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The Determination of Zirconium from North-Western Nigeria using PIXE Technique

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ABSTRACT

Proton induced X-ray emission (PIXE) technique was used to characterize fourteen geological samples collected from North-Western Nigeria to determine concentration of zirconium (Zr) and other trace elements. Samples were irradiated and analyzed at Centre for Energy Research and Development, Ile-Ife, Nigeria. 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.

Keywords: *PIXE, zirconium, Ile-Ife, Nigeria.*

1. INTRODUCTION

Zirconium has found usage in many areas of scientific application, notably as shield in nuclear reactor fuel. Zirconium is especially suitable in water-moderated reactors because of its low neutron-absorption cross section as well as an excellent corrosion resistance at moderately elevated temperatures, strength, ductility, and ease of fabrication. The high ionic conductivity (and a low electronic conductivity) makes it one of the most useful electroceramics [1].

Zirconium obeys traditional power-law creep with a stress exponent of approximately 6.4 over stain rates and temperatures usually associated with the conventional "five-power-law" regime. The measured activation energies for creep correlated with the activation energies for zirconium self-diffusion.

Consequently, dislocation climb, rather than the often assumed glide mechanism, appears to be rate controlling. The common zirconium alloys (*i.e.*, Zircaloys) have higher creep strength than zirconium. The stress exponents of the creep data in the five-power-law regime were determined to be 4.8 and 5.0 for Zircaloy-2 and Zircaloy-4, respectively. The creep strength of irradiated Zircaloy appears to increase relative to unirradiated material [2]. Again the review of 5 years clinical outcome and survivorship of a ceramic-surfaced oxidized zirconium femoral component implanted during 98 primary TKAs between April 2001 and December 2003. Survivorship was 98.7% at 7 years postoperatively. No revision was necessary and only one component failed because of aseptic loosening. Mean Knee Society score improved from 36 to 89. No adverse events were observed clinically or radiologically. These results justify pursuing the use of oxidized zirconium as an alternative bearing surface for a femoral component in TKA [3].
This work focused on establishing the accurate knowledge of zirconium content and other trace elements in North Western Nigeria.

2. MATERIALS AND METHODS

Fourteen samples collected across North-Western Nigeria were crushed to small pieces using mechanical crusher. The crushed samples were dried at 105 ^{o}C to constant weight. The dried samples were ground to form fine powder. Then the powdered samples were sieved using a standard set of sieves to a diameter range of less than 125. Every powdered sample was shaken using an electric shaker to be sure that the sample was homogenized. From each of the fourteen balk samples, pellets were made by hydraulic press (3 ton). Standards (NIST 278, BCS 355) were irradiated by thick target proton induced X-ray emission with 2.5 MeV and 3.0 MeV proton beams accelerator for accuracy and validation. The proton beam was collimated.

Characteristic X-ray were measured by three detectors, one detector was placed at 45^{0} for PIXE, the other at 135^{0} for Rutherford backscattering spectroscopy (RBS) and the third detector was for proton induced gamma ray emission (PIGE). Table 1 display the quality control from the standard reference material (SRMs) (Graham et al, 2002). Thereafter the pellets were subjected to same analytical conditions as the SRMs, subsequently analyzed by GUPIX (a program for the non-linear least-squares fitting of P1XE spectra).

Table 1: Elemental concentrations (ppm) in selected reference materials using PIXE.

	NIST 278 (Obsidian rock)		BCS 355 (Tin ore)	
Analyte	Reported value	This work	Reported value	This work
Si	341436	342392.3±9039	5000.0	5152.6±484
Cl	NA	609.1±140	NA	321.3±187
K	3453	3465.8±148	-NA	3215.6±562
Ca	7025	7057.4±114	2630	2688.5±528
Ti	1468	1475.9±30	3700	3693.7±76
Mn	403	378.8±15	NA	1795.6±39
Fe	14268	14321±72	170800	170282.8±255
Cu	5.9	6.4±7.3	850	848.8±35
Zn	55	56.4±17.3	590	589.5±32
Rb	127.5	127.8±21	-	-
Zr	NA	265.3±48	-	-
Cr	-	-	NA	60.7±25
As	-	-	1400	1398.5±50
Sn (K)	-	-	314200	314901.4±4881
Sn (LA)	-	-	314200	314969.2±1134
Ba	1140	1144.1±229	-	-
Ce	62.2	65±32	-	-
Cd	-	-	NA	1070±577
W		-	3500	3491.7±152

NA: Not analyzed.

