Investigation and Measurement of Ash Content of Coal in Zirab Coal Mine-Iran Using Dual Energy γ-Ray and X-Ray Fluorescence Methods

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ABSTRACT: *Coal with low ash content has an important role in the coal and steel industry. There are different methods to measure the ash content. The conventional method which is used in most coal mines of Iran, is to burn the coal and measure the remaining ash. A new method has been recently developed at Nuclear Research Center (NRC) of Iran, which works on the basis of the absorption of the dual energy γ-ray by coal. In this paper we present the results obtained from coal mine "Zirab, Central Alborz, Iran" to which we have applied this method, and compared the results with those obtained by the conventional method. In addition, the chemical components of the coal samples from six layers of this mine was obtained by X-ray fluorescence (XRF). We have found that for SiO_2, Al_2O_3, TiO_2, Na_2O and K_2O there exists a linear relationship between these components and the ash content, but such a relationship was not obtained for Fe_2O_3, CaO, SO_3 and MgO.*

KEY WORDS: *Coal, Ash, Dual energy γ-ray, X-ray fluorescence, Chemical Component*

INTRODUCTION

The Zirab coal mine is situated in the basin of the Alborz range in the northern part of Iran. The coal of this mine is of Clarodurite type and their ash contents vary from 1 to 37%. The ash content in these coals have been measured by using dual energy γ-ray and x-ray fluorescence methods [1-3]. In the former method, ^{241}Am and ^{137}Cs are used as sources of low and high energy γ-rays (60 Kev, 7.4 Gbq and 660

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Kev, 0.1 Gbq respectively). These sources are placed in the same container. The source container is positioned below the conveyor belt carrying the coal and an NaI detector is placed above it. Figs. 1-1 and 1-2 show the geometry of the coal analyzer device and typical spectrum of the NaI detector for ^{241}Am and ^{137}Cs. Theoretically, the intensity of γ-rays transmitted through the sample of thickness x is given by:

$$I_1 = I_{01} \exp(-\mu_1 \cdot \rho\, x) + I_{1b} \quad (1)$$

$$I_2 = I_{02} \exp(-\mu_2 \cdot \rho\, x) + I_{2b} \quad (2)$$

where I_{01} , I_{02} and I_1 , I_2 , are the initial and final intensities, I_{1b} , I_{2b} are the background intensities, with μ_1 , μ_2 being the mass absorption coefficients, and ρx is the mass per unit area of the coal. Since $I_{1b} << I_1$ and $I_{2b} << I_2$, by dividing equations (1) and (2), one obtains

$$\mu_1 = \mu_2 \, \mathrm{Ln}(I_1/I_{01})/\mathrm{Ln}(I_2/I_{02}) \quad (3)$$

For ^{241}Am which emits low energy γ-rays, the absorption depends both on the ash content and the mass per unit area of the coal, while for ^{137}Cs which emits high energy γ-rays, the absorption depends only on the mass per unit area of the coal and is independent of the ash content, therefore μ_2 is constant. By measuring I_1 , I_2 , I_{01} and I_{02} one can find μ_1 in terms of μ_2 which is a constant. It is known that there exist the following relationship between the mass absorption coefficient, μ , and the ash content, A^d [2,3]:

$$A^d = a + b\,\mu \quad (4)$$

where a and b are constants which depend on the mine being considered. The values of μ for each sample are measured using a device specially developed in the Nuclear Research Center for this purpose and the values of A^d are measured using the conventional method described in references [4-6]. By fitting a line through the values of A^d and μ , using the least squares method, a and b are found. These values of a and b as well as other parameter, when given to the NRC device, will yields the ash content of an unknown sample. A typical chart of the measurements by computer is shown in Fig. 2 and the histogram of the measurements of a sample by the NRC device is shown in Fig. 3. Furthermore, the ash content of different layers are analyzed using the XRF method. A relationship between the ash content and the chemical constituents of the ash in various layers of the mine were also found. In section "***experimental method and results***", the experimental results are presented and it is shown how the ash content of an unknown sample can be obtained. In section "***analysis of chemical components of ash content by XRF***", it is shown that a linear relationship can be found between some of the chemical constituents of the ash and the ash content in different layers of Zirab coal mine. These relationships can be helpful in determining the chemical composition in different layers of mines and in geological research.

