END-OF-LIFE CFRP AS A RAW MATERIAL IN STEEL AND OF CALCIUM CARBIDE PRODUCTION

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Abstract

CFRP has become more and more an established material of lightweight design in the recent years. In addition to the established sectors such as aerospace, sports and leisure, the material has been increasingly used in in the automotive sector, energy sector and mechanical engineering [1]. However, recycling is still a challenging process step at the moment. Fibre reduction [Fibre damage/ A Reduction of Fibre diameters] is intrinsic in recycling processes. Therefore additional processes for material and energy recovery are also necessary. Experiments for energy recovery in household waste and hazardous waste incineration plants have shown that these treatment plants are not suitable for energy recovery. [2].

Pilotscale test in the field of calcium carbide production have shown that up to 20% of the black material mixture can be replaced by CFRP. Workplace measurements have also shown that no relevant levels of WHO fragments occur in the workplace environment. In carbide furnace carbon fiber materials can be recycled, the carbon fibers react to carbide, the plastic matrix pyrolizes and can be supplied as gaseous fuel the process-related CO gas of thermal and material recovery.

Steel production trials (pilot scale) have shown that secondary metallurgical slag briquettes with 3% and 6% CFRP residues, respectively, were successful. The briquettes were added to a liquid slag melt at a temperature of 1830 ° C.

1. Introduction

Since 2012, the recycling technologies of carbon fiber reinforced plastics (CFRP) are developing rapidly. This process still goes on and it can be assumed that in a few years the developed innovations in industry are implemented [3]. Due to constantly new developments in the field of CFRP production technology there has been a steady growth of the produced products and components made of. In a few years or few decades, this will also have a significant impact on the necessary recycling or the market for recycling applications. Compared to other materials such as metals, paper or unreinforced plastics, however, the processed quantities of CFRP are still very small. As with other materials, economically attractive recycling plants can only be implemented if the mass flows also make high volume plants profitable for recycling. Despite this, there are already a multitude of ways to recycle CFRP. Basically, the material flows must be differentiated as follows:

- **Dry residues**: Dry residues have not been infiltrated with a matrix. Any binder or sizing residues are negligible. By dry residues are for example, materials such as remnants of fiber or fabric bobbins or tailings from the preforming process.

- **Wet residues**:wet residues have already been associated with the matrix. In addition to hardened cutting residues, wet residues are, for example, production rejects or end-of-life components. It is fundamentally to be distinguished between the type of polymer:
  - With thermoset matrix: Thermoset matrices have tightly crosslinked chain molecules. As a result, thermosets are not melted.
  - With thermoplastic matrix: Thermoplastic matrices have uncrosslinked chain molecules. As a result, thermoplastics are meltable.

2. Recycling

In the field of recycling, a distinction must be made between the different types of residues. Dry residues (fibers) with a certain length (about > 10 mm) can again undergo textile treatment. With nonwovens [4], yarns [5], tapes [6] or papers [7,8] very different processes have been developed so far that corresponding products made from recycled carbon fibers (rCF) are ready for the market. These semi-finished textile products can once again be used as raw materials for CFRP production. Dry fiber pulp, which are too short to be treated, can be used, for example, in injection molding [9, 10, 11]. Even the shortest fiber residues (< 20 mm in length) or fiber dust (<200 µm) increase the mechanical properties of plastics to a high degree [12]. Substantially, any type of fiber remains can be utilized, whereby the outstanding reinforcing properties of CFRP can be at least partially preserved.

For wet residues with thermoset matrix, the fiber must first be separated from the matrix. In addition to the already industrially used pyrolysis [12] there is a series of research and development works. Examples include electrodynamic fragmentation [13], solvolysis [14] including supercritical water [15] and inductive heating [16]. In most processes, the fiber is recovered, the matrix is lost. The exception here is solvolysis or treatment in supercritical water. In the future, procedures will have to be established which leave these substances economically attractive in the material cycle. After successful fiber-matrix separation, the fibers can be re-fabricated in textile form and then be introduced into new products (see above). In addition, these substances can also be crushed or ground and later used as a filler in other productions.

Wet waste with thermoplastic matrix can go the same way as dry residue with duromer matrix. In addition, these substances can also be crushed and processed directly. For example, injection molding granules can be produced from wet waste with a thermoplastic matrix (see above). These injection-molded granulates end up in products again.

This shows that it is technologically possible to keep the carbon fiber in the material cycle. However, as the length of the fiber decreases, so does the mechanical properties of the composite. However, at the end of the life cycle, a last recycling step may be that carbon fibers can be used as a reinforcing material in injection molding.

