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D. T2.2.2 Report on pilot scale tests undertaken for metal extraction on samples from DUFERCO site

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SUMMARY

The Materials Processing Institute together with its project partners has the objective of achieving a systematic, long-term beneficial outcome from recovery and regeneration of Past Metallurgical Sites and Deposits (PMSD) in the INTERREG region of Europe under an EU funded REGENERATIS project. Its aims are the innovative circularity to recover raw materials while regenerating the polluted sites.

This report is submitted in fulfilment of the requirements of work package T2 and deliverable DT2.2.2 for pilot scale metal extraction on samples from DUFERCO site.

1 INTRODUCTION

The NWE-REGENERATIS project (Interreg North-West Europe) aims to recover metals, minerals, and land from PMSDs using urban mining methods and valorise the site. The Materials Processing Institute will focus on recovering valuable metals from three different Past Metallurgical Sites and Deposits (PMSD's), by applying metallurgical processing techniques, especially pyrometallurgy. Based on non-intrusive geophysical prospecting techniques carried out by The University of Liege on the DUFERCO steelmaking waste stockpile in La Louvière (Belgium), three locations (S2, S6 and S8) with significant concentrations of potentially valuable metals were identified. Approximately 1 m^3 of samples were collected by CTP on 3rd December 2021.

An initial pre-treatment was performed on the samples by CTP in Belgium including crushing, screening and the use of magnetic separation equipment. Metal contents were separated from the mineral gangue through crushing. After crushing, particle size range was narrowed down through screening using various mesh sizes that increase the effectiveness of the subsequent separation steps. The recovery of precious metallic fractions (Fe, Al, etc.) and the concentration in some fractions of the metals that may be recovered through various following extraction operations by hydrometallurgy or pyrometallurgy are made possible by magnetic and eddy current separation.

Initial tests on several samples from different sites were carried out at the laboratory scale (300g) concentrating on the recovery of the major component, Iron. The most promising site was selected based on the results of the small-scale trials, site extraction and mineral processing activities. The sample selected was from Duferco[1].

2 EXPERIMENTAL METHODS

2.1 SAMPLE PREPARATION

Further sample was requested from CTP to perform the upscale tests. Unfortunately, the original sample was no longer available. A replacement was obtained from material gathered from the sample site location and put through the same pre-processing steps including grading and magnetic separation.

2.2 X-RAY FLUORESCENCE (XRF)

The chemical composition of the DUFERCO samples were analysed by X-ray fluorescence spectrometry (XRF), figure 1. This non-destructive method is used widely in many extractive and process industries, with its ability to detect trace elements at the parts per million (ppm) level. However, due to instrumental limitations and low X-ray yields for the light elements, it is often difficult to quantify elements lighter than sodium (atomic number 11).