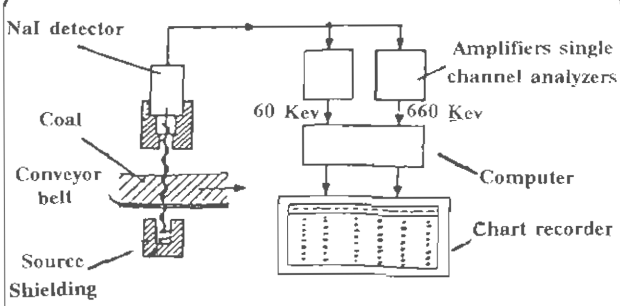

Fig. 1-1: Schematic diagram of the coal analyzer.

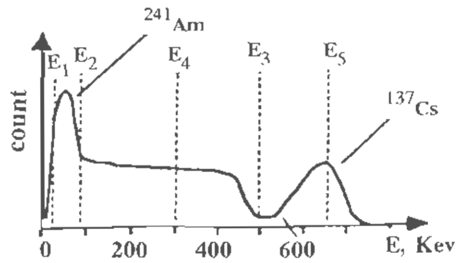

Fig. 1-2: Typical spectrum of NaI detector for ^{241}Am and ^{137}Cs.

EXPERIMENTAL METHOD AND RESULTS

In this method, the ash content of a coal sample is measured using a conventional method. The sample is initially powdered. Then one gram of it is burnt at 850°C for three hours. The resulting ash is weighed and the percentage of the ash is obtained. The mass absorption coefficients of the samples were

Fig. 2: A typical chart showing the computer read out.

No.	Year-mm:dd	hh:mm	A(%)	S(A)%	Km	μ_1(cm^2/g)	m(g/cm^2)	M(t/h)
253	1999-04:20	09:56	43.9	0.25	10.0	0.2370	7.1	70.68
254	1999-04:20	10:00	22.0	0.34	10.0	0.1829	6.2	62.23
255	1999-04:20	10:02	20.9	0.31	10.0	0.1816	6.3	62.58
256	1999-04:20	10:04	22.4	0.34	10.0	0.1834	6.4	63.91
257	1999-04:20	10:06	22.7	0.32	10.0	0.1838	6.4	63.65
258	1999-04:20	10:08	22.2	0.35	10.0	0.1831	6.3	63.02
259	1999-04:20	10:09	22.5	0.34	10.0	0.1835	6.3	62.88
260	1999-04:20	10:12	17.9	0.32	10.0	0.1780	6.5	65.22
261	1999-04:20	10:13	18.1	0.31	10.0	0.1783	6.5	65.03
262	1999-04:20	10:15	20.4	0.32	10.0	0.1810	6.3	62.95
263	1999-04:20	10:17	20.3	0.33	10.0	0.1809	6.3	63.01
264	1999-04:20	10:19	14.8	0.32	10.0	0.1744	6.3	62.59
265	1999-04:20	10:21	14.8	0.32	10.0	0.1744	6.3	62.56
266	1999-04:20	10:24	13.7	0.35	10.0	0.1731	5.6	55.55
267	1999-04:20	10:26	13.3	0.34	10.0	0.1726	5.6	55.74
268	1999-04:20	10:28	15.4	0.32	10.0	0.1751	6.3	62.69
269	1999-04:20	10:29	15.2	0.32	10.0	0.1748	6.3	62.68
270	1999-04:20	10:32	15.4	0.32	10.0	0.1752	6.2	62.01

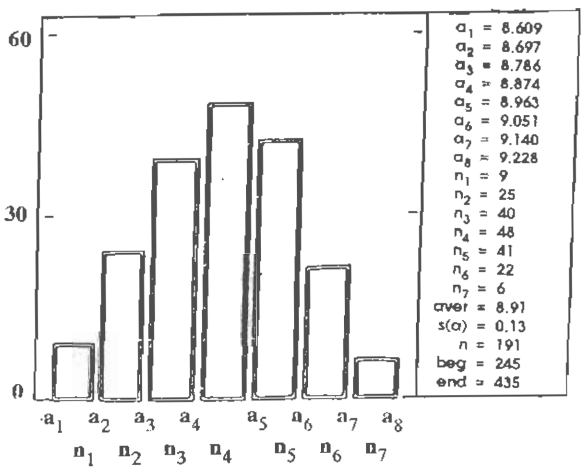

Fig. 3: A typical histogram of measurements on a sample by the NRC device.

also measured using a device developed in the Nuclear Research Center of Iran (NRC device). The results for twenty four samples, all extracted from the same mine, are presented in Table 1.

Considering $A^d_{con.}$ and μ values in Table 1, it is seen that there exists a linear relation between these two values. Using a least squares method, the following relationship is obtain:

$$A^d_{con.} = -132.8534 + 847.2307\,\mu$$

with a correlation coefficient of 0.9974 and a standard deviation of 0.4927. This line which we call the calibration curve, is shown in Fig. 4.

