Thermal treatment of rock phosphate: Phosphorus recovery and production of an alternative binder component

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552

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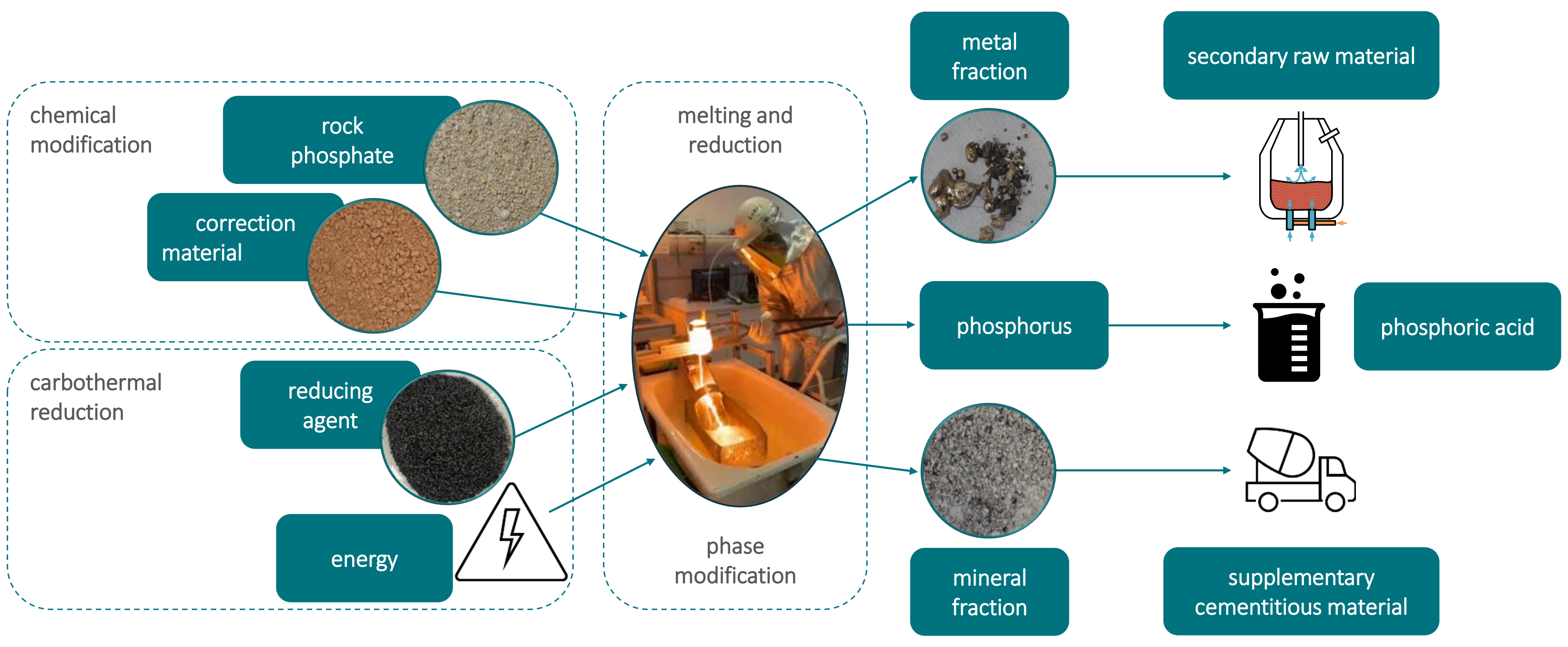
Introduction / Research Motivation

Rock Phosphate (RP) is an essential precursor for various industrial and agricultural applications (e.g. phosphoric acid production), with a global production of 220 million tons in 2021. [1] About 95 % of the world's phosphorus reserves are concentrated in a few countries, including Morocco, China, Jordan, South Africa, and the USA, with P_2O_5 contents ranging from 5 % to 37 %. [2] However, conventional processing methods cannot utilize the immense amounts of by-products. Furthermore, phosphoric acid production generated about 332 million tons of phosphogypsum in 2022, which must be landfilled due to a lack of practicable recycling solutions. [3, 4] Addressing these environmental challenges for sustainable P resource management is the motivation behind this research work, which examines the thermochemical treatment of RP to recover P and produce a reactive binder compound similar to granulated blast furnace slag (GBFS). GBFS is commonly used as a binder component in the building industry, but dwindling supplies necessitate the search for new alternative binder components both for blended Portland cements and alkali-activated binder systems.