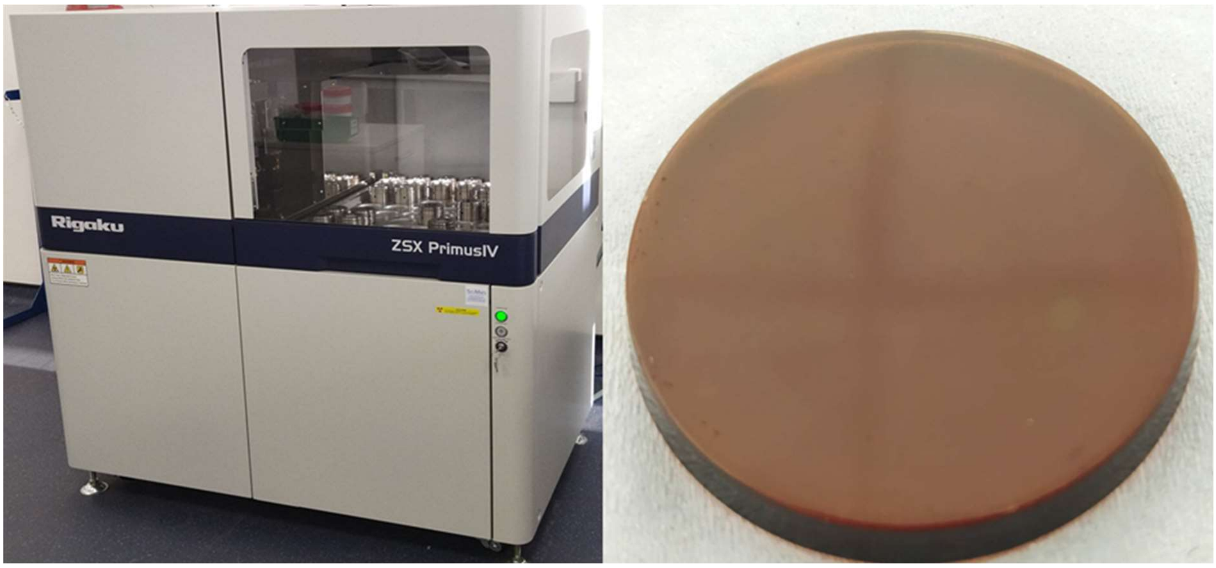

Figure 1: XRF device (left) on fused bead (right)

XRF was performed on the fused bead sample which showed higher homogeneity than the powdered sample. A semiquantitative analysis of the chemical composition was obtained from the instrument software.

Analysis of the new samples were compared to the material used in the laboratory scale trials.

Table I: XRF analysis of the DUFERCO samples

Sample	**Fe_2O_3**	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**MnO**	**Cr_2O_3**	**TiO_2**	**P_2O_5**	**CaS**	**V_2O_5**	**Na_2O**	**ZnO**
Lab Scale	45.13	24.54	10.90	5.21	5.63	5.73	1.074	0.50	0.493	0.192	0.167	0.037	
Pilot Scale	38.53	25.79	12.46	9.06	6.21	4.64	1.167	0.47	0.457	0.412	0.218	0.193	0.079
Sample	**BaO**	**Nb_2O_5**	**K_2O**	**SrO**	**CuO**	**WO_3**	**CoO**	**NiO**	**As_2O_3**	**ZrO_2**	**MO_3**	**Total**	
Lab Scale			0.028	0.026						0.02		99.8	
Pilot Scale	0.086	0.054	0.024	0.025	0.025	0.028	0.014	0.041	0.006	0.009	0.005	100.0	

The new sample was found to contain less iron oxide than the lab scale sample however it was still significant enough to justify extraction testing.

2.3 SAMPLE MODIFICATION

As shown in the lab scale tests it is necessary to modify the slag chemistry to facilitate iron recovery.

XRF analysis shows that DUFERCO material has high basicity, which is calculated to be approximately 2. Taking CaO-SiO_2 binary phase diagram into consideration, it is evident the current composition is in the region of 32 % SiO_2 and 68% CaO (Fig. 2). This makes the Fe recovery extremely difficult and uneconomical as the material is highly refractory and the liquidus is more than 2000 °C. As with the laboratory scale trials extra SiO_2 was added into the composition to bring the liquidus as low as possible.

