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Energy Efficient Recycling of in-Plant Fines

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***Abstract*—**Numerous amounts of metallurgical dusts and sludge containing iron as well as some other valuable elements such as Zn, Pb and C are annually produced in the steelmaking industry. These alternative iron ore resources (fines) with unsatisfying physical and metallurgical properties are difficult to recycle. However, agglomerating these fines to be further used as a feed stock for existing iron and steel making processes is practiced successfully at several plants but for limited extent.

In the present study, briquettes of integrated steelmaking industry waste materials (namely, BF-dust and sludge, BOF-dust and sludge) were used as feed stock to produce direct reduced iron (DRI). Physical and metallurgical properties of produced briquettes were investigated by means of TGA/DTA/QMS in combination with XRD. Swelling, softening and melting behavior were also studied using heating microscope.

***Keywords*—**Iron and Steel Wastes, Recycling, Self-Reducing Briquettes, Thermogravimetry.

I. Introduction

INTEGRATED steel plants generate large amounts of dust and sludge from cleaning of process gases that annually are put to landfill or intermediate storage. These by-products contain significant amounts of iron and carbon that could be used as replacement for virgin materials by recycling in existing iron- and steelmaking processes [1], [2]. However, due to high levels of impurity elements such as Zn, Pb and alkalis as well as unsuitable physical properties, direct recycling is not possible [3], [4].

Different recycling alternatives and characterization of these by-products have been investigated previously [5]–[7]. For instance, a part of the produced blast furnace dust is recycled via cold-bonded briquettes or injection in the blast furnace. Properties of different cold-bonded briquettes and pellets have also been studied. However, due to already quite high Zn load in the BF, both BOF and BF-sludge has to be recycled via another route. Alternatively, to enable internal recycling in the blast furnace for these by-products, a method must be identified in where the Zn-content can be significantly reduced.

Producing briquettes with self-reducing properties for production of DRI (Direct Reduced Iron) followed by charging in existing iron- or steelmaking processes has previously been suggested as a possible recycling method for dust and sludge that currently landfilled [6]. This method has the potential to utilize carbon and iron oxides within dust and sludge to produce DRI that can be used as replacement for scrap and thus reduce the need of virgin materials. In addition, production of DRI by heat treatment would also contribute to significant reduction of Zn, which enables introduction of by-products with high Zn-contents in the blast furnace. In fact, BOF-sludge and BF-sludge in combination with carbon-containing materials (BF-dust) in agglomerates have not been investigated previously.

In the present study, briquettes with self-reducing properties are produced. Reduction behaviour is monitored via mass loss, off-gas analysis as well as heat changes as a function of temperature by means of TG/MS/DTA. Change of existing phases as a function of reaction progress is also studied using high temperature XRD. Swelling, deformation and melting behaviour is monitored using heating microscope. Mechanical properties of produced briquettes were studied by means of standard mechanical testing machine (tumbling test strength – TTH).

II. Experimental

The following materials have been considered within this investigation;

– Blast furnace sludge and dust (BF-sludge, BF-dust)
– BOF fine sludge
– A mixture consisting of BOF- and desulphurisation dust

In Table I, chemical analyses (XRF and LECO) of by-products are given. The chemical analyses of by-products have been done on dry materials.

Average particle size distributions of BF-sludge, BF-dust and BOF-sludge are given in Table II. As can be seen, both BF-sludge and BOF-sludge are really fine material compared to BF-dust

Briquettes were prepared manually by first mixing by-products with cement, scrap mix and later water. To have 100% release of reducible oxygen atoms in iron oxides and thus achieve 100% reduction degrees, the amount of free carbon in the briquette was decided in a way to exceed the number of reducible oxygen atoms. The by-products ratios in the briquettes were decided based on the following rules;

- Fixed relation between BOF-sludge, BOF-dust and BF-sludge
- Content of BF-dust varied
- Molar ratio of carbon to reducible oxygen should be larger than 1 (C/O>1) and Fe(tot) as high as possible
- Simulate available proportions of generated byproducts

The proportions of dust and sludge in the designed briquettes as well other materials can be found in Table III.

