

Process Integration Analysis for Innovative Environmentally Friendly Recovery and Pre-Treatment of Steel Scrap

Giacomo Filippo Porzio^{*a}, Valentina Colla^a, Barbara Fornai^a, Marco Vannucci^a, Mikael Larsson^b, Håkan Stripple^c

^aScuola Superiore Sant'Anna, TeCIP - PERCRO, Via Alamanni 13b, 56100 Ghezzano, Pisa, Italy

^bSwerea MEFOS, Box 812 SE-971 25 Luleå, Sweden

^cIVL Swedish Environmental Research Institute Ltd., P.O. Box 210, 60 SE-100 31, Stockholm, Sweden

g.porzio@sssup.it

The use of zinc-coated steel (e.g. galvanized steel) in melting cycles based on Electric Arc Furnaces can increase the production of harmful dust and hazardous air emissions. A process to simultaneously preheat and remove the coating from the scrap surface is presented in this paper. The zinc in coating is removed in the gas phase by acid syngas combustion and collected in a dedicated recovery system. The article describes two possible process routes involving plastic waste pre-treatment, shredded plastic gasification/pyrolysis, scrap preheating and zinc recovery processes. The routes have been modelled in an integrated flowsheet, in order to allow a comprehensive simulation and optimization of the pre-treatment processes.

1. Introduction

Steel scrap is a valuable raw material for the steel industry, especially for the electric steelmaking route: in the EU-27 the percentage of steel produced through electric arc furnace (EAF) is 35.3 % with a net production of 50.8 Mt steel (World Steel Association, 2012). In order to increase the corrosion resistance, steel is sometimes subjected to a galvanization process, consisting in the creation of a zinc coating on its surface. At the end of its life cycle, when it is recycled as scrap into the EAF to produce a new product, steel is contaminated by zinc and organics creating harmful or toxic elements that contaminate EAF dust. Currently, pyrometallurgical processes such as Waelz Kiln, Rotary Hearth or Shaft Furnace are the mostly applied technologies for the recycling of dusty steel mill residues, even though they have some disadvantages: for example, the Waelz process has the significant disadvantage that the Fe content (and the valuable Ni) of the residues cannot be re-used in the steel industry. In the best case the Waelz slag is usable in road construction or cement production (Ruetten, 2010). Pre-treatment of scrap prior to its melting in steelmaking furnaces is another way to handle the problem with the coated scrap (Larsson et al., 2008): in literature there are several methods, e.g. electrochemically aided caustic leaching, but few concepts have reached industrial scale (Ijomah and Ijomah, 2003). In this article an innovative stand-alone method which combines scrap preheating and surface cleaning will be presented, using energy and chlorine containing plastic waste as a resource. Plastic is converted in a low pH syngas, which is burnt in a dedicated shaft. Such a concept has been suggested and developed first at Swerea MEFOS. The pre-treated and cleaned scrap is charged hot into the steelmaking furnaces giving direct savings of energy (Larsson and Angstrom., 2008) and improving the energy efficiency of the scrap melting process (Larsson et al., 2012): European manufacturing industries, e.g. the steel industries, are nowadays faced with such issues in order to maintain their competitiveness in the international panorama (Porzio et al., 2013a). In such context, process integration methods such as pinch analysis, as well as advanced optimisation techniques, combining flowsheeting models and artificial intelligence (Porzio et al., 2013a) can be helpful for both reduction of total energy (Larsson and Dahl, 2003) and for the conservation of resources (Sahu and Bandyopadhyay, 2011). The purpose of the present paper is to describe two possible process routes involving plastic waste pre-treatment, shredded plastic gasification/pyrolysis, scrap preheating and zinc

removal and recovery processes. It is organised as follows: Section 2 describes the approach to the problem that has been implemented; Section 3 describes the case studies and the results obtained; conclusions follow in Section 4.