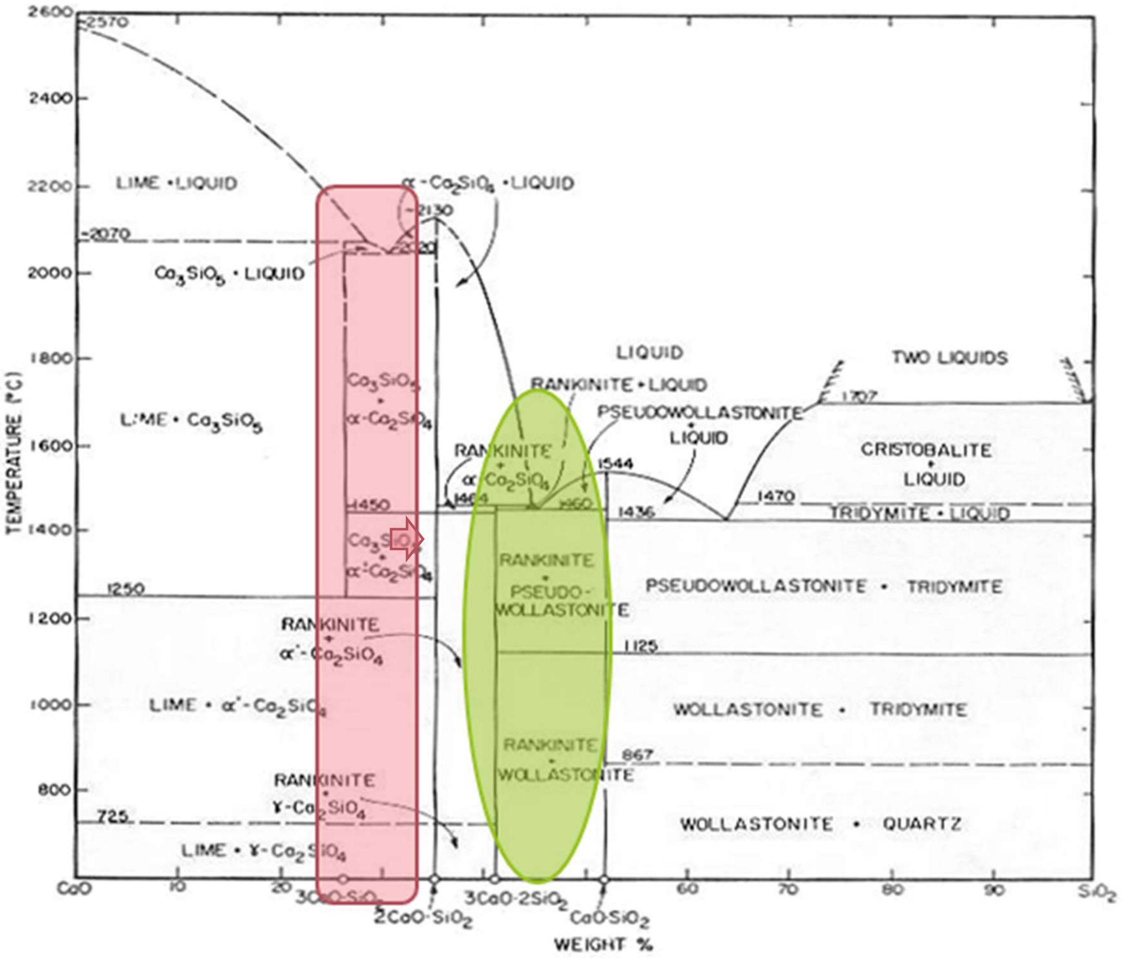

Figure 2: $CaO-SiO_2$ binary phase diagram

A Carbon addition is used as a reductant. The Carbon required to reduce the Iron in the Duferco sample was calculated taking into account the theoretical carbon required to reduce the Iron content is 10.1 g/100 g plus 4.5% dissolved Carbon. This also includes an allowance for 10% loss during the experiment and 98 wt% Carbon content in the graphite used.

A theoretical phase diagram of the compounded mixture was generated using Factsage 8.2 software. Figure 3a shows the phase diagram for the unmodified sample with just a carbon addition. The predicted slag liquidus is 1520°C. Figure 3b shows that the predicted liquidus is further reduced to approximately 1400°C using an addition of silica sand. Table II shows the overall composition of the final proposed sample.

Table II - Composition of DUFERCO sample with the addition of 10 g sand/100 g, mass%

Sample	**Fe_2O_3**	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**MnO**	**Cr_2O_3**	**TiO_2**	**P_2O_5**	**V_2O_5**	**Na_2O**
Duferco plus 10 g Sand/100g	35.01	24.19	19.38	8.42	5.67	4.22	1.06	0.46	0.42	0.20	0.18
Sample	**ZnO**	**Nb_2O_5**	**K_2O**	**SrO**	**CuO**	**CoO**	**NiO**	**As_2O_3**	**ZrO_2**	**SO_3**	**Total**
Duferco plus 10 g Sand/100g	0.07	0.05	0.15	0.02	0.02	0.01	0.04	0.01	0.01	0.41	100

