# Inorganic Constituents in Coal

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Coal contains not only organic matter but also small amounts of inorganic constituents. More than one hundred different minerals and virtually every element in the periodic table have been found in coal. Commonly found group minerals in coal are: major (quartz, pyrite, clays and carbonates), minor, and trace minerals. Coal includes a lot of elements of low mass fraction of the order of $w = 0.01$ or 0.001 %. They are trace elements connected with organic matter or minerals comprised in coal. The fractions of trace elements usually decrease when the rank of coal increases. Fractions of the inorganic elements are different, depending on the coal bed and basin. A variety of analytical methods and techniques can be used to determine the mass fractions, mode of occurrence, and distribution of organic constituents in coal. There are many different instrumental methods for analysis of coal and coal products but atomic absorption spectroscopy – AAS is the one most commonly used. Fraction and mode of occurrence are one of the main factors that have influence on transformation and separation of inorganic constituents during coal conversion.

Coal, as an important world energy source and component for non-fuels usage, will be continuously and widely used in the future due to its relatively abundant reserves. However, there is a conflict between the requirements for increased use of coal on the one hand and less pollution on the other. It's known that the environmental impacts, due to either coal mining or coal usage, can be: air, water and land pollution. Although, minor components, inorganic constituents can exert a significant influence on the economic value, utilization, and environmental impact of the coal.

Keywords: *Coal, inorganic constituents, mineral matter, trace elements, methods of determination, utilization*

## Introduction

Coal may become more important, both, as an energy source and as the source of organic chemicals in the 21st century. In the past several decades, the dominant use of coal has been combustion in power plants to generate electricity. But, other coal utilization, the so – called non-fuel uses, are also interesting. The non – fuel uses of coals include: high-temperature carbonization of bituminous and subbituminous coals to make metallurgical coke; use of coal in manufacturing carbon materials (activated carbons, carbon molecular sieves, carbon for production of chemicals), and specially carbon materials such as graphite, fullerene and diamond; gasification of coal to make synthetic gases and other chemicals; the use of coal tars from carbonization, gasification and pyrolysis for making aromatic and phenolic chemicals; the use of coal tar pitch for making binder pitch, mesocarbon microbeads, carbon fibers, activated carbon fibers and composite materials etc.

The inorganic constituents in coal are all elements (excluding C, H, O, N and S) in mineral form and organically bound inorganic elements. Effects of the inorganic constituents on coal utilization and evaluation is different. Small quantities of certain minerals and inorganic compounds are known to modify the behavior of coal during pyrolysis and gasification processes. They can cause technological problems such as fouling and slagging of coal – fired boilers, corrosion and erosion of combustors, abrasion of mining and grinding equipment, affect washability and oxidizability of coal, affect the heating value of coal, contribute to environment pollution, but also contain information on environment of deposition, diagenesis, source materials.[1-7]

## Range, mode of occurrence, and distribution of inorganic constituents

Practically all the elements of the Chemical Periodic Table are present in coal. According to contents, the elements can be divided into three groups: major elements (C, H, O, N, S) whose amounts are above $w = 1.0 \cdot 10^{-3}$; minor elements which include the coal mineral matter (Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti), and halogens (F, Cl, Br, I) present in ranges between $w = 1.0 \cdot 10^{-8}$ and $1.0 \cdot 10^{-9}$; trace elements which are the mass fraction with concentration below $w = 1.0 \cdot 1.0^{-6}$.

All coals contain a significant amount of mineral matter, organometallics, chelates and/or adsorbed species. More than one hundred different minerals and virtually every chemical element have been found in coal. Ninety-five per cent of the mineral matter in coal are classified into five components:

1. clay minerals (aluminosilicates) consisting mostly of kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($K_{1\text{-}1.5}\ Al_4(Si_{0.57}\ Al_{1\text{-}1.5}\ O_{20})(OH)_4$), montmorillonite $(Al, Mg)_2Si_4O_{10}(OH)_2$ and mixed illite – montmorillonites;

2. carbonate minerals, principally calcite ($CaCO_3$), siderite ($FeCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$) and other variously mixed carbonates of Ca, Fe, Mg and Mn;

3. sulphides and disulphides, mostly pyrite, $FeS_2$ (cubic) and markasite, $FeS_2$ (orthorhombic);

4. silica, the majority of which occurs as quartz ($SiO_2$);

5. sulphates, mostly present as iron hydrated sulphates and mixed Na, K, Fe sulphates.