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TABLE I
AVERAGE CHEMICAL ANALYSES (BY XRF AND LECO) AND MOISTURE CONTENTS OF BF-SLUDGE, BF-DUST, BOF-SLUDGE AND BOF-DUST

Analysis	BF-sludge	BF-dust	BOF-sludge	BOF-dust
Fe%	33.3	19.6	49.0	48.7
CaO%	7.7	8.3	18.7	11.6
SiO2%	5.3	5.9	1.27	1.5
MnO%	0.3	0.52	1.07	2.5
P2O5%	0.13	0.07	0.07	0.09
Al2O3%	2.2	2.3	0.18	0.5
MgO%	1.7	1.5	3.9	4.31
Na2O%	0.08	0.05	0.03	3.9
K2O%	0.12	0.31	0.08	0.40
V2O5%	0.26	0.33	0.34	0.62
TiO2%	0.30	0.35	0.09	0.11
Cr2O3%	0.03	0.04	0.05	0.12
C %	27.2	49.5	2.2	-
S %	0.4	0.47	0.02	0.74
Zn %	0.6	0.26	0.10	0.63

TABLE II
AVERAGE PARTICLE SIZE DISTRIBUTIONS OF BF-SLUDGE, BF-DUST AND BOF-SLUDGE

Cumulative undersize %		BF-sludge	BF-dust	BOF-sludge
1	mm		99.9	
0.5	mm		97	
0.12	mm		50	
45	µm	100	17	100
8	µm			50
6	µm	50		43
1.05	µm			10
1	µm	10		8

TABLE III
PROPORTIONS BETWEEN SCRAP MIX, CEMENT AND BY-PRODUCTS IN PREPARED BRIQUETTES FOR REDUCTION TRIALS

	BM1	BM2
BF-sludge (wt-%)	15	12
BF-dust (wt-%)	2	8
BOF-sludge (wt-%)	21.5	19
BOF-dust (wt-%)	<1	<1
Cement (wt-%)	11	11
Scrap mix (wt-%)	50	50

The prepared mixtures were then fed into special moulds, vibrating and applying a mechanical pressing force to shape- and compact the material into briquettes (briquette machine, TEKSAM VU600/6). Fig. 1 shows one of the studied briquettes as well as a schematic diagram of its dimensions and thermocouples assembly.

A Netzsch thermal analysis STA 409 instrument with simultaneous thermo-gravimetric measurement with sensitivity ±1µg (TGA) and differential thermal analysis (DTA) coupled with a quadruple mass spectroscopy (QMS) was used to study the reduction behavior of self-reducing briquettes. A schematic diagram of the thermal analysis instrument is given in Fig. 2.

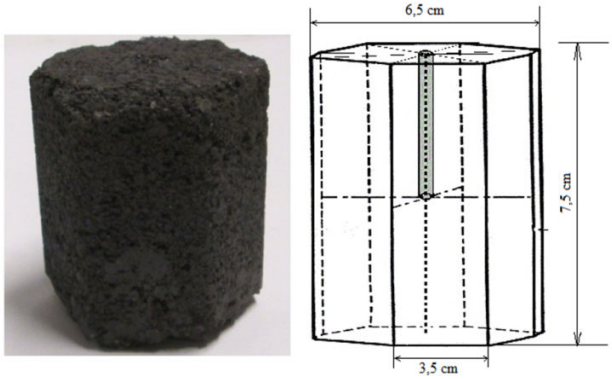

Fig. 1 Photo image as well as schematic diagram of used briquettes

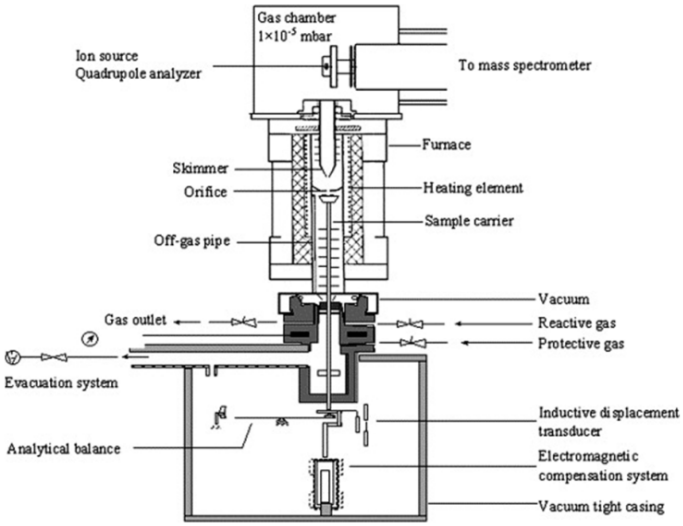

Fig. 2 Illustration of TGA/DTA/QMS

Single briquette reduction experiments were conducted in a Eurotherm vertical steel tube furnace with adjustable heating rate and maximum temperature of 1200°C. A schematic diagram depicting the furnace assembly, temperature monitoring positions and gas flow is shown in Fig. 3.

