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# Analytical determination of recycling quota through SRF co-processing in the cement industry

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**Abstract**

When solid recovered fuel (SRF) from non-hazardous municipal solid waste is used for co-processing in the cement industry, this waste treatment process is usually considered as thermal recovery according to the waste hierarchy. However, the ash that is formed during the combustion process becomes part of the product, the cement clinker. Certain components of the ash (e.g. $CaO$, $SiO_2$, $Al_2O_3$, and $Fe_2O_3$) that are incorporated into the clinker also represent important raw materials for the production of cement. For this reason, this share of SRF could be considered as being material recycled in the process. This paper, therefore, aims at determining the ash composition and the share of ash constituents that is material recyclable.

In a first trial, 12 samples of SRF were ashed and analyzed by ICP-OES and ICP-MS. Preliminary results show that $72 \pm 6\,\%$ of the ashes' mass is made up from four chemical compounds that represent main constituents of the raw materials used in cement manufacturing: $SiO_2$, $CaO$, $Al_2O_3$, and $Fe_2O_3$. Furthermore, the ash consists of other chemical compounds that are part of common raw materials or Portland cement clinker.

More analyses are required in order to identify the share of the SRF ash that can be considered as material recyclable when co-processed in the cement industry. However, based on the preliminary results obtained, it is suggested that a large proportion of the SRF ash can be attributed to this share.

**Keywords**

Solid recovered fuel, co-processing, co-incineration, cement industry, materials recycling.

# 1    Introduction

## 1.1    Solid recovered fuels

Solid recovered fuels (SRF) represent a subgroup of refuse derived fuels (RDF). While RDF can be made of various non-hazardous and hazardous, liquid and solid waste materials (e.g. sewage sludge, waste wood, used solvents), the term SRF only refers to solid fuels prepared from mixed or sorted non-hazardous solid wastes, that are furthermore quality assured, i.e. meet the criteria defined by EN 15359 [1].

Based on their lower heating values and grain sizes, solid recovered fuels can be further divided into three subgroups that suit different applications [2], compare Fig. 1:

- *SRF LOW quality*: SRF with a lower heating value between 8 and 12 MJ/kg$_{OS}$ (corresponding to class NCV 4 or 5 in EN 15359) and grain sizes up to 120 mm that can be used in co-incineration plants relying on fluidized bed combustion technology.
- *SRF MEDIUM quality:* SRF with a lower heating value between 12 and 18 MJ/kg$_{OS}$ (corresponding to class NCV 3 or 4 in EN 15359) suitable for the use in secondary firing (calciner, kiln inlet or hot disc combustion chamber) in the rotary kiln of cement manufacturing plants. Grain sizes can range up to 80 mm when used in a calciner or at the kiln inlet and up to 300 mm for a hotdisc combustion chamber.
- *SRF PREMIUM quality:* SRF with a lower heating value between 18 and 25 MJ/kg$_{OS}$ (corresponding to class NCV 1, 2, or 3 in EN 15359), and grain sizes below 35 mm suitable for the use as a main burner fuel in the rotary kiln of cement manufacturing plants.

The paper at hand focuses on the analysis of SRF PREMIUM quality and SRF MEDIUM quality, which are used in the cement industry for the manufacturing of Portland cement clinker.
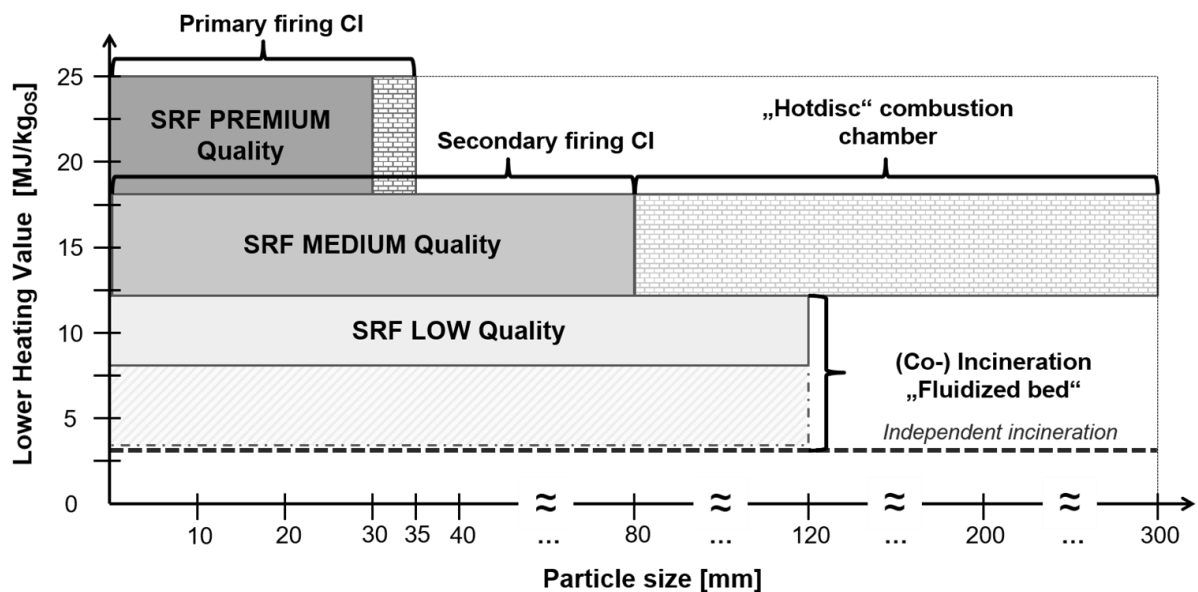


