

## Discussion about major and trace Elements behavior with a view to mineralogy in the coal mine Pabdana, East South Central Iran

Loghman Shirzadi<sup>\*1</sup> and Jamal Rasouli\*

\* PhD students, Department of Earth Sciences, Shahid Beheshti University, Tehran, Iran

**Introduction:** In Iran, most of the coal deposits are confined to two major basins, one in northern part called Alborz basin and another in Central part of Iran named Kerman basin. There are several studies on the coal deposits of Alborz basin. Much of the present knowledge on the geological aspects of Iranian coal are due to the works of Teichmuller (1982), Zadeh Kabir (1991), Razavi Armagani and Moinsadat (1994), Shariat Nia (1994), Stasiuk et al. (2003), Yazdi and Shiravani (2004) on the Alborz coal deposits. Studies on the various geological aspects of Kerman basin have not received any attention. Among the several coal seams of the 330 MT is thermal and the remaining coal has intermediate properties. Nayband Formation mainly consists of sandstone, shale, siltstone, and clay stone. Coal is predominantly confined to shale and argillite. These sediments with coal intercalations happened to be deposited under humid climatic conditions. In the Pabdana coal field, coal is being extracted by underground methods. The Pabdana coal field contains coal that is a cokable type and mining was started in 1977; and in 2009, as much as 1,62,000 tons coal have been extracted. Absolute reserve of the mine is estimated to be around 315 MT. In the Pabdana coal field, 13 coal-bearing layers (seams) with thickness varying from 0.1 to 2.5 m have been identified. Among these coal seams, coal seam numbered as d2, d4, d5, and d6 are more productive and economical. The present study involves quality characterization of these four coal seams of the Pabdana coal field which include the major and trace elements, geochemistry and mineralogy of representative samples of coals currently mined from Pabdana area.

**Sampling and analytical methodology:** A total of 16 samples (four samples each) were collected from four coal seams of the Pabdana underground mines and were analyzed for their mineralogical and geochemical compositions. Samples were collected adopting channel sampling technique. The sampling channel was 0.12 cm wide, 20 cm long and 5 cm thick. These samples were taken from fresh surface of the mine by driving channels across the beds and digging inside the coal bed (~0.5 m thickness) to avoid weathered surface. The coal samples are black in color, light weight, and massive without visible Three types of analyses were performed namely chemical and mineral. The bulk samples from the field were air dried and reduced to 0.5 kg by coning and quartering method. The coal samples were analysed (proximate, ultimate, major and trace element analyses) at the Organization of Geology and Exploration of Minerals in Tehran, Iran. The samples for proximate, ultimate and chemical analyses were pulverized to less than -200 mesh sizes and dried for 12 hours in a dessicator. These powdered samples were subjected to major and trace element determinations using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The procedures used for ICP-AES involve two different dissolution methods. A sinter digest was used to determine the concentration of major elements (Si, Al, Ca, Mg, K, Fe, Ti, P) and trace elements (B, Ba and Zr). An acid digest was used to determine the concentrations of Na, Be, Co, Cr, Cu, Li, Mn, Ni, Sc, Sr, Th, V, Y and Zn. Acid digest solution similar to the above was used to carry out ICP-MS analyses. Concentrations of As, Au, Cd, Cs, Ga, Ge, Mo, Nb, Pb, Rb, Sb, Sn, Tl and U were determined adopting the procedure described by Meier (1996). Hg and Se were determined directly on the coal samples by cold-vapor atomic absorption analysis and hydride generation atomic absorption, respectively as described by O'Leary (1997).

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<sup>1</sup>: Corresponding author

**E-Mail:** loghman.shirzadi@gmail.com

**Study area:** Pabedana coal mine is one of the important coal mines is situated in Kerman Province, SE of Iran and is bounded between 56° 23' 30" to 56° 31' 30" longitude and 31° 05' 00" to 31° 14' 00" latitude covering an area of 13 km<sup>2</sup>. The Pabedana coal mine is situated in the central part of the Central-East Iranian Microcontinent (CEIM; Takin 1972; Fig. 1). The CEIM, together with central Iran and the Alborz Mountains, forms the Iran Plate and occupies a structural key position in the Middle Eastern Tethysides (Sengor et al. 1988). The CEIM consists of three north–south oriented structural units (Lut, Tabas, and Yazd Blocks) which are aligned from east to west. The focus of the present study is confined to the middle of the three blocks, i.e., the Tabas Block, where the Pabedana coal mine is situated. In the Pabedana coal field, coal is being extracted by underground methods. The Pabedana coal field contains coal that is a cokable type and mining was started in 1977; and in 2009, as much as 1,62,000 tons coal have been extracted. Absolute reserve of the mine is estimated to be around 315 MT. In the Pabedana coal field, 13 coal-bearing layers (seams) with thickness varying from 0.1 to 2.5 m have been identified.

