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WASTE PLASTICS INJECTION: REACTION KINETICS AND EFFECT ON THE BLAST FURNACE PROCESS[1]

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Abstract

Over the past 10 years, as a consequence and to counter constraints of availability and price, voestalpine Stahl has implemented several projects to use injected reducing agents more flexibly. The use of waste plastics in the steel industry is an appropriate way to recycle industrial and municipal wastes and therefore contributes to the environmental protection. Furthermore the amount of coke replaced by injected reducing agents has a direct influence on the CO_2 balance in the blast furnace. In the BF A in Linz, up to 110,000 tons of plastics per year are now used as a reducing agent; this corresponds to an injection rate up to 40 kg/tHM. Despite the available experience in waste plastics injection, systematic investigation of its reaction kinetics is still missing. Four waste plastics types of different origin and treatment processes have been tested at RWTH Aachen University using an injection rig that simulates conditions in the tuyère, injection lance and in the oxygen area of the raceway. Conversion behaviour has been examined for various plastics concentrations characterised by the oxygen / carbon atomic ratio. Waste plastics of two grain sizes have been injected: 2-3 mm and the original size used at voestalpine Stahl. The change in the microstructure and the surface of injected substances were determined as well. The conversion degree depends on two mechanisms: the change in the particle-specific surface that is affected by its mass and shape factor and the change in the particle dimension or volume; respectively diffusion or reaction kinetics can be limiting factors depending on the balance between both mechanisms. Industrial experience including material preparation, replacement ratios and the analysis of trace elements and heavy metals such as Pb, Zn, Cd and Hg is discussed as well.

Key words: Waste plastics injection; Raceway; Reaction kinetics; Conversion degree; Trace elements.

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1 INTRODUCTION

The use of waste plastics in the steel industry aims at recycling of industrial and municipal wastes. Furthermore presence of hydrogen in this material may contribute to the CO_2 mitigation.

There are three ways to use waste plastics in ironmaking technologies:

- Gasification and subsequent injection of generated reducing gas.
- Incorporation into iron burden or into coal blends for cokemaking.
- Direct use by injection via tuyères.

This contribution deals with waste plastics injection into the blast furnace via tuyères. Despite of industrial experience of plastics injection into blast furnaces in Germany,(1) Japan(2) and Austria, where in 2006 a new treatment and injection plant was commissioned,(3) as well as studies on combustion behaviour of waste plastics depending on its grain size and pre-treatment method(4-6) systematic investigation of reaction kinetics of waste plastics has been started only recently.(7)

To investigate the reaction kinetics during the conversion in the raceway systematically, several factors have to be taken into account:

1. Chemical reaction
2. Free surface of the particle characterised by its
    a. Porosity
    b. Grain size
    c. Shape factor
3. Gas diffusion
4. Residence time in the raceway
5. Melting

Essential physical, chemical characteristics and kinetics data of four waste plastics types were gained from the experimental studies using several analytical and laboratory methods and facilities. Afterwards injection trials were conducted using the batch injection rig. The tests were performed with specially prepared fractions of 2-3 mm diameter and for one type with particles of original size.

Industrial data on waste plastics injection at voestalpine Stahl BF A including the balances of harmful elements are presented as well.

2 WASTE PLASTICS INJECTION AT VOESTALPINE STAHL

The key philosophy of voestalpine Stahl related to reductant matter at blast furnaces in Linz consists in flexible use of various auxiliary reducing agents like oil, tar, natural gas, coke oven or BOF gases, biomass and plastics including co-injection of mentioned substances depending on availability, costs and other factors. A plant for waste plastics preparation and injection into BF A with a capacity of 70,000 t per year was commissioned in 2006 and then extended to a capacity of 140,000 t per year. Figure 1 shows schematically the chain of plastics injection.

In the BF A in Linz, up to 110,000 tons of plastics per year are now used as a reducing agent; this corresponds to an injection rate up to 40 kg/tHM. The secondary raw materials replace primary resources like heavy oil.

