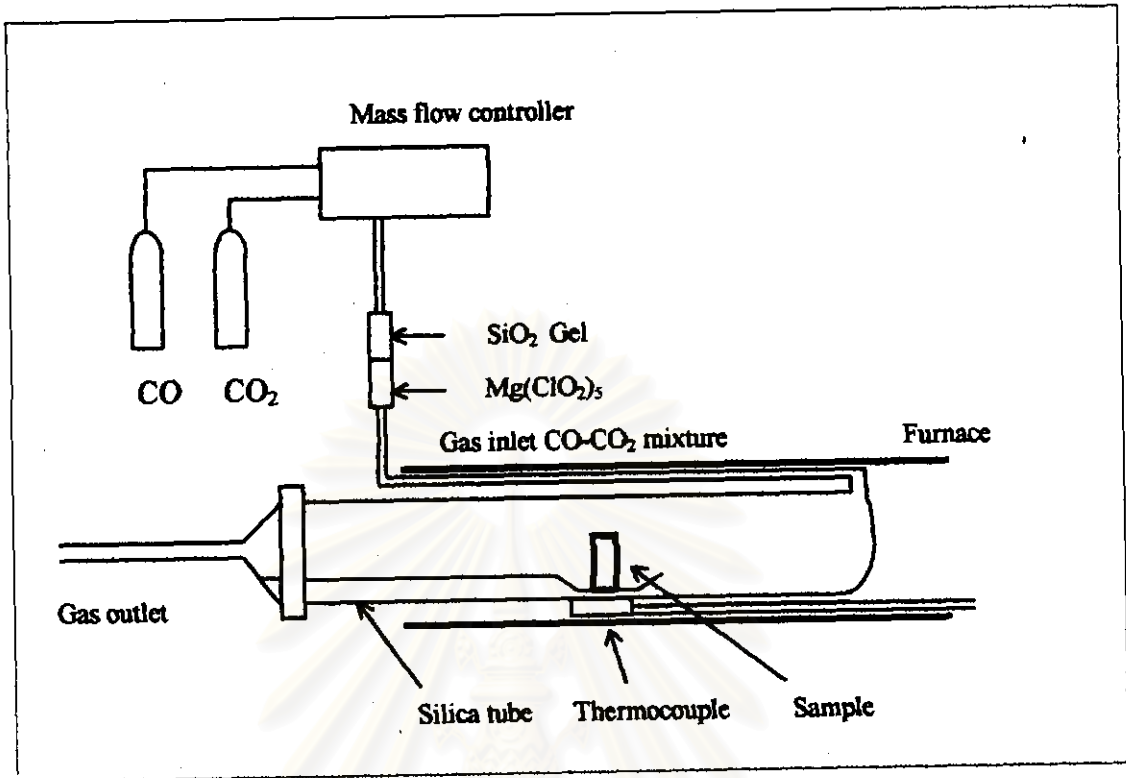


Figure 5.1: Schematic diagram of experimental set-up for the first reduction stage.

5.2.3 Procedure

For first reduction stage, the temperatures used were between 600 and 800 °C with the carbon monoxide/carbon dioxide gas ratio varied from 3 to 9 . The gas mixture, at a flow rate of 0.545 to 0.583 l/min, was passed through the SiO_2 gel and $\text{Mg}(\text{ClO}_2)_5$ to remove moisture. After that the gas mixture was passed over the sample for the required heating time. The temperature in the hot zone was measured by a R-type, Pt/Pt-13%Rh thermocouple and maintained within ± 5 °C. The sample was placed in the furnace for between 0.5 and 6 hours. After the reduction experiment, the sample was cooled to room temperature. The sample was then weighed and analysed for metallic iron. In order to obtain the metallic iron content, a sample was dissolved in bromine-methanol solution and then filtered. The method is described in Appendix B. The reduction ratio of iron R_{Fe} was defined as the ratio of metallic iron to initial total iron in the briquette. In

addition, the overall concentrations of iron, zinc, lead, cadmium, potassium, sodium, chlorine and chromium in a selected spent briquette were determined by the ICP-AES method. Characterisation of the phases present in the selected spent briquettes was based on XRDs.

The experimental conditions used for the runs are summarised in Table 5.1 .