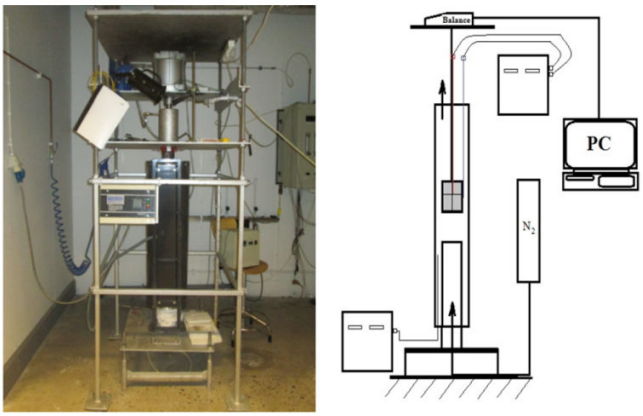

Fig. 3 Photo image and schematic diagram of the furnace assembly

In order to accurately monitor and control the briquettes temperature, two thermocouples (K-type) were carefully

attached to the briquette. A 3.5mm diameter hole was drilled in the briquette center and one of the thermocouples was placed there to monitor the briquette core temperature while the other one was positioned at the surface. The mass loss was noted manually by recording mass before and after the process.

In addition, the process has further investigated using high-temperature XRD and heating microscope. For high temperature XRD, Reaction progress and phase alteration were monitored by means of in-situ heating X-ray Diffraction analysis using PANalytical XRD instrument coupled with a heating furnace. The obtained X-ray spectra were evaluated using PANalytical software. The samples were introduced into the even temperature zone of a small furnace (the furnace is assembled in such a way to enable the in-situ X-ray scanning) and a flow of Ar-gas was maintained during the course of process. As shown in Fig. 4, the samples were subjected to the first scan at ambient temperature. The second scan was carried out at 300°C while the third was at 600°C with 10°C/min fixed heating rate. The sample was then scanned every 75°C until the temperature reached 1100°C.

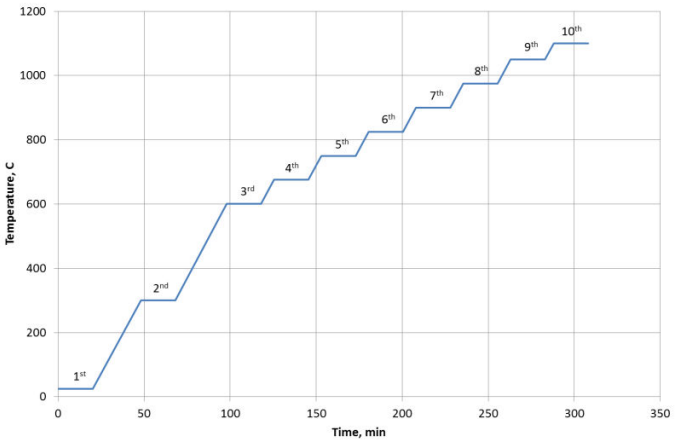

Fig. 4 Temperature profile during XRD analysis

Furthermore, swelling, softening and melting temperatures are essential values to capture, which significantly affect the process operation. LeitzWetzlar Germany heating microscope (Fig. 5) was used for this purpose. Fine ground samples were agglomerated into small briquettes (3mm height and 2mm diameter) using a specially designed mold provided by the same company. The briquette was then centered on a flat alumina pan and then introduced to the even temperature zone of a horizontal tube furnace. The two endings of the furnace are closed with transparent quartz stoppers to enable atmosphere control and imaging. An argon gas flow was maintained throughout the process. The sample was heated 15°C/min up to 600°C and thereafter 10°C/min up to the flow temperature of the sample. Imaging was set to carry out automatically according to preset parameters. Size alteration was monitored by analysis of the silhouette of the sample and the change of sample size was calculated accordingly.

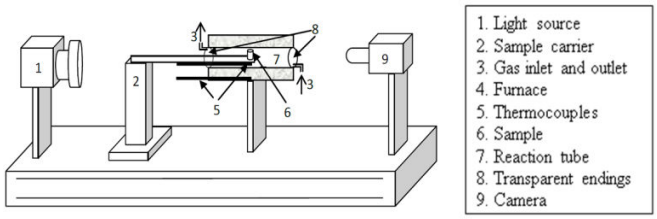

Fig. 5 Typical heating microscope

III. Results and Discussion

A. Characterization

X-ray diffraction patterns showed that hematite is the main iron baring phase in all studied by-products. However, traces of calcite and wustite phases could also be detected. Individual behavior of each by-product during heating was studied by means of thermogravimetry. Large variation in the net mass loss was observed. Mass loss of 12.8% was achieved for BOF-sludge, 5.5% for BOF-dust, 33.1% for BF-sludge and 18% for BF-dust. Detailed characterization of the applied materials as well as experimental condition and results are reported in an earlier publication [8].