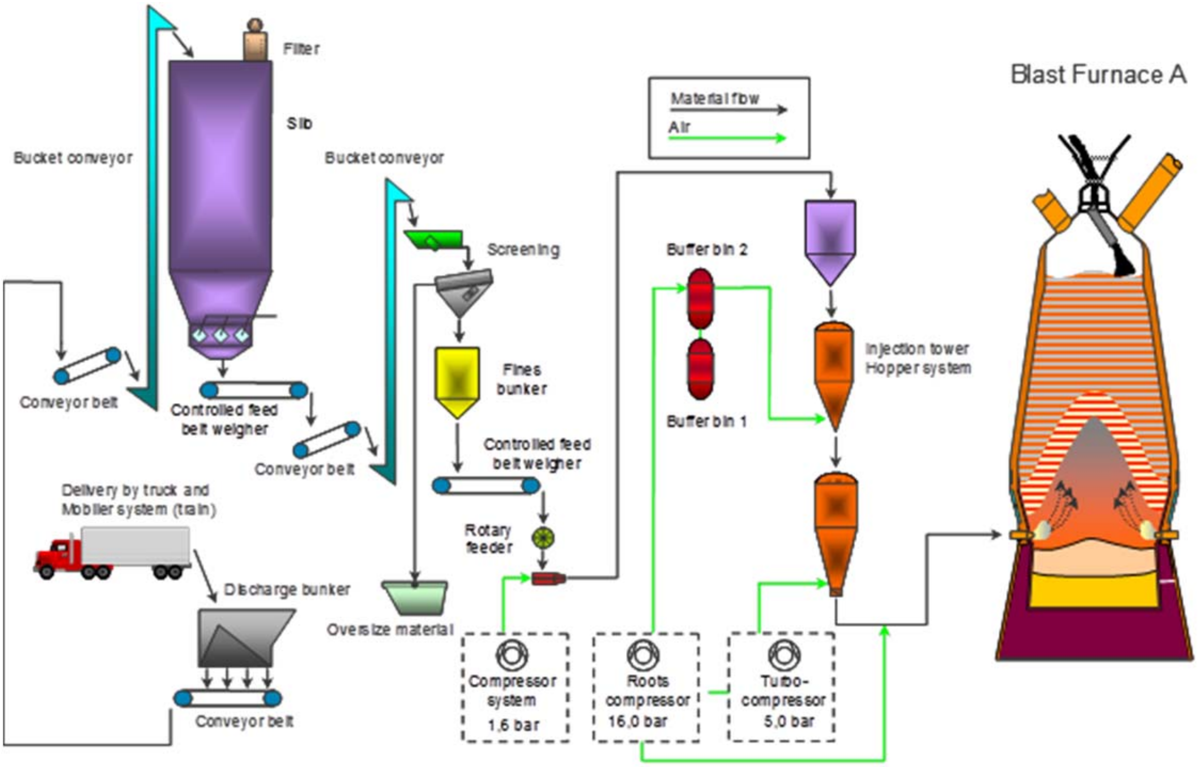

Figure 1. Layout of plastics injection at voestalpine Stahl BF A.

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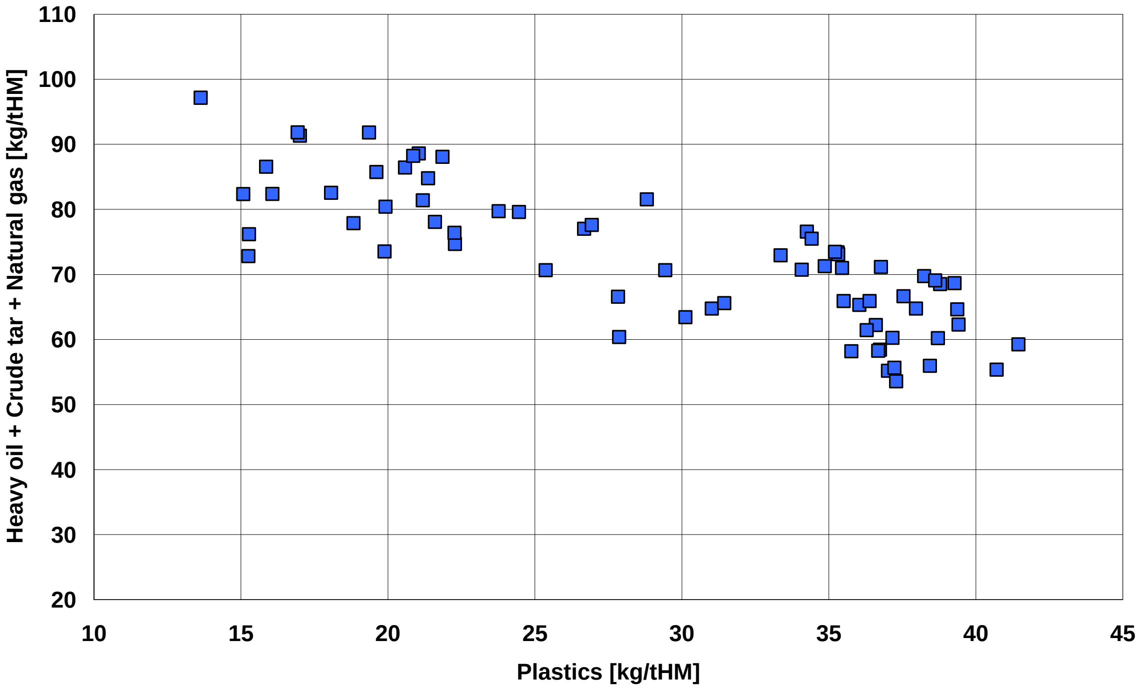


Figure 2. Injectant rates.

Secondary raw materials like plastics have usually higher contents of trace elements like Pb, Zn, Cd and Hg than conventional BF input materials. A substance flow analysis describes the process of production and shows in which product components the substance of interest can be found. All flows can be displayed in Sankey-style, i.e. the width of a flow is proportional to its value.