Table 5.1: Summary of Experimental Conditions for the First Reduction Stage.

Experimental runs	Temp(°C)	Time	Injected gases (volume %)		Gas flow rate (l/min)	Briquette type
			CO	CO ₂		
A-1	600	1.5 hrs	90	10	0.545	non-sintered
A-2	600	4.0 hrs	90	10	0.545	non-sintered
A-3	600	6.0 hrs	90	10	0.545	non-sintered
B-1	700	30 mins	90	10	0.545	non-sintered
B-2	700	1.0 hr	90	10	0.545	non-sintered
B-3	700	1.5 hrs	90	10	0.545	non-sintered
B-4	700	2.5 hrs	90	10	0.545	non-sintered
B-5	700	4.0 hrs	90	10	0.545	non-sintered
B-6	700	6.0 hrs	90	10	0.545	non-sintered
C-1	800	30 mins	90	10	0.545	non-sintered
C-2	800	1.0 hr	90	10	0.545	non-sintered
C-3	800	1.5 hrs	90	10	0.545	non-sintered
C-4	800	2.5 hrs	90	10	0.545	non-sintered
C-5	800	4.0 hrs	90	10	0.545	non-sintered
C-6	800	6.0 hrs	90	10	0.545	non-sintered
D-1	700	30 mins	75	25	0.583	non-sintered
D-2	700	3.5 hrs	75	25	0.583	non-sintered
D-3	700	5.0 hrs	75	25	0.583	non-sintered
D-4	700	6.0 hrs	75	25	0.583	non-sintered
E-1	700	30 mins	90	10	0.545	sintered
E-2	700	1.0 hr	90	10	0.545	sintered
E-3	700	1.5 hrs	90	10	0.545	sintered
E-4	700	2.5 hrs	90	10	0.545	sintered
E-5	700	4.0 hrs	90	10	0.545	sintered
E-6	700	6.0 hrs	90	10	0.545	sintered

Runs A-1 to A-3, B-1 to B-6, and C-1 to C-6 were used to study the effect of temperature. The same CO/CO₂ ratio of 9 was used for each of these runs.

Runs B-1 to B-6 and D-1 to D-4 were used to study the effect of gas composition at 700°C.

Runs B-1 to B-6 and E-1 to E-6 were used to study the effect of sintering the briquettes. The same CO/CO₂ ratio of 9 and temperature of 700 °C was used in each runs.

5.3 SECOND REDUCTION STAGE EXPERINEMTS

5.3.1 Materials

The completed first reduction stage briquette samples were used in these experiments. The non-sintered briquettes were reacted at 700 °C, a CO₂/CO gas ratio equal to 0.11 for a reduction time of two and a half hours. High purity nitrogen gas was used for runs carried out in a nitrogen atmosphere. Runs were also carried out under vacuum condition using a vacuum pump.

5.3.2 Experimental Set-up for Nitrogen Atmosphere

A schematic diagram of the experimental set-up is shown in Figure 5.2 . A vertical furnace with an alumina tube (4.2 centimeter inside diameter) was used for these experiments. The furnace created a uniform 11.6 centimeter constant temperature zone. The completely reduced briquette samples from the first reduction stage were chosen for these experiments. The sample was weighed and put in an alumina crucible and heated at specified temperatures in nitrogen gas. A mass flow controller, BRONKHORST HI-TEC, was used to manage the flow rate of nitrogen gas. Prior to the experiment, the furnace was flushed with the nitrogen gas for 20 minutes to ensure that no oxygen was present and also to allow the equilibration of the temperature in the hot zone of the furnace.

