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EXAMINATION OF COAL AND ASH
SAMPLES BY PIXE METHOD
FOR GAS TURBINE APPLICATIONS

S. RAJ* R. RAJ** G. HALL *

* Assistant Professor
Department of Chemistry, Rutgers, The State
University of New Jersey

** Associate Professor
Department of Mechanical Engineering & Director
Turbomachinery Laboratory
The City College of New York

ABSTRACT

A new technique, PIXE - Particle Induced X-Ray Emission, for analyzing concentration of trace elements with a detection concentration in parts per million is presented in this paper.

PIXE is performed on a sample by using a proton beam. The experimental results are obtained from a number of coal and ash samples useful for the combined cycle power plants. The technique is useful for deposit analysis and analysis of eroded and corroded surfaces. This technique can identify depth of deposit and chemical constituents simultaneously.

INTRODUCTION

Coal reserves in the United States currently estimated at 283 billion tons present an opportunity and challenge for its usage in various industries. However, for the effective usage of coal in chemical industry and utility, a wide range of problems need to be solved. Based on the application, these problems are not only related to the efficient transformation of polymeric coal structure into the compounds of CH, CH₂, CHOS and CHOSN but also to the direct combustion of coal into oxides of C, N and S. In addition, usage of coal in industry introduces a new dimension to the chemical problems which are related to corrosion and deposition (1). These problems are caused by the inorganic constituents inside the coal.

A number of analytical techniques may currently be employed in the analysis of the inorganic constituents of coal and its products. These techniques are reviewed by Weaver (2) and Fuller (3). An up-to-date state of these techniques is presented in References (4,5). The foregoing analytical techniques are related to atomic absorption, nuclear activation, x-ray fluorescence, x-ray diffraction, mossbauer and scanning electron microscope. Some of these methods are time consuming, some possess lower detection limits, and some do not provide multi elemental detections simultaneously with the depth

profile. The PIXE (Particle Induced X-Ray Emission) technique overcomes the above mentioned difficulties. Johansson et al (6) developed the PIXE technique in 1970. Since then, the PIXE technique has been used in study of aerosol pollutants (7,8), meteoritic samples (9), biological tissues (10), snow (11), rain (12), and uranium ore samples (13). According to Reference (14) the PIXE technique is reliable and repeatable.

In this paper the principle of the PIXE is summarized and experimental results using the PIXE on four coal samples and two ash samples are presented.

SUMMARY OF PIXE PRINCIPLE

The details of PIXE (Particle Induced X-Ray Emission) are given in Reference (6). A summary of this technique is given in this section. PIXE involves bombarding the electrons of K and L shell electrons of an element with a proton beam. These electrons after absorbing the proton energy migrate to higher energy level and leave the vacant spots in K and L orbits. The transition of electrons from higher energy "allowed" orbitals takes place to fill the vacant spot in the K and L orbits. The transition of electrons from higher energy to lower energy orbits accompanies with the emission of electromagnetic radiation. These emissions correspond to K and L x-ray radiations. The wavelength of the produced radiations are characteristics of the elements and varies from element to element. The corresponding K and L x-ray intensities are recorded in the form of a spectrum. The area covered under a peak in the spectrum directly relates to the concentration of individual element.

EXPERIMENTAL SECTION

The experiment program was conducted in three steps. The first step was involved with the generation of the homogeneous beam of protons with a given intensity. The second step dealt with the preparation of samples and exposing the samples to the beam of protons. The third step was carried out to obtain the elemental x-ray spectra and compare it with that of standard elements.