2. Materials and Methods

The technologies described in this article have been assessed during the RFCS (Research Fund for Coal and Steel) research Project (PROTECT), which consortium is formed by several research institutions and commercial companies, plus a steel producer (SSAB). All the involved processes have been modelled through the software Aspen Plus[®]. Flowsheeting models have been realised for all the sub-processes involved in the feedstock and scrap processing, and zinc recovery from the flue gas. The models, then, have been interconnected in a general flowsheet in order to carry out simulations that enable to evaluate the processes in its completeness. The applicability of the software Aspen Plus[®] to the simulation of ironmaking and steelmaking processes has been demonstrated in previous literature: (Schultmann et al., 2004) demonstrate that flowsheeting-based simulation can support in decisions related to the recycling concepts in metal industry; (Fröhling et al., 2009) examined which recycling rate is optimal considering transportation planning measures and recycling rates; (Porzio et al., 2013b) have presented an approach to the realization of a software system able to generate internal report and simulate the process plants behaviour in different conditions. The software has been used also for the simulation of biomass processes (Porzio et al., 2011) and as an opportunity to evaluate different process integration solutions and scale-up potential (Porzio et al., 2012). Moreover, as far as the work described in this article is concerned, Aspen Plus[®] has been used to join and combine within a same “virtual” location different technologies, which pilot plants are located in different European countries. The fundamental blocks in the model flowsheet of the PROTECT processes are: a plastic feedstock handling block, two parallel blocks reproducing plastic gasification/pyrolysis, a preheating shaft block and a block representing gas scrubbing and zinc recovery system.

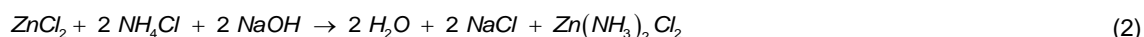
The simulation and modeling work started exploiting the laboratory analyses carried out by the industrial partners in order to feed the Aspen simulations with a material flow that closely reproduced the actual incoming stream: different feed materials have been treated as nonconventional components (e.g. tires, shredded granules + heavies, Shredded Light Fraction - SLF), and sent to RYield blocks that are responsible of the conversion of the material flows into their constitutive chemical elements. The conversion is made based upon experimental measurements of the feedstock composition in terms of ultimate and proximate analysis, coming from SiCon GmbH that developed the feedstock preparation and handling process. A selector block, then, allows choosing among different feeds to be sent to syngas production through gasification/pyrolysis; the stream is duplicated in order to supply both with the same inlet composition and flowrate.

The gasification model has been realized taking as a reference the pilot plant at Siegen University, exploiting experimental data conducted at 700 °C, 800 °C and 900 °C with steam as gasification medium and nitrogen as inert carrier gas. The Aspen Plus[®] gasification flowsheet, described in detail in (Kappes et al., 2013), is composed by a combination of equilibrium and separation reactors that estimate the syngas yield and composition in different operating conditions and processing different plastics. Every reactor represents a different reaction zone in the gasifier, individuated by different temperature level and reactants (e.g. steam). The results from the simulation of the plastic gasification process have been validated through comparison with experimental data from a lab-scale reactor, showing a good agreement between the simulation results and the experiments. The pyrolysis model has been realised exploiting the experimental results provided by Stena Metall. In the experimental setup microwave energy has been used to supply the processes with the necessary heat for the pyrolysis reactions to take place; however, since the full-scale process is foreseen to get the necessary energy by burning part of the process gases, a hypothetic layout representing such a situation has been chosen for implementation in the Aspen model. In this case, an equilibrium model reactor is put in series with a stoichiometric reactor in order to simulate the isothermal conversion of the fuel into a liquid and gaseous fuel and a solid residue without addition of air. In the modelled system it is assumed that the microwave energy provided to the pyrolysis reactor is converted to heat, which is supplied to the equilibrium reactor. Products are separated in order to separate ash from fuels and recover oil from the gas stream that is sent to the preheating shaft. The preheating shaft model has been realized following the layout of a pilot plant by SWEREA MEFOS in Lulea, Sweden. This model section is the heart of the whole process simulation, linking all the other parts together. Propane gas (necessary to sustain the combustion reactions) is supplied to an adiabatic reactor together with oxygen, syngas from either pyrolysis or gasification and a recycled gas stream from the scrubbing section. Combustion takes place in an equilibrium reactor (where the steel scrap is brought to its

preheating temperature), and the scrap preheating and simultaneous zinc removal is operated by means of the HCl content in the syngas in a stoichiometric reactor according to the reaction:



The preheated scrap is then separated from the gases, and the former is sent to the EAF, while the latter proceed to the gas scrubbing and zinc extraction sections. Such a process is based upon the Ezinex technology developed by Engitec Technologies S.p.A. Following gas washing and solution neutralization in the scrubber, the next step is a further neutralization where sodium chloride is formed together with zinc complex according to the reactions:



A solid residue is then separated and the liquid flow sent to a single stage cementation reactor. The main cementation reactions can be written as:



Solids are washed once again in order to recover valuable by-products, while the liquid stream proceeds to the subsequent electrolysis and crystallization stages. In the electrolysis the zinc solidification and deposition on the anode takes place, as well as some dissociation of ammonia into gaseous hydrogen and nitrogen:



Whereas in the crystallization step water is evaporated to produce steam and the concentrated salt sludge is sent to a centrifuge for extraction of NaCl (with about 3 % residual moisture). The weak solution is circulated back into the leaching reactor and goes through the subsequent steps of the process in order to enhance the zinc recovery efficiency. The described process allows a very efficient recovery of zinc, which can be sold on the market: it has in fact been estimated that Good Ordinary Brand (GOB) grade zinc - or higher quality - is recoverable, with a yield of almost 100 %.