Clays, quartz, pyrite and various carbonates are the dominant minerals in most coals. Minerals such as sphalerite (ZnS), pyrrhotite ($Fe_{1-x}S$), troilite (FeS), chalcopyrite ($CuFeS_2$), galena (PbS), apatite ($Ca_5(PO_4)_3$ (FCl, OH), barite ($BaSO_4$), monazite (Ce, La, Nd, Th)$PO_4$, rutile ($TiO_2$), zirkon ($ZrSiO_4$), ankerite $CaFe(CO_3)_2$, clausthalite (PbSe) are most often minor mineral coal components.

Coal, as a sedimentary rock, consists of an aggregate of variable materials mainly composed of organic constituents called macerals (lithotypes), which are associated with mineral matter that yields ash after the complete burning. Minerals can occur: as small granular inclusions (disseminated); as lenses or layers (partings); as concretions (nodules); within cracks or cleats (fissures) or as large masses of rock (rock fragments). Syngenetic minerals are incorporated within peat during the peat – forming process whereas epigenetic minerals are considered to be emplaced within cleats, cracks and cavities following the induration of coal. The epigenetic mineralization of cleats and cracks is considered to have resulted from the precipitation of pore fluids during burial and coalfication. Literature data[8-12] suggest that mineralization occurs in sequence, commencing with sulphides, followed by silicates and lastly carbonates. On a semi-quantitative basis, the mineral groups in coal, in decreasing order of importance, are: silicates > carbonates > oxyhydroxides > sulphides > sulphates > phosphates > others. A number of elements occur in wide fraction ranges.[13] Table 1 shows the range of the average fraction of some inorganic elements found in most types of coal produced in the world. Elemental fractions of coals reflect the elemental composition of the coal-forming material, properties of environment, and processes during the coal formation period and later. Although there is much information on different elements fraction in coal, there is much less knowledge about the forms in which such element occurs.

It should be mentioned that the conditions that prevailed in the peat swamp (especially the hydrological conditions that affected the transport of inorganic matter into the swamp) varied geographically and temporally within a given peat swamp. Therefore, the fraction of elements as, both, mineral matter and organically combined species, varies from one location to another in a coal bed and form one bed to another.

The inorganic content of coal always includes a number of elements at mass fractions below $w = 0.1 \cdot 10^{-3}$ collectively referred to as trace elements. The trace elements can occur in coal in organic or inorganic forms but most trace elements are found in both combination. The organic versus inorganic occurrence of trace elements in coal was discussed.[13] Float-sink, specific gravity separations of coal, often are used to determine organic versus inorganic affinity to trace elements. Washability curves and histograms of washability data are effective means of depiciting the mode of combination of elements in coal. They indicate whether the elements are associated with the organic or inorganic fractions of the coal. It is useful to quantify the information presented on the washability curves and produce an 'organic affinity' index.[14-17]

Table 1 – *Mass fractions of some elements found in most types of coal in the world*[13,19,21]

Tablica 1 – *Maseni udjeli nekih elemenata u većini svjetskih ugljena*[13,19,21]

| Element<br>Element | Mass fraction, $w = 10^{-6}$<br>Maseni udjel, $w = 10^{-6}$ | Element<br>Element | Mass fraction, $w = 10^{-6}$<br>Maseni udjel, $w = 10^{-6}$ |
|---|---|---|---|
| As | 0.5 – 80 | Nb | 1 – 20 |
| B | 5 – 400 | Ni | 0.5 – 50 |
| Ba | 20 – 1000 | P | 10 – 3000 |
| Be | 0.1 – 15 | Pb | 2 – 80 |
| Cd | 0.1 – 3 | Rb | 2 – 50 |
| Cl | 50 – 2000 | Sb | 0.05 – 10 |
| Co | 0.5 – 30 | Sc | 1 – 10 |
| Cr | 0.5 – 60 | Se | 0.2 – 10 |
| Cs | 0.3 – 5 | Sn | 0.2 – 4 |
| Cu | 0.5 – 50 | Sn | 1 – 10 |
| F | 20 – 500 | Sr | 15 – 500 |
| Ga | 1 – 20 | Th | 0.5 – 10 |
| Ge | 0.5 – 50 | Ti | 10 – 2000 |
| Hg | 0.02 – 1 | Tl | < 0.2 – 1 |
| Li | 1 – 80 | U | 0.5 – 10 |
| Mn | 5 – 300 | V | 2 – 100 |
| Mo | 0.1 – 10 | Zn | 5 – 300 |
| | | Zr | 5 – 200 |

Elements such as Fe, Ca, Zn, Mg, Si, etc., may occur predominantly in mineral species of these elements for example $FeS_2$, $FeCO_3$, $MgCO_3$, $SiO_2$, $CaCO_3$, ZnS, etc. However, for many elements such as Hg, As, Pb, Cd, Co, Ni, Se, etc., no specific mineral of the element may be present, but the element may be distributed among several mineral species.