Table IV shows the chemical analyses of green briquettes corresponding to BM1 and BM2. Fe% is the total iron content in each blend including Fe^{3+}, Fe^{2+} and metallic iron. Additional analyses have been conducted on Fe^{2+} and metallic Fe to know how the different states are distributed. Fe^{3+} have been estimated by subtracting Fe^{2+} and Fe metallic from Fe% in the XRF analysis, see Table V.

In the original XRF analysis, the sum of all compounds was <84% for both blends. After calculating the distribution between metallic iron and iron oxides the total reached 91.76% for BM1 and 92.98% for BM2. The other 7-8% that doesn't appear in the analysis might be an indication on presence of calcite or other volatile matter. Furthermore, compared to the estimated analyses of by-product blends without cement and scrap mix (see Table I), the metallic iron content is higher and might be explained by high metallic iron content in scrap mix.

TABLE IV
XRF Analysis of Green Briquettes BM1 and BM2

Analysis	BM1	BM2
Fe%	41.88	40.3
CaO%	18.56	17.85
SiO_2%	6.03	6.53
MnO%	0.95	0.94
P_2O_5%	0.117	0.119
Al_2O_3%	1.75	1.96
MgO%	2.93	2.87
Na_2O%	<0.070	<0.070
K_2O%	0.08	0.089
V_2O_5%	0.72	0.7
TiO_2%	0.6	0.54
C %	9.2	11.3
S %	0.55	0.52
Zn (ppm)	840	740
Ni (ppm)	149	95
Total	83.5	83.8
GLF%	-8.41	-10.78

TABLE V
ANALYSIS OF IRON (II) AND METALLIC IRON BY TITRATION

%	BM1	BM2
Fe^{2+}	5.17	5.52
Fe met	20.94	17.1
Fe^{3+}	*15.77*	*17.68*
Fe_2O_3	*22.55*	*25.28*
FeO	*6.65*	*7.10*
Total	91.76	92.98

XRD analysis of green briquettes is given in Fig. 6. Both blends are shown to contain Fe_2O_3, Fe_3O_4, C, $CaCO_3$, FeO, Fe and $Ca(OH)_2$ phases. However, the intensity peak of carbon is higher in BM1 than BM2 and the intensities for metallic iron are low in both blends which is contradictory to the chemical analyses. However, the contradiction can be solved by the fact that metallic iron in the chemical analysis comes mainly from the added scrap mix which is in most cases covered by layer of rust.

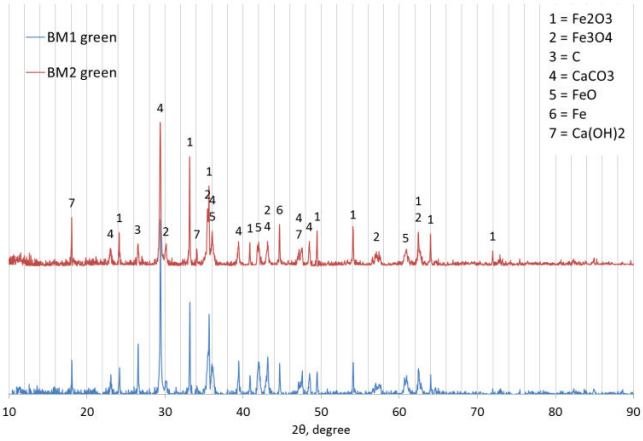

Fig. 6 XRD analyses of green briquettes BM1 and BM2

B. Thermogravimetric Studies

Figs. 7 and 8 show the mass loss (TG), first derivative of mass loss with respect to time (DTG), differential thermal analysis (DTA) and the off-gas analysis for BM1 and BM2, respectively. Those samples are composed of crushed briquettes which are expected to contain significant amount of moisture due to the water added during briquetting process.

The sample alteration starts by moisture evaporation which is indicated by the slight mass loss early beginning and the accompanied heat absorbance (endothermic peak in DTA curve) as well as evolution of H_2O (detected by MS). Later, the combined water get elaborated in addition to the dehydroxylation around 400-450°C. At 700-800°C, the detected endothermic peak as well as the appearance of CO and CO_2 in the off-gas and the determined mass loss suggests the dissociation of residual carbonate and/or reduction of higher oxides. Reduction of lower oxides and formation of CO then dominates in the temperature range 900-1000°C. This is also confirmed by the heat absorbance that synchronizes the strong appearance of a CO spectrum.