TABLE 1
COAL AND ASH SAMPLES

Sample #	Origin	Rank	%C dmmf	% MM dry
Coal - PSOC 95	Washington	HVA	84.39	23.75
Coal - PSOC 124	W. Virginia	HVA	83.48	9.71
Coal - PSOC 245	No. Dakota	Lignite	73.39	15.38
Coal - PSOC 251	Kansas	HVA	83.73	19.99
Coal - Ash	From coal sample #1			
Coal - Ash	From coal sample #3			

TABLE 2
GENERAL TREND IN
CONCENTRATION OF ELEMENTS (PPM)

Coal Sample	Concentration of Elements Na, Ca, Mg, Fe, Al, Si, K, Ba	Concentration of Elements Se, V, Ti, Co, Zn, Sc, Cr, As, Pb, Cu, Cd, Sr, Sb, Cs, Sm, Th, U
Washington HVA	Hundreds	Under One
W. Virginia HVA	To	To
Kansas HVA		
North Dakota LIGNITE	Thousands ppm	Under Hundred ppm
Coal Ash		
Coal Ash		

The high intensity beam of protons was obtained from Tandem/Van de Graff accelerators. The beam energy was of the order of 4 MeV and was sufficient to detect heavy elements in the sample. The beam passed through a diffuser foil, several collimators and finally through a 25 μm diameter Kapton window. The purpose to pass the beam through a number of obstacles was to scatter the beam to obtain uniformity and subsequently to refocus it to obtain homogeneity. The homogeneity of the beam was checked by using known standard element. The test section where the sample was introduced was filled with helium. The beam when projected on a sample covered an estimated diameter of 8 mm. The Kapton window in the set up was changed every 12 hours so as to avoid pick up of any interaction effects in the final spectra. The Faraday cup was used to integrate the charge. This cup was mounted downstream of the sample. The detection was done by the Ge Princeton Gamma Tech. detector. This detector possessed energy resolution of 150 eV at the Mn 5.9 KeV K line. Several other protective measures were taken in the PIXE set-up to maintain the sensitivity of the experiment. The sample slides were mounted in a slide projector. The insertion and the removal of the slides was controlled automatically.

Coal and ash samples were analyzed as a thin slide on kimfol film. Samples were mixed with an appropriate binding agent and mixture was then transferred on to kimfol film slides. Binding agent used for coal was cellulose acetate (Polystyrene) in toluene where as ash samples were mixed with 6f HNO_3 doped with 100 ppm yttrium. Coal and ash samples were mixed with their appropriate binding agent in the ratio of 300 mg to 300 μl . 50 μl of this mixture were deposited on the kimfol film slides and irradiated directly. Kimfol is a polyvinyl very thin material, easy to handle, resistant to chemical attack and can withstand high proton beam currents.

The concentration of an element in a sample was determined by comparing the area of the K (or L) peak of the element of interest with that of a reference element that contained Argon, Rhodium or yttrium as the internal standard. The standard reference spectra were obtained from bombarding high purity atomic absorption standards in a matrix of boric, perchloric, nitric, and hydrofluoric acid under the same conditions (i.e. target thickness, type of backing and its thickness, integrated charge, and current) as the samples. This normalization procedure removed uncertainties due to x-ray absorption and x-ray production cross-sections.

EXPERIMENTAL RESULTS, DISCUSSION AND CONCLUSIONS

The characteristics of coal samples analyzed by the PIXE methods are shown in Table (1).

Preliminary examination indicates that inorganic constituents in coal are detrital mineral grains and authigenic mineral grains. Major original detrital constituents include montmorillonite, quartz, plagioclase, alkali, feldspar, biolite, chlorite, volcanic glass and rock fragments. Major minerals consist of montmorillonite, chlorite and kaolite, pyrite, gypsum, hemalite, siderite and calcite are formed after diagenesis as a result of geochemically changes during the course of coalification process.

Na, Mg, Al, K, Ca, Ti, Fe, Sc, V, Cr, Mn, Co, Ni, Zn, As, Se, Ru, Ag, Cd, Sb, Cs, Ba, Sm, La, Ce, Yb, Th, U etc. are the inorganic elements responsible for the formation of the mineral matter in coals. Major mineral matter which is not bonded with the organic structure of coal is widely known and can be taken out in the cleaning processes by physical means. However, this is cumbersome, expensive and time consuming process and changes the chemistry of coal. These are also some of the reasons why a direct combustion of coal is encouraged.

