minerals

MDPI

Supplementary Information

For manuscript with title: "The fate of rare earth elements in South African coal fly ash during processing by wet, magnetic separation and zeolitisation."

1. Experimental

1.1. Characterisation by SEM

The mineralogical and elemental (major and trace) composition of solid products of the magnetic separation process were determined by XRD, XRF and LA-ICP-MS, respectively. XRD analysis was carried out on a powder Bruker D8-Advance X-ray diffractometer; measurements were carried out at 40 kV and 25 mA with Cu $K\alpha_1$ radiation (λ = 0.154 nm). XRF analysis of solid products was carried out on a PANalytical Axios Wavelength Dispersive spectrometer fitted with a Rh tube and scintillation detector, by using SuperQ PANalytical software; XRF conditions were set at 50 kV and 50 mA. LA-ICP-MS analysis was carried out on an Agilent 7500ce ICP-MS spectrometer, fitted with a Resonetics 193 nm Excimer laser. The morphological properties of the magnetic separation products were analysed by SEM; SEM analysis of powdered solid products was carried out on a Zeiss Auriga field emission gun (FEG)-scanning emission microscope at 5.0 kV.

2. Characterisation and Results

2.1. Morphology Analysis of Magnetic Separation and Zeolitisation Products

The variation in the morphology of CFA, MF and NMF was analysed by SEM (depicted in Figure S1). The morphology of the NMF material was similar to that of as-received CFA as expected; both materials were composed of spherical particles (0.5–40 μm) as well as relatively large, irregularly shaped particles (~60-175 μm). It is noteworthy that the MF material also exhibited a similar morphology to CFA, with spherical particles covered in rod-like structures attributed to iron-containing minerals magnetite and hematite. This may account for the presence of quartz (and minor mullite) diffraction peaks in the diffractogram of the MF material, as observed in Figure 2.