TG curves for both blends manifest discontinuity during the course of the reaction indicating the step wise process as the temperature goes up. DTG curves clarify the changeover of process mechanism as the temperature rises. By comparing these results with an earlier investigation [9], one can conclude that the reaction mechanism of carbon-iron containing waste materials is similar to the reaction mechanism of simple mixtures in where step wise reduction is clearly identified.

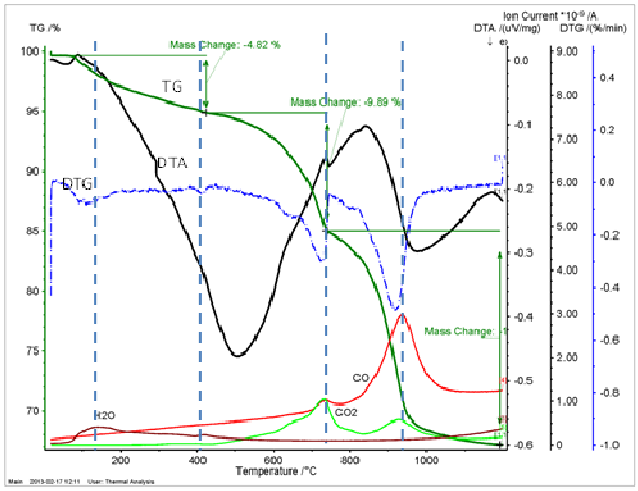

Fig. 7 Thermal analysis curves of BM1 as a function of Temperature

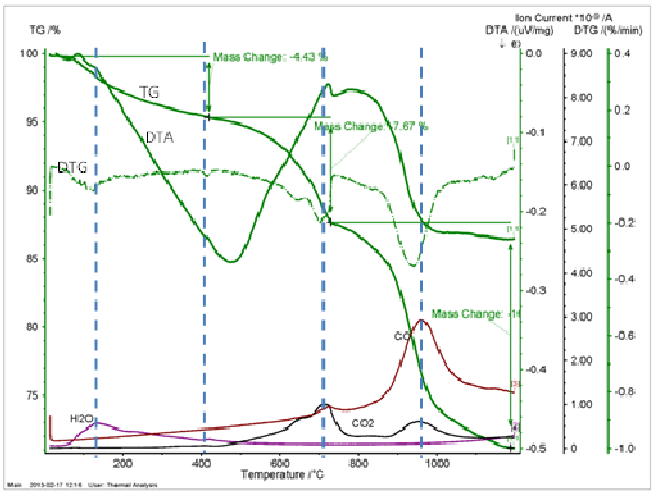

Fig. 8 Thermal analysis curves of BM2 as a function of Temperature

C. High Temperature XRD and Heating Microscope

Phase analysis was carried out using high temperature XRD to monitor phase changes during heating cycle. Figs. 9 and 10 show the corresponding detected phases and the XRD patterns of the processed samples.

It can be observed from the obtained XRD patterns that the dominating phases of the prepared blends prior the reduction are $Ca(OH)_2$, $CaCO_3$, Fe_2O_3, Fe_3O_4, FeO and Fe. On heating, the existing wustite and metallic iron get oxidized by the trapped oxygen in the sample or by oxygen transfer (solid

diffusion) from higher oxides to lower ones and in addition, the hydroxide phase disappear. Later at 750°C as a result of carbonate decomposition and primary slag formation, new phases appear like CaO, $Ca_2Fe_2O_5$ and $Ca_2Al_2SiO_7$. Reduction of hematite to magnetite was almost completed at 850°C and wustite phase start to be dominating. Metallic iron peaks were hardly detected in the in-situ heated samples of BM1 and BM2. This is can be explained by either defect atmosphere control during heating and scanning or by short residence time of locally produced reducing gases. The latter might be due to small sample thickness or high flow rate of inert gas (the inert gas flow rate in XRD test could not be controlled, one can only ensure the presence of continuous flow of inert gas). However, the step wise-reduction of waste material containing briquettes still can be approved from XRD observations and the reactions seem to be very sensitive to the experimental conditions. Furthermore, XRD patterns of samples heated externally at 1200°C indicated high metallization degree as no iron oxides was detected.

