



Assessment of Viability of Coal Mines in Tanzania for Extraction of Rare Earth Elements

Juma Sija^{1,2*} and Mohamed Mazunga¹

¹Physics Department, University of Dar es Salaam, P.O. Box 35063, Dar es Salaam, Tanzania.

²Department of Physics, Mathematics and Informatics, Dar es Salaam University College of Education, University of Dar es Salaam, P.O. Box 2329, Dar es Salaam, Tanzania.

Email addresses: juma.nghwani@udsm.ac.tz; mazungam@gmail.com

*Corresponding author

Received May 2023, Revised 2 Aug 2023, Accepted 16 Aug 2023 Published Oct 2023

DOI: <https://dx.doi.org/10.4314/tjs.v49i4.4>

Abstract

This study aimed at determining the concentrations of rare earth elements (REEs) in coal and coal fly ash (CFA) from three coal mines in Tanzania: Kiwira, Ngaka and Rukwa. The goal was to assess if these resources could be commercially viable for extracting REEs. Coal and CFA samples were analysed using X-ray fluorescence (XRF) spectrometry and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The total concentrations of REEs in the coal samples ranged from 89.48 parts per million (ppm) to 196.30 ppm, while in CFA samples, ranged from 362.55 ppm to 475.77 ppm. Computed percentage of critical REEs ($REY_{def, rel\%}$) and outlook coefficient (C_{outl}) values ranged from 27.41% to 50.74% and 0.62 to 2.00, respectively. Based on the evaluation criteria proposed for assessing coal and coal ash as sources of REEs, the results suggest that the studied coal and CFA samples have the potential to be used as sources of REEs for economic development. These findings have important implications for the Tanzanian government and other relevant authorities, as they provide valuable insights into the feasibility of investing in the coal and coal ash as promising sources of REEs. This is particularly significant considering the high global demands for REEs.

Keywords: Rare earth elements, coal, coal fly ash, X-ray fluorescence spectrometry, ICP-MS.

Introduction

Rare earth elements (REEs) are a group of 17 elements consisting of 15 lanthanides ($_{57}\text{La}$ through $_{71}\text{Lu}$) plus two transition metals ($_{21}\text{Sc}$ and $_{39}\text{Y}$) (Connelly et al. 2005). Sc and Y are included due to their similar geochemical properties and they are normally found in the same ore deposits as the lanthanides (Lin et al. 2017, Suli et al. 2017, Eterigho-Ikelegbe et al. 2021). REEs possess unique and specialised properties such as electrochemical, nuclear, thermal, magnetic and luminescent (Ganguli and Cook 2018, Eterigho-Ikelegbe et al. 2021), as a result, they find diverse applications in different sectors of the global economy (Lin et al.

2017, Lin et al. 2018, Balaram 2019). REEs endow products with improved efficiency, speed, low energy consumption, thermal stability and durability (Eterigho-Ikelegbe et al. 2021) with widespread applications in medical, defence, clean energy, oil refining as well as aerospace and automobile industries (Dutta et al. 2016, Lin et al. 2017, Suli et al. 2017, Ganguli and Cook 2018, Eterigho-Ikelegbe et al. 2021). Because of their strategic importance and diverse industrial applications, REEs are termed the “vitamins of industries” (Akinyemi et al. 2021, Okeme et al. 2022).

Due to their strategic importance and diverse applications, the demands for REEs

are rapidly increasing. However, the gap between the global demands and supply is widening due to limited conventional sources and production being concentrated in a few countries leading to export restrictions. For instance, China which has been a dominating producer of REEs since 1990s and accounts for more than 79% of REEs consumed worldwide (Huang et al. 2019, Okeme et al. 2022), has posed export restrictions in order to retain the limited REEs resources for domestic use and concerns for environmental effects of mining (Zhang et al. 2015, Mancheri et al. 2019). The increased demands have led to realisation and need for exploration and exploitation of nonconventional sources such as coal and its combustion ash. Coal and coal fly ash (CFA) have been recognised as promising alternative sources of REEs (Dutta et al. 2016, Dai and Finkelman 2018, Jyothi et al. 2020, Okeme et al. 2022). Extraction of REEs from coal and coal ash is extensively being investigated worldwide. A number of studies in regard to viability of coal and coal ash for extraction of REEs have been carried out in different countries, including China (Dai et al. 2017a, Dai et al. 2017b, Li et al. 2020), United States (Hower et al. 2016, Lin et al. 2018), India (Kumari et al. 2019, Mondal et al. 2019), Indonesia (Rosita et al. 2020), South Africa (Wagner and Matiane 2018), Nigeria (Akinyemi et al. 2021, Okeme et al. 2022), and others. In Tanzania, although studies have been conducted in regard to coal and coal ash (Mrema 1997, Shao 2012, Nyaki 2014, Makundi et al. 2018, Meza et al. 2021), but none has researched on the contents of REEs. Therefore, the present study focused on assessing the viability of coal mines in Tanzania for extraction of REEs.