The limitation for emissions of above mentioned heavy metals with the BF gas is a decisive factor for the use of secondary raw materials. Zn is dissolved in the hot metal and leaves the process by more than 90% during tapping with the hot metal and the BF slag (Figure 3). Pb with a lower evaporation temperature than Zn leaves the BF process mainly with the uncleaned top gas and can be found mainly in the solids after the scrubber. The major depression for Hg is the scrubber (Figure 4). The behaviour of Cd is similar to Pb. The high amount of approx. 75% in the solids after the scrubber and the flue dust shows that Pb and Cd are adsorbed by fine dust particles from the burden materials and the coke.

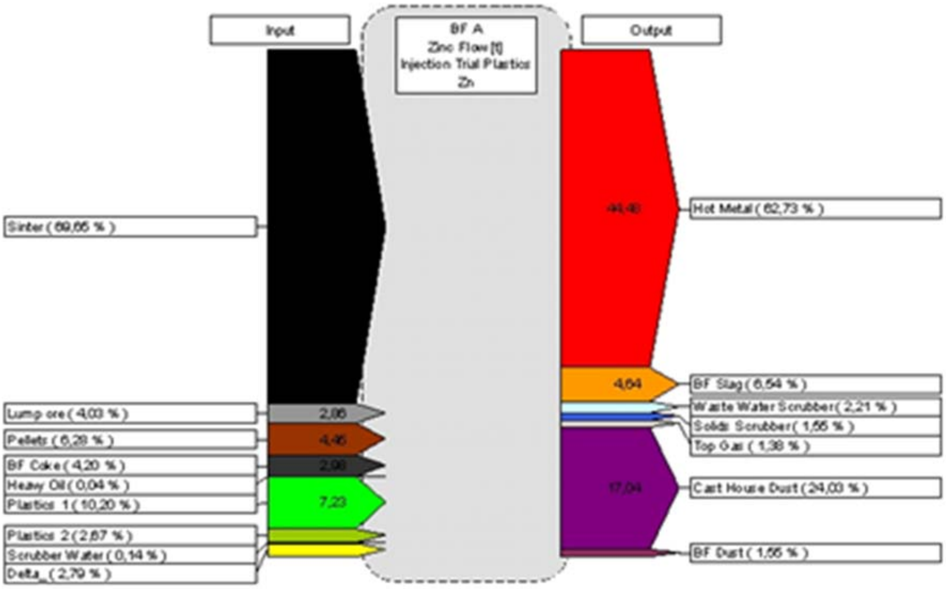


Figure 3. Substance flow analysis Zn for BF process with secondary raw materials.

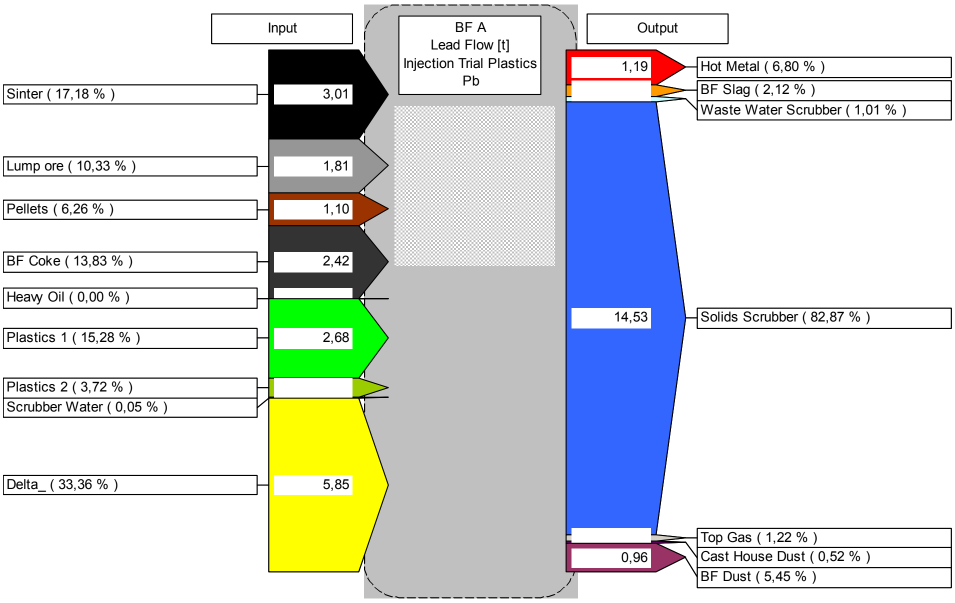


Figure 4. Substance flow analysis Pb for BF process with secondary raw materials.

3 CHARACTERISATION OF WASTE PLASTICS MATERIALS

The four waste plastics types used for injection into the blast furnace were examined: agglomerate, granulate and two sorts of pellets.

Agglomerate is produced from post-consumer packaging. After processing and separating different material fractions the remaining mixed plastics fraction is agglomerated. In this step heat is introduced, leading to partial melting. The softened material is quenched with water and shredded. The agglomerate structure is characterised by compact core and a coarse surface riddled with fibres.

Granulate is one product of the automotive shredder residue (ASR) treatment process. The particles have homogeneous structure and plane surface.

Pellets are produced from post-consumer packaging and other sources like industrial waste. Their surface is rough and cliffy. The original fractions can still be identified. In this research two types of pellets have been investigated; pellets B are more homogeneous than pellets A.

