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ESTIMATION OF THE ABUNDANCE AND DISTRIBUTION OF RARE EARTH ELEMENTS IN SOIL AROUND KADUNA REFINING AND PETROCHEMICAL COMPANY USING NUCLEAR TECHNIQUE

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ABSTRACT

Instrumental neutron activation analysis (INAA) technique was used to investigate the abundance and distribution of rare earth elements (REE) in soil around Kaduna Refinery. The aim of the study is to assess the rare elements potential of Nigeria for economic exploitation. Five REEs (La, Dy, Eu, Yb, and Lu) were detected in varying concentrations ranging from a minimum of 0.6 µg/g (Lu) to a maximum of 249.0 µg/g (La). The elements existed with trends consistent with the natural pattern of REEs in soil, showing significant Eu and Dy anomalies which characterize upper plains and flood plains. The levels of REEs in soil in the study area were generally slightly above background levels, with minimal (La, Dy, and Eu), moderate (Yb), and significant (Lu) enrichments and trending: Lu >Yb > Eu > Dy > La. The abundance of the REEs investigated cannot establish a potential of Nigeria for economic exploitation of the mineral, hence, rare earth project in the study area is not viable at the moment.

Keywords: INAA, REE, abundance, soil, Kaduna Refinery

INTRODUCTION

Rare earth elements (REEs) are members of a group of elements with atomic numbers 57 – 71 (La – Lu on the periodic table). The elements have similar chemical behaviour, therefore, they tend to stay together in any natural occurrence as a group rather than exist individually or as combination of a few of them (Wang and Liang, 2015; Šmuc *et al*., 2012). As such, any deviation from this natural pattern is an indication of a disruption of the geochemical environment. REEs occur in a wide range of minerals including silicates, phosphates, halides, oxides, and carbonates, with abundances that vary widely from one element to another (Wang and Liang, 2015).

Out of the over 200 known REEs-bearing ores, only three (basnasite, xenotime, and monazite) are most feasible for extraction of rare earth minerals (Tyler, 2004). REEs do not exist as independent elements in nature, rather, they are integral part of the host mineral's chemistry. This makes the extraction of REEs or their oxides a complex and difficult task. Their extractions have to first go through complex processing procedures to chemically break down their host minerals (Tyler, 2004).

The correlation between the soil texture and REE concentrations indicate that REEs (both light and heavy) tend to be hosted in the finer particles which is primarily attributed to the strong adsorption of REEs on minerals through hydroxyl-hydrated sites (Laveuf and Cornu, 2009). Rare earth elements are not necessarily rare. The rarest of the REEs (Tm and Lu) are even more abundant than the most valuable precious metals (Au, Ag, and elements that belong to the platinum group (Rudnick and Gao, 2003), while some are even more abundant than the crustal concentrations of some much more studied elements like Cu and Zn (Charalampides *et al*., 2015). The issue of concern here is that REEs only exist in low density ores and hard to extract. Despite this disadvantage, the quest to reduce greenhouse emission and obtain clean energy has driven a large number of investors into this promising industry. It is on record (Chen, 2011; Charalampides *et al*., 2015; Zhou *et al*., 2017) that several potential sources of supply of REEs are currently being explored, with Brazil even promising to surpass China and rank first in rare earth deposit. Several reports (Hong *et al*., 2000; Ding *et al*., 2006; Hu *et al*., 2006) also revealed highly elevated levels of some REEs (La, Ce, Sm, Eu, and Tb) in agricultural soils (the reason for this investigation). The fact that the amount/value of REEs in a site may be less important compared to the cost of processing is still a big source of discouragement from exploration. The future of rare earth industry promises to be viable however; the time is therefore ripe to invest in the rare earth production. It must be added however that the deposits/reserves must be economic to mine (must have net economic benefit) as almost all the deposits contain the radioactive thorium and uranium which could be of environmental concern. According to United States Geological