In the present investigation powder form of coal samples was used. Therefore, the PIXE analysis of coal samples presented contain elemental concentration of total mineral contents. Fig. (1) through Fig. (6) illustrates the concentration distribution of various major elements in the sample. Some of the peaks are not seen on the plots due to scaling. These hidden peaks represent the elemental concentration of the order of one ppm. In between the adjoining peaks, there are also elements less than 1 ppm which have not been identified due to presence of one of the elements in far excess compared to others and which controlled the vertical scale. Detection of the elements below 1 ppm concentration may be possible in future work. Since it was a preliminary investigation, it provided us an input to set up scales for future work on the coal structure and ash investigation. Nevertheless it was the first effort to analyze coal using the PIXE technique.

Presence of Na, Al, Si, K in large quantities also interfered with the Ar - standard used to identify trace elements. Fe, Ca, Al, Na, Si, K, Mg, Ba, etc. are not trace elements (concentration range is higher). These elements come from pyrite, clays and quartz incorporated into coal during the coalification process. Mn, Co, Ni, V, Zn, Sr, Cr, As, Se, Sm, Pb, Cu, Th, U etc. are the trace elements. Concentration of these elements vary from few ppm to below hundreds.

The results of PIXE analysis are summarized in Table (2). The identified elements and their concentration levels match with the ones obtained from other methods given in Reference (3) which demonstrates the accuracy of the method.

ACKNOWLEDGEMENT

The PIXE spectra were arranged by G. Hall.

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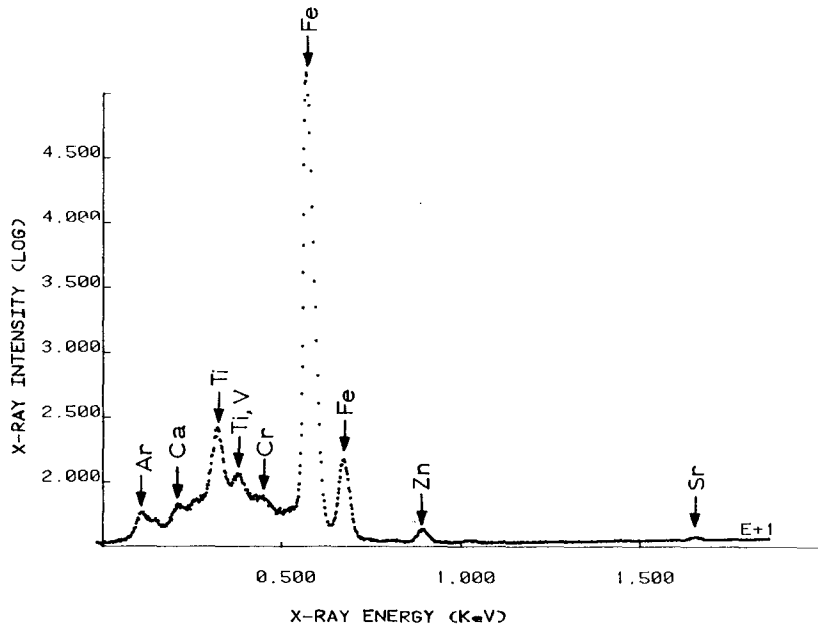