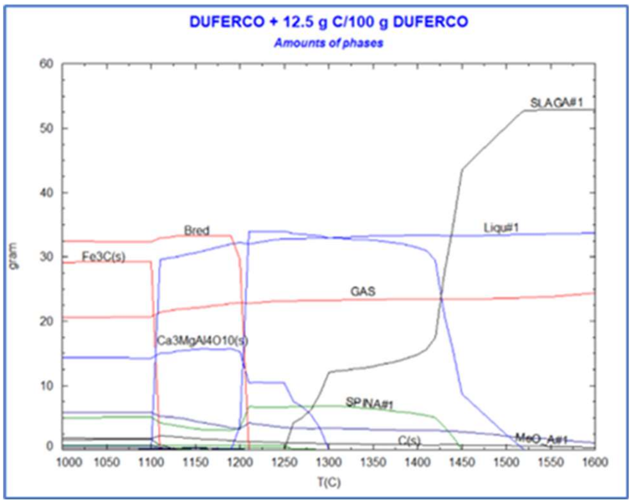

Fig. 3a – Duferco sample with Carbon only

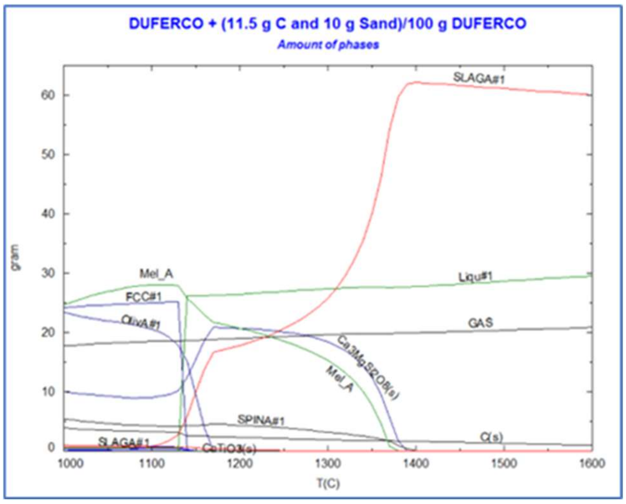

Fig 3b – Duferco sample with Carbon and Sand

2.4 EXPERIMENTAL METHOD

The sample was placed in an alumina circle fitted to the 100kW induction furnace at Materials Processing Institute light pilot plant. The metallic content of the slag was insufficient to effectively couple with the induction field, so the crucible was surrounded by a graphite tube to increase the heat input into the melt. The furnace was covered with a refractory lid though which an argon purge was applied and a thermocouple was inserted to measure temperature. The thermocouple position can be adjusted as the material melts. A schematic of the experimental set up is shown in Figure 4a and a photograph is shown in Figure 4b

