NUCLEAR TECHNIQUES APPLICATIONS IN SOLID MINERALS ANALYSIS

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ABSTRACT

Nigeria is gifted with large deposits of solid minerals located in different parts of the country. However, the country has not fully exploited the minerals because of the lack of knowledge of the available technology to find and process them. While many nuclear and radiations technology techniques for many solid minerals processing and exploration exist, this paper aims to review the applicability of the Neutron Activation Analysis (NAA) and Proton Induced X-Ray Emission (PIXE) techniques in Nigeria for the reason that it is most common in the country. NAA has not only been used for coal exploration but also to obtain the elemental composition of coal found in Enugu and Okaba areas of Nigeria. The PIXE technique has been used to analyze mining waste and the technique has been successful in identifying trace materials and heavy metals. Evidence indicate that a wide range of radiation techniques and technologies offer great advantages to the mining industry, be it for exploration, optimization of processes, troubleshooting, assessment of mining sites or ensuring environmental protection. A Nigerian National Policy to promote the use of nuclear and radiation technologies in the solid mineral industry should be put in place.
Keywords: *Nuclear, Radiation, Neutron, Proton, Optimisation*

1. INTRODUCTION

Nigeria is endowed with large deposits of several solid minerals located in different parts of the country. The minerals that investors are interested in include coal, lignite, granite, bitumen, gold, coltan, limestone, lead, zinc, cassiterite, iron ore, limestone, clay, barite, columbite, marble, and tantalite (Adetunji *et al*. 2005; Akpan *et al*. 2011; FMSMD, 2016). Despite the abundance of the afore-mentioned minerals, the solid mineral industry only contributed approximately 0.33% to the gross domestic product of Nigeria in 2015. Some of the challenges facing the solid minerals sector are (FMSMD, 2016):

i) weak mechanism for gathering, disseminating and archiving critical geological data required by investors and policy makers
ii) insufficient infrastructure such as railroad, competitive financing systems, mine and asset security as well as policy uncertainty for operators

With the passage of the Nigerian Minerals and Mining Act (2007) and the Nigerian Mineral and Metals Policy (2008) as well as the recently approved roadmap for the growth and development of the Nigerian mining industry by the Federal Executive Council, it is hoped that these challenges would be appreciably addressed. However, the use of nuclear techniques in the solid minerals sector was not addressed by these policy documents despite the fact that the Nigeria Atomic Energy Commission Act (1976) empowers the Commission to prospect for and mine radioactive minerals.

The full economic value of the solid minerals resources can only be attained after they have passed through the exploration, mining and processing stages. Available techniques that have been used to analyze the products from each of these stages are quite extensive; they are based on chemical, physical and nuclear characteristics. The nuclear techniques that have been used include Atomic Absorption Spectrometer (AAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Energy Dispersive X-ray Spectrometer Fluorescence (EDXRF), Scanning Electron Microscopy (SEM), Gamma-ray Spectrometry, X-Ray Fluorescence, Neutron Activation Analysis (NAA), Proton Induced X-ray Emission (PIXE) and Particle Induced Gamma Ray Emission (PIGE) (Smolka-Danielowska, 2006; Adedosu, *et al*., 2007; Funtua, *et al.*, 2012; Katrinak and Benson, 2014; Isaiah *et al*., 2015). Some of these techniques can be used during exploration while others are used to analyze the minerals. This paper aims to review the use of nuclear and radiations technology in the economic exploitation of the numerous solid minerals deposits that are available in Nigeria. Specifically, it focuses on NAA and PIXE since these techniques are readily accessible in the country.

2. NEUTRON ACTIVATION ANALYSIS (NAA)

NAA was first developed by G. Hevesy and H. Levi in 1936 when they used a neutron source (226Ra + Be) and a radiation detector (ionization chamber) and promptly recognized that the element Dy (dysprosium) in the sample became highly radioactive after exposure to the neutron source. They showed that the nuclear reaction may be used to determine the elements present in unknown samples by measuring the induced radioactivity. With the development of nuclear reactors later, providing neutron fluxes in order of $10^{16} m^{-2} \cdot s^{-1}$, the use of neutron activation analysis as a very sensitive

technique increased rapidly. Furthermore, the introduction of NaI(Tl) scintillation detectors of gamma-radiation and multichannel analysers as well as the introduction of semiconductor detectors made of germanium compensated by lithium (Ge(Li)) and high purity germanium (HPGe) detectors made neutron activation analysis much easier to use. Greenberg *et al.*, (2011), Hamidatou *et al.*, (2013) and Kubešová, (2016) have discussed extensively the history and development of NAA.