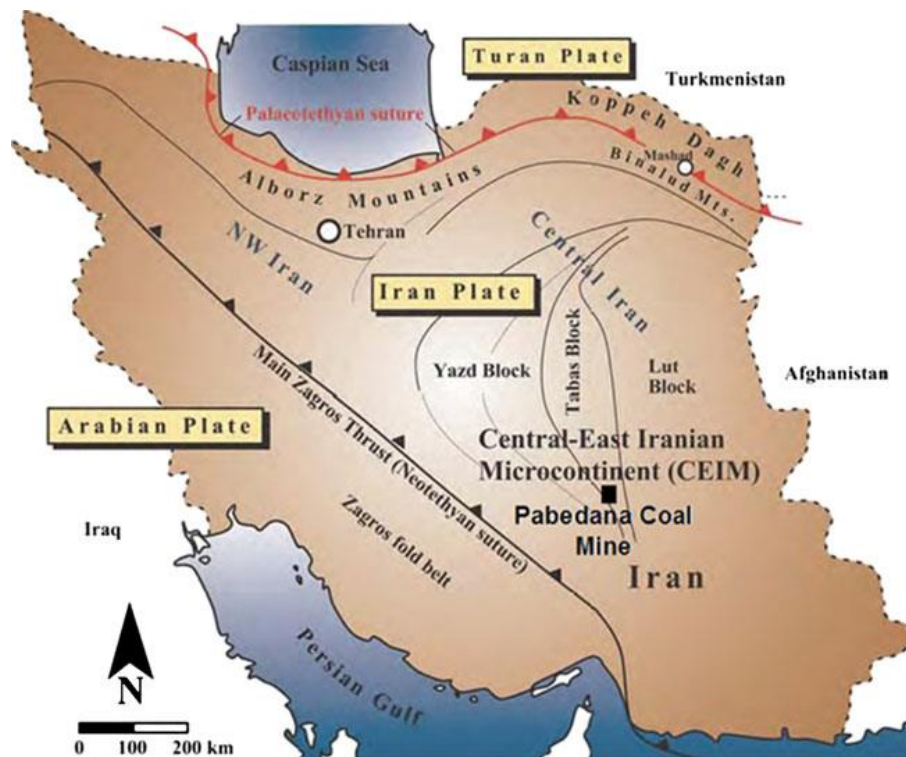


Fig. 1 Structural and geographic framework of Iran showing the main sutures, structural units, and geographic areas (modified after Wilmsen et al. 2009)

**Proximate analysis:** Coal quality of the study area has been evaluated through proximate, ultimate and calorific and described in the following sections. Results of the proximate analysis of the Pabedana coals are showed there are no major variations in the moisture, ash, volatile matter and fixed carbon contents in the coals of different seams of the study area. The coals of the study region are characterized by low moisture content (1.05-1.23%; mean 1.15%). The content of volatile matter ranges from 29% to 31% db, with an average of 30.47% db. Fixed carbon content ranges from 56.27% to 58.16%, with an average of 57.19%. Ash content in Pabedana coal samples varies from 9.82% to 12.95% with an average of 11.19%. Low ash contents in the Pabedana coal indicate relatively quick burial of vegetative matter. Further, moderately low ash content indicates short distance transportation. The slight variation in the volatile matter contents is probably due to the compounds released from organic and mineral matter in coals. The Pabedana coal contains high C (81.30-83.32%, mean 82.61%), relatively low H ( av. 5.04%) and O+N combined comprise 7.98%. Atomic H/C and O/C ratios determined for the Pabedana coals are indicative of humic nature of the coal, which are in agreement with the nature and origin.

**Calorific value:** The calorific value is related to carbon content, moisture, minerals and coal rank of coals (Liu et al., 2005). In study area flamy coal yields minimum Calorific value (7430 Kcal/Kg) and coking coal yields maximum calorific value (8900 Kcal/Kg).

**Mineral analysis:** Mineralogical investigations using XRD indicate that the inorganic fraction in the Pabedana coal samples is dominated by carbonates thus constituting the major inorganic fraction of the coal samples.

