

Characterisation and processing of some selected Nigerian solid mineral samples using short-lived nuclides of Neutron Activation Analysis (NAA)

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ABSTRACT

Two Nigerian iron samples, siderite and iron pyrite were analysed for minor and trace elements using short-lived nuclides of neutron activation analysis (NAA) technique. Results obtained showed that siderite contains traces ($\mu\text{g g}^{-1}$) of aluminium and manganese, while zinc was found to be a major element (34.4%) of iron pyrite along with traces of aluminium, manganese, samarium, chromium, barium dysprosium, copper and sodium. Due to the short life span of the nuclides, iron the major element in these ores could not be determined using NAA, so classical analytical techniques were used. It was found that iron pyrite contained 55.97% Fe and siderite contained 63.19% Fe. Other parameters like ash content, acid insoluble ash, moisture content, density were also determined. The results also show that iron pyrite and siderite have high contents of iron that may be exploited for production of iron salts and reagents for use in the laboratory.

INTRODUCTION

Nigeria like any nation in the world is blessed with abundant natural mineral and human resources. The economic development and growth of any nation depends upon how effectively these groups of natural resources are exploited. For a country to produce any commodity for sale and export, the known resources must be efficiently processed to marketable and competitive product. Every part of Nigeria is rich in one mineral resource or the other [1-2].

Most of the known resources in Nigeria still remain at the raw material level because their location have not been exhaustively identified and some of those identified have not had their actual quantities determined, surveyed and exploited [3-4]. These initial stages must be overcome before meaningful exploitation, refinement and exploration of the derivable project can happen [1-6].

In the past, especially during the colonial era, most of the mineral resources were mined and exported unprocessed, hence attracted little or no value thereby having low price with minimal effect on the economy. With the advent of structural adjustment programme (SAP) and the consequential downturn in the economy, the need to develop and diversify our resources to the quality that can be used as raw materials for our industries, higher institutions and also quality goods for export became expedient [3]. This led to the establishment of the Raw Material Research and Development Council (RMRDC), which was charged

with the responsibility to survey, map and advertise the nations raw materials, aiming at the eventual processing for industrial requirements and also for export [1-4]. There are many minerals such as fossil fuels, solid minerals and energy minerals. Fossil fuels include petroleum, natural gas, coal, lignite, bitumen and asphalt [5-9]. Solid minerals include iron ores, silver, gold, manganese, chromite, sphalerite, galena, iron pyrite, siderite and gypsum to mention a few. Energy minerals are the radioactive minerals that can be used to produce energy using nuclear reactor. Principal among energy minerals include uranium, plutonium and rare earth metals [7-9].

In this paper, efforts have been made to characterize and analyse two iron samples namely iron pyrite and siderite for major, minor and trace elements using short-lived nuclides of neutron activation analysis (N.A.A.). Classical analytical techniques were employed to determine other parameters.

Permanent sources of iron ore include China, Brasil, U.S.A., Russia, Ukrain, Canada, South Africa, Sweden, Liberia, Venezuela, Nigeria to mention a few [5-9]. In Nigeria sources of iron ore are South and North of Onitsha and Abah in Anambra state, Abakaliki, Onitsha and Ikon in Ebonyi State, Enugu South in Enugu State, Itakpe in Kogi State and Wukari in Taraba State of Nigeria. While the main sources of siderite and iron pyrite are South-West of Abakaliki in Ebonyi State, Ameri, Ameka, Enyeba, Onitsha toll gate and Enugu State. The exploitation of iron in Nigeria has not yet fully taken off due to the nation's economic

problems and the global steel glut. However, iron and steel industries have been built, using imported raw materials. The need to fully assess our local resources is very paramount. To accomplish this, the choice of multi-elemental technique such as the NAA technique has been used to obtain the much needed comprehensive information about the ores [9-14]. Neutron activation analysis based on thermal neutrons from a nuclear reactor in combination with high resolution gamma ray spectrometry was used. This method has the advantage of sensitivity, high level of accuracy and precision, and highly versatile in characterizing environmental, mineral, clinical, and food samples [9-23]. The samples siderite and pyrite were analysed along with the certified sample BCR-146, using the short-lived nuclides of neutron activation analysis. The major components of these minerals hitherto unaccounted for by this technique were determined using classical methods.

