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RECYCLING OF METALLURGICAL RESIDUES BY A COMBINED PROCESS OF CHEMICAL MODIFICATION, CARBOTHERMIC REDUCTION AND PHASE MODIFICATION

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Introduction

A zero-waste circular economy approach must be promoted to decrease environmental and climate impact, especially in heavy industries such as cement and steel. A large amount of unavoidable CO₂ is emitted during the production of Portland cement clinker - consequently, a reduction of the clinker-to-cement ratio is pursued by adding supplementary cementitious materials (SCM). Different metallurgical residues accumulate in the integrated steel mill and must be temporarily stored or landfilled due to the lack of recycling processes. In contrast, ground granulated blast furnace slag (GGBFS) is already heavily demanded as a SCM due to its benefits for the strength and durability of the resulting concrete. This contribution discusses the thermal treatment of metallurgical residues, which allows recovering their metal content for recycling as a secondary raw material (SRM) and utilising the generated slag content as a GGBFS-like SCM, see Figure 1.

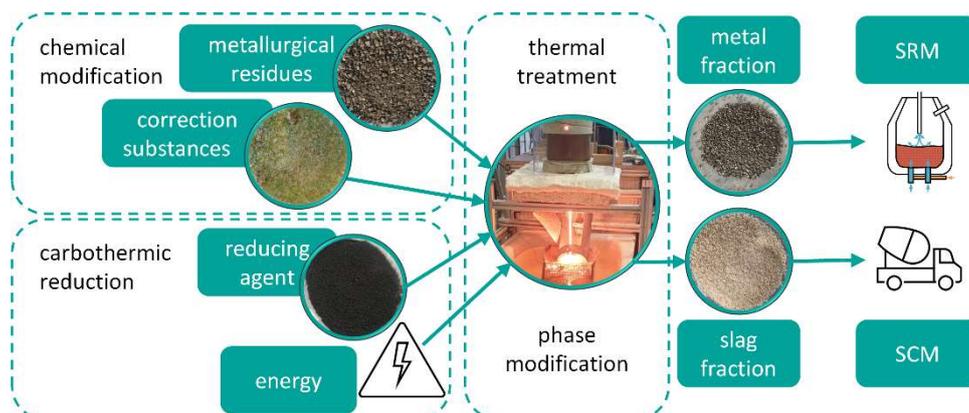


Figure 1: Flow chart of the recycling of metallurgical residues as secondary raw materials (SRM) and supplementary cementitious materials (SCM)

Materials and Methods

Various residues occur during steel production via the blast furnace/converter route. For the present investigation, slags from hot metal desulphurisation (HMDS) and secondary metallurgy/continuous casting (CCS) produced at the integrated steel mill of voestalpine Stahl Donawitz GmbH (VASD) were used. In addition, for the chemical modification of these residues, basic oxygen furnace slag (BOFS) and Siemens-Martin slag (SMS) from internal landfills were used as a source of calcium and magnesium and glass waste (GW) from glass recycling was used as silicon carrier. Based on the chemical and mineralogical analysis¹, see Figure 2, two different mixtures, M1 and M2, with an input mass of around 1.5 kg were calculated using an MS Excel Solver² according to the identified requirements for SCM³⁻⁵.

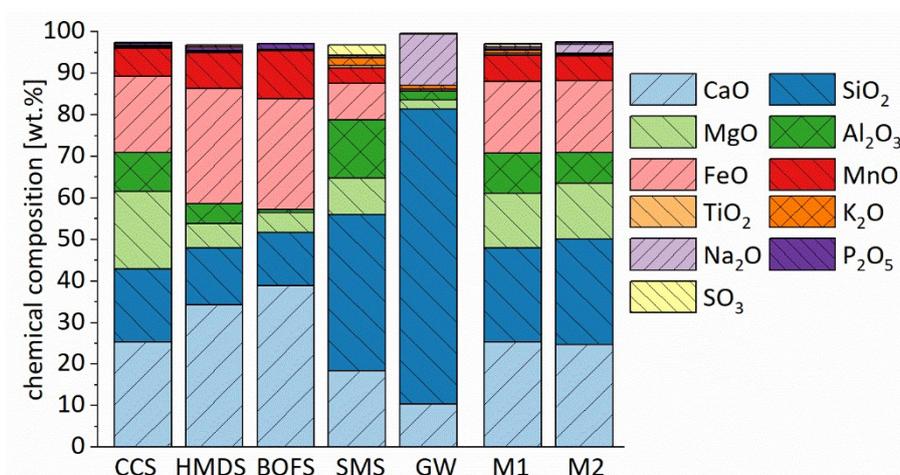


Figure 2: Main chemical composition of the metallurgical residues (CCS, HMDS), correction substances (BOFS, SMS, GW) and two mixtures before thermal treatment (M1, M2)

The treatment was conducted three times each for M1 (50.0% CCS, 16.0% HMDS, 30.0% SMS, 4.0% BOFS) and M2 (63.7% CCS, 19.9% HMDS, 16.4% GW) using an inductively heated crucible furnace at temperatures up to 1400°C⁶. The material was melted in a graphite crucible to achieve a carbothermic reduction, and the stoichiometric carbon needed with a surplus of 10% was added. A systematic cooling of the molten material was realised through wet granulation. The produced granulate was crushed, sieved and finally, the metallic and slag fraction were magnetically separated.