Survey (Zhou *et al*., 2017), China had the highest world reserve of rare earth oxide (REO) of about 55×10^6 metric tons, with Malaysia having the least of 0.03×10^6 metric tons of REO on the chart. At the moment, there are insufficient data on ground to be able to place Nigeria on the global chart of countries with rare earth projects. Different parameters are used to determine the feasibility or otherwise of a rare earth project including: individual rare earth distribution, the tonnage, the ore grade, among which the tonnage has been adjudged to be the most important parameter (Zhou *et al*., 2017). An individual rare earth element distribution is based on the individual REE as a fraction of the total rare earth element (TREE) expressed as $\left({}^{REE}/_{TREE}\right)\%$. Dy will be the critical material for clean energy in the near future (Zhou et al., 2017), hence, they will determine the success of the exploration of a new rare element project.

Rare earth elements are very vital to critical sectors of the economy such as information technology, energy, transportation, medicine, military, and a host of others. For instance, the microchip in the cell phone, LASERs, electric car batteries, glowing phosphors in monitors, LED, fibre optic networking *et cetera* make use of rare earth elements (Hanson, 1980; Henderson, 1984; Aubert *et al*., 2004; Han and Liu, 2006; Tyler, 2004; Willis and Johannesson, 2011). This has led to renewed interest in the search for REEs to break the global monopoly enjoyed by China. Despite the importance of REEs to the global economy, they are unfortunately in short supply; hence, the need to explore into the natural resources that Nigeria is endowed with (especially in the face of Government's drive towards diversification) and possibly contributes to the global supply. The aim of this study is therefore to assess the REEs potentials of Nigeria for economic exploitation in order to key into the fast-developing technology. Different techniques (AAS, XRF, INAA etc) can be employed for the elemental determinations, however, the instrumental neutron activation analysis (INAA) technique was used in this study due to its versatility, multi-elemental nature and availability.

In the neutron activation analysis technique, a stable isotope is made radioactive by bombarding the isotope called the target nucleus with a neutron.

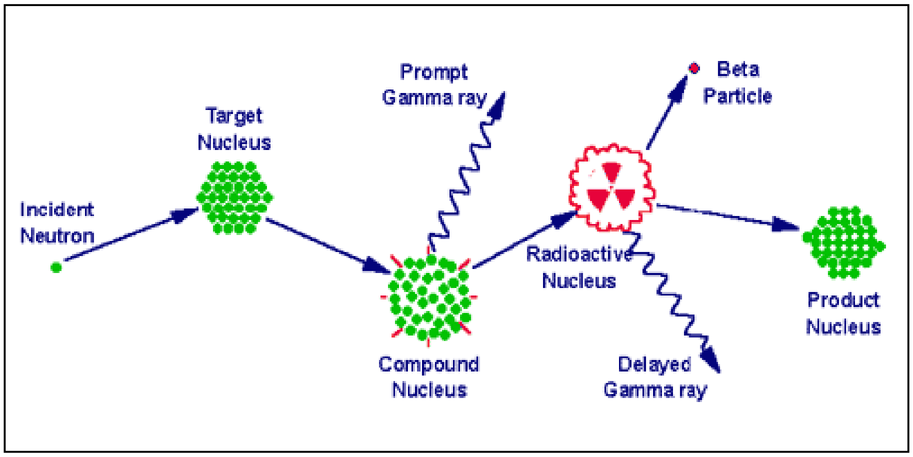

Figure 1. Illustration of the activation process (Glascock, 2005)

The radioactive nucleus emits prompt gamma rays immediately following activation, and after a period of decay, delayed gamma (decay gamma) corresponding to different energy peaks which are characteristic of specific elemental compositions (elements of interest) are emitted (Figure 1). These are then measured using the gamma ray spectrometric analysis. The element of interest in the unknown sample relative to the standard can be determined using the expression (Glascock, 2005):

$$c_x = c_s \frac{w_s}{w_x} * \frac{A_x}{A_s} \qquad (1)$$

where c_x and c_s are the concentrations of the sample and standard respectively, w_x, w_s, A_x, and A_s are the weight of the sample, weight of the standard, activity of the sample, and activity of the standard respectively.