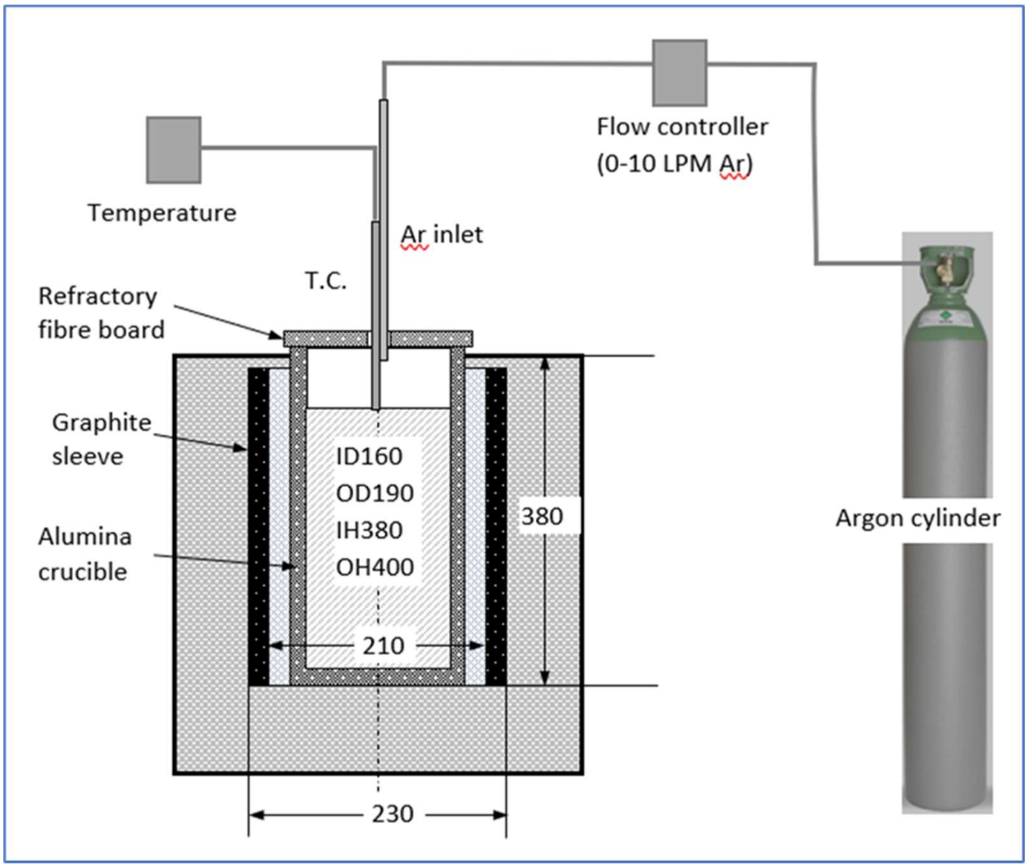

Figure 4a – Schematic of 100kW Induction furnace set-up

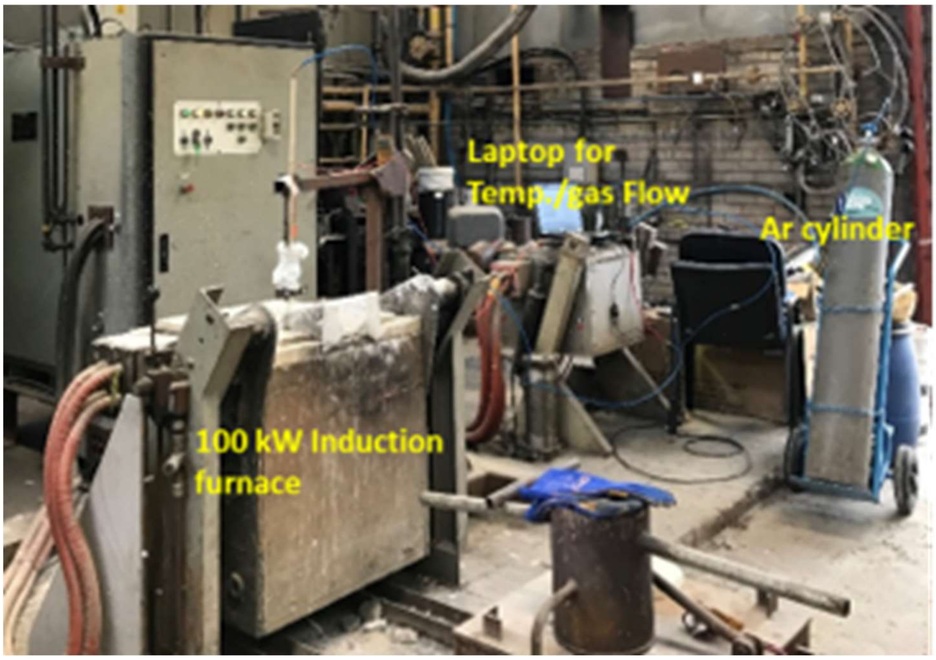

Figure 4b - Photgraph of 100kW Induction furnace set-up

3 MELTING TRIALS

3.1 TRIAL 1

3.1.1 Trial Set up

The induction furnace was charged with:

- 7 kg DUFERCO
- 0.7 kg Sand
- 0.826 kg graphite

For the first trial it was decided to use the Duferco material in the as received state without any further processing e.g. grinding, the particle size was relatively large as can be seen in Figure 5. The material was charged in 3 layers the Duferco sample then the graphite and finally the sand.

Figure 5 – Duferco input sample

Figure 6 shows the thermal profile of the trial The charge was initially heated at 10kw and power was increased power 5kw every 10 minutes. At power 50kW, the temperature at the top of the burden was 750°C and the power was further increased to 60kW, then to 70kW at 1000°C.