2.1 PIXE Calculations

The formula for calculating concentration [$Y(Z)$] in PIXE is given as:

$$Y(Z) = \frac{N_{av}\omega_Z b_Z t_Z \varepsilon_Z^{i\Omega/4}}{A_Z} N_p C_Z \int_{E_0}^{E_f} \frac{\sigma_Z(E) T_z(E)}{S_M(E)} dE$$

……1

Where N_p is the number of protons, Nav Avogadro's number, and σ_z (E) the K-shell ionization cross section for the proton energy E corresponding to depth x. The number of K X-rays in a particular spectral line is then obtained via the fluorescence yield $\omega_{k,z}$ and line intensity fraction $b_{k,z}$.

If we generalized angle α and Θ_{TO} for proton impact and X-ray take off en route to the detector, the X-ray intensity from the element of the path indicated suffers a transmission factor When specimens are thick enough to stop the beam, then we have $E_f = 0$ in Eq. 1. The matrix (M) effect (i.e., those due to proton slowing and X-ray attenuation) are contained in the

integral, which we denoted by $I_Z(M)$ where M denotes the specimen (SP) or the standard (ST).

$$\frac{C_Z(SP)}{C_Z(ST)} = \frac{Y_Z(SP)}{Y_Z(ST)} \frac{I_Z(ST)}{I_Z(SP)} \quad \ldots\ldots\ldots\ldots 2$$

Standards are usually single elements or very simple compounds containing the elements of interest or their near neighbors in the chart of nuclides.

The merit of this ratio process is its cancellation of instrumental factors such as solid angle, efficiency, and calibration factors for charge integration (Aung, 2002). This is important given the practical difficulties in obtaining accurate knowledge of the detector's lineshape and intrinsic efficiency at the low X-ray energies characteristic of the light elements that are so often the major elements in environmental specimens (Sven, 1995).

3. RESULTS AND DISCUSSION

The reported data is for the following elements: Fe, Cu, Rb, Cd, Ba, Ce, W, Bi, Sn and Zr. Zirconium were found to be deposited at several thousand times above the enrichment factor Figure I indicated the energypeaks of zirconium and other trace element in their channels against the count rate at the vertical. . We suggested that further investigation be carry out with a comparative technique to eliminate statistical errors associated the method used before exploitation can be embarked upon.