**Fig. 1** Different SRF qualities (defined by their lower heating value [MJ/kg$_{OS}$] and grain size [mm]) and their recovery options. Figure reprinted with permission of [2]

## 1.2    Cement manufacturing and raw materials

Portland cement clinker is an important constituent of any of the 27 types of common cement that are defined in EN 197-1 [3], and depending on the cement type amounts for 5 – 100% of the cement's mass [3]. The most common cement, Portland cement, consists of 95 – 100 % of Portland cement clinker, and 0 – 5 % of minor additional constituents[1] [3].

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[1] The European standard EN 197-1 defines minor additional constituents as „specially selected, inorganic natural mineral materials, inorganic mineral materials derived from the clinker production process or constituents as specified in 5.2 [main constituents] unless they are included as main constituents in the cement"

Raw materials used for the production of cement clinker need to provide the main chemical compounds required for the process, namely calcium oxide ($CaO$), silicon dioxide ($SiO_2$), and smaller amounts of aluminum oxide ($Al_2O_3$) and iron(III) oxide ($Fe_2O_3$) [4]. The following raw rock types are relevant primary resources for the production of cement clinker [4–8]:

- *Limestone and chalk:* consist of $CaCO_3$, which represents a source for $CaO$.
- *Clays:* are considered as a source for $Al_2O_3$ and $SiO_2$. Additionally, they contain feldspars, which are aluminosilicates that also consist of the chemical components sodium oxide ($Na_2O$) and potassium oxide ($K_2O$). Furthermore, clays contain iron minerals such as $FeOOH$, $FeS_2$, $FeO$ and $Fe_2O_3$.
- *Marl:* a natural mixture of $CaCO_3$ and clay.
- *Sand or quartz sand:* represent a source for $SiO_2$ and are added when the $SiO_2$ content of the raw materials mixture is too low.
- *Iron ores:* Source for $Fe_2O_3$. Its addition might be required as a correcting material to achieve the desired bulk composition.
- *Natural gypsum or anhydrite:* represents a source for sulfate ($SO_4^{2-}$) in the form of $CaSO_4$. Small amounts of sulfate are added to bind alkali metals when the content of alkali metals in the raw materials mix is too high or the sulfate content is too low.

To summarize, limestone or chalk, clay, and marl represent the most important raw materials, while sand, iron ores, and other correcting materials are usually added in order to achieve the desired bulk composition and to compensate for the lack of certain chemical components [6]. Apart from these raw rock types, secondary resources containing $SiO_2$, $Al_2O_3$, $Fe_2O_3$, and $CaO$ or $CaCO_3$ can be used in the cement plant [4]. Some of these alternative raw materials and the primary raw materials they can substitute are listed in Tab. 1.