Granulate has the lowest porosity. It is followed by Agglomerate and then the Pellets. All examined materials have porosity within a range from 17 to 28 %. The difference between Agglomerate and Pellets is not very high.

The waste plastics samples are characterised by very high volatile matter (VM) content as shown in Table 1; combustible matter (C_M) are determined as dry mass without ash.

Table 1. Chemical analysis of waste plastics(8)

	Agglomerate	Granulate	Pellets A	Pellets B
C_M	93.84	93.31	90.28	90.32
VM	88.69	89.03	81.11	84.27

4 REACTION KINETICS INVESTIGATIONS BY THERMO-GRAVIMETRIC MEASUREMENTS

To analyse the conversion behaviour in detail and to get more information about the pyrolysis, the vaporisation of volatile matter and the reaction with the atmosphere, investigations in a thermo balance were conducted. The experiments were carried out in inert and oxidising atmosphere. From these investigations the following three steps of conversion were determined: (8)

- 1st step: vaporization of moisture
- 2nd step: vaporization of volatile matter ➔ main reaction
- 3rd step: decomposition or burning of fixed compounds

The first step of weight loss is characterized by the vaporization of water (until 200°C) and the volatilization of low molecular weight species through scission of side chains from the polymers (until ~ 380°C). The second step of weight loss is caused by the vaporization of volatile matter (V_M) by means of thermal cracking. After 380°C the temperature is high enough to start the decomposition of the hydrocarbons through radical mechanisms. First long-chain polymers are cracked, ionic molecules are created and primary radicals emerge.(9) This reaction is characterised by high reaction rates and high weight loss due to the high content of volatile matter. After the second step of weight loss only fixed carbon and ash components remain. The conversion in air atmosphere in the third step of weight loss is linked to the decomposition and burning of the remaining carbonaceous residue. If polyvinyl chloride is present, this may lead to a two-stage weight loss. The conversion of PVC takes place in two stages: Firstly, chlorine vaporises, and secondly the radical polymerisation occurs.(10)

The differences between the reaction in argon and air atmosphere are small, which can be explained by the radical decomposition of the waste plastics which is mainly temperature dependent and faster than the chemical reactions.

To show differences and similarities of the examined materials, the reaction rate for the main reaction was calculated (Table 2).

Table 2. Reaction rate related to the main reaction (second step) of the waste plastics in [%/min]

	Argon, 5 K/min heating rate	Air, 5 K/min heating rate
Agglomerate	-0.20	-0.16
Granulate	-0.19	-0.15
Pellets A	-0.23	-0.06
Pellets B	-0.19	-0.09

The calculated reaction rates show only little differences between argon and air atmosphere. Within air atmosphere the main reaction starts earlier and extends over a wider temperature interval, so that the reaction rate is not as high as in argon atmosphere.

4.1 Heat Flow

Simultaneously to the weight loss, the specific heat flow of the samples was detected.

In inert atmosphere each type of waste plastic shows an endothermic peak in the heat flow. This negative peak correlates with the main weight loss, the vaporization of volatile matter (Figure 5). The endothermic effects appear because of cracking and radical decomposition of polymers, which consumes energy.

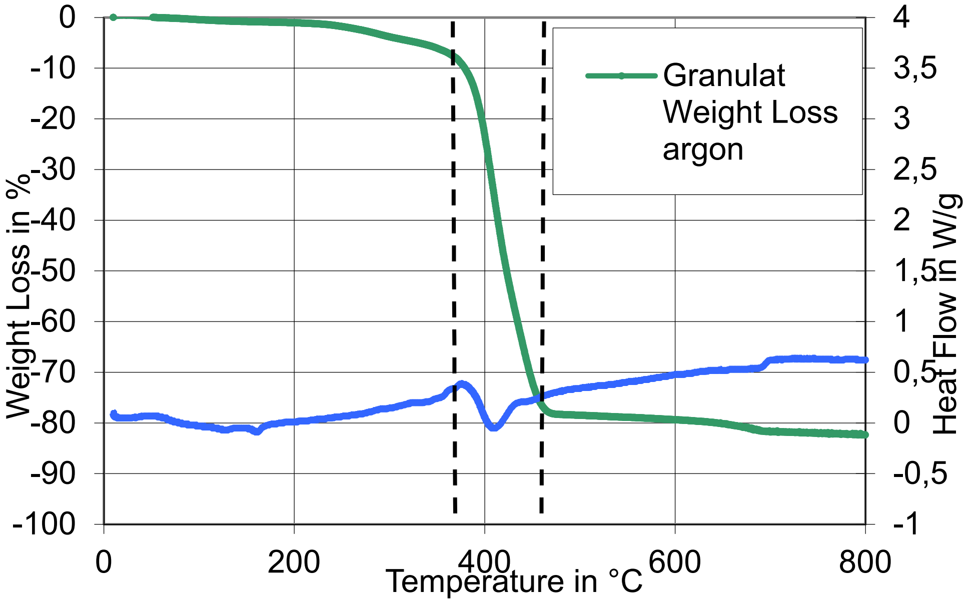


Figure 5. Specific weight loss and heat flow of granulate in argon atmosphere.