Materials and Methods

The main material for the experiments was RP from Morocco. To modify the chemical composition towards suitability as a binder component and to lower the melting temperature, industrial residuals such as brick waste (BW), waste incineration ashes, and glass waste were added. Possible mixtures of the materials were calculated using a Microsoft Solver Add-in. Limit values for the calculation, based on known compositional ranges for GBFS, were >25 % SiO_2, <10 % Al_2O_3, <15 % MgO, CaO+MgO+SiO_2 >67 %, and a CaO/SiO_2 mass ratio between 1.2 and 1.6. A hyper-stoichiometric amount of carbon powder (pulverized Carbolux® pellets) was added to the mixtures to enable carbothermal reduction. First, in a heating microscope (HM) of E. Leitz Wetzlar, approximately 0.1 g of the sample pressed to a standardized cylinder was tested for its melting behavior. Hence, in a furnace chamber under an argon gas flow of 2 l/min, the cylinder was heated up to 1600 °C and illuminated frontally by a light source. Finally, the cylinders silhouette is analyzed, while geometric parameters and characteristic temperatures are determined. Following these results, thermochemical treatment of the defined mixtures (200 g of input material and carbon in a graphite crucible) was carried out in an argon-purged elevator furnace (EF) from Thermconcept ELHT 16/18 at 1500 °C and 1600 °C. After a holding time of 30 min, the samples were water quenched. For each mixture, two replicate experiments were carried out in the HM and EF. The yielded granulate was dried at 105 °C for 24 h, followed by crushing (Retsch model BB50), sieving and magnetic separation into a mineral fraction (MI) and metal fraction (ME). XRF and XRD analysis or ICP-OES, respectively were carried out to characterize these fractions.

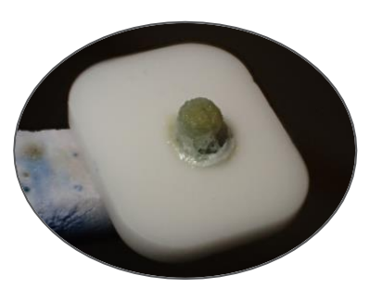
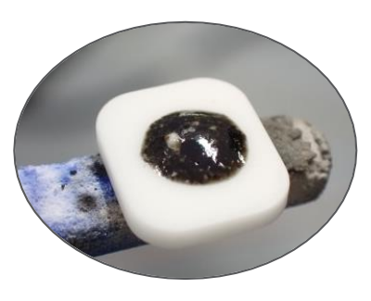

chemical modification
rock phosphate
correction material
carbothermal reduction
reducing agent
energy
melting and reduction
phase modification
metal fraction
secondary raw material
phosphorus
phosphoric acid
mineral fraction
supplementary cementitious material

Sequence of the EF experiments: input mixture preparation (left), thermal treatment with subsequent water quenching (middle), and separation of the output material (right) with their potential utilization possibilities