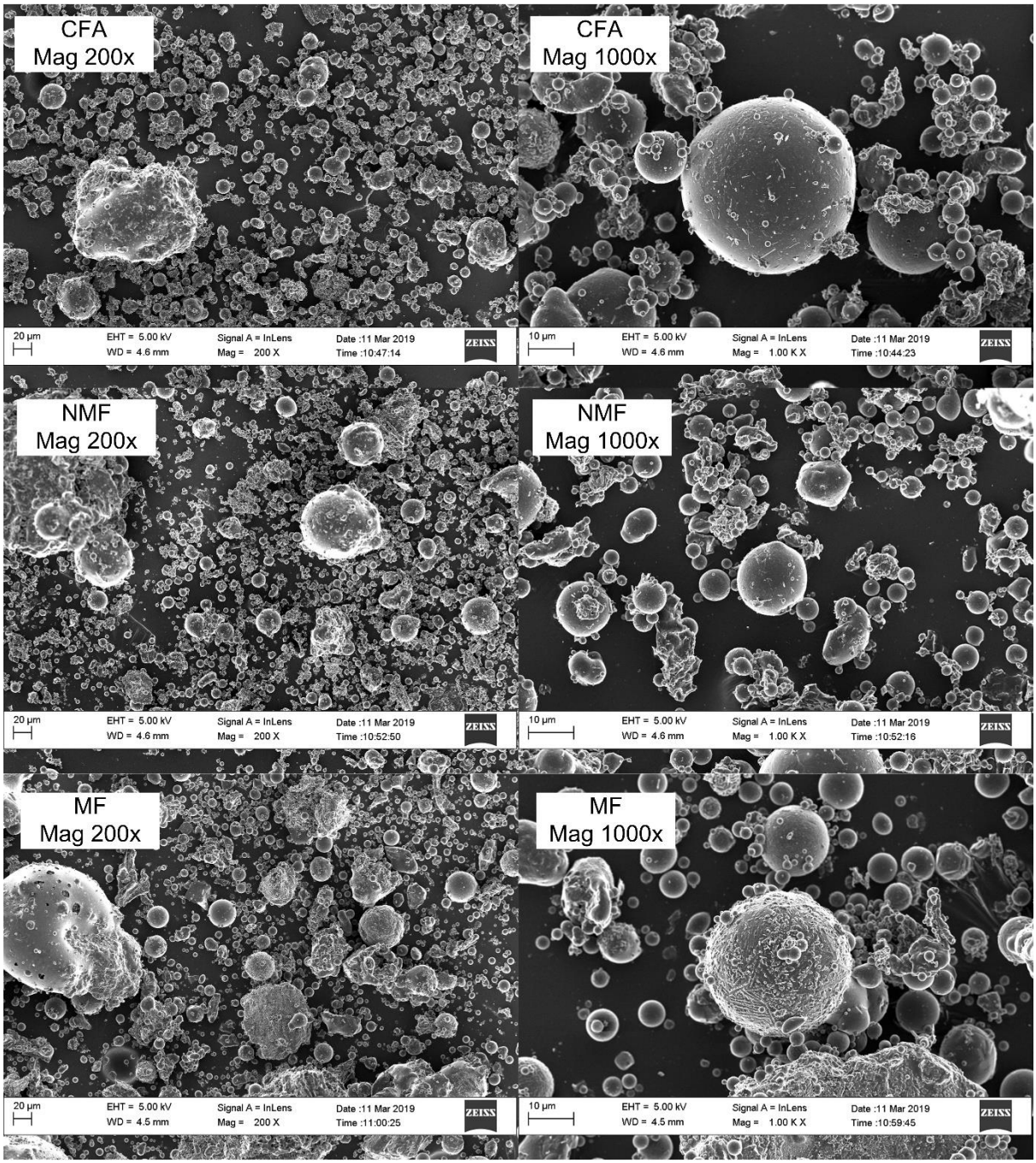

Figure S1. SEM micrographs of as-received CFA, magnetic fraction and non-magnetic fraction generated by wet magnetic separation.

The morphology of the Si extract was irregular in shape with varying particle sizes, as depicted in Figure S2. The relatively larger Si extract particles (ranged in particle size from 7 µm to up to 100 µm); these larger particles were composed of agglomerated small particles (with average particle size between 0.1 and 0.3 µm). The zeolite material exhibited the typical morphology of hydroxysodalite, as reported in literature [1], with an average particle size of ~6.7 µm.