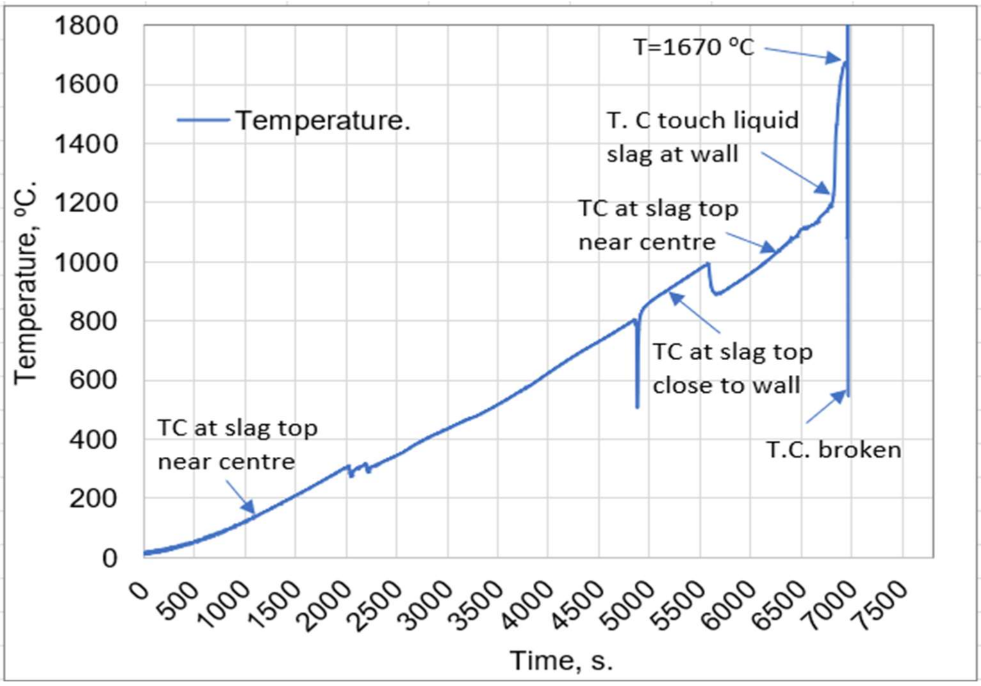

Figure 6 – Trial temperature plot

At 1200°C the material began to soften and after 5 minutes at 70kW, temperature quickly increased to 1670°C. Power was reduced to 50 kw.

The trial was aborted when the thermocouple failed. It was decided that the temperature was rising too quickly and had become too high. The reaction could not be suitably controlled.

3.1.2 Trial Results

Inspection of the crucible once cool revealed that the crucible had failed along with the thermocouple. There had been insufficient time at temperature to allow the slag material to be reduced. The resultant product was a small quantity of metallic material at the bottom of the crucible, unreacted porous slag and slag adhered to the sides of the crucible in the proportions:

- Total charge 8.526 kg
- 0.423 kg metal
- 4.83 kg slag particles and powder
- The remainder 3.27 kg as slag on the walls and gas evolved

3.1.3 Discussion

The trial was aborted due to excessive local temperature which also led to the failure of the crucible. The examination of the product showed that around 40% was melted with a recovery of metallic iron of 423 g. Poor reduction and heat transfer is thought to be due to the large particle size which meant that the contact area between the particles and graphite was limited. The action of the silica to reduce the liquidus was likely also limited.

The material was not held at temperature for sufficient time for the reduction reaction.

3.2 TRIAL 2

3.2.1 Trial Set up

For the next trial it was decided that the contact between the components of the charge must be improved. To Facilitate that a number of actions were taken:

- The Duferco charge size was reduced
- The Particle size was reduced to less than 5mm
- Reduce the heating rate to allow sufficient heat transfer and reducing time

The sample was crushed and graded. The size distribution can be seen in Table III

Table III - Size distribution of the ground DUFERCO, mass%

Size	Fraction Wt%
>5.6mm	0.835
4-5.6	26.504
2.8-4	14.820
2-2.8	9.823
1 ~ 2	19.898
0.5 - 1	10.495
<0.5	17.625
Total	100.000

The induction furnace was charged with (See Figure 7):

- 5.52 kg ground Duferco material
- 0.552 kg Sand
- 0.641 kg Graphite

From the analysis the theoretical iron content was 1.487Kg.

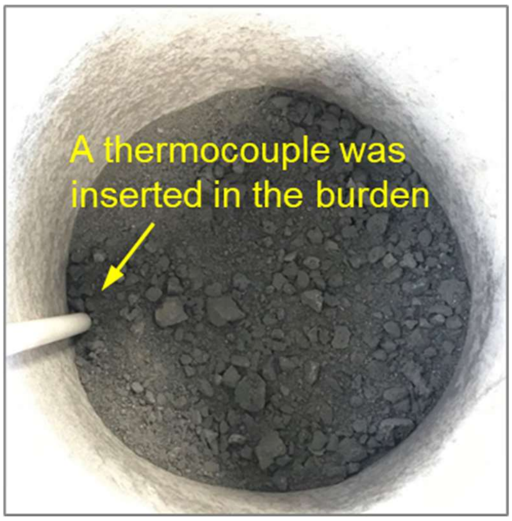

Figure 7 – Charged furnace crucible with thermocouple

Figure 8 shows the thermal profile for Trial 2. Temperature was slowly increased from 800 to 1400°C and then held over a period of 75 minutes to allow solid state reduction of the iron from its oxide in a solid state to avoid/reduce foaming the creation of a foaming slag due evolution of process gases such as Carbon Monoxide in the liquid slag.