Materials and Methods

Geographical description of the study area

Coal samples were collected from Kiwira, Ngaka and Rukwa coal mines which are the only active coal mines in Tanzania. CFA samples were collected from Kiwira coal-fired power plant, which is located within Kiwira coal mine premises. The Kiwira coal mine is located within Songwe-Kiwira

coalfield, in Mbeya Region. The Songwe-Kiwira coalfield is along the western rift valley, situated between latitude 9°20'S to 9°35'S and longitude 33°35'E to 33°45'E (Makundi et al. 2018). The Ngaka coal mine is located in Mbinga District, Ruvuma Region, south western Tanzania, within Ngaka basin, situated at latitude 10°29'12.9"S and longitude 34°55'38.7"E. The Rukwa coal mine is located within Rukwa coalfield, in Rukwa Region, southwest Tanzania, between Lake Rukwa and Lake Tanganyika. The mine is located at latitude 7°44'44.6"S and longitude 31°27'16.9"E, within a corridor trending northwest-southeast that extends south into Zambia and Malawi (EEP 2013).

Sample collection

The sampling of coal and CFA was carried out for about two weeks, from 15th to 28th April, 2022. Coal samples were collected from pits and stockpiles of the coal mines. Sampling locations were selected in such a way that representative coal samples could be obtained. A total of 30 coal samples (10 from each mine) of about 250 g each were collected. On the other hand, a total of 10 CFA samples (5 from stockpile and 5 from boilers) of about 250 g each were collected. At each sampling location, the CFA was loosened to a depth of 0–6 cm using a scoop and homogenised by stirring. After collection, coal and CFA samples were packed in clean plastic bags, sealed, labelled and transported to the laboratory for preparation and analysis.

Sample preparation

Coal and CFA samples were oven-dried at 60 °C for 24 hours to prevent interference and matrix alterations (Kodom et al. 2012). In order to obtain homogeneity, the dried samples were crushed and ground using jaw crusher and ball mill, and sieved using a sieve of mesh size 75 µm. Finely powdered samples were prepared as fusion discs of ~ 32 mm diameter and ~ 5 mm thickness by mixing a 1:10 ratio of sample (~ 0.7 g) to high purity trace and REEs-free flux (~ 7 g) using an automatic Claisse M4 gas fusion

instrument at temperature between 1100–1200 °C.

The prepared fusion discs of coal and CFA samples were firstly analysed by XRF spectrometry. XRF spectrometry is a non-destructive analytical technique that uses X-rays to measure the elemental composition of a sample. It can provide qualitative, semi-quantitative or quantitative results for a wide range of elements. In this study, XRF spectrometry was used to analyse the coal and CFA samples, allowing the researchers to determine the major element oxides served as internal standards (Longerich et al. 1996, Eggins 2003). XRF analysis was carried out using a PANalytical Axios wavelength dispersive X-ray fluorescence (WDXRF) spectrometer of the Central Analytical Facilities (CAF) laboratory, Stellenbosch University, South Africa. The WDXRF spectrometer used was fitted with a 2.4 kW Rhodium tube, two detectors; a gas-flow proportional counter which uses a gas mixture of 90% argon and 10% methane and a scintillation detector, analysing crystals LiF200, LiF220, PE002, Ge111 and PX1, and operated with SuperQ PANalytical software which corrects for matrix effects in the analysed samples.

The prepared fusion discs had flat surfaces that were suitable for LA-ICP-MS analysis (Eggins 2003), however, due to their large size, following XRF analysis, fusion discs were broken into small pieces of ~ 5 mm diameter and ~ 5 mm thickness using a hammer to enable LA-ICP-MS analysis of multiple samples at a time. The obtained small pieces of samples were mounted alongside up to 12 samples in a round resin disc with a diameter of 2.4 cm, then mapped and polished to be scratch-free.