Germanium, beryllium, boron, uranium, antimony are among elements that have a dominant organic association. However, with the exception of vanadium and nickel porphyrins, no other organic complex that has ever been isolated or identified in coal may be associated with phenolic, carboxylic, amide and sulphhydroxy functional groups in the organic fraction of coal.[18-20] Some elements exist in coal in a variety of forms. For example, selenium was found in coal from the Powder River Basin in at least six forms: selenium bearing pyrite, organically bound selenium, selenium bearing sphalerite, lead selenide, water soluble selenium and ion exchangeable selenium. Zirconium in coal occurs mostly as the mineral zircon but there may be some organically bound zirconium in lignites.[6] *Querol* et al.[21] performed a study on trace elements distribution, in both, coals and wastes and they found the following:

1. Elements showing inorganic affinity:

In clay minerals and feldspars: Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y and rare earth elements;

In iron sulfides: As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, Se, Ti, W and Zn;

In carbonates: Ca, Co and Mn;

In sulphates: Ba, Ca, Fe;

In heavy minerals (tourmaline): B.

In several mineral phases: Co and W (carbonates and sulphides); Ni, Cu, Pb (clay minerals and sulphides);

2. Elements showing organic affinity in coal: Be, B, Ge, V, W and Zr (boron exhibits partial association with tourmaline in the heavy fraction, and V with clay minerals).

In Table 2 the classification of trace elements as a function of the inorganic, organic or intermediate affinities is given. Indeed, both, trace elements contents and combinations in coal vary significantly with coal type.

The distribution of trace elements in coal was initially examined by *Gluscoter* and *Goldschmidt* and has been studied extensively since then.[16] Significant studies on trace elements in the US, Australian, British and Canadian coals have included those of *Valkovic, Finkelman* and *Swaine* et al.[13,14,17,19,23]

The mode of occurrence of inorganic elements in coal is one of the main factors that influence their transformation behavior during coal conversion.[3,24-26] During combustion, the inorganic elements in coal are concentrated in the by-products (fly ash, bottom ash, slag and flue gas desulphurization products). The studies of mineral matter transformation during coal combustion enabled the understanding of volatile minerals release from coal, chemical transformation of the minerals and interaction of minerals with organic matter.

The volatility of inorganic elements during coal conversion depends on many factors including the granulometric analysis of the coal, reaction conditions, the mode of occurrence of the element in the coal, and the interaction of the different elements. In the reaction conditions, temperature is the major factor influencing the volatility of elements. During combustion, the minerals in coal can become fluid or volatile, and may oxidize or undergo other gas phase

Table 2 – *Classification of trace elements in coals as a function of the affinities (inorganic, organic or intermediate)*[22]

Tablica 2 – *Klasifikacija elemenata u tragovima u ugljenima prema afinitetima (anorganski, organski ili prijelazni)*[22]