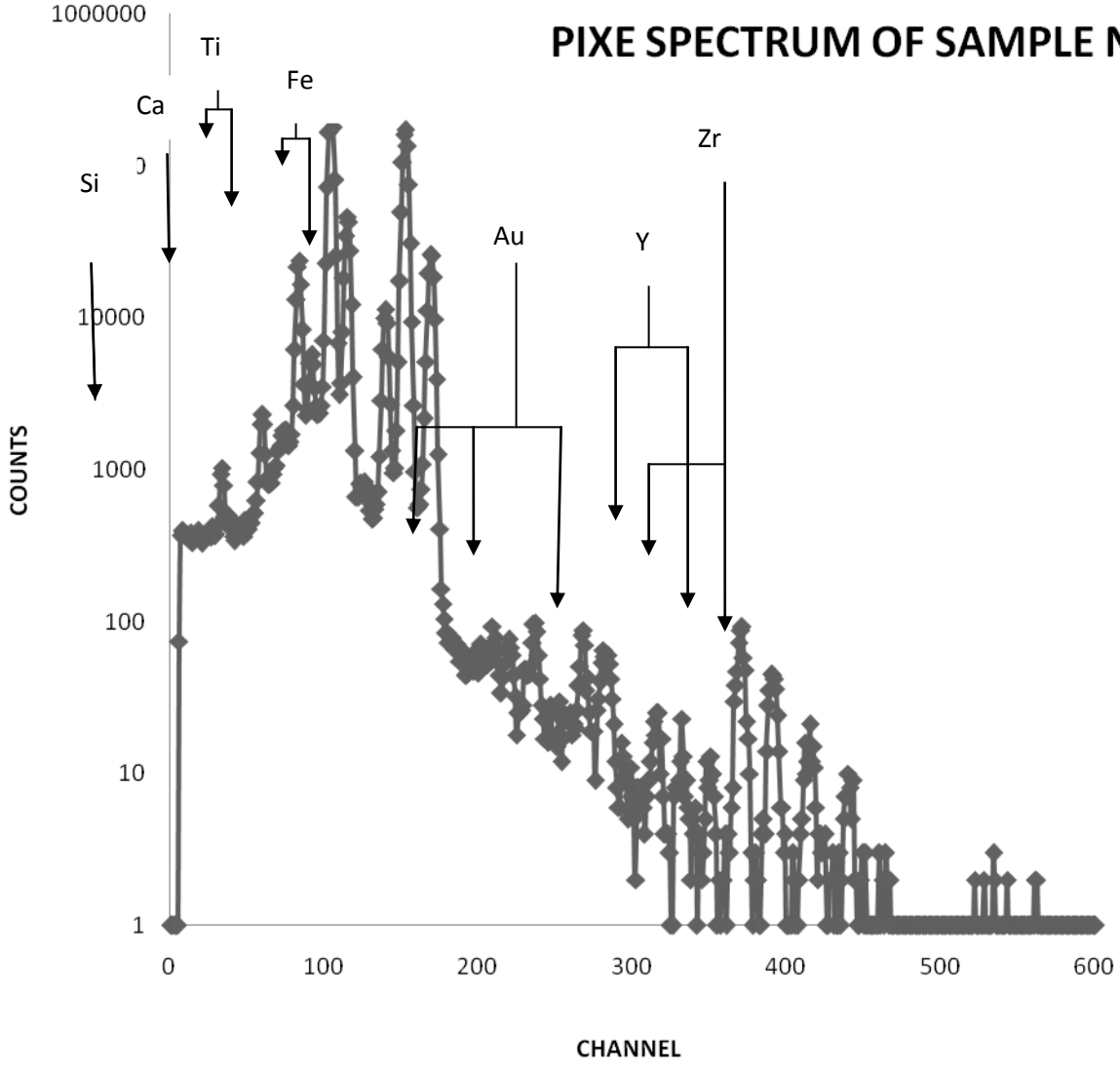

Figure 1: X-ray Spectrum of sample N

Table 2: Average Concentration (ppm) of Elements in the Samples

Sample	Fe	Cu	Rb	Zr	Cd	Ba	Ce	W	Bi	Sn
Sample A	48492.2±131	1697.1±35	29±25	87.7±39	1199.7±676	2931.7±321	79±47	759.6±58	226.6±289	BDL
Sample B	3446.1±35	114.2±13	BDL	BDL	BDL	549.7±106	BDL	90±39	82.1±145	727.3±266
Sample C	50494.4±121	847.5±25	BDL	BDL	BDL	288.3±159	32.5±29	432.3±63	BDL	BDL
Sample D	107527.4±204	BDL	BDL	2117.1±111	1073.2±303	BDL	BDL	BDL	BDL	BDL
Sample E	60871.1±128	2318.8±37	38.5±33	58.7±59	BDL	1030.5±305	BDL	299.7±66	BDL	1902.1±915
Sample G	242445.3±291	95.8±18	BDL	3636.9±122	BDL	BDL	BDL	57.6±59	BDL	78.7±226
Sample I	18641.9±71	658.2±19	25.2±24	140.9±45	268±647	BDL	BDL	575.343	250.9±127	BDL
Sample J	58651.9±123	1752.6±34	72.3±33	63.4±63	1020.6±505	1049.9±320	63.7±41	478.4±66	BDL	344.5±248
Sample K	350425.8±350	BDL	BDL	8325.7±177	BDL	BDL	BDL	BDL	BDL	BDL
Sample L	30871±93	981.3±24	34.8±15	157.3±35	BDL	2382.1±175	102.4±34	656.6±42	137.8±146	BDL
Sample M	53405.1±117	2167.6±34	33.6±24	121.9±38	467.2±810	1243.1±394	91.8±46	582.4±55	BDL	634.7±1267
Sample N	240563.6±337	BDL	BDL	4394.7±165	BDL	BDL	1250.9±734	294.7±72	BDL	BDL
Sample P	255474.1±332	BDL	BDL	10731.1±235	BDL	BDL	761.8±698	BDL	BDL	BDL
Sample Q	161424.8±226	BDL	BDL	730.7±62	BDL	BDL	BDL	49.4±44	BDL	BDL

BDL= below detection limit

Some regions in the study area indicated high deposit of Fe and Cu, but Fe seem to be more promising. All the samples have a deposit of Fe at a very high concentration; most at above the norm. Since Nigeria is making frantic effort in resuscitating its iron industries located at Ajaokuta (Nigeria), it would be prudent if these areas are further subjected to comparative analytical scrutiny. Even though not reported in this work, a close look at Fig. 1 indicated gold deposit. In figure 1, several energypeaks of gold are clearly seen, which suggested that gold content in sample N is appreciable.

4. CONCLUSION

From the result discussed, PIXE gave account of its proficiency in the analyses of geological samples. Sample N from site N is recommended for further investigation: the site appears endowed with several trace elements of commercial quantity.

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