Results and Discussion

Despite the complexity of the different residues used for M1 and M2, comparing the theoretically calculated via the MS Excel Solver Add-In and analysed reduced slag fractions shown in Figure 3 depicts good agreement between predicted and measured compositions. However, a higher deviation can be observed for MnO, for which the

content in the slag fraction was higher than predicted. This is because the transfer coefficient (TC), defined as the element content in the slag fraction in relation to the input mass in percentage, was above the previously assumed value of 50%, presumably due to certain process conditions and the influence of interfering substances such as phosphorus and sulphur⁷. Since the gaseous phase was not considered during the mixture calculation, the measured content of volatile components (K₂O, Na₂O, SO₃) also deviates from the predicted composition.

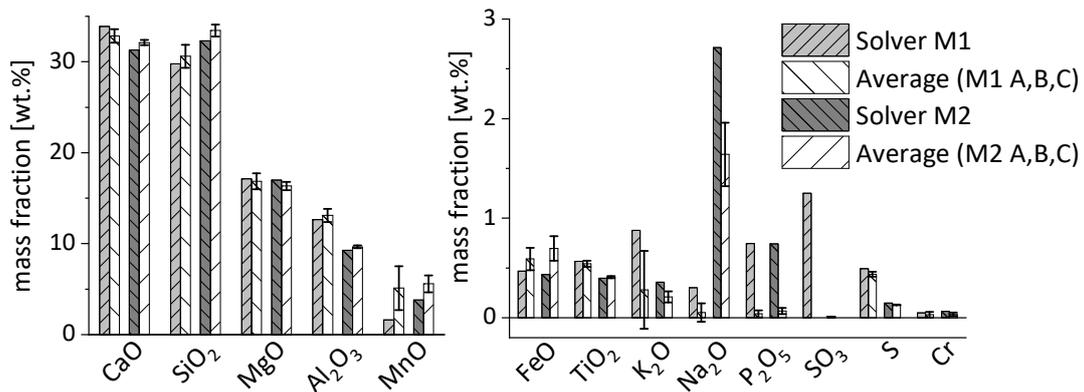


Figure 3: Comparison of the mass fractions calculated by the MS Excel Solver and the average composition of the slag of M1 and M2 after carbothermic reduction

Table 1 presents the properties of the generated metal and slag fractions after the treatment. Although all samples meet the requirements for slag compositions and reactivity, there are significant differences in the transfer coefficient (TC), especially for Mn, as mentioned above. This circumstance can be attributed to deviating furnace temperatures and holding times. For example, the holding time of M1B and M2C was under 30 minutes, leading to a high TC of Mn and Cr. Sample M1C shows the lowest TC_{Mn}, likely due to the higher furnace temperature than 1400°C.

Table 1: Comparison of properties of the reduced slag fraction to the assumptions and requirements

property	assumption*/ requirement [#]	M1			M2		
		A	B	C	A	B	C
TC _{Fe}	10%*	2	2	5	2	2	3
TC _{Mn}	50%*	60	79	18	57	41	22
TC _{Cr}	20%*	7	21	7	6	6	15
glass content	> 66% ³	100	99	100	99	92	97
CaO+MgO+SiO ₂	> 66 wt% ³	80	78	82	82	83	81
(CaO+MgO)/SiO ₂	> 1.00 ³	1.54	1.69	1.64	1.45	1.43	1.47
R ³ heat release after 7 days	> 250 J/g slag ⁴	525	411	542	407	396	423
activity index after 28 days	≥ 90% ⁵	100	90	97	96	97	94

Conclusions

The results of the trials showed that most of the metal content was reduced for reuse as SRM. Concerning the TCs, the recovery of Fe is more effective than that of Cr and Mn. At the same time, the required performance of the slag as a SCM was proven. These findings are to be deepened by further research projects to identify factors that influence metal recovery and slag reactivity. In particular, the impact of temperature, holding time, and phosphorus content are under investigation. Future work will also investigate possible recovery processes powered by renewable energy sources, such as plasma reactors or inline induction melting furnaces.

Acknowledgement

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