LA-ICP-MS sample analysis

LA-ICP-MS is a highly sensitive analytical technique that combines laser ablation (LA) with inductively coupled

plasma mass spectrometry (ICP-MS). It enables the precise and rapid analysis of trace elements, including REEs, in solid samples. By using this analytical technique, the study was able to obtain more detailed information on the concentrations of REEs in the coal and CFA samples. Analysis of coal and CFA samples for REEs with LA-ICP-MS was carried out at Central Analytical Facilities laboratory, Stellenbosch University, South Africa. The LA-ICP-MS machine used was operated by Mass Hunter software version 4.5, and Geostar software version 10.12 to control laser ablation. The spectrometer employs a 193 nm ArF excimer laser sampling instrument that is coupled to an Agilent 7700 Q ICP-MS and equipped with electron multiplier detector.

Samples were ablated in helium gas, a low-density gas with high thermal conductivity. As stated elsewhere (Eggins 2003), helium gas minimises post-ablation surface condensation, thereby maximising the transport efficiency of samples to the ICP-MS. After exiting the ablation cell, helium gas containing ablated sample was mixed with argon and nitrogen gases prior to delivery to the ICP-MS.

Prior to analysis, the LA-ICP-MS machine was optimised for sensitivity and low oxide ratio maintaining ThO^+/Th^+ ratio below 0.3% (Eggins 2003) by adjusting the ICP-MS and laser parameters while ablating on the standard reference material (SRM) NIST 612. Four replicate measurements were performed on each sample of coal and CFA. Table 1 summarises the operational parameters of the LA-ICP-MS utilised in the analysis. The concentrations of elements in the analysed samples were determined using an equation reported elsewhere (Longerich et al. 1996), and data processing was carried out utilising the software package LADR version 1.1.06 from Norris Scientific (Norris and Danyushevsky 2018).

Table 1: Operational parameters of the LA-ICP-MS utilised in the analysis

Parameter	Value	Parameter	Value
Laser wavelength	193 nm	Ablation time	45 s
Spot size	100 μm	Washout time	25 s
Frequency	8 Hz	Sample depth	4.5 mm
Energy fluence	4.5 J/cm ²	RF power	1450 W
Carrier gas flow rate	He; 0.5 L/min, Ar; 0.9 L/min, N ₂ ; 0.0035 L/min	Background acquisition time	20 s

Calibration and quality assurance

BE-N and NIM-G were used as calibration standards for the XRF machine. In addition, to ensure the quality of XRF measurements, SRMs BE-N, JB-1, BHVO-1 and JG-1 were analysed and absolute relative percentage difference (RPD) values determined using equation (1) (US EPA 1998) were used to verify the accuracy of the analytical results. The results showed a strong agreement between measured and certified values of major element oxides in all SRMs. As depicted in Figure 1(a), the absolute RPD values for all SRMs were within the acceptable range, with the exception of MgO in JG-1 (10.83%), which was marginally above; for the analytical data to be considered sufficiently accurate, the absolute RPD value should not exceed 10% (US EPA 1998).

$$RPD = \frac{C - M}{Average(C, M)} \times 100\% \quad (1)$$

Where, *C* and *M* are respectively the certified and measured concentrations of element of interest in the analysed SRM.

External calibration with internal standardisation protocol was employed in the

LA-ICP-MS analysis. SRM NIST 612 glass was used as an external calibration standard, while ²⁹Si as an internal standard element. ²⁹Si was tested and used as an internal standard element due to its presence in large amount for majority of geological samples. The recommended concentration of SiO₂ for each SRM and that obtained from XRF analysis for each coal and CFA sample were used for this purpose. The calibration standard NIST 612 was run after every 15 samples. Besides, to ensure the quality of LA-ICP-MS measurements, two SRMs BCR-2G and BHVO-2G from United States Geological Survey (USGS) were analysed as unknowns between each calibration. Also, to verify ablation on fused material, two fusion control standards BCR-2 and BHVO-1 (also from USGS) were analysed at the beginning of each sequence. As depicted in Figure 1(b), almost all absolute RPD values in all SRMs were at most 10%, except for Y (12.68%), Ce (10.56%) and Pr (11.46%) in SRM BHVO-2G, and Y (10.08%) in SRM BCR-2G which were marginally above 10%. In addition, the minimum detection limits (MDLs) of the LA-ICP-MS for REEs in coal and CFA ranged from 0.001 ppm to 0.124 ppm (Table 2).