MATERIALS AND METHOD

Sample collection and preparation

The siderite and pyrite samples were obtained from Onitsha toll gate in Anambra State and Abakaliki in Ebonyi State of Nigeria. The certified reference sample was supplied by International Atomic Energy Agency, Vienna-Austria. The samples were prepared for both neutron activation analysis [NAA] and the classical analytical determination by grinding the siderite and iron pyrite samples into small pieces with heavy hammer and crushing machine in the Chemical Engineering Department of Ahamadu Bello University and regrinding into semi-powder at Geology Department, Ahamadu Bello University, Zaria. The powdered sample was regrinded using the finest sieve of the grinding machine. This was refined by regrinding the fine powder using agate portable mortar. The samples were divided into two portions and each portion was stored in the polyethylene plastic containers for NAA and classical analysis.

Neutron activation analysis

1.0 gram of each of the samples and the certified references sample BCR-146 was accurately weighed into NAA polythene capsules, and inserted into aluminium capsule and irradiated for 3 minutes and cooled for 5 minutes before counting the Ge/ Li detector coupled to a multi-channel analyzer. The facility of the international Atomic Energy Agency's Reactor centre, in Vienna, Austria was used for this purpose.

Classical Analysis Method

The parameters that could not be determined by neutron activation analysis [NAA] were determined by various classical techniques (8). Parameters of interests included moisture content, acid insoluble ash content, density content loss on ignition contents, Nickel, iron and sulphur contents.

The pyrite prior to milling into fine powder was weighed in order to determine the density of the ore. The moisture content was determined by drying the sample in air oven set at 105 degree C until constant weight was obtained in the ore sample.

Ash content and loss on ignition were determined by igniting a weighed sample at 850 degree C in Gallenkamp Muffle furnace for five hours. The acid-insoluble ash content of the samples were determined by weighing 1.00g each of the ore and dissolved in 1.1 concentrated hydrochloric acid (HCl) and distilled water. The resulting product was filtered using a sintered glass funnel. The filtrate was collected and made up to 250 cm³ with distilled water in a standard flask. The residues obtained was the carbonized and ignited at 860 degree C, and determined as the acid-insoluble ash content of the ore sample. The filtrate solution made, was used as a stock solution of the ore for subsequent analysis.

The iron [Fe] content was determined gravimetrically using cupferron as the precipitant from homogeneous solution. 25 cm³ cube of the ore stock solution was mixed with 10 cm³ cube of 1% w/v solution of cupferron and small quantity of 2M NH₄OH solutions for the generation of the precipitate. The precipitate was collected on an ashless filter paper [No. 40] for carbonization and ignition as 550 degree C. The resulting residue was weighed and determined as Fe₂O₃.

Nickel was also determined gravimetrically as Nickel dimethylglyoxime. 25 cm³ cube of the aliquot stock solution was withdrawn and mixed with 10 cm³ cube of alcoholic solution of dimethylglyoxime and enough quantity of dilute ammonia solution was added to generate the desired precipitate. The precipitate obtained was quantitatively collected on pre-weighed ashless filter paper, dried at 150 degree C and weighed as the Nickel complex (8). The sulphur content obtained from HNO₃ digestion of the ores, notably the iron pyrite were collected, dried and weighed.

RESULTS AND DISCUSSION

The Table 1, shows the result of the neutron activation analysis of BCR-146, the certified reference material, while similar analysis carried out on siderite and iron pyrite are shown in Table 2. Table 3 contains the result of the classical analysis of the ore samples.