The temperature was then increased >1540°C for 20 minutes to allow the reduced iron to melt and separate from the slag.

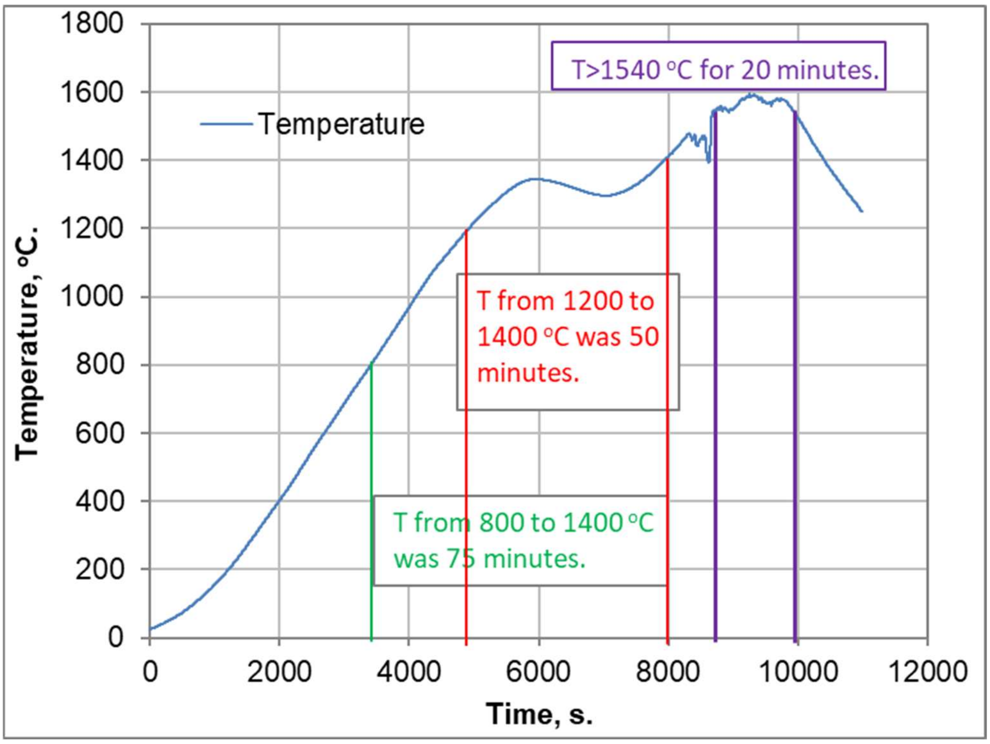

Figure 8 - Trial temperature plot

3.2.2 Trial Results and discussion

The contents of the crucible were examined. Figure 9 shows a photograph of the crucible after removal from the induction furnace.

Figure 9 – Photograph of contents of the crucible

Figure 9 - Iron Ingot

A single piece of iron (Figure 10) was recovered which weighed 713g which accounted for approximately 50% of the theoretical iron content of the sample. The magnetic fraction of the slag was seen to contain a significant proportion of reduced iron which had not been consolidated into the lager ingot. The slag was ground and the magnetic fraction extracted. See figure 11.

Figure 11 - Iron particles after grinding and screening to remove the slag

Table IV – Iron Recovery by particle size

	Initial Weight (g)	Weight after Grinding/ Screening (g)	With remelt the ground/screened portion (g)
Big piece	713.7	713.7	713.7
>6.3 mm	369.71	294.93	788.42 (Remelted)
4-6.3	163.5	178.02	
2.0 - 4.0	235.21	203.61	
1.0 - 2.0	147.83	88.65	
0.5 - 1.0	74.34	5.49	
<0.5	33.77	21.79	
Total	1738.1	1524.19	1502.12
Iron in the ingots, g	-	-	662.33+715.47=1377.80
Recovery rate, %	-	-	**92.66**
Carbon utilization rate, %			**79.73**

The magnetic fraction following crushing and screening totalled 1.524Kg. This was reheated under inert atmosphere with no further reductants added to melt the iron and allow it to consolidate into a single piece.