The sequence of events occurring during NAA is shown in Fig 1. A neutron interacts with a target nucleus by non-elastic collision, thus forming a highly excited compound nucleus. The compound nucleus has a short lifetime and can de-excite in different ways which usually involve emission of nuclear particles or gamma rays. Prompt Gamma NAA is based on the in-situ measurement of the latter. In most cases, the new nucleus is radioactive and will further evolve towards stability. Its nuclear decay is often accompanied by the emission of very characteristic gamma rays, "which can be considered as a fingerprint". A statistical correlation exists between the number of target nuclei and the amount of gammas in the activation spectrum recorded by a spectrometer (Pomme *et al.*, 1997). In practice, the first step in NAA is to irradiate the sample with neutrons in a nuclear reactor which then excites the sample to form a stable nucleus; in this transition state it emits prompt gamma rays. In some cases, the stable nucleus after absorbing neutrons may become a radioactive nucleus, if this happens a delayed gamma ray would be released with very high energy (see Fig. 1). The radioactive nuclei emit characteristic gamma rays, which can be measured to determine which element is present (Win, 2004). NAA can be used to detect the elements that are shaded in Fig 2.

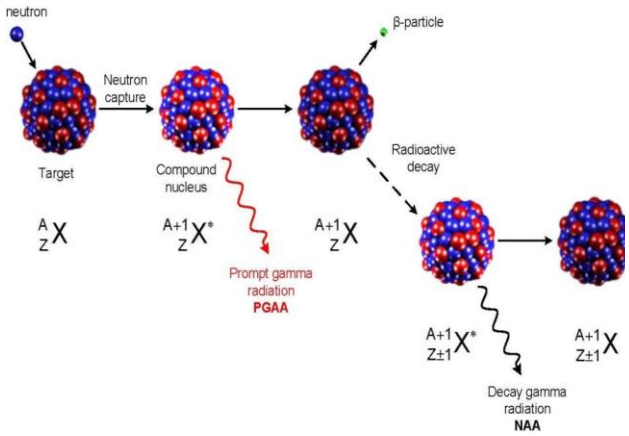

Fig 1: Schematic illustration of the physical phenomena involved in Neutron Activation Analysis (Hamidatou *et al.*, 2013).

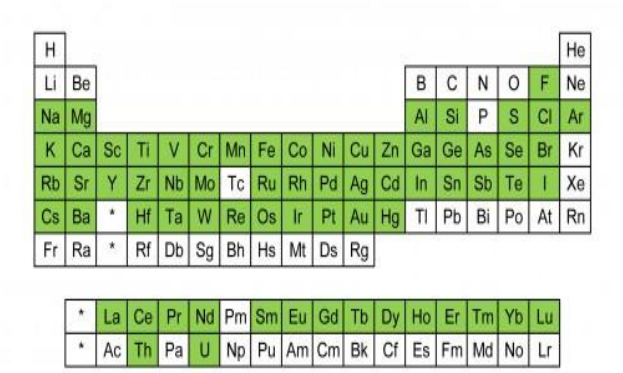

Fig 2: Shaded elements are detected by NAA (Kubešová, 2016).

NAA has several advantages and a few disadvantages. These are summarized below (De Corte, 1987; Avino *et al.* 2007; Win, 2004; Kogo *et al.*, 2009; Gwarzo *et al.*, 2014; Win, 2004; IAEA, 2001; Kučera and Řanda, 2001; Kubešová, 2016):

Advantages:

1. Wide possibilities of applications for different types of samples
2. Low detection limits down to 10^{-6} mg·kg^{-1}
3. The relative freedom from interference and matrix effects.
4. The possibility of non-destructive analysis
5. The high specificity based on characteristics of induced radionuclides.
6. A completely independent nuclear principle, in contrast to electron nature of most of other analytical methods.
7. The method is theoretically simple and well understood, which makes it possible to evaluate and model sources of uncertainty of results.
8. The neutron energy and neutron flux density can be chosen to certain extents, which allows obtaining of the best results using simple optimization means, such as selective activation.
9. The isotopic basis, which makes it possible to use analytically independent routes of determination of many elements and to cross-check the results, obtained using so called internal self-verification principle.