**1) Major elements:** The major elements in coal generally occur in minerals (Liu et al., 2005) rather than in organic matter (Pike et al., 1989). Therefore, major elemental analyses can be used as a tool for discriminating element-mineral associations. The SiO<sub>2</sub> content varies narrowly from 10.38 to 19.93. The Al<sub>2</sub>O<sub>3</sub> content ranges from 12.24 to 16.54% and Fe<sub>2</sub>O<sub>3</sub>, from 8.44 to 12.56%. MgO and CaO are the dominant components of the inorganic constituents and vary between 19.70 and 24.72%, and 28.00 and 36.04% respectively. The Na<sub>2</sub>O content varies from 0.87 to 2.63%, K<sub>2</sub>O, from 0.1 to 0.35%, MnO, from 0.48 to 0.61, P<sub>2</sub>O<sub>5</sub>, from 0.40 to 0.78 and Cl<sub>2</sub>O, from 0.96 to 1.12%. The content of TiO<sub>2</sub> ranges from 2.55 to 3.98%. The variation in major elements content is relatively narrow between different coal seams. The elements Si, Al, Ti and K are mainly associated with quartz and clay minerals. The significantly positive correlation between K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> ( $r = 0.94$ ), the positive correlation between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> ( $r = 0.20$ ) and between TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> ( $r = 0.62$ ), no correlation between K<sub>2</sub>O and SiO<sub>2</sub>, demonstrate that Si, Al, K and Ti mainly originate from illite and not from kaolinite. Illite has been reported as one of the major clay minerals in the coal deposits of Iran. By assuming that Al in the coal is exclusively derived from detrital alumina-silicate sources (Pike et al., 1989), the positive correlation between Al and Si, K, Ti and P ( $r = 0.20, 0.94, 0.62$  and  $0.25$  respectively) indicate the detrital origin of these elements, which may occur as detrital clay minerals. Ti is present in concentration close to 3% in pabedana coals. This range of Ti contents is high when compared with the usual Ti content in coal elsewhere (0.05-0.2%). The Ti/Al ratio is close to 0.04-0.05, but when high Ti levels are present, this ratio increases up to 0.2. The small variation in the Al/Ti ratios in the Pabedana coal implies that the detrital material supplied to the site of deposition had near equal values of Al/Ti ratio. The constant Ti/Al ratio supports an association of Ti with the aluminium fraction, but the presence of significant amounts of anatase or rutile may be deduced when high Ti/Al ratios are sporadically measured. In sediments rutile is known to form during the reconstitution processes in clays and shales and also known to occur as a common detrital mineral.

The Pabedana coals are characterized by high contents of Ca, Mg, Mn, Ba and Sr which in turn reflect the high carbonate and phosphate contents. The MgO wt.% (which ranges from 19.70% to 24.72%) and CaO wt.% (which varies from 28% to 36.04%), are positively correlated ( $r = 0.81$ ). Optical and X-ray studies and the ratio of Mn:Fe  $\leq 4:1$  confirm the undoubted presence of ankerite as the most dominant constituent among the carbonate minerals in the coal samples. Megascopic studies of coal reveal the occurrence ankerite along cleavages and joints. Ankerite may be of low temperature metasomatic origin. However, some amount of CaO in coals may be present as minor amounts of calcite. This is in contrast to the coal fields of Alborz region of northern Iran, wherein it is reported that carbonates are largely made up of dolomite and calcite (Zadeh Kabir, 1991; Razavi Armagani and Moinosadat, 1994; Yazdi and Shiravani, 2004). Further, minor amounts of Ca, along with P<sub>2</sub>O<sub>5</sub> and Cl<sub>2</sub>O may be contributed by apatite. The strong positive correlation between P<sub>2</sub>O<sub>5</sub> and ash content ( $r = 0.86$ ) further shows that P is mainly present in the form of phosphate minerals.

The positive correlation between Na<sub>2</sub>O and ash content, ( $r = 0.46$ ) and the negative correlation between Na and Cl ( $r = - 0.51$ ) indicate that Na mainly occurs in minerals rather than in pore water, the latter is generally considered as a source of Na. The presence of feldspar group of minerals accounts for Na in coals. The Fe<sub>2</sub>O<sub>3</sub> content in coals ranges from 8.44 to 12.56 wt.% and indicates the presence of variable amounts of pyrite. Low sulfur content indicates low contents of sulphates (barite and gypsum). There is a positive correlation between Fe and S, showing association of these elements with sulfide minerals, pyrite in particular. Some exceptionally high content of Fe suggests the presence of iron oxides (hematite) and Fe-bearing clay minerals.

**2) Trace elements:** The relationships between trace element concentration and ash yield have been widely reported (Finkelman, 1983; Spears et al., 1999; Dai et al., 2005). The ash content of coal and its

geochemical character depends on the environment of deposition and subsequent geological history. It is generally considered that most trace elements in coal are associated with the mineral matter.