| Authors / Autori | Affinity / Afinitet | | |
|---|---|---|---|
| | inorganic / anorganski | organic / organski | intermediate / prijelazni |
| *Minchev* and *Eskenazy* (1972) | Be, Sc, Zr, Ti, Cr | Ge, As, Ag, Y, Mo, Yb, Sr, Ba, V, Mn, Cu, Ni, Sn, Zn, Co | |
| *Gluskoter* et al. (1977) | Zn, Cd, Mn, As, Mo, Fe | Ge, Be, B, Sb, Cr, Se | Co, Ni, Cu |
| *Ward* (1980) | Cu, Pb, Zn, Mn, Sr, Cr | B, Ni, V, Zr, Co, Be | Ge |
| *Azambuja* et al. (1981) | Mn, Zn, Pb | Cu, Co, Ni, Cr, V | |
| *Harvey* et al. (1983) | As, Ba, Cd, Mn, Mo, Pb, Tl, Zn | B, Be, Br, Ge, Ni, Sb, U, V | |
| *Kojima* and *Furusawa* (1986) | Mn | Ti, V, Sr, B | Ba, Sn, Cr, Ni, Sc, Y, Be, Co, Cu, Zn, Zr, As |
| *Kortenski* (1986) | Mn, Zn, Bi, Sn, Sr, Tl | Ag, As, Ge, Mo, Ni, W, Ba, Co, Cr, Cu, Pb, Ti, V, Zr | |
| *Warbrooke et* al. (1986) | | Ge, Mo, Ni, Be, Br | |
| *Goodarzi* (1987) | | As, B, Br, Cl | |
| *Goodarzi* et al. (1987) | Ti, Cr, Hf, Ta, Th, V | Br, Mn, Cl | |
| *Miller* and *Given* (1987) | Ce, Zr, Pb, Zn | Cu, Be, Y, Yb, V, Ge, Ti, Ni, Ga, Sr, Ba, Mn | |
| *Rimmer* (1991) | Ba, Mn, Rb, Sr, Zn, Zr | Be, Ni | Cu, V |
| *Beaton* et al. (1991) | Ti, Sb, As, Be, Cs, Li, Ni, Pb, V, Zn, Rb, Mn | Sr, B, Br | As, Ba, Co, Mo, Ce, Dy, Lu, Sc, W, U |
| *Querol* et al. (1992) | Ba, Ce, Cr, Rb, Co, Ni | Be | As, Cd, Cu, Dy, Er, Eu, Gd, Ge, Ho, Lu, Mo, Nd, Pb, Pr, Sm, Sb, Sr, Tb, Th, Tm, U, Yb, Zn |
| *Martinez–Tarazona* et al. (1992) | Cu, Ni, Zn, Pb | Mn, Zr, Nb | Rb, Ba, Cr, Sr, V, Y |
| *Spears* et al. (1993) | Pb, Cu, Ni, Zn, Mn | V, Sr, Ba, Zr, Nb | |
| *Querol* et al. (1995) | Al, K, Mg, Na, P, Ti, Li, Cr, Ni, Cu, Ga, Rb, Sr, Y, Sn, Cs, Ba, Ta, Pb, Bi, Th, U, REEs, Fe, Co, Zn, As, Se, Mo, Cd, Sb, Hg, Tl, Ca, Mn, Co | | |
| *Lu* et al. (1995) | As, Co, Cr, Cu, Ni, Pb, V | Be, Ge | |

reactions. For example, the iron in pyrite is converted to iron oxide, and calcium can react with $SO_2$ and $O_2$ to form $CaSO_4$. Silicates and clay particles, may remain chemically unchanged, if they are excluded from the coal particle, but become fluid and solidify during cooling. Previous paper [22] reported that Pb and Cd are mainly associated with mineral matters, such as galena and sphalerite, Cr is present predominantly as $Cr^{3+}$. It was shown that Pb and Cd are semi-volatile elements, while Cr is hardly vaporized up to 1300 °C during coal combustion.

In fly ash, the primary silicate compounds are quartz, mullite or sillmanite, clays and feldspars. Oxides (hematite, magnetite and other spinels) and sulphates (gypsum or anhydrite) are dominant non-silicate minerals identified in fly ash. The major cations are Si, Al, Fe and Ca with lesser amounts of Na, Mg, Mn, K, Sr and Ti. Trace elements include As, B, Be, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, and Zn. Data on the association of trace elements with specific inorganic phases in fly ash, are limited. *Huggins* et al.[27] determined that several elements had a preferred oxidation state in non-silicate oxyanions. In the examined samples, the primary Cr oxyanion in fly ash is Cr(III) rather than the more toxic Cr(VI). Arsenium was primarily present as less toxic As(V), although, As(III) could be produced in oxygen-lean furnace conditions. Using the selective leaching method, it was estimated that approximately 50 % of the As is in a silicate matrix, while other authors found As to be associated with an iron rich glass phases.[28] Approximately 80 % of As in the fly ash was found to be associated with non-silicates. *Finkelman* et al.[29] found Cr, Ni, Co and Zn to be primarily associated with spinels, but with a significant fraction in silicate inclusions. *Rousseau* et al.[30] identified three mechanisms that determined trace element distribution in fly ash particles: a) trace elements remained associated with unaltered mineral phases; b) minerals containing trace elements were dissolved in larger particles; c) volatile trace elements reacted with molten fly ash particles.