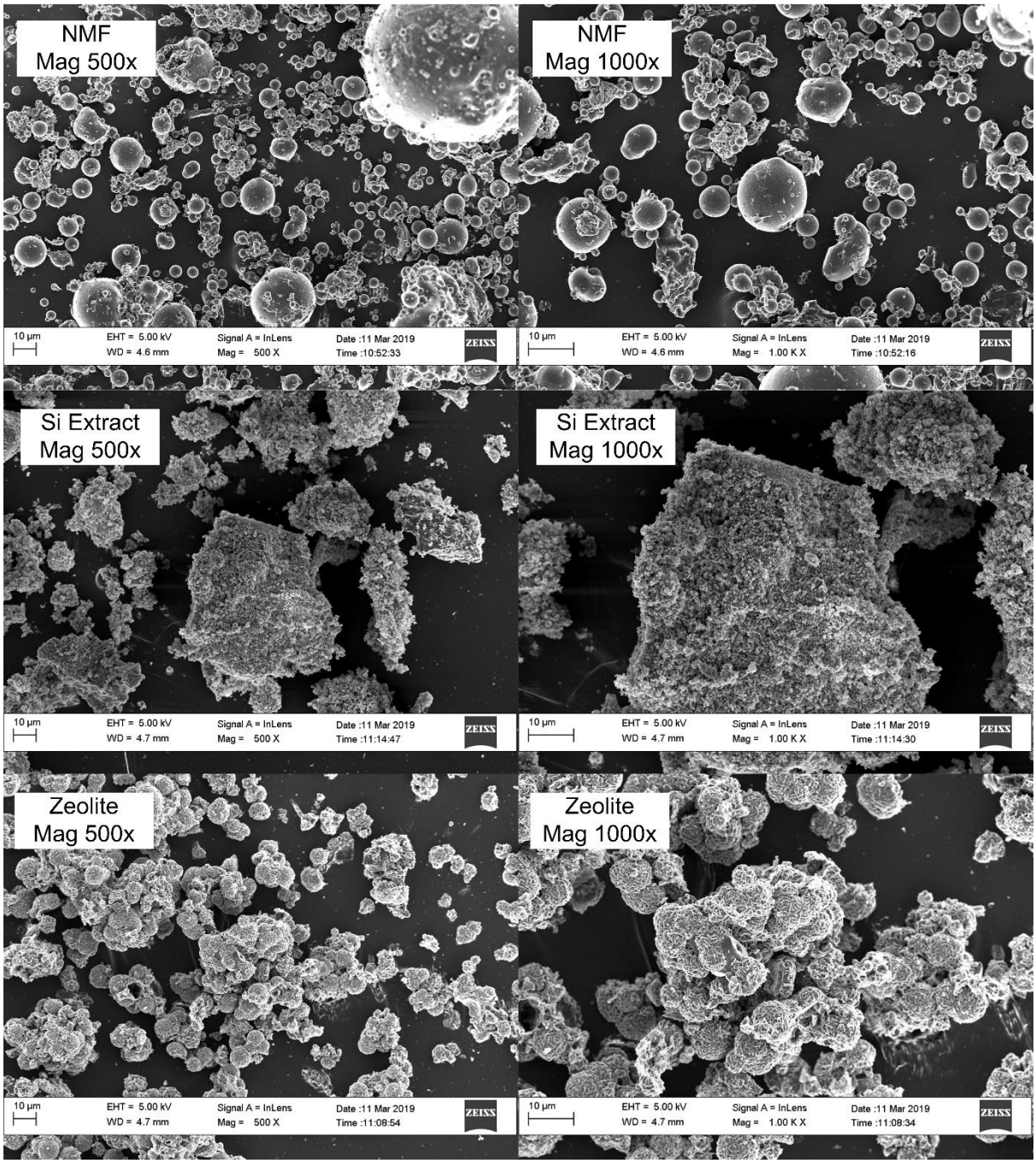

Figure S2. SEM micrographs of the non-magnetic fraction of CFA as well as the zeolite product and Si extract generated by liquid phase alkaline treatment and precipitation.

2.2. Recovery of CFA Components

The wet magnetic separation process resulted in MF and NMF products with mass yields of 8.4 and 91.6 wt%, respectively, calculated according to Equation S1. The recovery of the main components in CFA was calculated (as listed in Table S1); the recovery of major oxides was calculated based on the mass yield of each component in the magnetic separation product (MF or NMF) compared to CFA, according to Equation S2.

$$Yield\ of\ fraction\ (wt\%) = {Mass_{Fraction}}/{Mass_{x_{CFA}}} \times 100\% \quad \text{Eq (S1)}$$

$$Recovery\ \%\ (Element\ x) = {Mass_x}/{Mass_{x_{CFA}}} \times 100\% \quad \text{Eq (S2)}$$

Table S1. Recovery of main components of CFA in magnetic separation products (non-magnetic and magnetic fraction).

Major Oxide	Magnetic Fraction	Non-Magnetic Fraction
SiO_2	4.6	94.1
Al_2O_3	4.5	99.1
Fe_2O_3	62.5	40.8
CaO	7.2	85.4
TiO_2	4.9	95.7
MgO	10.0	88.7
K_2O	4.0	97.5
P_2O_5	6.8	94.3
Na^2O	3.0	89.3
MnO	30.0	75.2
Cr_2O_3	9.8	92.6

The majority of the main components in CFA (SiO_2, Al_2O_3, TiO_2, MgO, K_2O, P_2O_5 and Cr_2O_3) remained in the bulk of CFA (i.e., the NMF material) with recoveries of ≥90 %, as depicted in Figure 7. The oxides of Ca and Na were also largely retained in the NMF material. However, it is noteworthy that only a total of ~90% of these soluble components were retained in the solid products; with ~10% of CaO and NaO ending up in the supernatant. The majority of MnO (~70%) also remained in the NMF, with ~30% recovered in the MF material (proposed to be due to Fe-Mn oxide mineral complexes present in CFA) [2–5]. The Fe recovery from CFA into the MF material corresponded to 64%. The efficiency of the Fe removal process in this study was therefore improved compared to a study in literature, which reported an Fe recovery of 26% from South African CFA (from the Matla power station) using a similar magnetic separation process [6]. However, a relatively more efficient magnetic separation with an Fe recovery of 82% was reported from a different source of CFA (from the Hendrina power station) [7]. Differences in Fe recovery may be due variation in coal processing which impacts the mineralogical and chemical compositions of the different sources of CFA. This study reported the potential recovery of iron (~64%) from CFA sourced from the Arnot power station in Mpumalanga, South Africa.

References

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