In oxidising atmosphere the same effect appears followed by an exothermic reaction. At the beginning of the main weight loss the endothermic effect starts. After the vaporization of volatile matter, the heat flow rapidly rises, which indicates the exothermic reaction. This correlates with the third step of weight loss and is referring to the oxidation of the carbonaceous residue.

In Table 3 the calculated reaction enthalpies during conversion in argon and air atmosphere are shown. These reaction enthalpies refer to the endothermic and exothermic peaks in the temperature interval between 350 and 520°C.

Table 3. Reaction enthalpies during conversion of waste plastics in DTA in J/g, heating rate at 5 K/min

	Argon		Air	
	endothermic	exothermic	endothermic	exothermic
Agglomerate	122	-	661	-2323
Granulate	116	-	276	-2083
Pellets A	166	-	274	-3638
Pellets B	57	-	112	-4591

4.2 Mass Change

The trials using the Tammann furnace experimental set simulate the conversion of the waste plastics entering the hot blast.(11) For simulating these conditions the mechanisms of thermo-shock and heat transfer by radiation were considered. The conversion behaviour was tested in isothermal conditions at 1,000°C. In Figure 6 exemplarily the weight loss of agglomerate and granulate in inert atmosphere and oxidising atmosphere is shown. It can clearly be seen that the conversion in oxidising atmosphere starts earlier and is faster than in inert atmosphere. The reaction rate in air atmosphere is only little higher than in inert atmosphere.

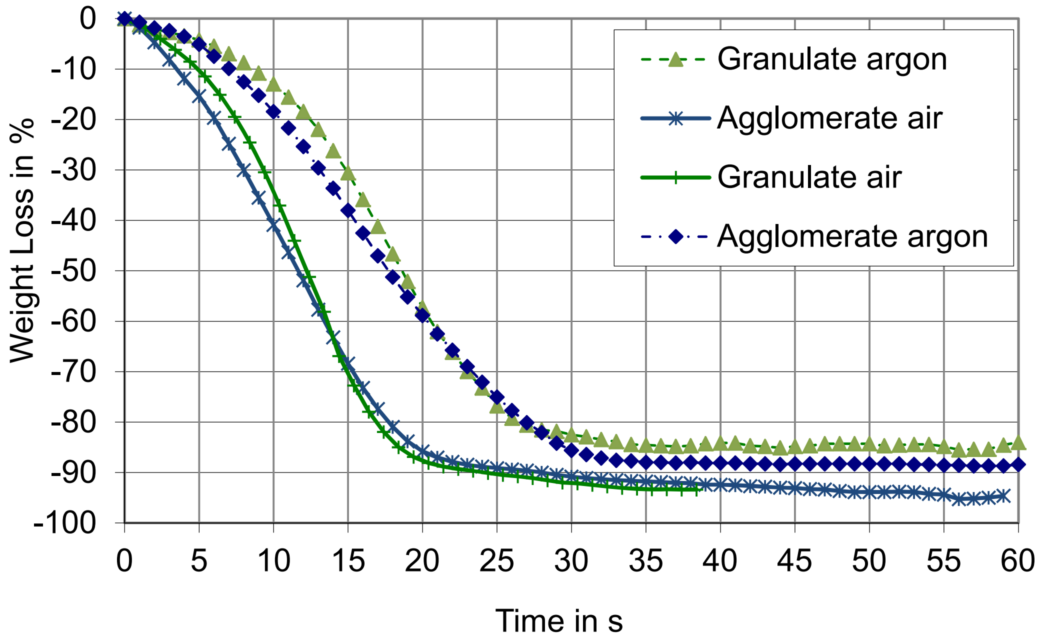


Figure 6. Weight loss of waste plastics in argon atmosphere.

5 INVESTIGATION OF CONVERSION UNDER BLAST FURNACE CONDITIONS IN THE INJECTION RIG

The laboratory injection rig at IEHK, RWTH Aachen University simulates the conversion behaviour of solid injectants in the blast furnace tuyères and oxidising part of the raceway (Figure 7). The high pressure part simulates the conditions in the injection lance; the low pressure part simulates the situation in the blast furnace tuyère and oxidising part of the raceway. On the top of the rig a furnace in the low pressure part is heated up to 1,100°C and a second furnace generates a local zone with temperatures of 1,700°C. The sample is filled in at position “E” and blown through the rig by expansion of the high pressure part. Passing the simulation zone the sample converts into reaction gas and a residue, which consists of unconverted carbonaceous material and ashes. The residue is collected on a filter at position “F” and cooled with nitrogen to prevent a further conversion. The reaction gas is collected in a gas mouse and analysed. The results are computed to diagrams which show the conversion degree vs. the O/C atomic ratio of sample and gas atmosphere. The conversion degree can be defined as the amount of analysed carbon containing product gas (CO and CO_2) divided by the theoretically possible CO_2-product.(12)