The trace elements release from coal combustion is affected, to a great extent, by their occurrence modes in coal i. e. their chemical affinities. The elements associated mostly with the coal organic and sulphide fractions tend to vaporize firstly and then they are easily adsorbed on fine particles during flue gas cooling. In contrast, elements combined with the mineral matters more often remain in the ash matrix. The most volatile trace elements (Hg, Se, As), to which we have often paid attention, and halogens remain mostly in the vapor phase as they pass through heat transfer sections of a boiler. For example, the percentages of the total in-stack fractions of these elements in the vapor phase: Cl, up to 99 % as HCl; F, up to 90 % as HF; Br, 25-98 % as HBr; Hg, up to 98 % as Hg, HgO and $(CH_3)_2Hg$; Se, up to 59 % as Se and $SeO_2$; As, 0.7-52 % as $As_2O_3$. Although fraction of Hg in coal is usually extremely low, significant attention is focused on its emission, because it is highly toxic to humans and it bioaccumulates.[31]

Finally, elements, such as Al, Ba, Ca, Ce, Cs, Fe, K, Mg, Mn and Th, remain condensed at the temperature of coal combustion, and divide equally between fly-ash and bottom ash. Some of other elements (As, Cd, Cu, Pb, Sb, Se and Zn) are volatilized and will therefore be depleted from the slag and bottom ash, and condense out on the smaller fly-ash particles. The third group of elements, (Br, Hg, I) most often remain in the gas phase. Thay are depleted in all ashes. Elements, such as Cr, Ni, U and V, display intermediate behaviour between these element groups.

## Determination of inorganic elements

Many different methods are applicable to the analysis of inorganic elements in coal. A few elements (Cl, F, P) are determined routinely by chemical methods. The majority of elements are determined by instrumental methods. There is no single method for determing all of the elements in coal. But, the instrumental methods very often employed by coal analyst are: instrumental neutron activation analysis (INAA), atomic emission spectroscopy (AES), atomic absorption spectroscopy (AAS), mass spectroscopy (MS), X-ray fluorescence (XRF), and electron microscopy. All of these methods give rapid and accurate multielement results for the bulk analyses of coal and their products. Multielemental instrumental methods used for analysis of coal are shown in Table 3. Every inorganic element can be determined by at least two of the multielement instrumental methods.[15,17,19,32-42]

Several different INAA techniques for analyzing coal samples include: thermal INAA (TNAA), epithermal INAA (ENAA), high-resolution prompt gamma INAA (PGNA), and radiochemical INAA (RNAA).

INNA methods utilize whole coal samples (not only coal ash). Analytical errors, because of incomplete sample dissolution, volatization of elements during ashing, and by the contamination during preparation, have been reduced. These methods are automated and sensitive ($w = 10^{-7} – 10^{-5}$) for the first-row transition elements, rare-earths, alkali, and alkaline earth elements.

Direct-current arc (DC)-AES is a technique often used in inorganic elemental coal analyses. Another AES technique is inductively-coupled plasma-AES (ICP-AES) as a multi-elemental, rapid, quantitative technique, that offers excellent precision for most elements (± 5 to 10 %).

AAS is widely used in determing elements in coal and their products because it is relatively inexpensive, rapid, and sensitive methods, and is free from many interferences. Different most often used AAS techniques are: flame (FAAS), hydridegeneration (HAAS), and graphite furnace (GAAS).

Of the many mass spectroscopy techniques used to analyze geological samples, spark source MS (SSMS) and inductively coupled plasma – MS (ICP-MS), are the ones most often used in the analysis of coal. A third specialized technique, isotope-dilution MS (IDMS), is sometimes used to determine selected elements in coal such as U, Pb, and Zn.[19]

IDMS is extremely accurate and sensitive technique, but it is seldom used on coal because it is labor intensive and expensive. SSMS is a quantitative method and it has been used to determine the concentration of all elements with at least two stable isotopes. ICP-MS is a newer quantitative technique that is capable of determining many elements simultaneously.