Table 2: MDLs (ppm) of the LA-ICP-MS for REEs in coal and coal ash samples

Element	MDL	Element	MDL	Element	MDL	Element	MDL
Sc	0.124	Pr	0.001	Gd	0.010	Er	0.004
Y	0.003	Nd	0.008	Tb	0.002	Tm	0.001
La	0.002	Sm	0.009	Dy	0.006	Yb	0.007
Ce	0.002	Eu	0.002	Ho	0.001	Lu	0.002

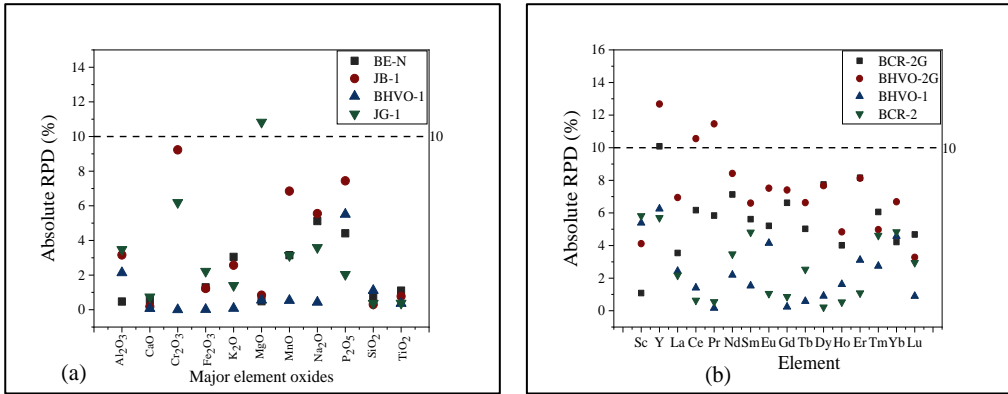


Figure 1: Absolute RPD values for (a) XRF measurements (b) LA-ICP-MS measurements.

Evaluation of economic significance of coal and coal ash for extraction of REEs

Full evaluation of coal and coal ash for extraction of REEs, requires a number of parameters to be considered, including the minable amount of coal, the modes of occurrence of REEs, extraction methods, environmental issues, as well as the demand and supply relationship (Dai et al. 2017a). However, for initial evaluation, data on REEs grade and the individual REEs composition may be sufficient (Seredin and Dai 2012). A concentration of 1000 ppm of REEs oxides (REOs) in coal ash or 800–900 ppm (ash basis) for coal seams with a thickness of greater than 5 m is considered as the cut-off grade for economic recovery of REEs (Seredin and Dai 2012). Besides, based on the REEs average abundance in the world coal, Zhang et al. (2015) estimated the cut-off grade at 115–130 ppm for coal and 677–762 ppm for coal ash.

The criterion of individual REEs composition requires the REEs source to contain as many critical REEs (Y, Nd, Eu, Tb, Dy and Er) as possible and as few excessive REEs (Ce, Ho, Tm, Yb and Lu) as

possible (Seredin and Dai 2012). A plot of $REY_{def,rel\%}$ versus C_{outl} is used as a further criterion to evaluate the economic significance of the REEs sources (Dai et al. 2017b). Where, $REY_{def,rel\%}$ is the percentage of critical REEs and C_{outl} (outlook coefficient also referred to REEs ore quality index) is the ratio of the relative amount of critical REEs to the relative amount of excessive REEs determined using an equation documented elsewhere (Seredin and Dai 2012). Based on a plot of $REY_{def,rel\%}$ versus C_{outl} , REEs sources can be classified as unpromising, promising or highly promising (Figure 2(a)) (Seredin and Dai 2012, Dai and Finkelman 2018). Besides, a plot of C_{outl} versus REOs content has also been used to evaluate the economic significance of coal ashes (Dai et al. 2017a, Dai et al. 2017b, Dai and Finkelman 2018). Similarly, based on a later plot, there are also three categories; unpromising, promising and highly promising (Figure 2(b)). These criteria were adopted and used in the present study to evaluate the economic significance of coal and CFA from Kiwira, Ngaka and Rukwa coal mines for extraction of REEs.

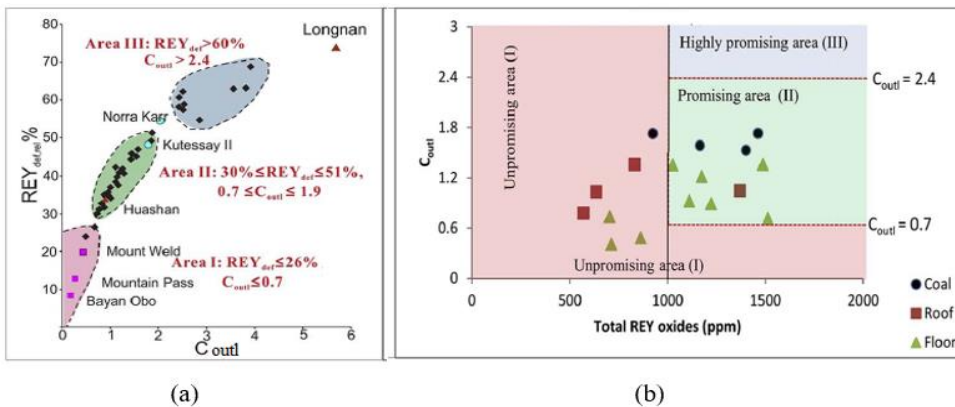


Figure 2: Classification of REEs sources: a plot of (a) $REY_{def,rel}\%$ versus C_{outl} (b) C_{outl} versus REOs (Dai and Finkelman 2018).