MATERIALS AND METHODS

Sample Collection and Preparation

Near surface soil samples were collected using a core sampler from depths of 0 - 20 cm from farmland along the effluents discharge track and other farmland surrounding the Kaduna refinery complex. These samples were air-dried at ambient temperature and stored in polyethylene bags which were thoroughly washed prior to sampling. While sampling, attention was given to farm lands where the river-water mixed with the effluents, was being used for irrigation. Soil samples were also collected from the sludge pit where oil wastes were dumped.

The dried samples were transferred to the laboratory at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria and pulverized into near-uniform particles and each was weighed into a pre-cleaned polyethylene bag and sealed with a hot soldering iron into a 7 cm^3 rabbit capsule. Thereafter, the sample capsules were packaged into bigger vials for irradiation.

Sample Irradiation

Irradiation is simply the exposure of a sample to nuclear radiation. The vials containing the rabbit capsules were sent to the reactor irradiation sites using the pneumatic transfer system called the rabbit system. The irradiation was done using the 31 kW tank-in-pool Miniature Neutron Source Reactor (the Nigeria Research Reactor-One, also called NIRR-1) with a neutron flux of 10^{11} n/cm^2/s. The software, WINSPAN was used for the spectrum analysis. Table 1 gives the details of the irradiation and counting regimes used in this work. Gamma energy lines free of interference were used for peak integration and are shown in Table 2 with other nuclear data.

Table 1: Typical irradiation and counting schemes used for this work

Neutron flux/irradiation channel	Procedure	$T_{irradiation}$	T_{decay}	$T_{measuring}$	Activation products
$1x10^{11}$n/cm^2 s /outer irradiation channels (B4, A2)	S1	2 min	2-15 min	10min	^{28}Al, ^{27}Mg, ^{51}Ti, ^{52}V, ^{66}Cu
	S2	2 min	3-4h	10min	^{165}Dy, ^{152m}Eu
5×10^{11}n/cm^{2}s /inner irradiation Channels (B1, B2, B3, and A1)	L1	6h	4-5d	30min	^{140}La
	L2	6h	10-15d	60min	^{152}Eu, ^{177}Lu, ^{175}Yb, ^{181}Hf.

Table 2. Nuclear Data for the elements of interest used for this work

Target Isotope	Product isotope (n,γ)	Half-life	Gamma energy (keV)
^{139}La	^{140}La	40.30 h	1596.21
^{151}Eu	^{152}Eu	13.30 y	1408.50
^{164}Dy	^{165}Dy	2.33 h	94.70
^{174}Yb	^{175}Yb	4.19 d	396.33
^{176}Lu	^{177}Lu	6.71 d	208.36

A high-resolution gamma-ray spectrometer (MAESTRO – 32) was used to detect the delayed gamma for both qualitative and quantitative analysis. The energy determined which elements were present, while the number of gamma rays of specific energy gave the amount of a particular element.

EVALUATION OF THE ENRICHMENT FACTOR (EF)

Enrichment factor (EF) is a quantity used to estimate the anthropogenic effects on the elements in the host. It is expressed as (Wang and Liang, 2015, Loska *et al*., 2004, Tang *et al*., 2009, Guimarães *et al*., 2011, Khan *et al*., 2020):

$$EF = {(C_i/C_r)_{Sample}} \Big/ {(C_i/C_r)_{Crust}} \qquad (2)$$

where C_i and C_r are the concentrations of the elements of interest and the reference element, either of the sample or the earth crust (Reference elements are elements that are not influenced by anthropogenic activities and not significantly affected by weathering processes).

The reference materials often used include: Ca, Al, Fe, Li, Mn, Sc, and Sr (Wang and Liang, 2015, Loska *et al*., 2004, Tang *et al*., 2010). Generally, an EF > 1is termed an enrichment while an EF < 1 on the other hand is termed a depletion. In this work, Fe, having a crustal concentration of 30890 µg/g (Wedepohl, 1995) was used as the conservative element for normalization.