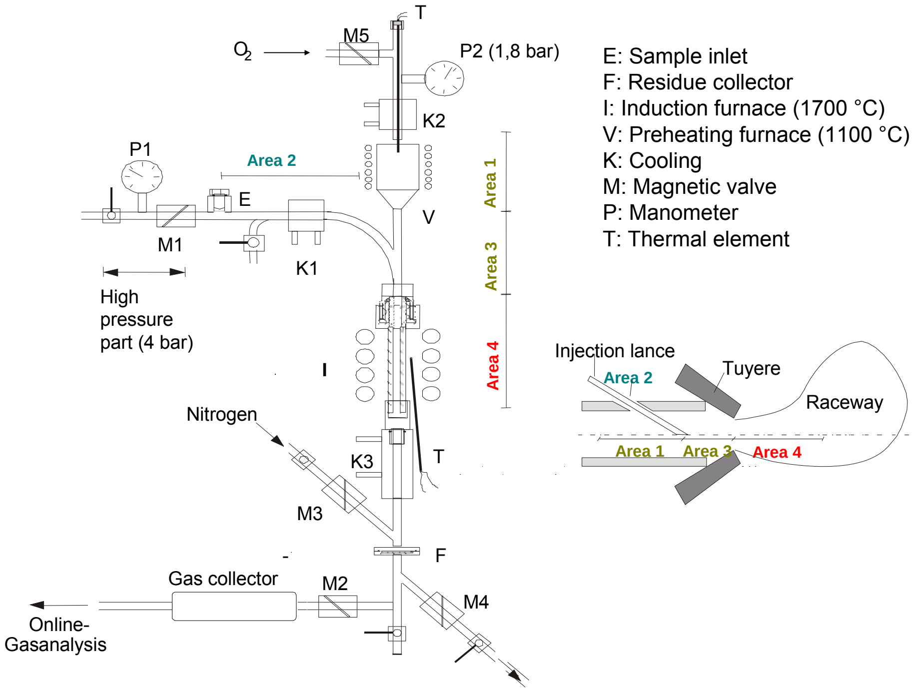


Figure 7. Scheme of the Batch Injection Rig at the IEHK. (12)

For each type of waste plastics 3 series with 10 different weights of the samples were conducted. The sample weight was changed from 75 to 275 mg within steps of 25 mg; the grain size of the particles was kept constant at 2-3 mm.

Figure 8 shows the conversion degree of the 4 types of waste plastics against the O/C atomic ratio. The different types of waste plastics show different conversion behaviour. Pellets A react with the highest conversion degree, followed by Pellets B. Granulate and agglomerate show worse conversion behaviour.

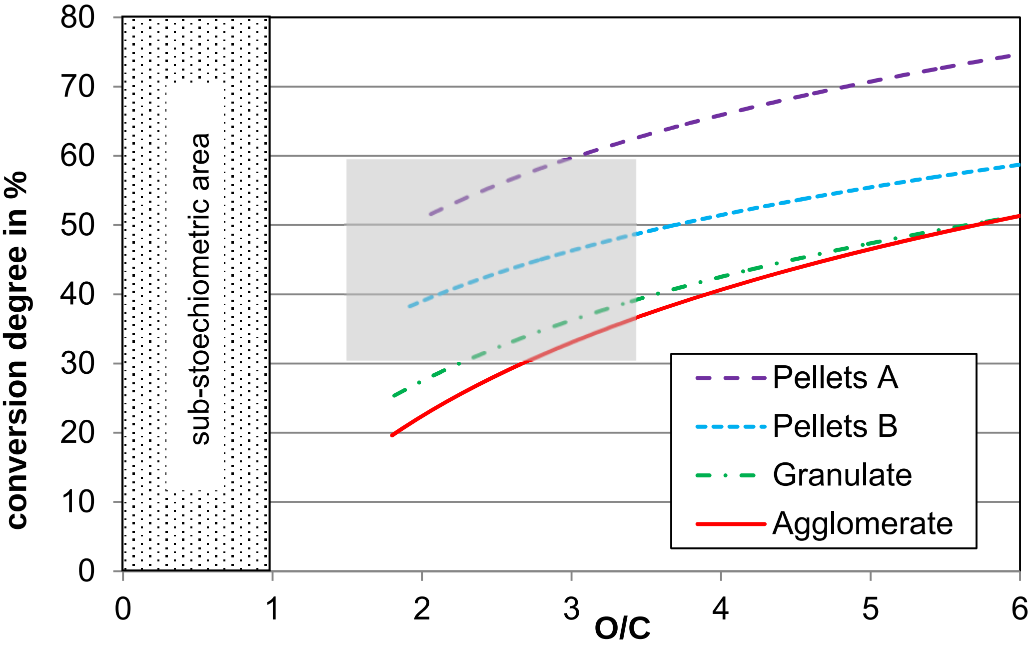


Figure 8. Conversion degree against O/C atomic ratio for the 4 types of waste plastics.

The conversion degree is clearly dependant on the type of waste plastics in accordance to the free surface area and the shape factor, as well as the concentration of injected material. With increasing sample weight the O/C ratio decreases. At low O/C ratios, i.e. at higher injection rate, the samples are not converted completely, as the available amount oxygen decreases.