Results and Discussion

Concentrations of REEs in coal samples

Tables 3 and 4 display the ranges and average concentrations of individual and total REEs for the coal samples, while Figures 3(a), 3(b) and 3(c) present the total concentrations of REEs for individual coal samples. The total concentrations of REEs were in the ranges of 89.48–140.82 ppm (Table 3), 138.66–196.30 ppm (Table 3) and 158.68–191.97 ppm (Table 4) for coal samples from Ngaka, Kiwira and Rukwa mines, respectively. Despite the fact that some coal samples originated from the same locations, such as NC7 (89.48 ppm) and NC8 (140.82 ppm) (Figure 3(a)), both of which were obtained from the same pit of Ngaka mine, the dispersed distribution of total concentrations of REEs could be attributed to the origin of coals (different coal seams). Twenty two (22) out of 30 coal samples (two from Ngaka, ten from Kiwira and ten from Rukwa) had total concentrations of REEs above the proposed cut-off grade for coal (115–130 ppm; Zhang et al. 2015). Consequently, based on the cut-off grade for coal proposed by Zhang et al. (2015), 22 coal samples equivalent to 73.33% of the investigated coal samples could be considered as promising sources for the economic recovery of REEs.

However, based on the composition of individual REEs, not only total concentration of REEs in the coal is significant, but also the percentage of critical REEs ($REY_{def,rel}\%$)

within the total concentration and the ratio of the critical REEs to the excessive REEs expressed as outlook coefficient (C_{outl}) are essential. Large C_{outl} and $REY_{def,rel}\%$ values means more critical REEs can be recovered and at high profitability. Computed $REY_{def,rel}\%$ values for coal samples from Ngaka, Rukwa and Kiwira mines were in the range of 27.41–34.34% (Table 3), 32.00–50.74% (Table 3) and 28.76–29.80% (Table 4), respectively. In addition, computed C_{outl} values were in the range of 0.62–0.87 (Table 3), 0.83–2.00 (Table 3) and 0.68–0.71 (Table 4) for coal samples from Ngaka, Rukwa and Kiwira mines, respectively. Based on a plot of $REY_{def,rel}\%$ versus C_{outl} , 21 coal samples (seven from Ngaka, four from Kiwira and ten from Rukwa) had $REY_{def,rel}\% > 26\%$ and $C_{outl} \geq 0.7$. Thus, about 70% of the investigated coal samples present opportunities for commercial extraction of REEs based on $REY_{def,rel}\%$ and C_{outl} values computed in the present study. Furthermore, among the three investigated coal mines, Rukwa coal mine was found to be the most promising for economic development; total concentrations of REEs for all the coal samples were above the cut-off grade for coal (115–130 ppm; Zhang et al. 2015), and $REY_{def,rel}\%$ and C_{outl} values for all the coal samples fall into the promising category ($30\% \leq REY_{def,rel}\% \leq 51\%$, $0.7 \leq C_{outl} \leq 1.9$; Seredin and Dai 2012, Dai and Finkelman 2018).

Concentrations of REEs in CFA samples

The ranges and average concentrations of individual and total REEs for the CFA samples are presented in Table 4, while the total concentrations of REEs for individual CFA samples are presented in Figure 3(d). As anticipated, CFA samples had higher concentrations for all the REEs than those found in the coal samples because REEs are non-volatile, as documented elsewhere (Wagner and Matiane 2018). The total concentrations of REEs for the CFA samples were in the range of 362.55–475.77 ppm. The obtained total concentrations of REEs in all the CFA samples were below the proposed cut-off grade for coal ash; 1000 ppm or 800–900 ppm (Seredin and Dai 2012) and 677–762 ppm (Zhang et al. 2015).