The values obtained for a and b are calibration constants for each mine. These constants along with other relevant parameters are fed into the NRC device. The device is then ready to measure the ash content of unknown samples.

To check the accuracy of the measurements, the ash content of sixteen unknown samples were measured using the NRC device and the conventional method. The results are shown in Table 2.

The following relation is obtained between $A^d_{dev.}$ and $A^d_{con.}$.

$$A^d_{dev.} = 0.0118 + 0.9859\,A^d_{con.}$$

with a correlation coefficient +0.9969, and a standard deviation of 0.4424. It is seen that the slope of the line is very close to unity, indicating that the NRC device gives agreeable results, Fig. 5.

***Table 1:** Determination of mass absorption coefficient and the ash content of the coal using the NRC device and the conventional method respectively*

No.	Computer code	μ (cm^2/gr)	$A^d_{con.}$ (wt%)	No.	Computer code	μ (cm^2/gr)	$A^d_{con.}$ (wt%)
1	466	0.1631	6	13	628	0.1796	20.6
2	467	0.1784	19	14	629	0.1825	22
3	468	0.1687	11	15	630	0.1821	21.7
4	469	0.1658	7.1	16	631	0.1773	18.2
5	470	0.1636	6.3	17	633	0.1667	8.2
6	472	0.1763	17.3	18	635	0.1646	6.8
7	474	0.1721	13.8	19	638	0.1629	5.8
8	480	0.1802	21	20	640	0.1625	5
9	486	0.1726	14.2	21	642	0.1681	10.2
10	621	0.1843	23.2	22	643	0.1807	21.2
11	622	0.1835	22.3	23	645	0.1671	9.1
12	623	0.1852	24	24	647	0.1674	9.9

***Table 2:** The results of the measurement of the ash content using the NRC device, $A^d_{dev.}$ and the conventional method, $A^d_{con.}$*

Computer code	μ (cm^2/gr)	$A^d_{dev.}$ (wt%)	$A^d_{con.}$ (wt%)	Computer code	μ (cm^2/gr)	$A^d_{dev.}$ (wt%)	$A^d_{con.}$ (wt%)
258	0.1831	22.2	22.88	274	0.1736	14.1	14.8
260	0.1780	17.9	17.54	276	0.1733	13.9	14.54
262	0.1810	20.4	20.9	278	0.1758	16	15.67
264	0.1744	14.8	15.48	280	0.1655	7.2	7.41
266	0.1731	13.7	13.37	282	0.1639	5.9	5.55
268	0.1751	15.4	15.18	284	0.1613	3.7	4.34
270	0.1752	15.4	15.66	286	0.1618	4.1	4.26
272	0.1718	12.6	12.27	288	0.1755	15.7	16

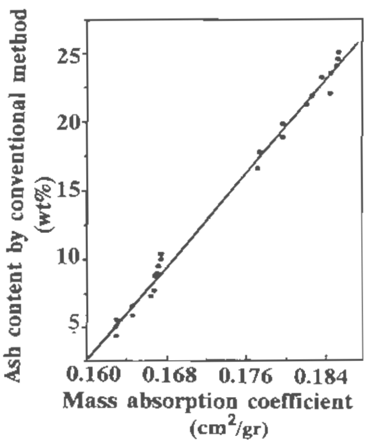

***Fig. 4:** Relationship between ash content and mass absorption coefficient*

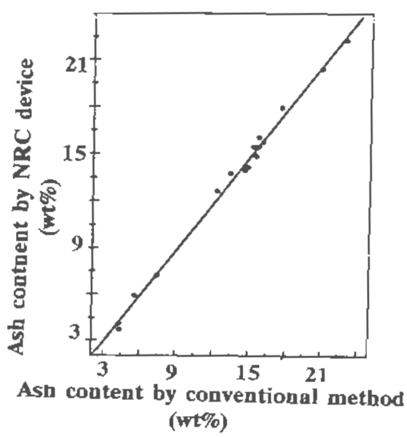

***Fig. 5:** Comparison between meusurement of ash by conventional and the NRC method*

Table 3: The chemical concentration of various components of the ash.