The free specific surface is decisive for the reaction of the waste plastics. The calculation for the specific surface (in m^2/kg) in dependence of the shape of the particle can be calculated from equation 1. The samples of granulate and agglomerate are in shape close to a ball and the pellets are closer to a rectangle plate.

$$f = F/M = F/(V^{*}\gamma) = D^2/(D^{3*}\ \gamma) = L^2_C/(L^3_C{}^{*}\ \gamma) \qquad \text{(eq. 1)}$$

Where:

- F = total surface of the whole combustible material in m^2
- M = mass of the combustible material in *kg*
- V = volume of the combustible material in (m^3)
- D = diameter of the combusted particle (average) in *m*
- L_C = characteristic length of the combusted particle in *m*
- γ = density of the combusted particle in kg/m^3
- characteristic length for a ball: $L_C = D$
- characteristic length for a rectangle plate: L_C = edge length/10

From eq. 1 the calculated specific surface of the pellets is 10 times higher than the specific surface of granulate and agglomerate, Table 4. Because of the higher free surface, pellets react much faster than granulate and agglomerate.

Table 4. Specific surface of injected waste plastics

Type of waste plastics	density in g/cm³	characteristic length L_C in m	specific surface in m^2/kg
agglomerate	1.125	$2.5*10^{-3}$	0.356
granulate	1.166	$2.5*10^{-3}$	0.342
pellets A	1.223	$2.5*10^{-3}/10$	3.135
pellets B	1.160	$2.5*10^{-3}/10$	3.584

To investigate the injection behaviour of samples of the original fraction, tests with agglomerate (5-8 mm) were performed. Agglomerate has the highest homogeneity of the waste plastics due to their production process. For these tests single particles with a weight of about 90 mg (Figure 9) were tested in the injection rig.

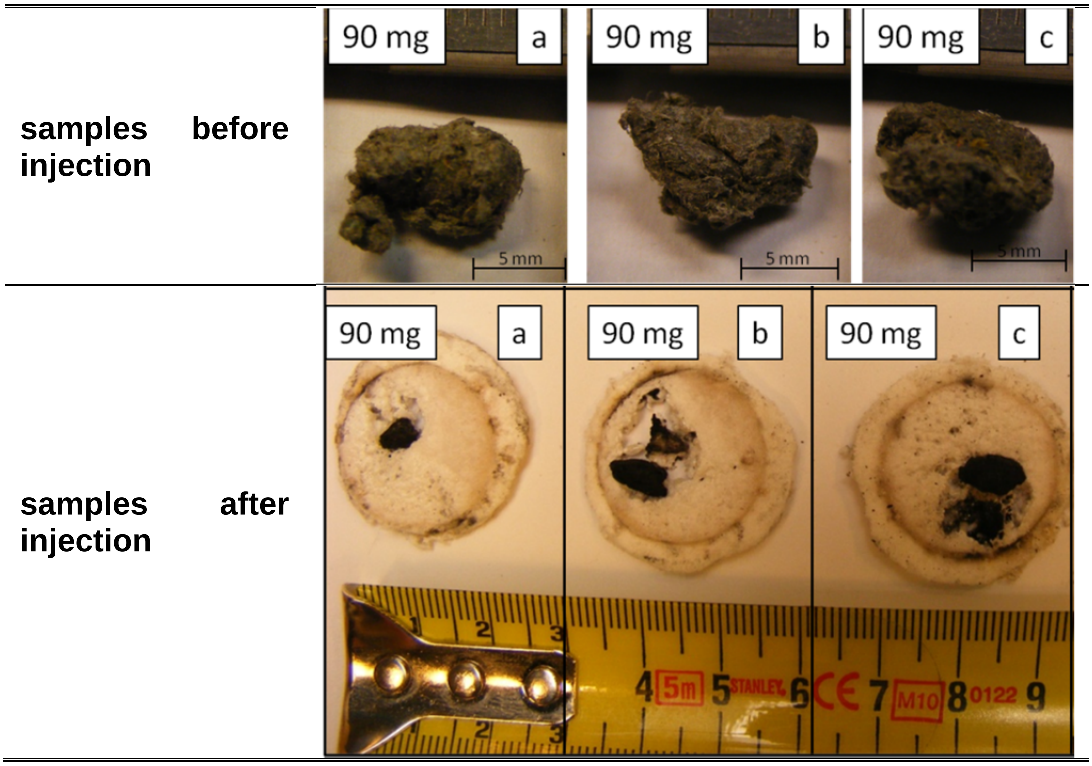


Figure 9. Samples before and after the tests in the injection rig.

The sample sizes were measured before and after the tests and the changes in dimensions were calculated (Table 5).

Table 5. Change in dimensions during injection

90 mg sample	change in dimensions in %				
a	-7.2	x	-17.3	x	-5.7
b	-10.0	x	-16.7	x	2.5
c	-13.7	x	-3.2	x	-3.0

To calculate the conversion degree, the weight change (Δm) of the samples was measured (Table 6). Comparing the mass change to the volume change, calculated from the measured dimensions, it can be clearly seen, that the mass loss is almost completely covered by the volume shrinkage of the particle.