Table 3 – *Instrumental methods used for elemental analysis of coal*[32]

Tablica 3 – *Instrumentne metode za analizu elemenata u ugljenu*[32]

| Element<br>Element | Instrumental methods<br>Instrumentalne metode | | | | |
|---|---|---|---|---|---|
| | INAA | AES | AAS | MS | XRF |
| Ag | + | + | + | + | |
| Al | + | + | + | + | + |
| As | + | + | + | + | + |
| Au | + | + | | + | |
| B | + | + | | + | |
| Ba | + | + | + | + | |
| Be | | + | + | + | |
| Bi | | + | + | + | |
| Br | + | | | + | |
| Ca | + | + | + | + | |
| Cd | + | + | + | + | |
| Cl | + | | + | + | + |
| Co | + | + | + | + | + |
| Cr | + | + | + | + | |
| Cs | + | | + | + | + |
| Cu | | + | + | + | |
| Er | + | + | + | + | + |
| Eu | + | + | + | + | + |
| F | | | | + | |
| Fe | + | + | + | + | + |
| Ga | + | + | | + | + |
| Gd | + | + | + | + | |
| Ge | + | + | | + | |
| Hf | + | + | | + | + |
| Hg | + | | | + | |
| Ho | + | + | + | + | + |
| I | + | | | + | |
| In | + | + | + | + | |
| Ir | + | + | | + | |
| K | + | + | + | + | + |
| La | + | + | + | + | + |
| Li | | + | + | + | |
| Lu | + | + | | + | |
| Mg | + | + | + | + | + |
| Mn | + | + | + | + | + |
| Mo | + | + | + | + | + |
| Na | + | + | + | + | + |
| Nb | | + | | + | |
| Nd | + | + | + | + | + |
| Ni | + | + | + | + | + |
| Os | | + | | + | |
| Pb | + | + | + | + | + |
| Pr | + | + | + | + | + |
| Pt | + | + | + | + | + |
| Rb | + | + | + | + | + |
| Re | + | + | | + | |
| Rh | + | + | + | + | |
| Ru | + | + | | + | |
| Sb | + | | + | + | |
| Sc | + | + | + | + | + |
| Se | + | + | + | + | + |
| Si | + | + | + | + | + |
| Sm | + | + | + | + | + |
| Sn | | + | + | + | + |
| Sr | + | + | + | + | + |
| Ta | + | + | | + | + |
| Tb | + | + | + | + | + |
| Te | | | + | + | + |
| Th | + | + | | + | + |
| Ti | + | + | | + | + |
| Tl | + | + | + | + | + |
| Tm | + | + | + | + | + |
| U | + | + | | + | + |
| V | + | + | + | + | + |
| W | + | + | | + | |
| Y | | + | | + | + |
| Zn | + | + | + | + | + |
| Zr | + | + | | + | + |

Both wavelength-dispersive and energy-dispersive XRF instruments are used in the analysis of coal. Either type can be used to determine the major elements in coal ash (Si, Al, Fe, Mg, Ca, Na, K, Ti, and Mn). However, energy-dispersive instruments offer greater sensitivity so they are commonly used to determine trace elements. For example, *Evans* et al.[43] reported accuracies of ± 10 % for Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce in eight whole coal and ash samples. *Hower* et al.[44] used principle component analysis on XRF-generated major and trace element data of mineral matter in the Blue Gem Coal Bed. They determined that Ni, Cu, Cr, and Co were associated with organic material and Ti, Zr, K, and Rb were associated with clastic material. XRF is moderate in price yet it does not have the sensitivity that some of the other more expensive techniques have.

Electron microscopy is used to analyze micrometer-sized areas in coal and coal combustion products. Energy-dispersive X-ray units are attached to most modern electron microscopes allowing for quantitative or qualitative determinations of elemental contents in individual particles. However, electron microscopy methods are expensive and are not used for bulk analyses. The electron microprobe (EMP), scanning electron microscope (SEM), and transmission electron microscope (TEM) are instruments which use an electron beam to generate X-rays, whereas the ionprobe micro-analyzer (SIMS) uses an ion beam, and the particle-induced X-ray emission (PIXE) uses a proton beam to generate the characteristic X-rays.

Electron microscopy sometimes allows the direct determination of the mode of occurrence of trace elements in coal and coal ash, making the techniques especially valuable to coal chemists, geochemists, and geologists. A good review on coal chemistry, as determined by SEM can be found in *Finkelman*.[45] He includes a table of 47 trace elements and their suggested modes of occurrences. *Wert* et al.[36] applied TEM to coal. They were able to identify inorganic and organic elements in coal macerals.