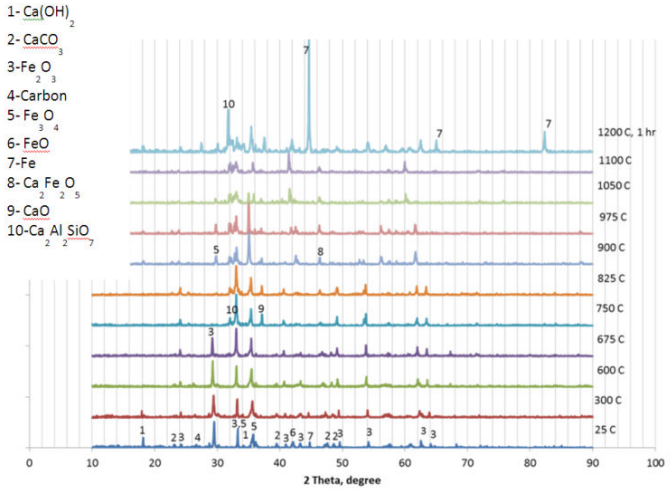

Fig. 9 XRD patterns of *in situ* heated sample of BM1

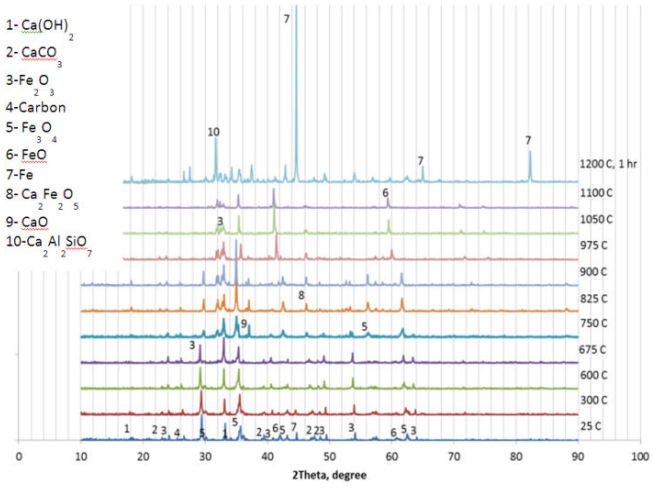

Fig. 10 XRD patterns of in situ heated sample of BM2

Further, for heating microscope tests, small briquette was produced from finely ground sample which is introduced to the even furnace temperature zone as previously mentioned. On the right hand side of Fig. 11, three images show the change of sample silhouette as the temperature goes up; (a) green, (b) deformed and (c) completely melted briquette. On the left hand side of Fig. 11, the change of sample silhouette area as a function of temperature is plotted. Bothe blends show thermal stability (no size change) up to around 700°C. Gradual swelling can be observed only above 700°C which is found to be significantly composition dependent. Swelling degree of about 20% is detected on heating BM2 while less the 15% swelling was observed on heating BM1. The difference in the swelling degree might be attributed to BF-dust content, the higher the BF-dust content the higher the swelling percentage. Irrespective of composition, deformation and hemisphere temperatures of both briquettes are quite close. On the other hand, flow temperature seems to be lower for higher BF-dust briquettes (see Fig. 11)

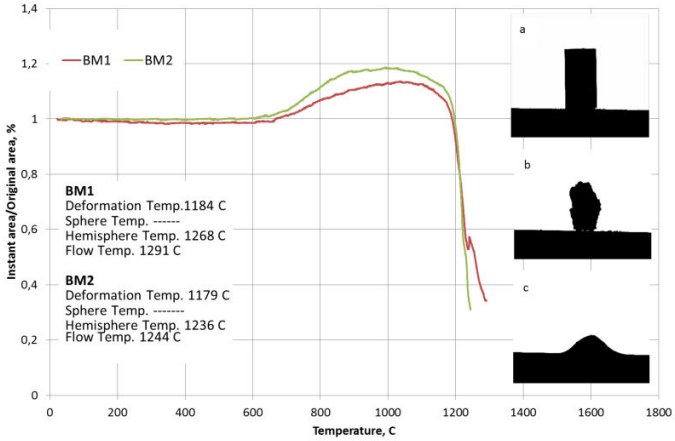

Fig. 11 Selected images show the sample deformation and melting (on the right hand side) and the change of sample silhouette area as a function of temperature (On the left hand side)

TABLE VI
SUMMARY OF STEPS OCCURRING DURING HEATING OF IRON-MAKING WASTE MATERIALS CONTAINING BLENDS IN AN INERT ATMOSPHERE