No.	Com.[a]	Con.[b] (wt%)	No.	Com.	Con. (wt%)	No.	Com.	Con. (wt%)
1	SiO_2	54.21	14	Cr	0.0655	27	Au	0.0146
2	TiO_2	1.29	15	Zn	0.0516	28	Ga	0.0145
3	Al_2O_3	29.35	16	Y	0.0317	29	La	0.0131
4	Fe_2O_3	3.14	17	Nb	0.0293	30	Th	0.0098
5	MgO	2.32	18	Sn	0.0036	31	Hg	0.0094
6	CaO	1.15	19	Cu	0.0442	32	Ta	0.0083
7	R_2O[c]	5.00	20	Rb	0.0398	33	U	0.0027
8	SO_3	0.03	21	Mn	0.0334	34	Ge	0.0026
9	P_2O_5	2.35	22	Ni	0.0308	35	Ag	0.0009
10	Sr	0.21	23	Ce	0.0308	36	Sb	0.0009
11	Zr	0.15	24	Pb	0.0211			
12	Ba	0.13	25	Sc	0.0201			
13	V	0.12	26	Co	0.0187			

a) component , b) concentration , c) $R_2O=Na_2O + K_2O$

Table 4: The chemical concentration of the main oxides of the ash from different layers of the Zirab coal mine.

No. (layer)	SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	TiO_2 (wt%)	CaO (wt%)	MgO (wt%)	SO_3 (wt%)	R_2O (wt%)	Depth(m)
1	54.21	29.3	3.14	1.29	1.15	2.32	0.03	5.00	100
2	52.97	28.99	2.34	1.35	1.75	3.39	0.57	4.93	160
3	50.86	28.00	7.92	1.29	1.14	2.31	0.22	4.82	200
4	50.98	25.64	4.74	1.21	2.53	5.49	2.24	4.68	300
5	56.57	24.30	5.18	1.27	2.23	4.94	0.46	4.98	380
6	47.34	25.37	11.1	1.05	1.92	3.73	1.93	4.13	430

Table 5: The ash content and the chemical components of the coal from different layers of the Zirab coal mine.

No. (Layer)	A^d (wt%)	SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	TiO_2 (wt%)	CaO (wt%)	MgO (wt%)	SO_3 (wt%)	R_2O (wt%)	Depth(m)
1	36.62	19.85	10.75	1.15	0.47	0.42	0.85	0.01	1.83	100
2	29.14	15.43	8.45	0.68	0.39	0.51	1.01	0.17	1.45	160
3	34.23	17.41	9.58	2.71	0.44	0.39	0.79	0.08	1.65	200
4	33.15	16.90	8.50	1.57	0.4	0.84	1.82	0.74	1.55	300
5	25.10	14.20	6.10	1.30	0.32	0.56	1.24	0.11	1.25	380
6	10.44	4.94	2.65	1.20	0.11	0.20	0.39	0.20	0.43	430

Analysis of chemical components of ash content by XRF

In each coal mine, the ash content and the chemical components change from one layer to another. To determined the amount of these constituents, coal was collected from six different layers and their ash contents were measured. Then the concentration of various chemical components of the samples were measured by XRF. Table 3, shows the results of the measurement by XRF of a sample for the first layer of Zirab coal mine.

As can be seen from Table 3, thirty six different chemical constituents were found in the ash, in which some of them have a very low concentration and can be easily ignored. Table 4, shows the chemical concentration of the main oxides which are obtained by XRF and Table 5, shows the amounts of the ash content and the chemical components of the coal from all six layers.

Using Table 5, and the least square method the following linear relationships were found between the amount of the various chemical components and the ash content. Linear relationships were also found between the chemical components themselves. The results of these relationships are shown in Table 6.

CONCLUSIONS

The method presented here for measuring the ash of coal is very quick, inexpensive and easy to do. The results show that the precision of the method depends on the accuracy of the calibration curves. A high accuracy can be achieved by preparing appropriate samples, increasing the number of samples and the number of measurements on each sample. The results obtained by XRF show that linear relationships exist between SiO_2 , Al_2O_3 , TiO_2 and R_2O with the ash content, Fig. 6-1. Such linear relationships

Table 6: The relationship between the chemical components with the ash, and between the components.

No.	Relationship	Correlation coefficient	Standard deviation
1	$SiO_2 = -0.3373 + 0.5380\ A^d$	0.9917	0.7468
2	$Al_2O_3 = -0.7026 + 0.2979\ A^d$	0.9821	0.6107
3	$TiO_2 = -0.0256 + 0.0135\ A^d$	0.9938	0.0162
4	$R_2O = -0.0891 + 0.0515\ A^d$	0.9958	0.0507
5	$Al_2O_3 = -0.3661 + 0.5435\ SiO_2$	0.9722	0.7590
6	$TiO_2 = -0.0134 + 0.02449\ SiO_2$	0.9921	0.0183
7	$R_2O = -0.0477 + 0.0952\ SiO_2$	0.9977	0.0378
8	$TiO_2 = 0.0149 + 0.0443\ Al_2O_3$	0.9868	0.0236
9	$R_2O = 0.0714 + 0.1680\ Al_2O_3$	0.9841	0.0982
10	$R_2O = 0.0140 + 3.7916\ TiO_2$	0.9980	0.0350
11	$MgO = -0.0839 + 2.2614\ CaO$	0.9967	0.0437