3. Results and Discussions: Case Studies Presentation

Several case studies for the pre-treatment plant have been carried out based on realistic scenarios in order to assess the validity of the proposed models. The selection of such cases allowed to feed the simulation with a consistent set of input variables. The resulting combinations of I/O variables from these case studies were then exploited to assess the performances of the proposed technologies.

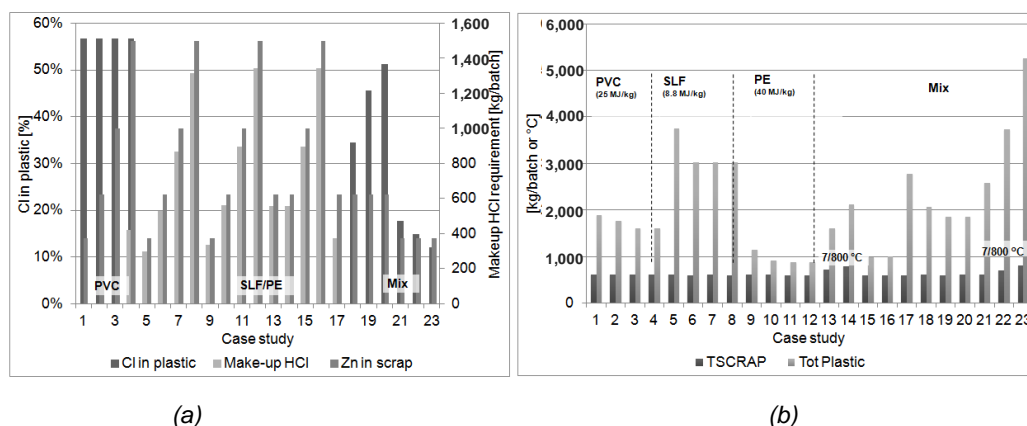


Figure 1: Case study: Make-up HCl requirement and Cl content in plastics as a function of Zn content (a) and Plastic Consumption for the preheating process (b)

The case studies referred to the production of 50 t of hot scrap as output, mainly varying the input plastic mix (Polyethylene, PE, Polyvinylchloride, PVC, and SLF). The varied factors have been Zn in the incoming scrap, outgoing scrap temp, and ingoing plastics mixture: % PE, % SLF, and % PVC varied in fact significantly. The experiments have been first carried out considering pure PVC, then SLF, then PE, followed by different mixtures of the three plastics (note in particular that the plastics differ for their chlorine content as well as heating value). The preheated scrap outgoing temperature has been set in all cases to 600 °C, except for four cases where it has been increased to 700 and 800 °C. All the outputs were calculated exploiting the process model, focusing in particular on the following:

- Mass of cold scrap;
- Mass of plastics required to supply the necessary heat;
- Mass of makeup-HCl in case not enough chlorine is supplied by the plastics usage;
- Mass of CO₂ emitted from the process (gas scrubbing and zinc removal) processes.