Reaction equation	Temperature, °C	
	BM1	BM2
Water evaporation	70-200	70-200
Dehydroxylation, $Ca(OH)_2 = CaO + H_2O$	400-430	400-430
Oxidation of iron to higher oxides	Below 750	
Calcination and primary slag formation; $CaCO_3 = CaO + CO_2$, $3CaCO_3 + Fe_3O_4 + Fe = Ca_2Fe_2O_5 + 3FeO + CaO + 2CO + CO_2$	675-790	675-790
Hematite reduction; $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$	600-700	600-690
Magnetite reduction; $Fe_3O_4 + CO = FeO + CO_2$	770-830	790-870
Wustite reduction; $FeO + CO = Fe + CO_2$	830-1140	875-1170
Gasification reaction; $CO_2 + C = CO$	830-1140	875-1050
Swelling	Above 670	
Deformation temperature	1184	1179
Hemisphere temperature	1268	1236
Flow temperature	1291	1244

Based on TG/DTA/QMS, XRD and heating microscope results, reduction behavior of iron-making waste materials containing mixtures is considered to go through simultaneous and consecutive steps which are summarized in Table VI.

D. Single Briquette Experiment

Reliable production of 50% dust and sludge containing briquettes was industrially successful. The trials also showed that the material treatment before briquetting is important and a drying step for sludge is crucial. The rolling- and abrasion strength (tumbling test strength – TTH) of produced briquettes is given in Table VII. The ordinary briquettes are cured for at least 28 days and require a TTH-value of 60 before they are charged to BF. These test briquettes did not need the same strength as the material was going to be reduced and charged in steel ladle before desulphurisation. The strength after two weeks curing time was considered enough for continued processing.

TABLE VII
CHANGE OF COMPRESSIVE STRENGTH MEASURED AFTER 1-, 2-, 7- AND 14 DAYS AFTER PRODUCTION FOR BM2

	Day 1	Day 2	Day 7	Day 14
TTH	23	39.6	52.4	53.7

In order to clarify the role of process conditions like atmosphere on the reduction behavior of industrial produced BM2-briquettes, a set of experiments were conducted under different atmosphere with heating rate 10°C/min up to 1150°. The experiment conditions as well as the results are summarized in Table VIII.

TABLE VIII
SUMMARY OF EXPERIMENTAL CONDITIONS IN VERTICAL TUBE FURNACE

No.	N_2 gas flow rate, l/min	Weight loss, %
B1	No gas flow	20.5
B2	4	25.5
B3	8	26.6
B4	12	25.4

It is known that that the pressure inside self-reducing briquettes or pellets will be higher than the pressure outside as long as the reduction is carrying on due to generation of CO from the gasification reaction. However, surface oxidation might occur, also when the reduction tends to end i.e. CO production rate becomes low comparable to oxygen diffusion into the briquettes, the reduced iron as well as residual carbon may get oxidized by the diffused oxygen. On the other hand, homogenous reduction could be achieved on conducting the process under controlled atmosphere. This phenomenon is approved by XRD of different positions within a single briquette.

The reduced briquettes were subjected to phase analysis using X-Ray Diffraction. Four samples were taken from each briquette, top, center, bottom and another representative sample for the whole briquette. The samples were then pulverized and then placed in the sample holder for analysis. To avoid repeatability and for the sake of brevity only some of the results will be shown. Figs. 12 and 13 show XRD of two selected samples (B1 and B4, see Table VIII). Generally, metallic iron was the main peak detected in the representative samples. Some residual higher oxides, calcium oxide and calcium aluminum silicate slag phases could be also detected. XRD of B1 shows high degree of metallization in the whole briquette except the top part which is exposed to air, where metallic iron peaks were hardly detected. Unlike, B1, XRD of B4 shows homogenous composition through the whole briquette even at its top side. High degree of metallization was recognized everywhere in the briquette and the intensity peaks of metallic iron were even higher in relation to iron oxides than in B1. There is no detected significant difference in the composition along the briquette.