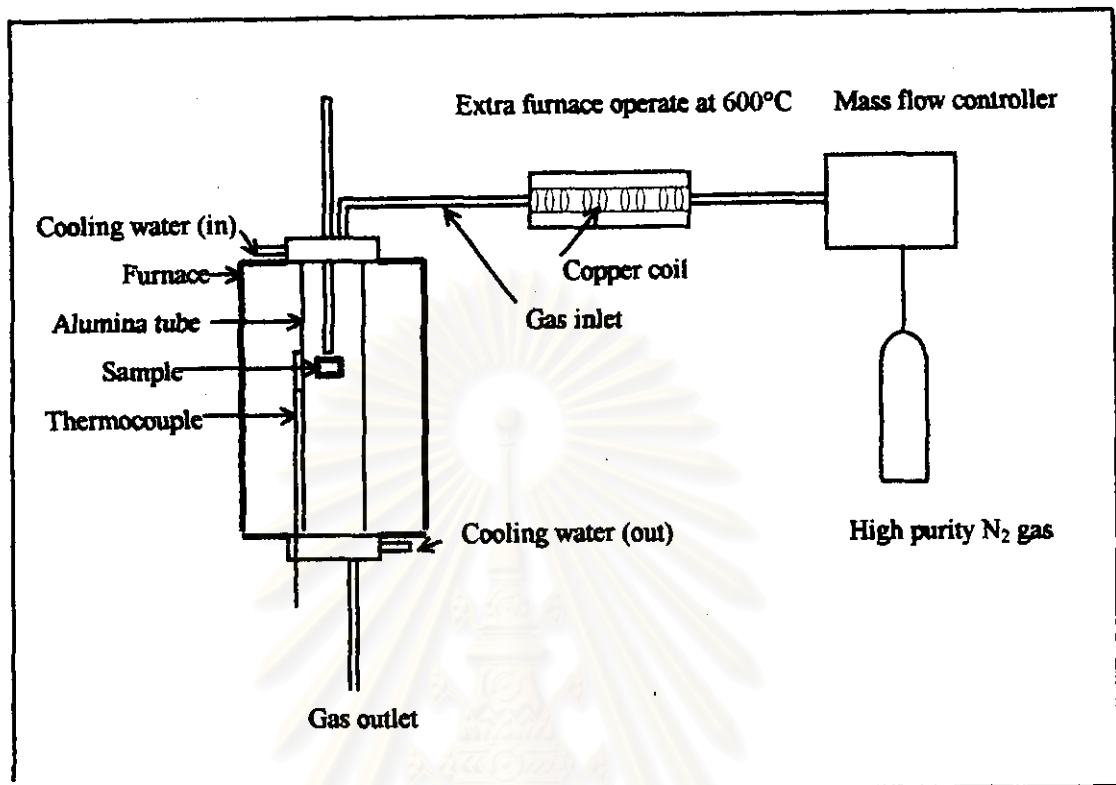


Figure 5.2: Schematic diagram of experimental set-up for the second reduction stage for nitrogen atmosphere.

5.3.3 Procedure in Nitrogen Atmosphere

The temperatures used were between 900 and 1200 °C. The nitrogen gas, at a flow rate of 1.200 l/min, was passed through a furnace containing a copper coil operated at 600°C for lower the oxygen content in the nitrogen gas. Then, the gas was passed over the sample for the required heating time. The temperature in the middle of hot zone was measured by a R-type, Pt/Pt-13%Rh thermocouple and maintained within ± 5 °C. The sample was placed in the furnace for between 10 minutes and 7 hours. After the reduction experiment, the samples were brought up to the cold part for 20 minutes and quenched in nitrogen gas. After that the samples were removed to determine the weight loss and put back for the next run. The reduction ratio of zinc R_{Zn} was calculated from

the loss of zinc during the experiment divided by the initial zinc in the briquette. The outline and calculation method are given in Appendix C. In addition, the overall concentrations of iron, zinc, lead, cadmium, potassium, sodium, chlorine and chromium in the selected spent briquettes were determined by the ICP-AES method. Characterisation of the phases present in the selected spent briquette was based on XRDs.

The experimental conditions used for the runs are summarised in Table 5.2 .

Table 5.2: Summary of Experimental Conditions for the Second Reduction Stage in Nitrogen Gas.