Computed $REY_{def,rel\%}$ and C_{outl} values for the CFA samples were in the range of 32.20–33.09% and 0.81–0.86, respectively (Table 4). When applying a plot of $REY_{def,rel\%}$ versus C_{outl} , the CFA samples could be considered as potential sources of REEs as their $REY_{def,rel\%}$ and C_{outl} values fall into the cluster of promising sources ($30\% \leq REY_{def,rel\%} \leq 51\%$, $0.7 \leq C_{outl} \leq 1.9$; Seredin and Dai 2012, Dai and Finkelman 2018). However, based on a plot of C_{outl} versus REOs applied by Dai et al. (2017a), Dai et al. (2017b) and Dai and Finkelman (2018) which requires the REOs content ≥ 1000 ppm (refer Figure 2(b)), the CFA samples do not qualify as potential sources of REEs as they fall into an unpromising category; their total REEs contents were below 1000 ppm although their C_{outl} values were all above 0.7.

Table 3: Concentrations of REEs for Ngaka coal (NC) and Rukwa coal (RC) samples

	NC (N = 10, n = 4)		RC (N = 10, n = 4)	
	Range (ppm)	Av \pm SEM (ppm)	Range (ppm)	Av \pm SEM (ppm)
Sc	5.44–9.84	6.98 \pm 0.42	6.75–10.52	8.66 \pm 0.41
Y	8.92–16.71	12.30 \pm 0.66	15.21–38.95	21.57 \pm 2.10
La	14.76–26.63	19.57 \pm 1.05	14.35–35.22	28.23 \pm 2.08
Ce	32.37–55.50	39.78 \pm 2.06	29.72–67.40	55.68 \pm 3.82
Pr	3.17–4.99	3.85 \pm 0.18	3.84–7.83	6.75 \pm 0.43
Nd	10.34–17.89	13.52 \pm 0.69	16.79–32.59	27.73 \pm 1.67
Sm	2.00–3.68	2.62 \pm 0.16	4.71–7.90	6.29 \pm 0.29
Eu	0.43–0.88	0.57 \pm 0.04	0.86–1.53	1.19 \pm 0.07
Gd	1.71–3.22	2.34 \pm 0.15	3.96–7.88	5.33 \pm 0.37
Tb	0.29–0.51	0.39 \pm 0.02	0.59–1.18	0.75 \pm 0.06
Dy	1.82–3.24	2.41 \pm 0.14	3.54–6.94	4.33 \pm 0.32
Ho	0.37–0.65	0.48 \pm 0.03	0.66–1.37	0.83 \pm 0.07
Er	0.99–1.75	1.32 \pm 0.06	1.74–3.57	2.21 \pm 0.16
Tm	0.14–0.24	0.18 \pm 0.01	0.22–0.44	0.30 \pm 0.02
Yb	0.92–1.57	1.20 \pm 0.06	1.42–2.63	1.89 \pm 0.11
Lu	0.13–0.22	0.17 \pm 0.01	0.20–0.37	0.27 \pm 0.02
REEs	89.48–140.82	107.68 \pm 5.04	138.66–196.30	171.99 \pm 6.05
REY	83.14–132.45	100.70 \pm 4.74	131.44–186.16	163.34 \pm 5.73
C_{outl}	0.62–0.87	0.73	0.83–2.00	1.04
$REY_{def,rel\%}$	27.41–34.34	30.33	32.00–50.74	35.80

N: number of investigated coal samples, n: number of replicate measurements for each sample, Av: average, SEM: standard error of the mean.

Table 4: Concentrations of REEs for Kiwira coal (KC) and Kiwira power plant CFA (KA)

	KC (N = 10, n = 4)		KA (N = 10, n = 4)	
	Range (ppm)	Av ± SEM (ppm)	Range (ppm)	Av ± SEM (ppm)
Sc	6.94–10.37	9.17 ± 0.45	22.21–28.52	25.12 ± 0.65
Y	16.56–19.99	18.48 ± 0.41	45.26–59.53	50.63 ± 1.39
La	30.57–36.03	33.10 ± 0.64	65.43–84.70	74.26 ± 2.15
Ce	60.54–74.34	68.41 ± 1.53	123.58–166.29	144.25 ± 4.61
Pr	6.09–7.27	6.70 ± 0.13	13.74–17.98	16.01 ± 0.48
Nd	21.31–25.77	23.71 ± 0.50	49.89–63.94	58.58 ± 1.69
Sm	3.79–4.67	4.27 ± 0.10	9.50–12.34	11.25 ± 0.30
Eu	0.72–0.89	0.81 ± 0.02	1.73–2.28	2.10 ± 0.06
Gd	3.08–3.76	3.49 ± 0.08	8.40–10.56	9.63 ± 0.24
Tb	0.49–0.60	0.55 ± 0.01	1.34–1.76	1.55 ± 0.04
Dy	3.10–3.61	3.42 ± 0.07	8.27–11.25	9.55 ± 0.29
Ho	0.60–0.73	0.68 ± 0.01	1.73–2.22	1.92 ± 0.05
Er	1.70–2.09	1.92 ± 0.04	4.86–6.45	5.48 ± 0.15
Tm	0.24–0.29	0.27 ± 0.01	0.71–0.94	0.79 ± 0.02
Yb	1.66–2.03	1.83 ± 0.04	4.66–6.12	5.33 ± 0.15
Lu	0.24–0.29	0.26 ± 0.00	0.68–0.89	0.77 ± 0.02
REEs	158.68–191.97	177.08 ± 3.91	362.55–475.77	417.19 ± 12.01
REY	151.74–181.68	167.91 ± 3.50	339.97–447.25	392.07 ± 11.39
C _{outl}	0.68–0.71	0.69	0.81–0.86	0.84
REY _{def. rel%}	28.76–29.80	29.12	32.20–33.09	32.63