From Table 1 it was evident that the results obtained from the neutron activation analysis of BCR-146 compared favourably with the certified value obtained for this sample. For instance, the concentration of Al, Mn, V, Mg, Na and K were similar to their

Table 1: Neutron activation analysis of BCR-146 a certified reference sample

Element	Certified value	NAA value	NAA/certified value
Al	29.9 ±14	29.9 ±2.0	1.01
Mn	588 ±24	681 ±30	1.16
V	38.0 ±2.0	441 ±2.0	1.16
Mg	16.2 ±2.0	23.1 ±2.0	1.42
Na	220 ±20	2500 ±22	1.13
K	5100 ±50	6130 ±6.0	1.2
Sm		4.52 ±0.5	
Cl		510 ±10	
In		0.28 ±0.01	
Ba		2280 ±30	
Sr		248 ±10	

Concentration in µg/g

Table 2: Concentration of elements in iron ore samples

Element	Siderite	Pyrite
Zn	Nd	34.4 ±0.31
Al	1140 ±10	1130 ±11
Mn	6550 ±64	1710.1 ±10
Sm	Nd	35.1 ±2.0
Cl	Nd	200 ±3.0
Ba	Nd	446 ±10
Dy	Nd	7.52 ±1.0
Cu	Nd	817 ±50
Na	Nd	161 ±2.0

Concentration in µg/g

Table 3: Concentration of elements using classical methods

Parameter	Siderite	Pyrite
Ash content	97.5	74.7
Loss on ignition	2.51	25.3
Acid-insoluble ash	84.74	13.63
Iron	63.29	56.98
Nickel	Nd	5.35
Sulphur	Nd	15.37
Density (g/cm ³)	3.84	3.93

Concentration in %

respective certified values. The ratio of NAA to certified value for these elements were close to 1.0. In addition, other short-lived nuclides were also detected

and determined in the sample. These elements occurring in trace amounts include, Sm, Cl, In, Ba and Sr. To a great extent, this technique could be relied upon for accurate, precise and reproducible analysis of samples with complex matrix.

The results of neutron activation analysis of the ore samples reported in Table 2 showed that siderite contained only two elements, which are Al and Mn in measurable quantities. The iron pyrite also an iron rich sample was found to be rich in Zn, which accounted for 34.4% of the ore. On the other hand, Al, Mn, Sm, Cl, Ba, Dy, Cu and Na were determined in measurable quantities in this sample. The occurrence of zinc in the ore may be attributed to simultaneous crystallization of both minerals out of a common melt or deposition of ore bearing melts from independent sources in the same rock vein. The Abakaliki mines is reputed for lead and zinc ores. The solid mineral was brownish-gray in colour, and it was readily soluble in concentrated nitric acid to give a yellow coloured salt, hydrogen sulphide and sulphur.

From results of classical analysis shown in Table 3, the two ores had similar density (siderite, 3.84gcm⁻³ and pyrite, 3.93gcm⁻³). The siderite was a white marble-like stone with grayish metallic spikes or encrustation within it, while the pyrite was a brownish-grey stone with dull metallic appearance. The iron content of the siderite was found to be 63.29% while that of the pyrite was 56.98%. The high iron content of the siderite ore was probably responsible for the high ash and the acid insoluble ash contents and the relatively high silica content in the ore sample. The ore was readily soluble in hot HCl to give a reddish-brown solution of ferric chloride.

The pyrite on analysis was found to contain 56.98% iron, 15.37% sulphur and 5.35% nickel. These three elements were the major elements as determined by classical analysis and nic was determined as another major element by neutron activation analysis. The ore was readily soluble in hot nitric acid giving a solution of iron salt and sulphur, and hydrogen sulphide and nitrogen dioxide as byproducts.

CONCLUSION

The neutron activation analysis (NAA) complemented with the classical technique have been found useful in this analysis. Siderite was found to contain 63.29% of Fe and Al and manganese as trace elements. The ash content of siderite was found to be high and acid insoluble. Pyrite ore was found to contain sulphur, zinc and nickel as bulk elements. The two ores were found contain high concentration of iron and therefore can be exploited for commercial purposes.

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