**Tab. 1** Primary and alternative/secondary raw materials for the cement industry [4, 6, 9]

| Primary raw material | Major elements contained by primary raw material | Alternative/secondary raw material |
|---|---|---|
| Limestone, chalk | Ca | Lime mud, residues from lime burning, calcium fluoride |
| Marl | Si, Ca, Al, Fe | Fly ash, ashes from the paper industry, bottom ash, slags, crushed concrete |
| Clay, bentonite, kaolinite | Si, Al, Fe | Waste bentonite and fuller's earth |
| Sand, quartz sand | Si | Used foundry sand, contaminated soil, |
| Iron ores | Fe | Materials from iron and steel industries, e.g roasted pyrite, contaminated ores, dust, mill scale, bauxite tailings (Fe and Al) |
| Gypsum or Anhydrite | S | Gypsum from flue gas desulfurization |

To manufacture Portland cement clinker, the required raw materials are milled, mixed and sintered at temperatures of about 1450°C. During the sintering process, clinker phases are formed. Typical Portland cement clinkers consist of approximately 63 - 70 wt% $CaO$, 19 - 24 wt% $SiO_2$, 3 - 7 wt% $Al_2O_3$ and $TiO_2$, and 1 - 5 wt% $Fe_2O_3$ [5]. The main clinker phases and some other constituents of cement clinkers and their properties are listed in Tab. 2.

**Tab. 2**. Possible composition of German cement clinkers [4, 5]

| Clinker phase/compound | Chemical formula | Content [mass %] | Comment |
|---|---|---|---|
| Alite (tricalcium silicate) | $3\,CaO \cdot SiO_2$ | 45 – 85 % | Main phase giving cement its crucial properties. |
| Belite (dicalcium silicate) | $2\,CaO \cdot SiO_2$ | 0 – 32 % | Is formed when the clinker is not saturated with calcium oxide. |

| Calcium aluminoferrite | $2\,CaO \cdot (Al_2O_3, Fe_2O_3)$ | 4 – 16 % | Major part of Fe- and Al-oxides are bound in this phase. |
|---|---|---|---|
| Tricalcium aluminate | $3\,CaO \cdot Al_2O_3$ | 7 – 16 % | Form of Al-oxides that are not bound as calcium aluminoferrite. |
| Free CaO and free MgO (Periclase) | CaO<br>MgO | 0.1 – 5.6 %<br>0.5 – 4.5 % | Free MgO originates from dolomite $(CaMg(CO_3)_2)$, which is a constituent of many limestones, and clay, while free CaO can be a consequence of oversaturation of the system with Ca. High contents of MgO and CaO lead to problems due to expansion, which is why the content of MgO shall not exceed 5 % according to EN 197-1. The smaller the grain size of the cement, the larger the amount of free MgO and CaO that is acceptable. |
| Alkali sulfates | $Na_2SO_4$, $K_2SO_4$, $(Na, K)_2SO_4$, $K_2Ca_2(SO_4)_3$, $K_2SO_4 \cdot 2\,CaSO_4$ | 1 – 2 % | Are formed during the clinker burning process from a reaction between $Na_2O$ and $K_2O$ (originating from feldspars) and sulfate (originating from raw materials and fuels). Alkaline sulfates in cement alter the chemical reactivity with water. |

In general, the sintering process is very energy intensive. In 2017, the production of 1 metric ton of clinker required 3.839 GJ of thermal energy in Austria [10], and 2.824 GJ in Germany [6]. To provide this energy, increasing amounts of alternative fuels (i.e. RDF) are used. The share of the energy demand that was covered by RDF amounted for 65 % in Germany [6] and more than 80 % in Austria [10].

### 1.3    SRF co-processing in the cement industry

The co-incineration of RDF in the cement industry is often referred to as co-processing. Co-processing comprises industrial processes that simultaneously enable energy recovery and recycling of the mineral content of waste material, thereby replacing both mineral resources and fossil fuels [11, 12]. This applies to the cement clinker burning process because irrespective of the use of fossil or alternative fuels, the fuel ash that is formed during the combustion process is incorporated into the clinker. For this reason, the fuel that is used influences the required raw material mix and is accounted for. For example, the $CaCO_3$ content of the raw material mix is adjusted to compensate for the low amounts of CaO in the ash of coal, which mainly consists of $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ [5]. Hence, besides fulfilling the function as a fuel, the ash of the burnt fuels is utilized on a material level [13]. This implicates that, in reverse, in co-processing technologies a certain proportion of the SRF (or RDF) used can be considered as material recycled.