Figure 1 Identification of Inorganic Elements in Sample 1

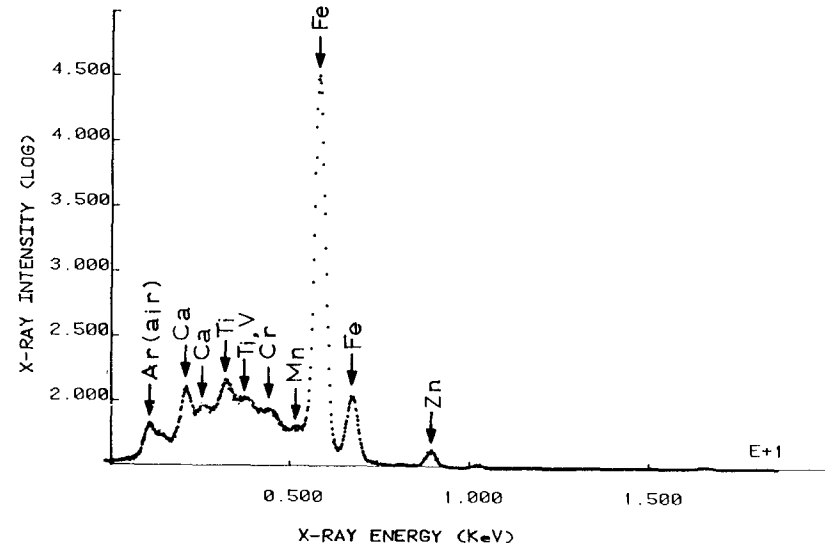


Figure 2 Identification of Inorganic Elements in Sample 2

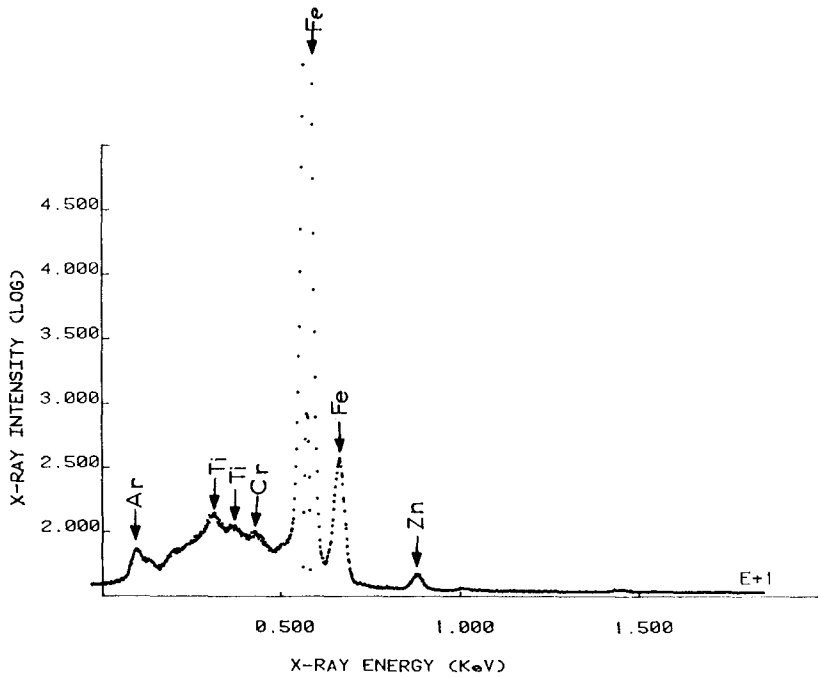


Figure 3 Identification of Inorganic Elements in Sample 3

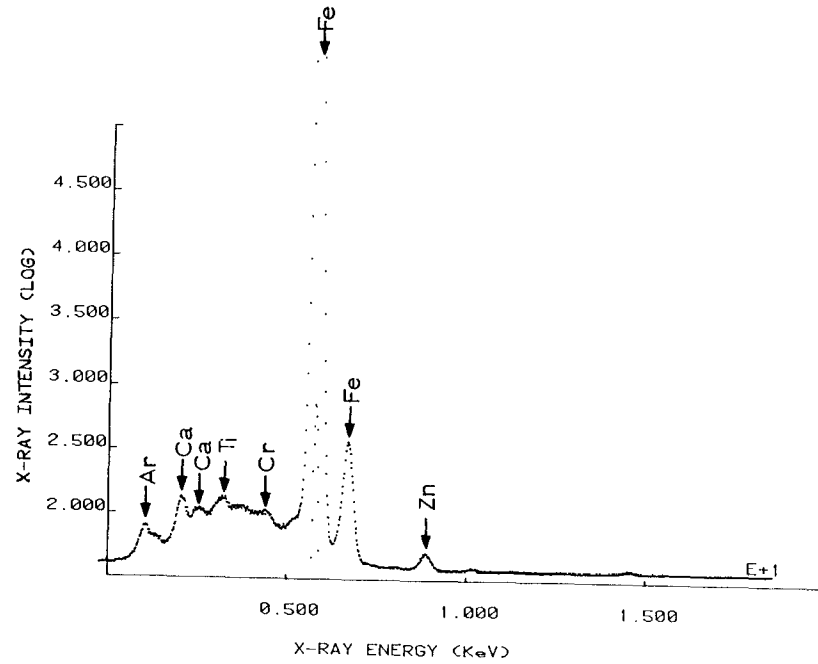