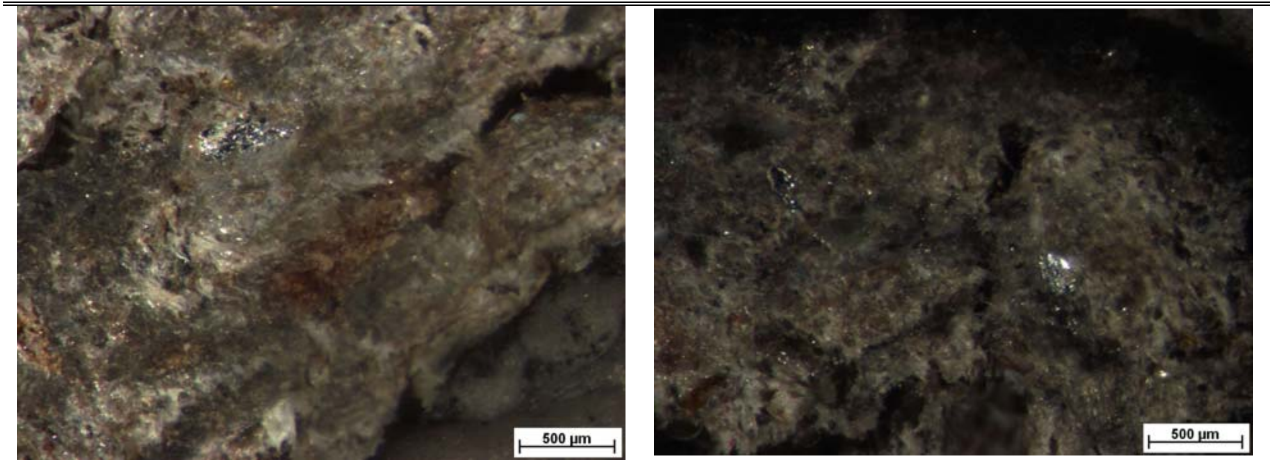
Table 6. Volume and mass change

sample	volume before reaction in mm³	volume after reaction in mm³	ΔV in mm³	Δm calculated from ΔV, mg	Δm measured in mg	conversion degree in %*
a	105	76	29	33	34	39.7
b	134	103	31	35	34	37.7
c	136	109	26	29	36	41.6

* conversion degree based on combustible matter

The single waste plastics particles cannot be converted fully due to the short reaction time, though the percentage of combustible matter is about 93% (almost volatile matter). A 90 mg single particle corresponds to an O/C ratio of 5.4. For this value the conversion degree is lower for single particle than from the experimentally curve determined (Figure 5). These results were expected, as for the determination of the curves several particles with a diameter of 2-3 mm were injected. Several small particles offer have a higher surface/volume ratio than a single particle.

Figure 10a shows the cross section of an agglomerate particle in initial state. At the border some cracks can be seen. In total the inner part is very dense and compact. In Figure 10b the cross section of an agglomerate particle after the injection is shown. It can be clearly seen, that small pores increased a little in size and a little more pores in total can be seen. The weight loss is mainly dependent on the change in dimensions/volume and the porosity of the sample. A much higher porosity after the trials was not observed with the stereomicroscopy.



(a) before injection (b) after reaction

Figure 10. Surface cut of an agglomerate particle before and after the injection.

The biggest part of the weight loss is caused by the volume shrinkage of the particle, about 90%. The remaining 10% of weight loss are caused by the higher porosity of the particle after reaction.

Because of the short residence time in the injection rig, the heat does not penetrate the whole particle till the inner core. The particles react mainly on the surface and the reaction is less dependent on diffusion.

6 CONCLUSIONS

Injection of 25-40 kg/tHM of waste plastics is practiced at voestalpine Stahl BF A. The reaction kinetics of plastics conversion was studied experimentally in detail.

The characterisation of the waste plastics points out a hierarchy in the porosity. Granulate has the lowest porosity, followed by agglomerate and the pellets with the highest porosity. The producing process is probably responsible for pores of bigger size, whereas the plastics origin may account for small pores. The porosity directly affects the conversion behaviour. Granulate and agglomerate show similar behaviour, as well as both types of pellets. The high free surface area of the pellets leads to a faster conversion in air atmosphere.

The results gained by thermo-gravimetric analysis in argon atmosphere point out the fast reaction rate of the waste plastics by the vaporisation of volatile matter. The reaction is more dependent on the temperature than on the atmosphere, as the weight loss is sharp and does not differ much from argon to air. The endothermic cracking reaction, due to the decomposition of the hydrocarbons, before the exothermic oxidation reactions is significant for the reaction of all examined materials in air.

The Tammann furnace experimental set the scenarios of conversion closer to raceway conditions by using thermo-shock and fast heat transfer mainly through radiation. Granulate and agglomerate show similar conversion behaviour as well as pellets A and B. This fact leads to the conclusion that the shape and the size of the substances have a high influence on the conversion.

The investigations in the injection rig show that the reaction takes place almost only on the surface. Heat transfer through the inner core of the particle is not high and the porosity does not increase much. The reaction is dominated by the shape and due to that the free surface of the particle.

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