Disadvantages:

1. The need of a nuclear reactor
2. The use of highly radioactive materials and the resulting consequences
3. The feasibility of determination of traces of some toxicologically important elements, such P, Cu, Ga, Ge, Gd, Y, Nb, Mo, Pr, Mn, Dy, Er, Hg and Pb is limited, because they do not form radionuclides with suitable properties
4. Samples for NAA should preferably be dried (or freeze-dried), because the presence of water radiolysis occurs on irradiation in a nuclear

reactor. This may increase pressure in the sample container and may cause explosion during handling.

5. The time of analysis can be quite long; up to about six weeks for elements, which produce long-lived radionuclides.
6. NAA is not available as a simple apparatus with software, which can easily be operated in any analytical laboratory.

For the solid minerals, NAA, especially INAA, has always played an important role in characterizing raw mineral materials, such as ore bodies and other valuable raw materials. The main task of NAA was not only to determine the elements of interest, but also to study various inter-element correlations, such as those of rare earth elements, which help in elucidating of origin and formation of geological structures. Nigeria has a Miniature Neutron Source Reactor which is designated as NIRR-1. NIRR-1 is the first Nigeria research reactor and its first criticality was achieved on 03 February 2004. It is specifically designed for use in NAA and limited radioisotope production (Jonah *et al.,* 2007). NIRR-1 has a tank-in-pool structural configuration and a nominal thermal power rating of 31 kW. It is located at Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria. A number of authors have used NIRR-1 for NAA of solid minerals.

Isaiah *et al.* (2015) analyzed Nigerian coals from Enugu and Okaba using NAA and found that seventeen elements were detected from Enugu coal while sixteen were present in Okaba coal with a total of twenty two elements detected from either the Enugu or Okaba coals. The elements found in both Enugu and Okaba were Al, Ti, K, Na, V, Mn Ba, La, Th, Hf, Fe, and Cr while that found in only Enugu were Lu, Ta, Rb, Eu and Co and elements found in Okaba are Sc, Br, Yb, and U. For coal an energy source, the major elements of interest are carbon, oxygen, hydrogen, nitrogen and sulphur. However, as can be seen from Fig 2, NAA cannot be used to detect these elements; Isaiah *et al.* (2015) results confirmed this. Ewa (2004) also used NAA determined element abundances (Al, As, Ba, Br, Ca, Ce, Cs, Dy, Eu, Fe, Ga, Gd, Hf, K, La, Lu, Mg, Mn, Na, O, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, Ti, U, V, Yb, Zn and Zr) of prepared and run-of mine coals from eight principal mines (Onyeama, Ogbete, Enugu, Gombe, Asaba-Ugwashi, Okaba, Afikpo and Lafia) in Nigeria. Ogugbuaja, and James (1995) also used NAA to analyse Nigerian bituminous coal and ash. Funtua *et al.,* (2012) evaluation of the composition of some geo-standard reference materials (Fly ash 1633b, SO-2, SARM-1, SARM-52, W-2, DNC-1, BIR-1, AGV-1, IAEA SL-3, and IAEA Soil-7) using NAA and their results indicated an insignificant maximum deviation error of 0.304 to 0.393% in all the geo-standard reference materials.

3. PROTON INDUCED X-RAY EMISSION (PIXE)

PIXE is based on the fact that irradiation of a material with proton or other charged particles of a few megaelectron volts per nucleon gives emission of characteristic X-rays of the present elements. PIXE analysis consists of two parts. The first is to identify the atomic species in the target from the energies of the characteristic peaks in the X-ray emission spectrum and the second part is to determine the amount of a particular element present in the target from the intensity of its characteristic X-ray emission spectrum. This normally requires knowledge of the ionisation cross-sections, fluorescence yields and absorption coefficients. Depth profile analysis may be performed if the PIXE is combined with other methods like Rutherford Back Scattering (RBS) and/or sample etching techniques (Govil, 2001).

The basic principle of PIXE analysis is shown in Fig 3. If an atom is ionized on an inner shell, its energy state is less stable than that of a simple ion. First, before any chemical reaction, it should lose energy. The energy loss usually takes place by the emission of a photon. These photons are called characteristic X-rays because they characterize the elements emitting them (Nagy, 2009). The incident ions themselves may undergo further elastic or inelastic scattering during the collision. The excited target atom seeks to regain a stable energy state by reverting to its original electron configuration. In doing so, the electronic transition, which takes place, may be accompanied by emission of electromagnetic radiation in the form of X-rays characteristic of the excited atom. The emission consists of K, L, M,... lines produced by electron transitions to the K, L, M,... shells of the target atom (Govil, 2001). These X-rays are usually detected by using a solid-state detector such as a Si(Li) detector and the spectrum obtained results in qualitative and quantitative information on the elements of interest (Alfassi and Peisach, 1991).