N: number of investigated coal samples, n: number of replicate measurements for each sample, Av: average, SEM: standard error of the mean.

Comparison of concentrations of REEs in coal and coal ash determined in the present study and other data from other studies

Table 5 displays the average total concentrations of REEs for coals from Ngaka, Kiwira and Rukwa coal mines determined in the present study and other data from some coal-producing countries such as South Africa, China, Columbia, Turkey, Democratic People’s Republic of Korea (DPR Korea), United States (US) and the global average. As shown in Table 5, the average content of REEs for Kiwira coal (177.08 ± 3.91 ppm) was the highest, followed by Rukwa coal (171.99 ± 6.05

ppm), Chinese coal (140.27 ppm), South African coal (130.85 ppm), Turkish coal (116.02 ppm), and Ngaka coal (107.68 ± 5.04 ppm). In addition, the average contents of REEs for Kiwira and Rukwa coals were nearly 2.5 times the global average (72.37 ppm), Columbian coal (74.39 ppm) and DPR Korea coal (77.30 ppm). Also, the average content of REEs for Ngaka coal was comparable to that of Turkish coal, but higher than the global average, the United States, Columbian and DPR Korea coals. Furthermore, the average contents of REEs for Ngaka, Kiwira and Rukwa coals were significantly lower than those for REE-rich coals identified by Seregin and Dai (2012).

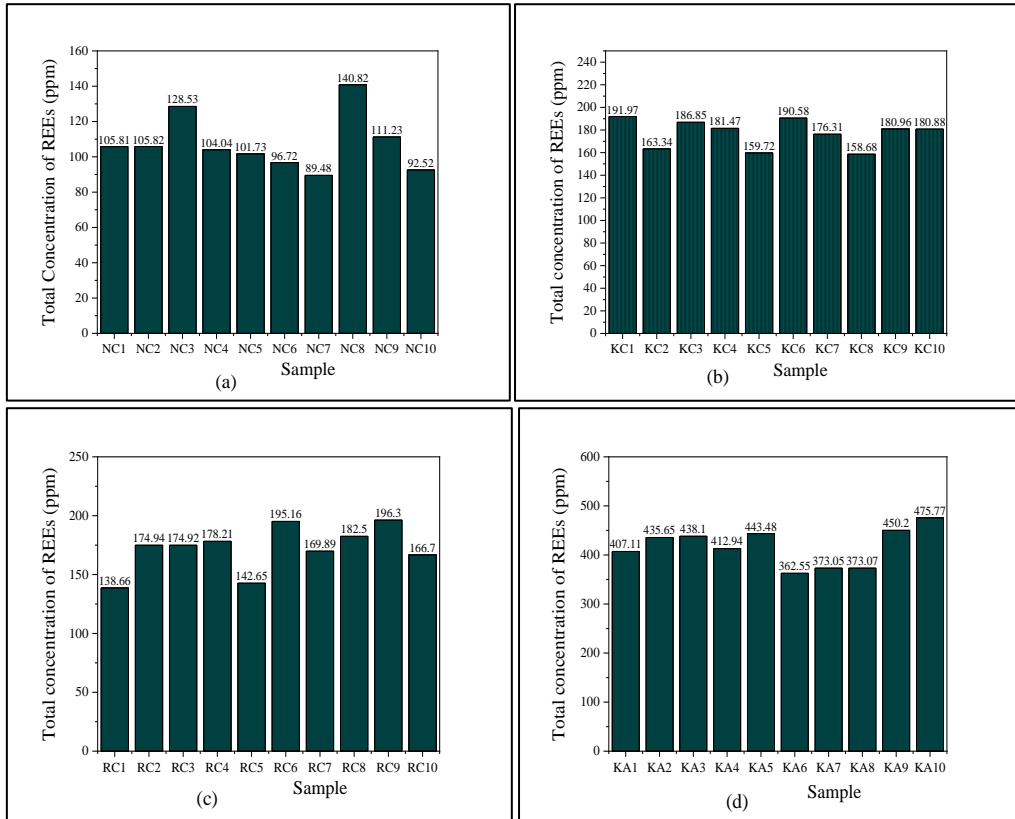


Figure 3: Total concentrations of REEs for (a) Ngaka coal (NC) samples (b) Kiwira coal (KC) samples (c) Rukwa coal (RC) samples and (d) Kiwira power plant CFA (KA) samples.