Elements exhibiting positive correlation with ash yield indicate inorganic affinity (Nicholls, 1968). The inorganic affinity may be explained as a result of the causes such as : (1) presence of the element in the inorganic detritus accumulating together with the peat from which the coal is formed, (2) sorption from circulating waters by the inorganic detritus during original peat accumulation, (3) sorption from groundwater by the inorganic fraction during diagenesis, (4) precipitation from circulating waters of compounds stable under physico-chemical environment of peat formation, (5) precipitation from groundwater by reaction with compounds already present in the formation during diagenesis and (6) introduction of mineral matter into coals at a late stage in their formation or even after their formation operating in isolation or in union.

Based on the values of correlation coefficients between elements and ash yield, the elements are classified into four groups. The first group of elements (Be, Co, Mn, Th, B, V, Au, Cd, Ga, Ta, P, Ca, Al, Fe) has a very high positive correlations with ash yield ( $r_{\text{ash}} > 0.7$ ): These elements have high inorganic affinity. Most of these elements have a high positive correlation coefficient with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  ( $r_{\text{Si+Al}} > 0.7$ ). The second group includes eight elements (Cu, Sr, Y, Rb, Na, Mg, La, K) and shows medium positive correlations with ash yields ( $r = 0.51$  to  $0.69$ ). This group of elements also exhibits inorganic affinity. The third group of elements (Sn, Te, Ti, S) exhibits weak correlation with ash yield ( $r = 0.21$  to  $0.50$ ). Only one element, namely Cs, belongs to fourth group which shows the lowest correlation with ash yields ( $r < 0.20$ ).

Many researchers have reported that some elements including As, Hg, Sb, Co and Se are associated with pyrite (Ward et al., 1999; Ding et al., 2001). In the coals of the study area, these elements are not clearly related with pyritic sulphur except As. Elements like As, Ni, Be, Mo and Fe show relatively high positive correlation coefficients with pyritic sulphur ( $r = 0.53$  to  $0.80$ ).

Elements Sc ( $r = -0.85$ ), Cr ( $r = -0.83$ ), Zr ( $r = -0.74$ ), Ga ( $r = -0.77$ ), Ge ( $r = -0.66$ ), La ( $r = -0.62$ ), As ( $r = -0.59$ ), W ( $r = -0.55$ ), Ce ( $r = -0.51$ ), Sb ( $r = -0.44$ ), Nb ( $r = -0.45$ ), Th ( $r = -0.44$ ), Pb ( $r = -0.42$ ), Se ( $r = -0.40$ ), Tl ( $r = -0.39$ ), Bi ( $r = -0.39$ ), Hg ( $r = -0.38$ ), Re ( $r = -0.29$ ), Li ( $r = -0.28$ ), Zn ( $r = -0.12$ ), Mo ( $r = -0.12$ ) and Ba ( $r = -0.11$ ) show varying negative correlation with ash yield. These elements possibly have an organic affinity. These elements may be present as primary biological concentrations either with tissues in living condition and/or through sorption and formation of organometallic compounds.

**Conclusions:** Pabedana coal is a medium ash coal, with relatively low sulfur content and belongs to subbituminous rank. Pabedana coals generally are comparable in quality with the extensively developed coal deposits in the Alborz region of Northern Iran. Atomic H/C and O/C ratios of Pabedana coal aspect of the coal indicate it as humic coal. The coal of the study area is characterized by low ash, low moisture, and high volatile matter indicating short distance transportation of the parent plant debris. The moderately low sulfur content in the Pabedana coals indicates that the coals were formed in freshwater/ deltaic environment. Pabedana mines produces primary coking coal. Mineralogical investigations using optical microscope and XRD indicate that the Pabedana coal samples are dominated by carbonates which are mainly represented by ankerite. Ankerite along with pyrite is commonly found as crack fillings in the coals. Illite, kaolinite, muscovite, quartz, feldspar, apatite, and hematite occur as minor or trace phases. The Pabedana coals are characterized by high contents of Ca, Mg, Mn, Ba, and Sr values which in turn reflect the high carbonate and phosphate contents. The high content of epigenetic ankerite mineralization is responsible for the higher Ca, Mg, Fe, and Mn contents in coals. Elements Be, Co, Mn, V, Au, Cd, Ta, P, Ca, Al, Fe, Cu, Sr, Y, Rb, U, Na, Mg, K, Sn, Te, Ti, S, and Cs exhibit positive correlation with ash yield thus suggesting them to be of inorganic origin. Elements Sc, Cr, Zr, Ga, Ge, La, As, W, Ce, Sb, Nb, Th, Pb, Se, Tl, Bi, Hg, Re, Li, Zn, Mo, and Ba show varying negative correlation with ash yield. These elements may be present as primary biological concentrations.

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