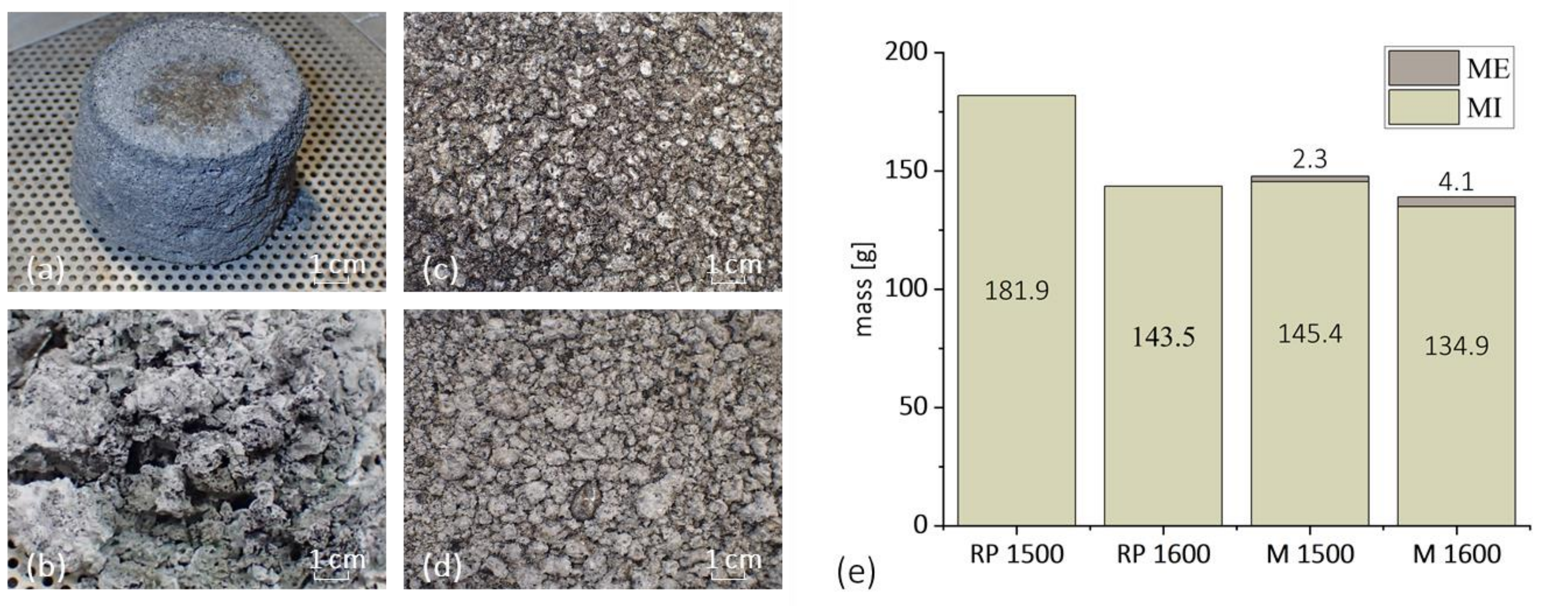
Results

In the following, the results merely compare pure RP and an input mixture containing RP, BW, and carbon as a reducing agent denoted as M. Generally, the melting behavior of the treated input mixture is essential for the course of chemical reactions. For this reason, the flow temperature was determined in a HM. While pure RP could not be converted into a molten phase in the analyzed temperature range (maximum 1600 °C), the addition of a silicon-rich correction substance in the form of BW and carbon leads to a significant reduction in the flow temperature to below 1450 °C.

Melting interval expressed as the flow temperature with specimen appearance after thermal treatment in the HM