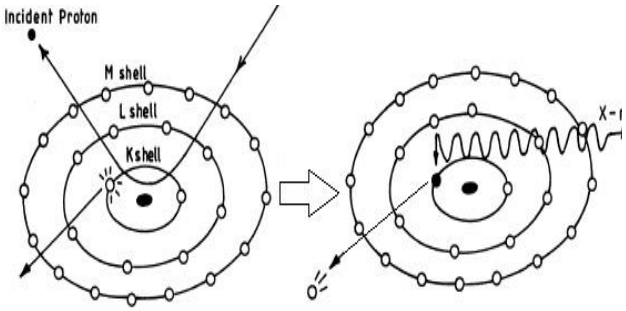

Fig 3 Basic Principle of PIXE analysis

Elements that can be detected using the PIXE are: Ca, Si, Mg, Mn, Al, Fe, K, Ti, V, S, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Pb, Bi, P, Sr, Cl, Zn, Na, Cr, Co, Cu, Ni, Ge, Ga, As, Se, Br, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th and U

(Deconninck, 1976; Ene *et al.,* 2009; Akpan *et al.*, 2011). Some of the advantages and disadvantages of PIXE are the followings.

Advantages:

1. PIXE is able to detect between 10 – 20 element, making it a multi-element detector
2. It takes the PIXE about 17 minutes to complete a single analysis, making it a fast analyzer
3. In most case, sample does not need preparation
4. Just a little amount of sample is required during sampling and detection
5. It cost very little to run a sample using the PIXE
6. PIXE is non-destructive during analysis
7. It is easy to focus on very small sample area of less than $1mm^2$

Disadvantages:

1. During irradiation, volatile compounds could be lost
2. PIXE functions better in a well-equipped accelerator facility
3. Samples containing liquid must be dried before irradiating to avoid explosion

PIXE needs a collimated beam of positively charged particles. This can be produced by a radioactive alpha source or by particle accelerators. The Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria has a 1.7MeV Tandem accelerator that can be used to produce proton beams. A number of authors have used this facility to PIXE analysis of solid minerals. Akpan *et al.* (2011) carried out PIXE analysis of Yandev and Odukpani limestone deposits using proton beams produced by Ion Beam Analysis (IBA) facility at the CERD, They concluded that all waste from industries mining the limestones (especilally the one from Yandev deposit) should be closely monitored since it was found to contain some rare earth elements (Ti, S, Rb, P, Mn, Sr, Cl and Zn). Wilberforce (2015) analyzed four different tubers and the soil where they were grown within Enyigba lead-zinc derelict for heavy metals using PIXE technique. The results revealed that heavy metals in soil decreased in the order Pb > Zn > Cu > Mn > Cd > Ni > As > Cr. PIXE was used by Abdullahi (2012) to characterize fourteen geological samples collected from North-Western Nigeria to determine concentration of zirconium (Zr) and other trace elements. The result obtained indicated that zirconium is of commercial deposit at some of the regions. Alongside zirconium, Fe, Cu, Rb, Cd, Ba, Ce, W, Bi, and Sn were determined. Also element Fe and Cu concentrations appears to be deposited in commercial quantities. Abdullahi and Funtua (2012) used PIXE to characterize Lead and other elements in fourteen samples of gold ores from North Western Nigeria. Olabanji, (1991), on the other hand, used PIXE with the protons produced from another accelerator in Lund to measure the concentrations of the major, minor and trace elements in Nigerian coal samples. The results show that Nigerian coals have a low (0.82–0.99)% sulfur content.

4. CONCLUSIONS

Two of the available nuclear techniques (NAA and PIXE) for analyzing solid minerals have been presented. NAA has many advantages and few disadvantages. Luckily, Nigeria has a nuclear reactor which is required for NAA. PIXE is a multi-element detector and a fast analyzer. PIXE also requires a proton or particle generator such as an accelerator which is available in Nigeria. Available evidence indicate these facilities can be used to analyze solid minerals such as coal, gold, phosphate, bitumen, zirconium, copper, cadmium and other trace elements in the country. Both NAA and PIXE are non-destructive during analysis and require that the sample be irradiated before being analyzed. Despite the numerous applications that have been enumerated in this work, there is no clear Nigerian National Policy on the use of nuclear and radiation technology in the solid mineral industry and we recommend that one should be put in place by Federal Government.

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