The first result is relative to the consumption of makeup HCl in the preheating shaft. Such an addition is necessary in those cases where not the hydrochloric acid carried within the syngas is not enough to support the surface zinc removal reactions. In case a plastic with a high Cl content is processed (e.g. PVC, cases 1-4), there is no or little requirement for makeup HCl. The lack of Chlorine in SLF or PE (cases 5-12) is compensated by the addition of a make-up. If a mixture of the 3 plastics is considered, the presence of PVC allows not to use an additional chlorine source. The addition of makeup HCl/exploitation of the Cl incoming with the feedstock is also proportional to the Zn contained in the scrap to be processed. This behavior is visible in Figure 1 (a) (Zn in the incoming scrap and makeup HCl are both reported on the secondary axis): the calculated rate of zinc recovery from such a process shows an almost constant value for all cases (81.3 % on average, min 80.2 %, max 82.7 %). Plastic consumption (that supplies the process with the energy required for preheating) is a function of the scrap temperature as well as feedstock heating values. From Figure 1 (b), it is clear that the higher the plastic heating value, the lower the requirement to reach the set scrap preheating temperature. An optimization study has been carried out in order to estimate the potential impact of a reduction in the plastic feedstock on the preheating temperature and makeup HCl consumption. The aim is to minimize simultaneously the consumption of plastic waste as well as the need of additional HCl, by maintaining an acceptable scrap preheating temperature level (at least 600 °C). The base case, calculated through the LCA software KLC-ECO, is related to the consumption of about 49 kg/t scrap of a plastic mixture of 68 % PVC and 32 % SLF by weight, and already included the addition of a small amount of HCl (roughly 2.1 kg/t scrap). The temperature of the preheated scrap is around 790 °C. According to simulation results, the consumption of plastic waste can be cut down to 29 kg/t without violating the constraint on the temperature. In such a case, however, the consumption of HCl would be increased up to 9 kg/t scrap (450 kg/batch of preheating). The results in Figure 3 also show that in case the plastic was the only source of chlorine, an amount of at least 56 kg/t would be needed, potentially bringing the scrap to a temperature of almost 850 °C, close to the upper scrap temperature limit that has been set at 900 °C to avoid ignition of scrap surface ignition phenomena. Since the model incorporated a limit at such temperature level, the calculation results for temperatures above 900 °C are not reliable (at 900 °C, the temperature stabilizes and increases for higher plastic consumption). Such an analysis is the basis for a potential economic evaluation. The variables utilized for the calculation of the cost function would then be the scrap preheating temperature, the plastic consumption and the makeup HCl consumption (assuming a constant yield of the zinc recovery process). The function $f(T, HCl, plastic)$ to be minimized can be written as:

$$f(T, HCl, plastic) = HCl \cdot \text{cost}_{HCl} + plastic \cdot \text{cost}_{plastic} - \text{energy saving}(T) \cdot \text{cost}_{energy} \quad (10)$$

The minimization of such objective has been carried out considering a constant zinc yield and only evaluating the impact of the plastic consumption. The following assumptions were taken into account:

- Heat capacity for steel at high temperature taken from Bentz and Prasad, 2007;
- EAF heating efficiency of 95 %;
- Electric energy cost of 0.01 €/MJ;
- Plastic processing cost of 0.18 €/kg (including 0.07 €/kg from plastic shredding operating costs and 0.11 €/kg for the gasification operating costs);
- HCl cost of 0.15 €/kg.

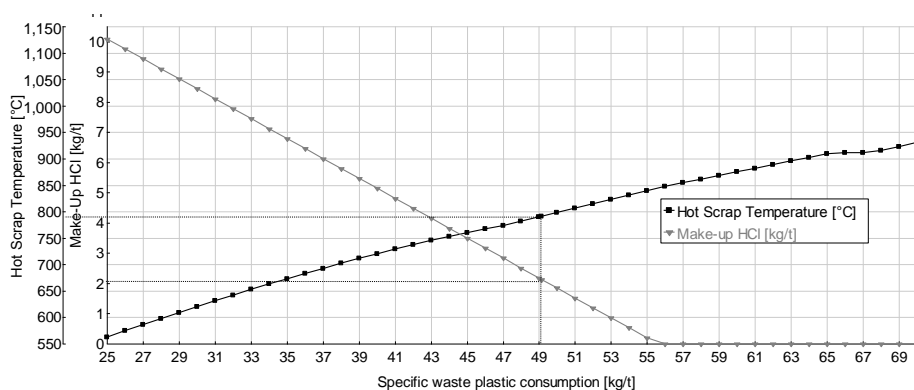


Figure 3: Impact of waste plastic consumption on HCl make-up and scrap preheating temperature

Table 1: Optimization results

Variable	Base case	Optimization result	Unit
Final scrap temperature	790.95	617.72	°C
Makeup HCL consumption	2.13	8.50	kg/t
Plastic feedstock consumption	49.14	29.80	kg/t
Incoming scrap mass flowrate	1,015.13	1,015.13	kg/t
Objective function value (cost)	€ 4.64	€ 3.24	[€/t]

The results from such an optimization are shown in Table 1. The achievable reduction in cost is of about 30 % in relative terms, caused by the combination of a 39 % reduction in plastic consumption, a three-fold increase in the HCl consumption, and a reduction of the scrap preheating temperature by 22 %. The energy saving in the EAF has been quantified for such scenario in about 320 MJ/t preheated scrap. Such an optimization is obviously a parametric study; therefore its results strongly depend upon the cost values that are utilized.