RP	RP+C	BW	RP+BW	M
>1600 °C	1566 °C – 1573 °C	1402 °C – 1419 °C	1535 °C – 1544 °C	1429 °C – 1446 °C
				

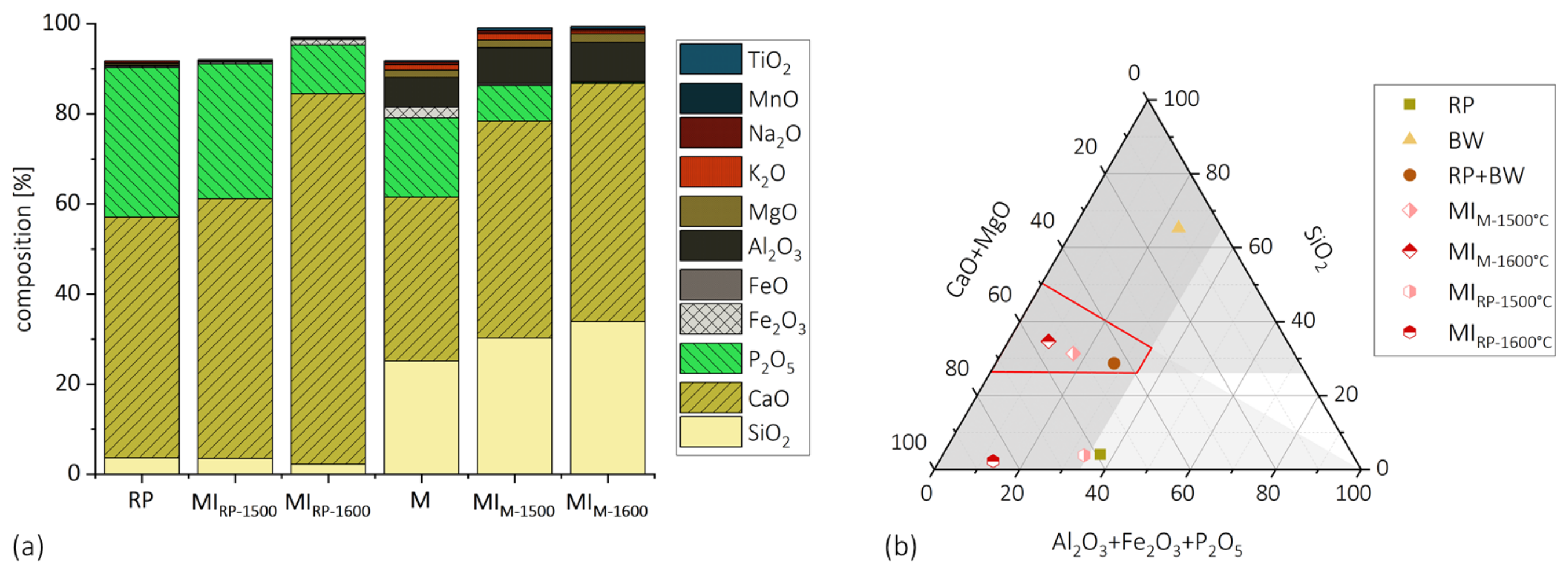
Molten material in the graphite crucible was rapidly cooled by water-quenching after the thermal treatment in the EF. The wet-granulated output-material was then separated by downstream post-processing steps and the weight was determined of the obtained fractions (MI and ME). For M, a ME is formed by reduction of iron oxide originating from the BW, whereby RP is nearly free of iron oxide.



Material after water quenching of 200 g input material in the EF – (a) sintered material of RP at 1500 °C, (b) granulate of RP at 1600 °C, (c) granulate of M at 1500 °C, (d) granulate of M at 1600 °C, (e) gravimetric determination of gained fractions divided into MI and ME