There are many other specialized techniques such as Mossbauer, laser microprobe mass analyzer (LAMMA), Fourier transform infrared spectroscopy (FTIR), glow dischange mass spectrometry (GMS) and X-ray absorption fine structure (XAFS). Sometimes the choice of methods and techniques is difficult for the analyst because each offers distinct advantages and disadvantages.

## Coal utilization

Coal has been an important source of energy in the World since the 17$^{th}$ century. Its use as a fuel and non a fuel material has been included in nearly every industry from textile to iron and steel. In the future, coal will keep its important position as a world energy source, because of its relatively abundant reserves in comparison to the decreasing reserves of, both, petroleum and natural gas. The iron and steel industry will continue to use coal which is considerably competitive against other sources of energy in producing steel.[1,2]

The environmental impacts of coal usage can be grouped into three categories: air, water and land pollutions. The pollutant emissions from coal utilization may cause serious environmental and health risks. The emissions of $CO_2$, $SO_x$, $NO_x$ and some of volatile inorganic elements (especially As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se), and their compounds in flue gases from coal combustion, may have important environmental impacts such as global temperature rising and direct hazards of volatile compounds to agriculture, soil, water, and human health. The inorganic constituents in fly ash, bottom ash, and slag disposed are other types of land pollution. Once released into the atmosphere, these pollutants can be transformed by a variety of chemical reactions.

A number of technical and technological options are available for the use in industrial plants in an environmentally acceptable manner. The following alternatives can be the choice: selecting a type of coal that eliminates the pollutant; controlling the combustion temperature to minimize the emission of volatile inorganic elements or gaseous oxides; removing the pollutant from the process input (such as desulphurization of coal); removing the pollutant from the process effluent (eg., passing polluted air through dust collectors with filters); replacing the process with one that does not generate or will minimize the pollutant (eg., pressurized fluidized bed combustion instead of pulverized coal burning).

## Conclusion

In the future, many of field utilization will continue to consume increasing quantities of coal. The inorganic constituents in coal have a significant effect on almost all aspects of coal conversion and utilization (specially pyrolysis and combustion). Knowledge of range, distribution, and affinities of the inorganic elements is one of the main factors that influence their transformation and separation during coal conversion process. There are many techniques and instrumental methods available for the analysis of elements in coal and their products.

The pollutant emissions from coal utilization may cause serious environmental and health risk, so it is an important issue with respect to environmental protection.

### References
### Literatura


1. *K. H. van Heek,* Fuel **79** (2000) 1.
2. *H. H. Schobert, C. Song,* Fuel **81** (2002) 15.
3. *M. Xu, R. Yan, C. Zheng, Y. Qiao, J. Han, C. Sheng,* Fuel Process. Techol. **85** (2004) 215.
4. *W. T. Reid,* Chemistry of Coal Utilization, John Wiley and Sons, New York, 1981, p. 1389-1445.
5. *R. B. Finkelman,* in "Organic Chemistry", Plenum Publishing Corporation, New York, 1993, p. 593-607.
6. *R. B. Finkelman* in "Coal", Istanbul Technical University, Mining Faculty, Istanbul, 1994, p. 115-125.
7. *S. L. Bend,* Fuel **71** (1992) 851.
8. *M. Th. Mackowsky,* "Minerals and Trace Elements Occurring in Coal" in Stach's textbook of Coal Petrology, Gebruder Borntraeger, Berlin, 1982.
9. *H. H. Damberger, R. D. Harvey, R. D. Ruch, J. Thomas,* in "The Science and Technology of Coal and Coal Utilization", Plenum Press, New York 1984, p. 7.
10. *D. A. Spears* in "Coal and Coal-bearing Strata: Recent Advances", Geological Society of London, Oxford, 1987, p. 171.
11. *S. V. Vassilev, C. G. Vassileva,* Fuel Process. Technol. **48** (1996) 85.
12. *S. Vassilev, K. Kitano, C. G. Vassileva,* Fuel **75** (1996) 1537.
13. *D. J. Swaine, F. Goodarzi,* Environmental Aspects of Trace Elements in Coal, Kluwer, Dordrecht, 1995.
14. *V. Valković,* Trace Elements in Coal, CRC Press, Boca, Raton, 1983.
15. *N. Limić, V. Valkovic,* Fuel **65** (1986) 1099.
16. *H. J. Gluskoter,* Trace Elements in Coal: Occurrence and Distribution, Illionis State Geological Survey, Urbana, 1977, p. 154.
17. *F. Goodarzi,* Fuel **66** (1987) 250.
18. *D. J. Swaine,* Trace Subst. Environ. Health **11** (1997) 107.
19. *D. J. Swaine,* Trace Elements in Coal, Butterworths, London, 1990.
20. *F. Goodarzi, A. E. Foscolos, A. R. Cameron,* Fuel **64** (1986) 1599.
21. *X. Querol, T. J. L. Fernandez, S. A. Lopez,* Fuel **74** (1995) 331.
22. X. Querol, T. J. L. Fernandez, S. A. Lopez, M. Duran, Appl. Geochem. **7** (1992) 547.
23. *F. Goodarzi,* Fuel **81** (2002) 1199.
24. *H. Lu, H. Chen, W. Li, B. Li,* Fuel **83** (2004) 39.
25. *B. M. Gibbs, D. Thompson, B. B. Argent,* Fuel (2004) 2271.