Table 3. Enrichment Factor Scale (Khan *et al*., 2020)

Enrichment Factor (EF)	Description
EF < 1	Depletion to minimal enrichment
2 < EF < 5	Moderate enrichment
5 < EF < 20	Significant enrichment
20 < EF < 40	Very high enrichment
EF > 40	Extremely high enrichment

Enrichment factors are categorized according to factor scales as presented in Table 3 (Khan *et al*., 2020). The level of the EF value determines the severity or otherwise of the anthropogenic contributions.

RESULTS AND DISCUSSION

Five rare earth elements (La, Dy, Eu, Yb, and Lu) were detected in soils around Kaduna refinery in varying concentrations. Plots of $(REE)_{cn}$ values against their corresponding ionic radii showed patterns that were consistent with REE trends with clear europium anomaly (Onoja *et al*., 2018). The concentrations of the REEs of interest in the upper continental crust in the study area are presented in Table 4, while the average values are represented by the chart in Figure 2. Table 5 presents the enrichment factors for the various rare earth elements. The REEs were detected in the ranges of 43.8 – 249.0 µg/g (La), 4.6 – 11.4 µg/g (Dy), 0.8 – 62.0 µg/g (Eu), 3.1 – 29.2 µg/g (Yb) and 0.6 – 87.3 µg/g (Lu), with average concentrations of the elements as 76.6 ± 54.5, 7.3 ± 1.9 , 2.8 ± 3.2, 9.1 ± 6.8, and 6.9 ± 22.3 µg/g for La, Dy, Eu, Yb, and Lu respectively. The concentration of each REE were generally higher (except Eu), but compare fairly well with those reported by Šmuc *et al*., (2012).

Table 4. Concentrations (µg/g) of REEs in soil around Kaduna Refinery

SAMPLE ID	La	Dy	Eu	Yb	Lu
S01	104.1 ± 0.3	8.8 ± 0.4	6.3 ± 0.4	15.0 ± 1.0	1.7 ± 0.1
S02	66.2 ± 0.3	5.7 ± 0.4	1.5 ± 0.1	6.2 ± 0.2	0.8 ± 0.0
S03	99.6 ± 0.3	8.4 ± 0.5	12.0 ± 0.4	15.4 ± 0.5	1.6 ± 0.1
S04	105.5 ± 0.3	8.7 ± 0.3	6.1 ± 0.4	12.5 ± 0.5	1.5 ± 0.1
S05	15.4 ± 0.1	6.1 ± 0.3	1.5 ± 0.2	3.5 ± 0.2	0.8 ± 0.0
S06	53.8 ± 0.3	9.0 ± 0.3	1.0 ± 0.1	6.6 ± 0.2	0.9 ± 0.0
S07	45.6 ± 0.2	8.6 ± 0.3	1.8 ± 0.3	29.2 ± 0.5	3.7 ± 0.1
S08	43.8 ± 0.3	11.4 ± 0.3	0.8 ± 0.1	5.8 ± 0.2	0.9 ± 0.0
S09	46.1 ± 0.3	5.3 ± 0.2	0.8 ± 0.1	4.7 ± 0.2	0.6 ± 0.0
S10	46.1 ± 0.2	5.3 ± 0.2	0.8 ± 0.1	5.1 ± 0.2	0.6 ± 0.0
S11	98.5 ± 0.3	5.8 ± 0.3	4.3 ± 0.4	8.6 ± 0.4	1.4 ± 0.1
S12	60.6 ± 0.4	7.7 ± 0.3	1.0 ± 0.1	5.9 ± 0.2	87.3 ± 2.9
S13	59.0 ± 0.4	5.9 ± 0.3	0.9 ± 0.1	5.4 ± 0.2	0.7 ± 0.0
S14	55.1 ± 0.3	8.7 ± 0.3	1.1 ± 0.1	9.5 ± 0.2	1.0 ± 0.0
S15	249.0 ± 1.0	4.6 ± 0.3	1.3 ± 0.1	3.1 ± 0.2	0.5 ± 0.0
Mean	**76.6**	**7.3**	**2.8**	**9.1**	**6.9**
Min.	**15.4**	**4.6**	**0.8**	**3.1**	**0.5**
Max.	**249.0**	**11.4**	**12.0**	**29.2**	**87.3**
SDev.	**54.5***	**1.9**	**3.2**	**6.8***	**22.3***