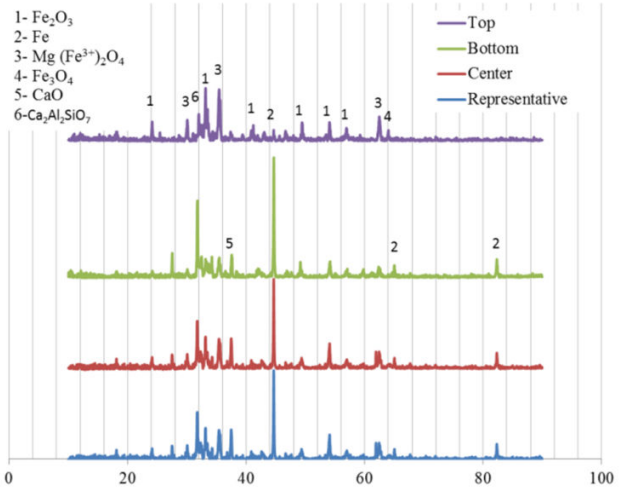

Fig. 12 XRD of reduced briquette (B1)

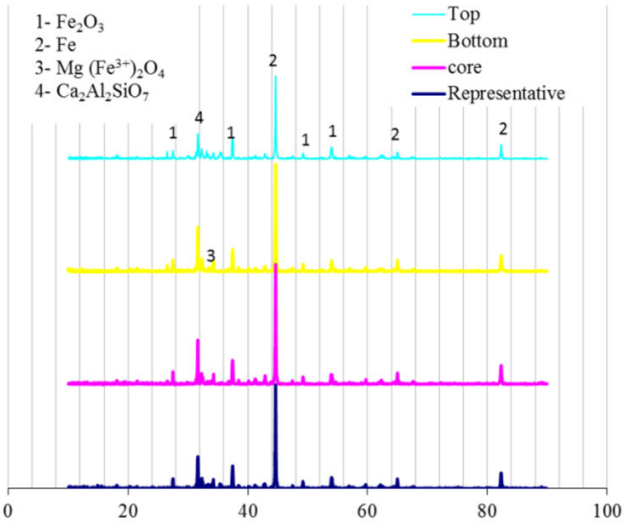

Fig. 13 XRD of reduced briquette (B4)

IV. CONCLUSION

Reduction studies of lab-scale briquettes showed that high reduction degrees could be reached for both studied briquettes, the following remarks can be drawn;

– Briquettes produced at the briquette plant were shown to

have sufficient mechanical strength for handling and reduction after two weeks of hardening. Moreover, the material treatment before briquetting and pre-drying of sludge was shown to be crucial for briquetting.

- Reduction behavior studies have shown that the reduction proceed in accordance with seen behavior of simple mixtures of carbonaceous materials and hematite, namely through three consecutive reduction steps; hematite to magnetite, magnetite to wustite and wustite to metallic iron.
- Cold briquetting tests have shown that briquettes with sufficient mechanical properties and self-reducibility can be prepared from available by-products and used for recycling.
- High reduction degree achievement was confirmed by single briquette experiment. Potential for even higher reduction degrees were stated during thermal analyses.
- Reduction trials showed that 95-97% of initial zinc content in briquettes can be removed during process, achieving final contents in the very low range.

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REFERENCES

[1] Das B, Prakash S, Reddy PSR, Misra VN."An overview of utilization of slag and sludge from steel industries. ResourConserv Recycling". 2007 3;50(1):40-57.

[2] Trung ZH, Kukurugya F, Takacova Z, Orac D, Laubertova M, Miskufova A. "Acidic leaching both of zinc and iron from basic oxygen furnace sludge". J Hazard Mater. 2011 9/15;192(3):1100-7.

[3] Sammut ML, Rose J, Masion A, Fiani E, Depoux M, Ziebel A. "Determination of zinc speciation in basic oxygen furnace flying dust by chemical extractions and X-ray spectroscopy". Chemosphere. 2008 2;70(11):1945-51.

[4] Makkonen HT, Heino J, Laitila L, Hiltunen A, Pöyliö E, Härkki J. "Optimisation of steel plant recycling in finland: Dusts, scales and sludge". ResourConserv Recycling. 2002 4;35(1–2):77-84.

[5] Singh M. Studies on "the cement-bonded briquettes of iron and steel plant by-products as burden material for blast furnace" [dissertation]. Luleåtekniskauniversitet: Luleåtekniskauniversitet; 2002.

[6] Robinson R. Studies in "low temperature self-reduction of by-products from integrated iron and steelmaking" [dissertation]. Luleåtekniskauniversitet: Luleå tekniska universitet; 2008.

[7] Fröhling M, Rentz O. "A case study on raw material blending for the recycling of ferrous wastes in a blast furnace". J Clean Prod. 2010 1;18(2):161-73.

[8] Ahmed H, Persson A, Sundqvist L, Bjorkman B. "Studies on Utilization of BF and BOF Dust and Sludge as Feed Stock to Existing Iron- and Steel- Making Processes" not submitted.

[9] Ahmed H, Viswanathan N, Bjorkman B. "Isothermal Reduction Kinetics of Self-Reducing Mixtures" not submitted.