During the melting process although the plan was to reduce as much as possible in the solid state, a foaming slag was produced when the melt temperature was increased to melt the iron. This indicates that the reduction reaction had not been completed after the 50 minutes that the melt was held between 1200°C and 1400°C. For a commercial process the production of the foaming slag could be avoided by more effective mixing of the feedstock either before charging or during process along with accurate control of melt temperature.

Table V shows an analysis of the residual slag. Iron oxide remaining in the slag is 3.89% which equates to approximately 109.07g. Compared to start composition which had a theoretical iron content of 1486.87g, the iron recovery rate is 92.66%

Table V - Analysis of the slag, wt%

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	V_2O_5
0.032	9.605	14.789	20.089	0.142	0.502	0.074	38.491	0.991	0.282
Cr_2O_3	**MnO**	**Fe_2O_3**	**NiO**	**ZnO**	**SrO**	**ZrO_2**	**Nb_2O_5**	**BaO**	**Total**
1.669	8.713	3.890	0.311	0.012	0.074	0.101	0.129	0.106	100

Analysis of the 2 iron ingots is shown in Table VI. The initial ingot has an iron content of 92.80% equivalent of 662.33 g iron. The second, remelted ingot, had an iron content of 90.75% equivalent of 715.47 g iron. A Total of 1377.80 g iron which compared to the theoretical iron content equates to 92.66%.

Table VI – Composition of iron ingots recovered from melting trial 2

	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Co	Cu	Nb	Ti	V
1st Ingot	4.5	0.02	0.924	0.101	0.107	0.84	0.007	0.034	0.059	0.103	0.03	0.014	0.006	0.088
Remelted Ingot	4.5	0.120	1.980	0.400	0.030	1.030	0.006	0.035	0.019	0.004	0.031	0.025	0.018	0.210
	Pb	**Sn**	**As**	**Zr**	**Ce**	**Sb**	**Ta**	**B**	**Zn**	**La**	**N**	**O**	**Fe**	**Tot**
1st Ingot	0.015	0.03	0.017	0.024	0.05	0.013	0.132	0.007	-	0.028	0.024	0.025	92.80	100
Remelted Ingot	0.006	0.008	0.006	0.013	0.025	0.110	0.108	0.002	-	0.052	0.045	0.47	90.75	100

The initial Zinc content of the Duferco material was relatively low but the Zinc in the collected iron was very low. The laboratory process did not collect the zinc but the residual analysis showed that it had been effectively driven off. In a commercial process this would need to be captured in the off-gas processing.

CONCLUSION

Following the laboratory scale trials the Duferco from La Louvière (Belgium) material recovered from landfill and enriched by mineralogical pre-processing and magnetic separation was identified as a good candidate for further study regarding scale up of the pyrometallurgical process.

The material tested had an iron content of approximately 38.5%. Basicity of the composition was high with the predicted liquidus of the slag being above 2000 °C. The charge material was modified using silica in the form of sand and a reductant, carbon, was added. Recovery of iron from this material was shown to be approximately 93%.

Feasibility of iron extraction has been shown in the laboratory and scaled up to the pilot (Kg) scale. By carefully tuning the chemical composition of the sample, the metals can be extracted at the lowest temperature possible. Reducing minimising the energy input required.

Slag foaming was observed during the trial due to the gas evolution and will need to be considered during the scale up melting.

To conclude, DUFERCO samples have potential for pyrometallurgical recovery of iron.

4 THE FUTURE

Although feasible a recovery process will still need to be designed. There is considerable scope for process optimisation and potential for iron recovery to be only one stage in a sequential process route that valorises different components. To extract the full potential, it may be possible to use a mixture of techniques such as hydrometallurgy and pyrometallurgy.

For a commercial process the requirements would need effective mixing and control of thermal profile. Use of existing technologies such as TBRC (top blown rotary converters) which although a batch process would potentially be suitable.

A full commercial viability study will need to be undertaken.

5 REFERENCES

1. D. T2.2.1 Report on lab scale tests (<25 kg) undertaken for metal extraction on samples from DUFERCO site