4. Conclusions

The present paper describes a process integration study on an innovative process for simultaneous steel scrap preheating and surface cleaning. Flowsheeting simulation has been utilised for the simulation of the process, which is under assessment in an RFCS research project. The simulations allowed an assessment of different process configuration and potentials for energy saving and waste materials re-use that would otherwise be sent to landfill. Process optimization has also been carried out in order to minimise the specific plastic and hydrochloric acid consumption, maintaining a satisfactory by-product recovery (valuable commercial Zn) and hot scrap temperature.

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References

- Fröhling M., Bartusch H., Schwaderer F., Schultmann F., 2009, An Inter-Company Approach to Improve Resource and Energy Efficiency and Reduce Greenhouse Gas Emissions in Metal Industries by Linking Flow Sheet Models, *World of Metallurgy – ERZMETALL*, 62(5), 288-298.
- Ijomah M.N.C., Ijomah A.I., 2003, Chemical recycling of galvanized steel scrap, *Indian Journal of Chemical technology*, 10, 159-165.

- Kappes M., Porzio G.F., Colla V., Vannucci M., Krumm W., 2013, Steam gasification process of chlorine-rich shredder granules: experiments and flow-sheeting modelling for process evaluation and scale-up, *Chemical Engineering Transactions*, 35, 1321-1326.
- Larsson M., Angstrom S., 2008, A novel process for simultaneous scrap preheating and surface rinsing, SCANMET 3th, International Conference on Process Development in Iron and Steelmaking, 8-11 June 2008, Lulea, Sweden, 1, 485-492.
- Larsson M., Hahlin P., Angstrom S., 2012, The future of scrap preheating and surface cleaning, SCANMET 4th, International Conference on Process Development in Iron and Steelmaking, 10-13 June 2012, Lulea, Sweden, 1, 83-92.
- Larsson M., Dahl J., 2003, Reduction of the specific energy use in an integrated steel plant—The effect of an optimisation model, *ISIJ International*, 43(10), 1664–1673.
- Bentz D.P., Prasad, K.R., 2007, Thermal Performance of Fire Resistive Materials – I. Characterization with Respect to Thermal Performance Models, NIST (National Institute of Standards and Technology) Report NISTIR 7401, Gaithersburg, MD, USA <ciks.cbt.nist.gov/~bentz/nistir7401.pdf> accessed 28.04.2014.
- Ozturk B., Fruhean R.J., 1996, Vaporization of Zinc from Steel scrap, *ISIJ International*, 36, supplement, 239-242.
- Porzio G.F., Colla V., Matarese N., Nastasi G., Branca T.A., Amato A., Fornai B., Vannucci M., Bergamasco M., 2013a, Process integration in energy and carbon intensive industries through exploitation of optimization techniques and decision support, *Chemical Engineering Transactions*, 35, 193-198.
- Porzio G.F., Fornai B., Amato A., Matarese N., Vannucci M., Chiappelli L., Colla V., 2013b, Reducing the energy consumption and CO₂ emissions of energy intensive industries through decision support systems – An example of application to the steel industry, *Applied Energy*, 112, 818–833.
- Porzio G.F., Prussi M., Chiaramonti D., 2011, Process analysis and modeling for 2nd generation lignocellulosic bioethanol production, *Chemical Engineering Transactions*, 25, 869-874.
- Porzio G.F., Prussi M., Chiaramonti D., Pari L., 2012, Modeling lignocellulosic bioethanol from poplar: estimation of the level of process integration, yield and potential for co-products, *Journal of Cleaner Production*, 34, 66-75.
- Ruetten Dr J., 2010, The topical Waelz process for recycling of EAF dust, State-of-the-art and future challenges, Proceedings of the Lead-Zinc 2010 International Symposium on Lead and Zinc Processing, 3-6 October 2010, Vancouver, British Columbia, Canada, 871-881.
- Sahu G.C., Bandyopadhyay S., 2011, Minimization of resources requirement and inter plant cross flow across resource allocation networks, *Chemical Engineering Transactions*, 25, 279-284.
- Schultmann F., Engels B., Rentz O., 2004, Flowsheeting-based simulation of recycling concepts in the metal industry, *Journal of Cleaner Production*, 12(7), 737-751.
- World Steel Association, 2012, Steel production 2012 report <www.worldsteelorg./statistics/statistics-archive.html> accessed 24.02.2014.