3. Material Recycling / Exploitation

However, if it is not possible to recycle the fibers, the following recycling methods are currently being investigated on an industrial scale:

3.1. CFK as a raw material for calcium carbide production

CFRP consists of carbon fibers embedded in a plastic matrix. The high-quality carbon fibers are a source of carbon for resource-intensive carbide production. The recycling of resinated CFRP waste to calcium carbide has been successfully implemented in an pilot scale. The chemical reaction proceeds as follows:

$$CaO \; + \; 3C \; \rightarrow \; CaC_2 \; + \; CO \qquad \Delta H_R = 465{,}3 \frac{kJ}{mol}$$

The following figure shows with which different materials the production of calcium carbide was tested. It turned out that CFK in a size of about 5 cm chip size should be available for optimal recycling.

Figure 1. CFRP Waste as raw material [17]

Principle of CFRP utilization: The plastic matrix protects the light carbon fibers on their way into the electric arc furnace and holds the clutch together. On the way through the furnace (temperature gradient ΔT> 2000 ° C), the plastic gasses and coagulates. The pure carbon fibers remain in the furnace thanks to the cover over them and finally move into the main reaction zone, where they are converted with lime to carbide.

Requirements for potential material flows: If possible no foreign substances, in particular (heavy) metals and glass fibers (GRP), if possible no dust or fiber flour, no tangle, maximum edge length 70 mm and clean, undamaged as possible edges, use theoretically also possible in briquetted form, if og Requirements are met. Fine or exposed fibers end up in the raw material or furnace gas filters rather than in the main reaction zone of the carbide furnace.

Challenges in the use of CFRP: Fiber accumulation in carbide production (short circuits of electrical equipment, exposure to employees), transfers in the raw material transport routes, in the bunkers and their outlets, laying of cooling and sealing water circuits by discharged fibers, modification of the properties of carbide and furnace dusts (Flow, agglomeration behavior, pyrophoricity, etc.), resulting in the need to optimize technical and organizational processes.

Conclusion: Experiments have shown that at least 20 % of the black substance mixture can be replaced by CFRP. Workplace measurements have shown that no relevant levels of WHO fragments occur in the workplace environment. Carbide content, spec. Electricity etc. were in the range of the standard mixture (hard coal coke + burnt lime). In carbide furnace carbon fiber materials can be recycled, the carbon fibers react to carbide, the plastic matrix pyrolyzed or gasified and is fed as gaseous fuel with the process-related CO gas of thermal and material utilization within the AlzChem. Unfortunately, emission measurements in the exhaust gas of the TeCO were so heavily occupied due to the high amount of dust that an evaluation by means of REM-EDX was only possible to a limited extent. Qualitative carbon fibers could be detected (see picture on the right), a classification, whether they met the WHO criteria ($l < 3\mu m$; $l > 3d$) could not be made.

3.2. CFK as a raw material for steel production

The demands made on the by-products of the steel industry are growing, but at the same time it is becoming much more difficult to generate new landfill space. The task here: to find intelligent solutions, so that only valuable substances exceed the company boundary to the outside. The Georgsmarienhütte offers solutions for the thermal and material recycling of residues:

- ELO electric arc furnace: Use of polymer recyclates as a replacement for primary carbon carriers for process control
- Possible applications of recyclates in the ELO are in close coordination with the authorities

The Georgsmarienhütte uses 100% scrap for the production of electrical steel for approx. 20,000 t p.a. Primary coal. The use of the primary coal in the electric arc furnace (see the following figure) is carried out for two different purposes and thus also at two different times:

- Charcoal is charged together with the scrap at the beginning of a melt in the ELO and should dissolve in the resulting crude steel to minimize the iron slags during the oxygen blowing.
- Foaming coal is blown into the slag floating on the liquid steel in the last phase of the melt and generates a foaming effect for enveloping the arc.

Preliminary investigation in the experimental electric arc furnace at the BAM Federal Institute for Materials Research and Testing in cooperation with TEER Technology of Fuels, RWTH Aachen (Prof. Quicker). Two preliminary tests with briquettes have been carried out so far. The briquettes consisted of secondary metallurgical slag and 3% and 6% CFK residues, respectively. Higher CFRP shares could not be realized so far. The briquettes were added to a liquid slag melt at a temperature of 1830 ° C. The slag composition did not correspond to the real conditions in the ELO because of the partially lower adjusted iron oxide contents. The briquettes floated in the slag melt and did not disintegrate, but gradually dissolved. CFRP swam visibly on the melt for a while. During the second preliminary test exhaust samples were taken; C-fibers could not be detected either in the oven room or in the oven environment.

Conclusion: The production of steel with CFRP as a primary carbon deposit seems promising, but it will have to be further investigated in the future.

Conclusion

The aim is to keep the carbon fiber in the material cycle, technologically this is possible. An economic implementation in corresponding large systems must be done as soon as the return mass flows are available. If the recycling of CFRP no longer makes economic sense, CFRP can currently be used as a raw material in steel or the production of calcium carbide.

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