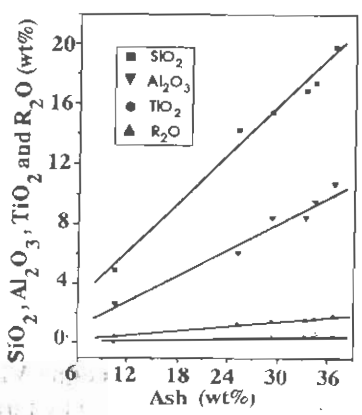

Fig. 6-1: Relationship between SiO_2 , Al_2O_3 , TiO_2 and R_2O and the ash content.

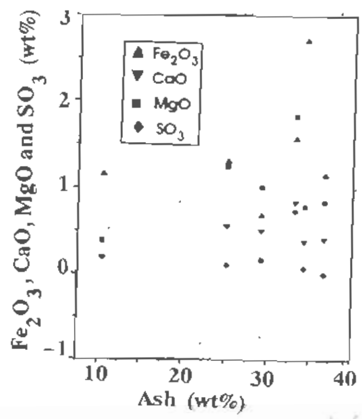

Fig. 6-2: Relationship between Fe_2O_3 , CaO, MgO and SO_3 and the ash content.

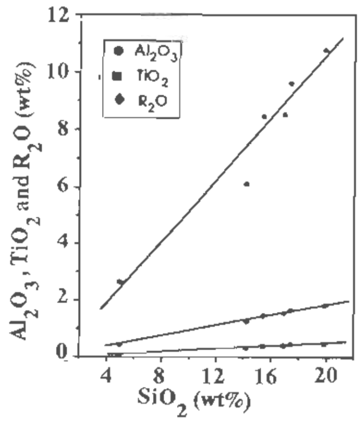

Fig. 6-3: Relationship between Al_2O_3 ,TiO_2 and R_2O and SiO_2 .

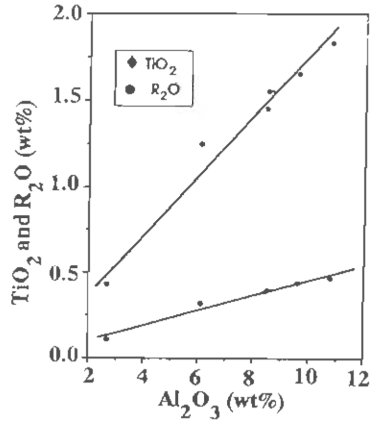

Fig. 6-4: Relationship between TiO_2 and R_2O and Al_2O_3 .

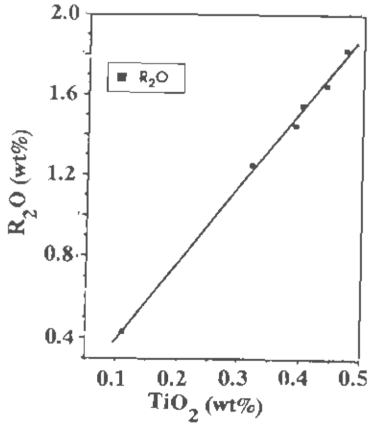

Fig. 6-5: Relationship between R_2O and TiO_2 .

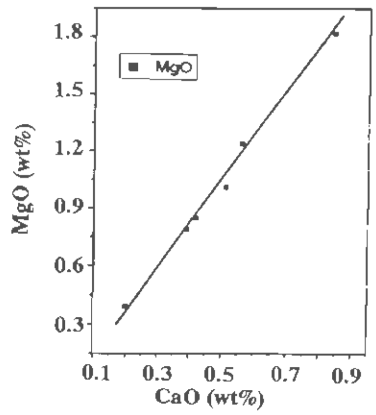

Fig. 6-6: Relationship between MgO and CaO .

were not found between Fe_2O_3 , CaO, SO_3 and MgO with the ash content, Fig. 6-2. Linear relationships between Al_2O_3 , TiO_2 and R_2O with SiO_2 - TiO_2 and R_2O with Al_2O_3 -R_2O with TiO_2 and MgO with CaO were also found, Figs. 6-3 to 6-6.

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