Figure 4 Identification of Inorganic Elements in Sample 4

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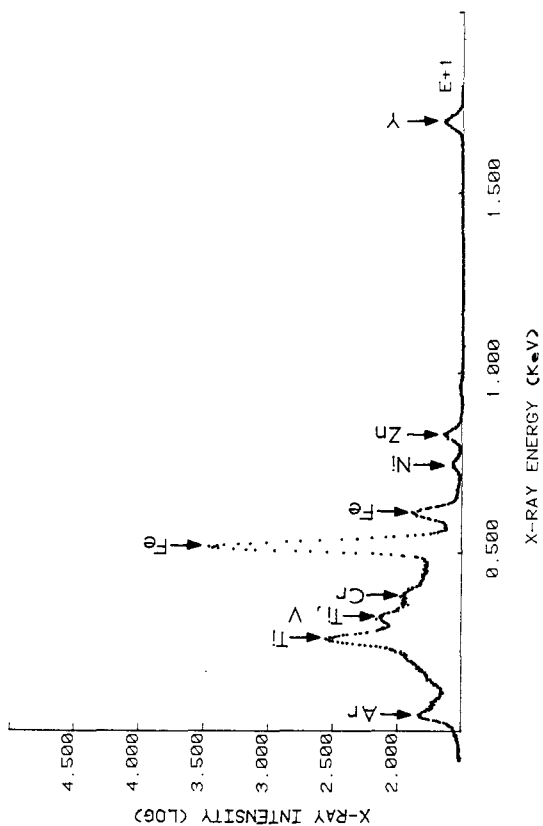


Figure 5 Identification of Inorganic Elements in Sample 5

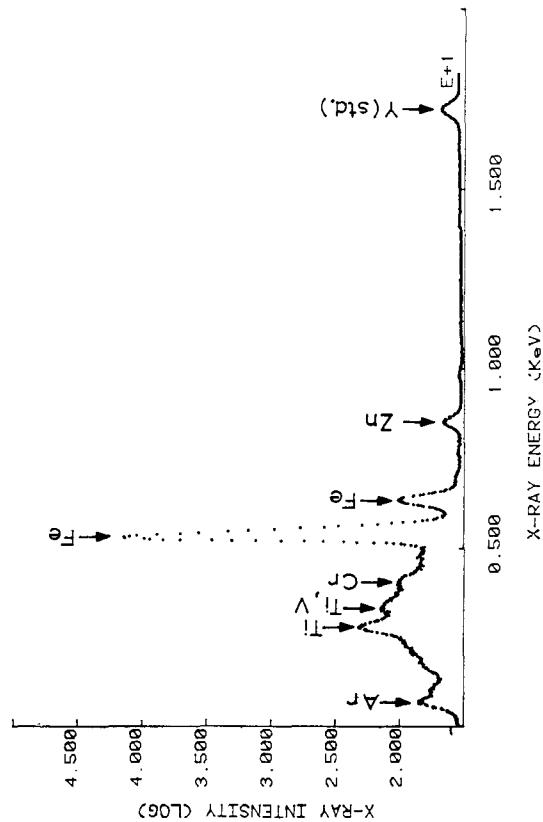


Figure 6 Identification of Inorganic Elements in Sample 6