Experimental runs	Temp(°C)	Time	Injected gas (volume %), N ₂	Gas flow rate (l/min)
F-1, F-8	900	1.0 hr	100	1.20
F-2, F-9	900	2.0 hrs	100	1.20
F-3, F-10	900	3.0 hrs	100	1.20
F-4, F-11	900	4.0 hrs	100	1.20
F-5, F-12	900	5.0 hrs	100	1.20
F-6, F-13	900	6.0 hrs	100	1.20
F-7, F-14	900	7.0 hrs	100	1.20
G-1, G-8	1000	1.0 hr	100	1.20
G-2, G-9	1000	2.0 hrs	100	1.20
G-3, G-10	1000	3.0 hrs	100	1.20
G-4, G-11	1000	4.0 hrs	100	1.20
G-5, G-12	1000	5.0 hrs	100	1.20
G-6, G-13	1000	6.0 hrs	100	1.20
G-7, G-14	1000	7.0 hrs	100	1.20
H-1, H-6	1100	30 mins	100	1.20
H-2, H-7	1100	1.0 hr	100	1.20
H-3, H-8	1100	2.0 hrs	100	1.20
H-4, H-9	1100	3.0 hrs	100	1.20
H-5, H-10	1100	4.0 hrs	100	1.20
I-1, I-8	1200	10 mins	100	1.20
I-2, I-9	1200	20 mins	100	1.20
I-3, I-10	1200	30 mins	100	1.20
I-4, I-11	1200	1.0 hr	100	1.20
I-5, I-12	1200	2.0 hrs	100	1.20
I-6, I-13	1200	3.0 hrs	100	1.20
I-7, I-14	1200	4.0 hrs	100	1.20

For each series F, G, H, and I, the same samples were used in the same series. In order to verify the reproducibility of the reduction experiments, two control samples were reduced under identical conditions.

5.3.4 Experimental Set-up for Vacuum System

A schematic diagram of the experimental set-up is shown in Figure 5.3. A vertical furnace with an alumina tube (4.2 centimeter inside diameter) was used in these experiments. The furnace created a uniform 17.5 centimeters constant temperature zone. The completely reduced briquette samples from the first reduction stage were chosen for these experiments. The sample and the INCONEL⁴ nickel alloy container pan were weighed and placed in the furnace. The container pan was connected to a weight transducer. The KYOWA⁵ transducer micro-load cell, model LVS-50GA, with the rated load 50 grams, was situated directly above the furnace, and provided a continuous measurement of the sample mass. The stainless steel wire, which supported the container pan, was connected to the transducer. The transducer was housed in a cold box, which has cooling water inside, to keep the temperature fluctuation and air disturbances to a minimum. The deflection of the transducer, due to the mass change, was converted to a signal. The signals which came from the mass loss of the sample during reduction stage were passed from the load cell to the transducer amplifier, HEWLETT PACKARD⁶ 34401A multimeter, instrumentation interface board and LABVIEW software respectively. The transducer and LABVIEW software recorder were calibrated using known masses. The change in mass during the reduction process was therefore known at every instant. In each of the experiments, a small amount of zinc vapour condensed on the container pan but most of it was removed in the cold trap (see Figure 5.3).

⁴ INCONEL is a trademark of INCO Alloys International, Inc., Huntington, WV.

⁵ KYOWA is a trademark of Kyowa Electronic Instruments Co., Ltd. Tokyo, Japan.

⁶ HEWLETT PACKARD is a trademark of Hewlett-Packard Co., Ltd. WA.