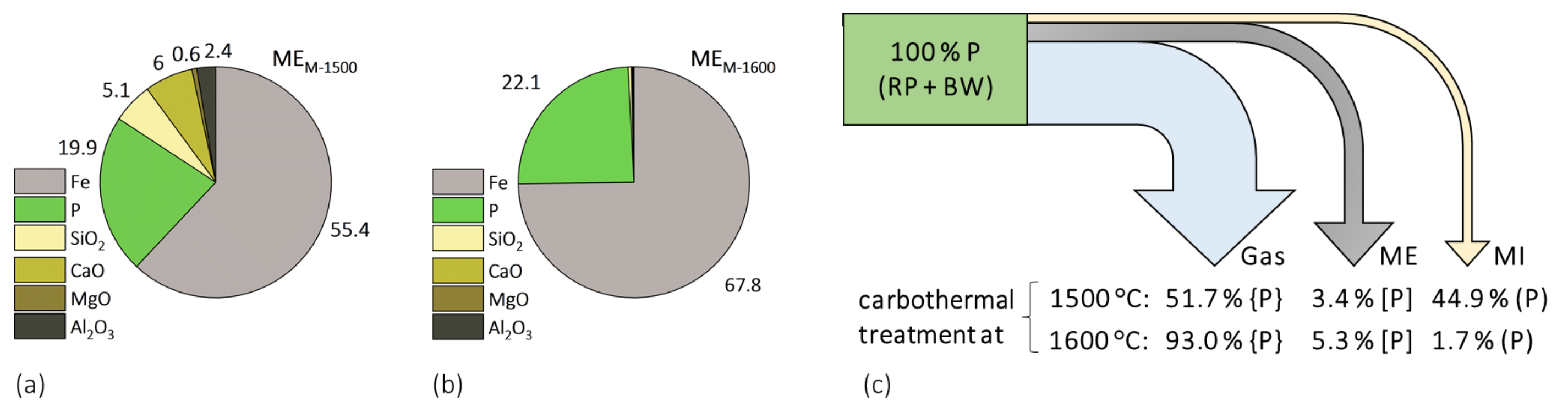
Results

After post-processing of the wet-granulated output material from the EF, the chemical characterization of the MI was analyzed by XRF and XRD. Furthermore, the ME was analyzed by ICP-OES. It can be noted that a separation into a Ca-/Si-rich but P-/Fe-poor MI and an Fe- and P-rich ME could be achieved. In the ternary system of [Al_2O_3+Fe_2O_3+P_2O_5] – [SiO_2] – [CaO+MgO] the path of the experimental series in the EF for pure RP and M at 1500 °C and 1600 °C is shown. The area marked in red indicates the normative requirements for GBFS.



Analysis results in mass percentage (m.-%) – (a) composition of input material (RP and RP+BW) in comparison to the composition of the MI at 1500 °C and 1600 °C, (b) path in the ternary system for the carbothermal treatment of pure RP and M at 1500 °C and 1600 °C

XRD results show that the MI fraction of treated M showed almost no discernible X-ray reflections, proving that the material is mostly glassy (>99 % amorphous content) with traces of crystalline phases in M treated at 1500 °C. The allocation of transferred P into the gas phase, ME, and MI indicates that for 1600 °C a P-gasification rate of >90 % could be achieved.



Analysis results in m.-% of ME and mass balance of P for M after EF-treatment – (a) ME composition at 1500 °C of treated M, (b) ME composition at 1600 °C of treated M, (c) P mass balance

Discussion and Conclusions

By adding a Si-rich residual material such as BW and carbon as a reducing agent the flow temperature can be reduced to well below 1450 °C compared to pure RP (>1600 °C). The results of carbothermal treatment in the EF show the advantages in removing P from the investigated input-mixture M via the gas phase compared to pure RP. Temperature and Si-content play a vital role in the reduction behavior of fluorapatite, the main oxidic P-compound in Moroccan RP. The Fe-oxide originating from BW was almost completely reduced at 1500 °C (FeO < 0.5 % in MI). P, on the other hand, is largely removed from the MI at 1600 °C (P_2O_5 < 0.3 % in MI). In contrast, poor dephosphorization rates could be achieved for pure RP. P can be detected in the recovered ME, which can be attributed to the formation of undesired metal phosphides. By the carbothermal reduction of fluorapatite highly reactive gaseous P is formed, which dissolves into the molten metal on contact, impairing the metal quality for further utilization and reducing the P-recovery rate. [6] The probability of contact increases significantly as the Fe content in the mixture increases. Based on the results of the analysis, the MI of treated M fulfills the principal requirements for GBFS, as given in EN-15167. Judging from these chemical and mineralogical similarities to GBFS and other treated slag-like residues [7], the MI are likely highly reactive in Portland cement and alkali-activated binder systems and can be used as a suitable replacement for GBFS.

Results from this experimental series show the feasibility of carbothermal treatment of chemically modified RP at 1600 °C, separating a Fe-rich metal fraction and yielding P in a gaseous, reclaimable form for further processing (e.g. into P_2O_5 or H_3PO_4). The wet-granulated mineral fraction has a high amorphous content and optimized chemical composition. Its suitability as a reactive binder compound will be examined in detail in ongoing future research. Treatment trails are planned for further mixtures, such as a combination of P-and Fe-rich sewage sludge ash and RP. The aim is to test the removal of P using highly Fe-rich residues. To treat larger quantities of up to 1.5 kg of input material, a switch is to be made to an induction furnace operated by the Chair of Thermal Processing Technology at the University of Leoben. [8] This has considerable advantages over other reduction units, particularly in treating input materials with increased P and Fe content, suppressing the undesirable formation of phosphides. The findings of this study are to be applied to Moroccan ore tailings and low- and medium-grade ores in future steps.

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