Table 5: Comparison of concentrations of REEs for coals from Ngaka, Kiwira, Rukwa mines and some other coal-producing countries around the world

Location	Av ± SEM (ppm)	Reference(s)
Ngaka, Tanzania	107.68 ± 5.04	Present study
Kiwira, Tanzania	177.08 ± 3.91	Present study
Rukwa, Tanzania	171.99 ± 6.05	Present study
South Africa	130.85	Wagner and Matiane 2018
Columbia	74.39	Huang et al. 2019
China	140.27	Dai et al. 2012
Turkey	116.02	Karayigit et al. 2000, Zhang et al. 2015
DPR Korea	77.30	Hu et al. 2006
United States (US)	66.29	Zhang et al. 2015
Worldwide	72.37	Ketris and Yudovich 2009, Zhang et al. 2015

Av: average total concentration of REEs, SEM: standard error of the mean.

Table 6 shows the average total concentrations of REEs for coal ashes from Kiwira and some other places such as South Africa, Indonesia, India, Poland, United Kingdom (UK), China and United States

(US) as well as the global average. The average content of REEs for the Kiwira coal ash (417.19 ± 12.01 ppm) was higher than the average contents of REEs for coal ashes from Indonesia (243.63 ppm), the United Kingdom

(340.33 ppm), Poland (341.67 ppm) and India (376.68 ppm), but it was lower than the global average (445 ppm), the United States (459.61 ppm), China (473 ppm) and South Africa (566.42 ppm). In addition, the average total concentration of REEs for the Kiwira

coal ash was considerably lower than those reported by Seredin and Dai (2012) (up to 8426 ppm), Dai et al. (2017b) (average of 1387 ppm) and Li et al. (2020) (up to 1257 ppm).

Table 6: Comparison of concentrations of REEs for coal ashes from Kiwira coal-fired power plant and some other places around the world

Location	Av ± SEM (ppm)	Reference(s)
Kiwira, Tanzania	417.19 ± 12.01	Present study
South Africa	566.42	Wagner and Matiane 2018
Indonesia	243.63	Rosita et al. 2020
India	376.68	Mondal et al. 2019
Poland	341.67	Blissett et al. 2014
United Kingdom (UK)	340.33	Blissett et al. 2014
China	473	Fu et al. 2022
United States (US)	459.61	Fu et al. 2022
Worldwide	445	Franus et al. 2015

Av: average total concentration of REEs, SEM: standard error of the mean.

Conclusion

For the first time, the concentrations of REEs in coal and CFA from Tanzanian coal mines have been determined, along with the viability for commercial extraction. The examined coal and CFA samples suggest the possibility of using them for the economic recovery of REEs. Moreover, among the three investigated coal mines, Rukwa mine was found to be the most promising for economic development; total concentrations of REEs for all the Rukwa coal samples were above the cut-off grade, and computed $REY_{def,rel\%}$ and C_{out} values for all the Rukwa coal samples fell within the range of recommended values for promising category. Overall, the combination of XRF spectrometry and LA-ICP-MS provided a comprehensive determination of the concentrations of REEs in the coal and CFA samples, offering valuable insights into the viability of the coal mines for extraction of REEs in Tanzania.

This investigation on coal and CFA revealed variations in the total concentrations of REEs among different coal and CFA samples, consequently, future research is recommended to consider coal samples obtained by stratified sampling in order to identify specific horizons of coal seams

enriched in REEs. In addition, as the examined samples indicate a potential for economic recovery of REEs, future research is recommended to consider the economic viability of potential extraction methods.

Acknowledgement

The authors are grateful to the Dar es Salaam University College of Education for the financial support, Central Analytical Facilities, Stellenbosch University, South Africa for their XRF and LA-ICP-MS facilities. The authors are also thankful to the management of Kiwira, Ngaka, and Rukwa mines for permission and assistance in sampling at their premises, and to staff members of the Physics Department of the University of Dar es Salaam for the support during this study.

Competing interests

The authors declare that no competing interests exist.

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