### 1.4    Legal framework

In the waste hierarchy, the use of SRF as substitute fuels in the cement industry is currently considered as thermal or energy recovery, an R1 process ("*use principally as a fuel or other means to generate energy*" [14]). In May 2018, the European Parliament and the council have amended directive 2008/98/EC on waste, i.e. the waste framework directive [14], with directive 2018/851 [15]. In the course of the amendment, a paragraph was added stating that it is considered to acknowledge that certain minerals are incorporated in co-processing, and to count the share of these minerals towards recycling targets:

*"The Commission shall assess co-processing technology that allows the incorporation of minerals in the co-incineration process of municipal waste. Where a reliable methodology can be found, as part of this review, the Commission shall consider whether such minerals may be counted towards recycling targets." [15]*

## 1.5 Aim

In light of this amendment of the waste framework directive, and considering the new recycling quota defined by the European Union's Circular Economy Package (CEP), information on the composition of SRF ashes and the share to which these ashes can contribute to reaching the recycling targets will likely be of interest in the near future. The paper at hand represents a first attempt to determine the composition of SRF ashes and presents the preliminary results for some SRF samples from different countries. It is part of a larger project in cooperation with FH Münster that aims at

- determining the share of SRF or SRF ash that can be considered as material recycled when co-processed in the cement industry,
- building up a database with ash compositions of a large variety of SRF samples, and
- developing a simple, but acknowledged and scientifically proven methodology for the analytical determination of both ash composition and the share of SRF that is material recycled.

## 2 Materials and methods

The first analytical determination was carried out for 12 Samples of SRF (7 PREMIUM Quality and 5 MEDIUM quality materials) from four different European countries (Austria, Croatia, Slovakia, and Slovenia). A sampling concept for the representative sampling of SRF from the storage depots of the SRF production plants was elaborated considering SRF particle size ($d_{95}$), bulk density, and other parameters according to EN 15442 [16]. Total masses of the representative samples ranged from 3 – 26 kg for SRF MEDIUM quality and 5 – 22 kg for SRF PREMIUM quality. The detailed sampling method is described elsewhere [17].

The samples were dried to constant weight at 105°C, comminuted to a grain size of < 0.5 mm using a cutting mill, and ashed at 550°C according to EN 15403 [18]. Applying the method of DIN 51729-11 (for solid fuels) [19], the ash residue was fused with lithium metaborate and dissolved in 2 molar HCl. The digest solution was subsequently analyzed by ICP-OES according to EN ISO 11885 [20] and the concentrations of Ca, Al, Si, Fe, Na, K, Ti, P, and S were determined. Assuming (for simplicity) that these elements are mainly present as oxides in the ash, the corresponding concentrations of the respective oxides (i.e. $SiO_2$, $Al_2O_3$, $Fe_2O_3$, etc.) were calculated.

The applied analytical methods and processes were optimized and validated. Comparative measurements by ICP-MS and XRF spectroscopy were carried out and showed good agreement. An alternative digestion method (microwave-assisted acid digestion using HCl, $HNO_3$, and HF) was tested as well. The results again confirmed the concentrations of the main components obtained by ICP-OES after fusion decomposition.

## 3 Results and discussion

Analyses using the current methodology show that on average approximately $72 \pm 6$ wt%$_{DM}$ of the SRF ash consists of $SiO_2$, $CaO$, $Al_2O_3$, and $Fe_2O_3$, the four main chemical components that are required for the production of cement clinker. It has to be noted that this percentage was not normalized to 100 %, as summarizing the analytes as oxides only $88 \pm 5$ % of the ashes' mass was recovered. This is probably linked to the low ashing temperature of 550°C, which will be discussed shortly. The average ash content of the samples was found at approximately $20 \pm 6$ wt%$_{DM}$.

The results regarding the four main chemical components imply that SRF ash can to some degree substitute raw materials that are required for the production of cement clinker. Fig. 2 shows a comparison of the ratio of $SiO_2$, $CaO$, and $Al_2O_3+Fe_2O_3$ of the 12 SRF ashes with those of the ashes of other common fuels, alternative raw materials, or cement clinker. Based on their composition, the analyzed SRF ashes are mainly located between Portland cement clinker and lignite coal, or in the overlapping area between lignite coal and sewage sludge. It is therefore assumed that SRF ash can contribute materials in a similar manner as these materials. Due to the higher content of CaO, some SRF ash samples feature an $SiO_2 : CaO : Al_2O_3+Fe_2O_3$ ratio that is even closer to the desired ratio of these components in cement clinker than the ratio of these components in other fuels, e.g. brown coal or pit coal.