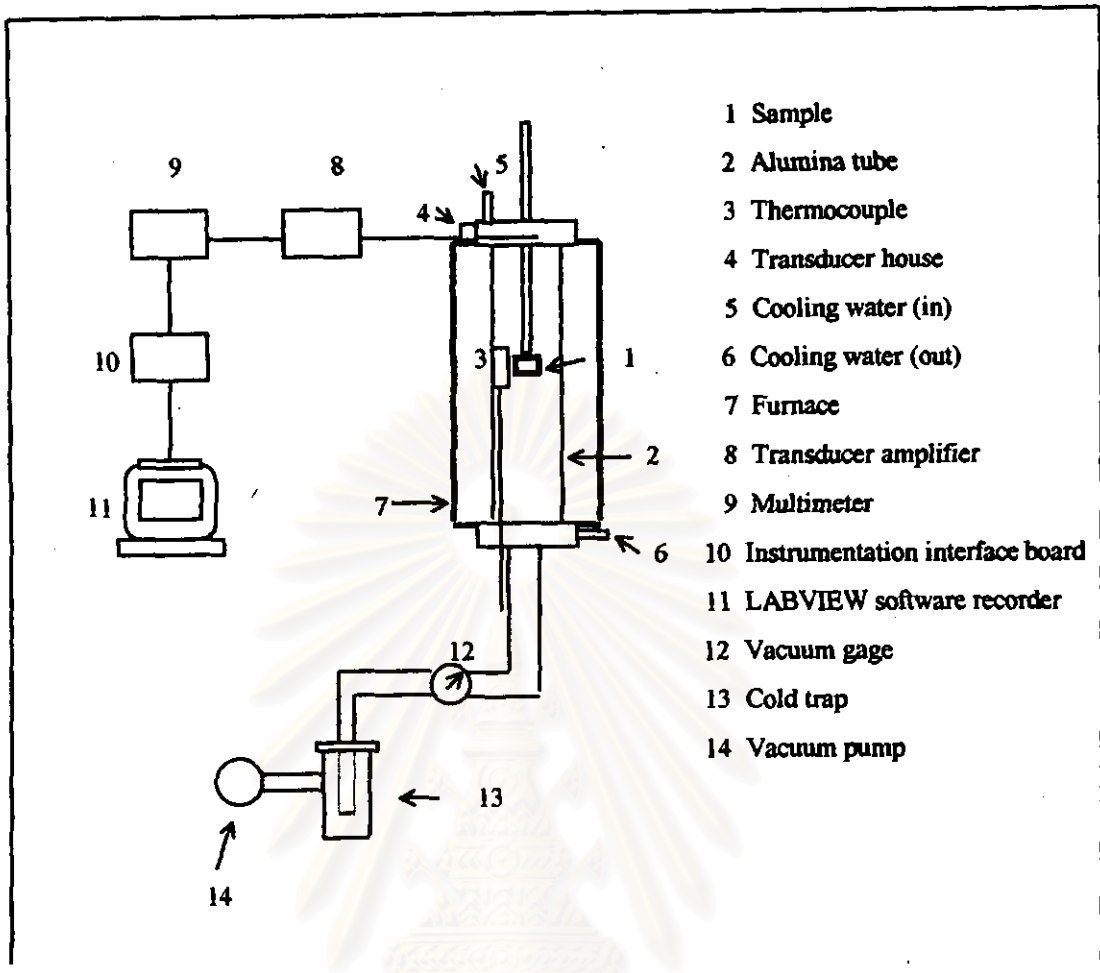


Figure 5.3: Schematic diagram of experimental set-up for the second stage reduction for vacuum system.

5.3.5 Procedure in Vacuum System

For the second reduction stage in the vacuum system, the temperatures used were between 800 and 1000 °C with a vacuum of 2.0×10^{-3} atmosphere (about 1.0-1.8 torr). The temperature in the middle of the hot zone was measured by a Pt-20%Rh / Pt-40%Rh thermocouple and maintained within ± 5 °C. The vacuum pump was operated for an hour concurrently with setting the temperature for zinc oxide reduction and the sample was placed inside the furnace at cold zone. After equilibration of system, the

sample was moved down in the hot zone of the furnace for between 50 and 120 minutes. During the reduction experiment, the weight loss was determined by the transducer and the data collected by the LABVIEW software program in computer. When the reaction was finished, the sample was cooled to room temperature by bringing up to the cold part of the furnace. This change in mass was due to the vaporisation of zinc. The reduction ration of zinc R_{Zn} was calculated from the loss of zinc during the experiment divided by the initial zinc in the briquette. In addition, the overall concentrations of iron, zinc, lead, cadmium, potassium, sodium, chlorine and chromium in a selected spent briquette were determined by the ICP-AES method. Characterisation of the phases present in the selected spent briquette was based on XRDPs.

The experimental conditions used for the runs are summarised in Table 5.3 .

Table 5.3: Summary of Experimental Conditions for the Second Reduction Stage under Vacuum.

Experimental runs	Temp (°C)	Time (min)	Pressure (atm)
J1	800	120	$2.0 \cdot 10^{-3}$
J2	800	120	$2.0 \cdot 10^{-3}$
K1	900	90	$2.0 \cdot 10^{-3}$
K2	900	90	$2.0 \cdot 10^{-3}$
L1	1000	50	$2.0 \cdot 10^{-3}$
L2	1000	50	$2.0 \cdot 10^{-3}$

In order to verify the reproducibility of the reduction experiments, two control samples were reduced under identical conditions.