*Abnormal SDevs are due to Outliers observed in the concentrations of the various elements

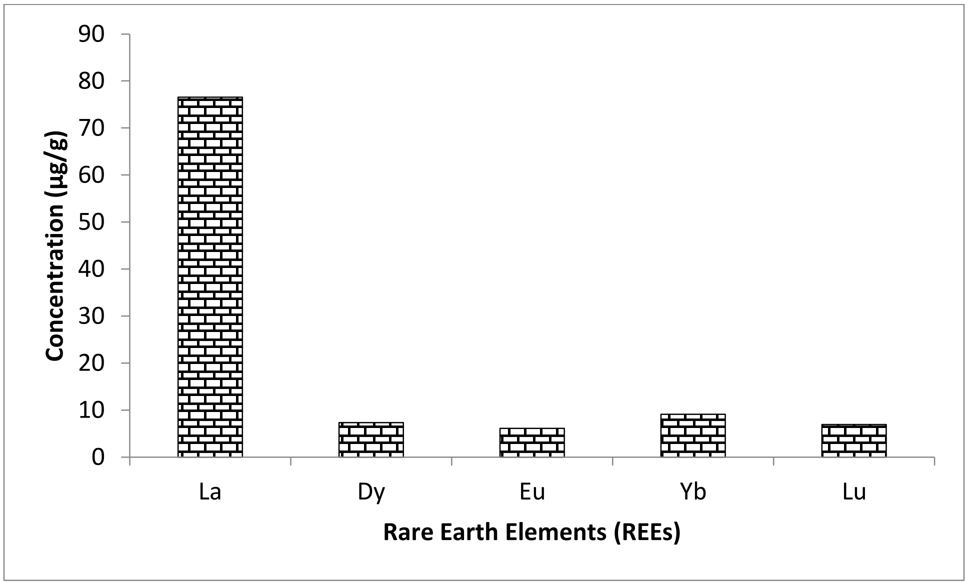

Figure 2. Average abundances of some REEs in soil around Kaduna Refinery

Table 5. Enrichment factors for REEs of interest

Element	Enrichment Factor (EF)
La	1.37
Dy	1.46
Eu	1.67
Yb	3.51
Lu	14.83

ENRICHMENT FACTORS

The measured REEs were enriched between 1.37 and 14.83. Though all the REES were enriched (Wang and Liang, 2015), the concentrations of La, Dy, and Eu in most of the samples tended towards the background. Comparison with Table 3 shows that La, Dy, and Eu acquired minimal enrichment, Yb achieved moderate enrichment, while Lu enjoyed significant enrichment. According to Zhang and Liu, (2002), an EF between 0.5 and 1.5 suggest that the metal may be totally from crustal materials; but if the EF is greater than 1.5, it is an indication that a significant percentage of the metal is of anthropogenic origin. Based on the foregoing, we can infer that Yb and Lu had their origin from anthropogenic activities, while La and Dy were of crustal origin. Eu, though having an EF greater than 1.5 may be of crustal origin since most of the samples had the metal in concentrations at the background levels. In summary, the EF values of the REEs followed the trend: Lu >Yb > Eu > Dy > La. EF alone, however cannot be solely relied upon to tell the source of REEs accurately (Tang *et al*., 2010) but are very useful indicators that can tell whether or not anthropogenic processes contribute to the distribution of the elements in a medium.

CONCLUSION

The INAA technique has been used to determine five rare earth elements. The results of this study revealed that the REE concentrations in agricultural soils of the study area are generally at the background levels with one or two spikes in a few samples. The concentration of an individual element in the crust does not imply the resource can be exploited; the viability depends on factors such as the economic benefits accruable from the resource *vis-a-vis* the cost of production and the environmental issues associated with its exploration and exploitation.

It is therefore quite uneconomical (based on measurements and observations) to venture into tapping of this natural resource in the area. The authors however suggest that the search be extend to the three principal mineral ores – bastanite, xenotime, and monazite at the various locations across Nigeria to fully establish the potentials of Nigeria for rare earth resources on a global scale.

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