The full results for the SRF ash compositions (not normalized to 100%) are shown in Fig. 3, standard deviations for the analytical results are given in Tab. 3. The ash analyses show that, besides the four main components, the ash also contains other chemical compounds that are also present in the raw materials used, e.g. $Na_2O$ or $K_2O$

which are components commonly occurring in feldspars. Furthermore, MgO and $TiO_2$, both of which are minor constituents of Portland cement clinker, are as well present in the analyzed SRF ashes.
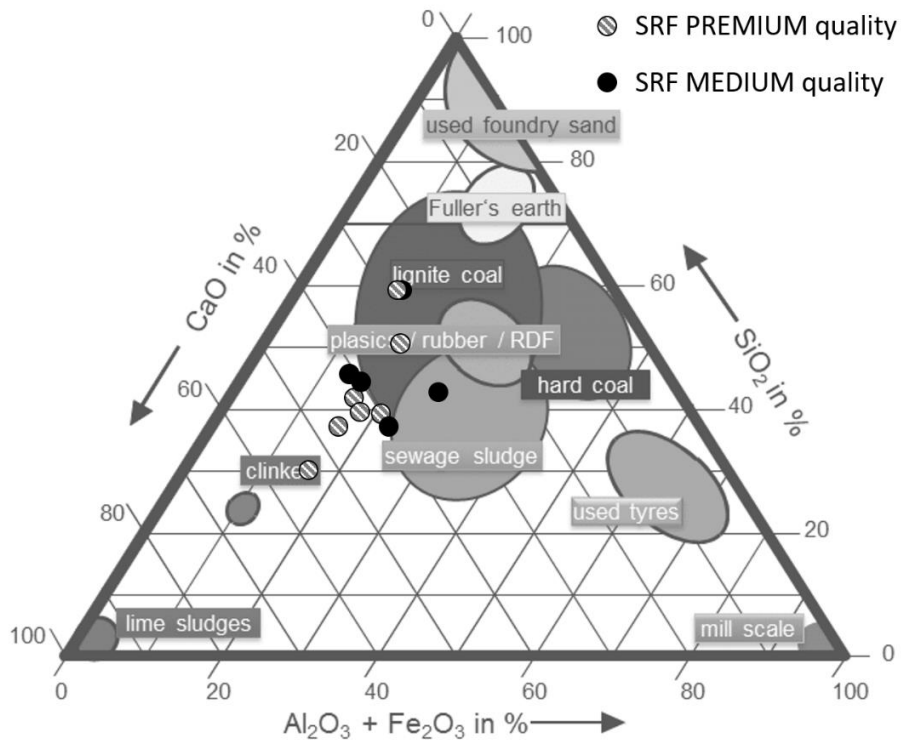


**Fig. 2** Comparison of the SRF ash composition of the current 12 samples with other fuels and raw materials relevant to the cement industry. Ternary diagram of fuels and raw materials ©VDZ supplemented with own results with permission of VDZ.
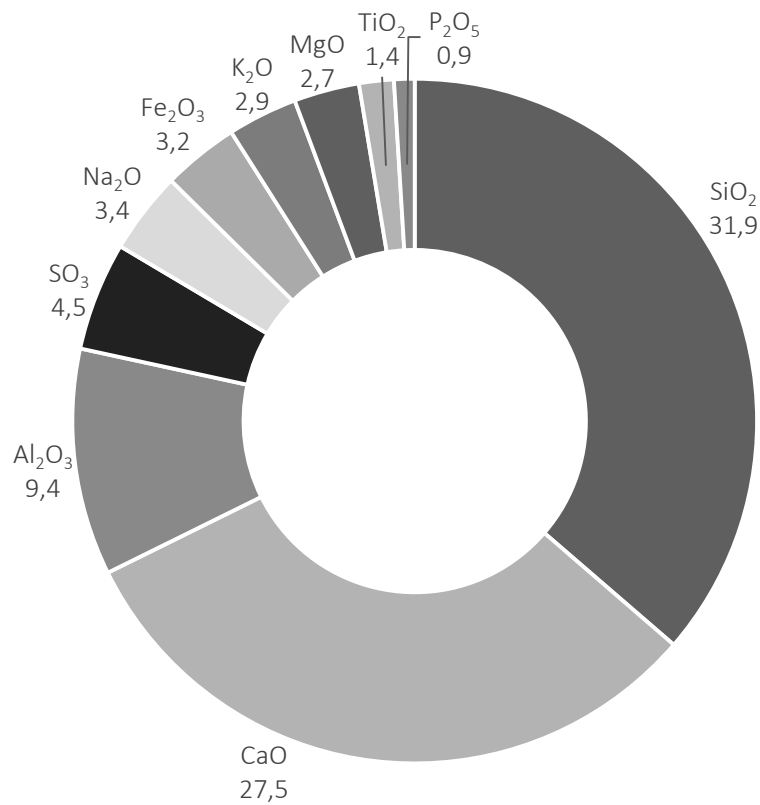