26. *Q. Liu, H. Hu, Q. Zhou, Sh. Zhu, G. Chen,* Fuel (2004) 713.
27. *F. E. Huggins, J. Zhao, N. Shah, G. P. Huffman,* Int. Ash Utilization Symp., Center for Applied Energy Research, University of Kentucky, Lexington, 1997, p. 682-689.
28. *P. K. Mukhopadyay, G. Lajeunesse, A. L. Crandlemire,* Int. J. Coal Geol. **32** (1996) 279.
29. *R. B. Finkelman, A. Kolker, C. A. Palmer,* Int. Ash Utilization Symp. Center for Applied Energy Research, University of Kentucky, Lexington, 1997, p. 239-246.
30. *P. D. S. Rousseau, W. J. Przybylowicz, R. Scheepers, V. M. Prozesky, C. A. Pineda, C. L. Churms, C. G. Ryan,* Nuclear Instrum. Methods Phys. Res. B**130** (1997) 582.
31. *S. A. Benson,* Fuel Process. Techol. **85** (2004) 423.
32. *U. Koklu, S. Akman, L. Ruppert,* in "Coal", Istanbul Techical University, Mining Faculty, Istanbul, 1994, p. 97-113.
33. *R. N. White, J. V. Smith, D. A. Spears, M. L. Rivers, S. R. Sutton,* Fuel 68 (1989) 1480.
34. *M. Legin-Kolar, A. Rađenović,* Kem. Ind. **42** (1993) 441.
35. *J. P. Willis, R. J. Hart,* J. of Coal Quality **8** (1989) 3.
36. *C. A. Wert, K. C. Hsieh, M. Buckentin, B. H. Tseng,* Scanning Microscopy **2** (1998) 83.
37. *C. A. Palmer,* Energy and Fuels **4** (1990) 436.
38. *A. H. Ali, B. W. Smith, J. D. Winefordner,* Talanta **36** (1989) 893.
39. *M. W. Doughten, J. R. Gillison,* Energy and Fuels **4** (1990) 426.
40. *K. Matsuoka, E. Rosyadi, A. Tomita,* Fuel **81** (2002) 1433.
41. *M. K. Baruah, P. Kotoky, G. C. Borah,* Fuel **82** (2003) 1291.
42. *D. A. Spears, M. R. Martinez-Tarrazona,* Fuel **83** (2004) 2265.
43. *J. R. Evans, G. A. Sellers, R. G. Johnson, D. V. Vivit, J. Kent,* Energy and Fuels **4** (1990) 440.
44. *J. C. Hower, S. M. Rimmer, A. E. Bland,* Int. Journal of Coal Geology **18** (1991) 211.
45. *R. B. Finkelman,* Scanning Microscopy **2** (1988) 97.

## SAŽETAK

### Anorganski sastojci u ugljenu

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Anorganski sastojci u obliku minerala i organski vezanih anorganskih elemenata nalaze se u ugljenu kao sporedni elementi različitih masenih udjela i elementi u tragovima ($w = < 100 \cdot 10^{-6}$). Za ispitivanje udjela, pojavnih oblika i raspodjele anorganskih sastojaka u ugljenu primjenjuju se različite, uglavnom instrumentalne, metode. Poznavanje anorganskih sastojaka važno je radi mogućeg predviđanja ponašanja i uklanjanja pojedinih elemenata za vrijeme procesa konverzije ugljena. Anorganski sastojci znatno utječu na raznoliku uporabu ugljena, a posebno na okoliš i zdravlje ljudi zbog čega su, s nekoliko aspekata, opisani i u ovom radu.

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