**Fig. 3** Average ash composition of the analyzed SRF ashes in mass percent dry mass (wt%$_{DM}$); percentages not normalized to 100 %

**Tab. 3** Average ash composition of SRF MEDIUM and PREMIUM Quality [wt%$_{DM}$], standard deviation and relative standard deviation, *n=12*. Components representing main constituents of cement clinker are labeled bold

|  | **SiO$_2$** | **CaO** | **Al$_2$O$_3$** | SO$_3$ | Na$_2$O | **Fe$_2$O$_3$** | K$_2$O | MgO | TiO$_2$ | P$_2$O$_5$ | Σ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Average [wt%$_{DM}$]* | **31.9** | **27.5** | **9.4** | 4.5 | 3.4 | **3.2** | 2.9 | 2.7 | 1.4 | 0.9 | 87.8 |
| *Standard deviation [wt%$_{DM}$]* | **8.2** | **4.0** | **3.1** | 1.2 | 0.9 | **0.6** | 0.9 | 0.4 | 0.5 | 0.5 | |
| *RSD [%]* | **26** | **14** | **33** | 27 | 28 | **20** | 31 | 15 | 37 | 56 | |

Regarding the methodology, the first analyses showed that - for the purpose of determining the material-recyclable share of SRF - the ashing temperature of 550°C has to be discussed. The temperature was chosen based on the standard EN 15403 [18], but even compared to the standard ashing temperature for solid fuels (DIN 51719) of 815°C [21], 550°C is rather low. Since the temperatures in the rotary kiln are much higher, higher ashing temperatures might be more suitable for this analytical approach.

The ashing temperature directly influences the ash content of the SRF, and it influences the ash composition with respect to the chemical species that are present. As a consequence, the assumption that all elements are present as oxides, that was made for simplicity, will probably be more suitable at higher temperatures. At 550°C, for example calcium might still be present as calcium carbonate (CaCO$_3$, m = 100.09 g/mol) instead of calcium oxide (CaO, m = 56.08 g/mol). On the other hand, other elements such as aluminum and iron might still be present in their elemental form, and not as oxides. Therefore, it is possible that the current method causes lower shares for calcium compounds in the ash, while shares of iron or aluminum compounds might not be as high in the ash itself as indicated in the method. Although this does not influence the concentration of the determined elements in the ash, it is an important issue for determining the material recyclable share of the ashes, and it is likely to be an explanation why only 88 ± 5 % of the ashes' mass was recovered when all analytes were summed up as oxides. For all these reasons, higher ashing temperatures have to be taken into consideration, tested, and compared.

The identification of the share of the SRF ash that can be considered as material-recyclable will not only require additional speciation information on the compounds present in the ash, but will also require more detailed information on the role of the different chemical compounds in cement manufacturing. Depending on the interpretation of the term "materials recycling", possibilities range from counting 100 % of the SRF's ash content as materials recyclable to considering only the part of the SRF ash that consists of the four main chemical components SiO$_2$, CaO, Al$_2$O$_3$, and Fe$_2$O$_3$ as the material recyclable share. Currently, there is not enough data to reliably estimate this share, and the methodology needs further development.

## 4    Outlook

In order to extend the database, the sample number is significantly increased in ongoing experiments. Currently, more than 50 samples from Austria and other European Countries are being analyzed. Furthermore, Lafarge has kindly provided analytical data of several other SRF samples. Simultaneously, similar analyses of SRF samples of 9 different quality assuring SRF production plants in Germany are coordinated and evaluated by FH Münster.

In future experiments the ashing temperature will be varied and increased, the results will be compared. Furthermore, the carbonate content will be assessed more closely at different ashing temperatures.

## 5    Acknowledgments

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