

The Effect of Trace Element Associations and
Mineral Phases on the Pyrolysis Products from Coal

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The initial mode of occurrence of trace and minor elements in coal influences their ultimate fate during the processing and/or utilization of coal materials. A float-sink procedure and an acid-leaching procedure have been developed independently and used to estimate the trace and minor element associations with the organic and mineral phases in coal. Values obtained by the two methods were in agreement within the limits of analytical error. Ion exchange studies and internal surface area studies indicated that major differences that were observed could be explained in terms of exchangeable and/or chelated elements on the exposed surfaces of the coal. When these two factors were considered, results from these two methods were sufficiently reliable to allow their values to be used as indicators of an element's organic association.

Representative data for 50 elements from 9 coals are presented for both methods. The mean values for the same elements determined in the acid demineralized coals are given for 27 coals from 3 geographical areas. These values were compared to elemental values for crustal abundance and plant material; only S, Se, and Te had concentrations of organically associated elements significantly in excess of Clarke values (by factors of 20 to 50). Other elements, such as Pb, varied from virtually no organic association, to those, such as Ga, which averaged about 40 to 50 percent organic association.

Although many elements had some organic association, the major amounts of accessory elements in coal were present in the mineral phases. Semiquantitative mineral analysis of the low-temperature ashes (plasma ashing at $<150^{\circ}\text{C}$) was performed on the coals; clay, ranging from 20 to 80 percent and a mean of about 50 percent, was the predominant mineral phase in the inorganic fractions. The sulfide minerals were second and carbonates generally were the third most abundant mineral phase. In any particular coal, however, this order may be mixed or even inverted. Also frequently present in the coals is quartz and many other minerals in lesser amounts.

The mobilities during pyrolysis of the various elements were determined at 450°C , 600°C , and 700°C through the use of both batch and continuous-feed processes. This range in temperature was selected in order to produce chars with minimum sulfur content and with both maximum and minimum surface areas. The coals reached their most plastic (fluid?) state within this temperature range.

The concentrations of 50 elements were determined in 6 whole coals, also their corresponding char residues and condensed volatile products. For most of the coals studied, the data showed significant increase in mobility (volatilization) during pyrolysis for P, Cl, S, As, Br, I, Se, Te, and Zn. Elements that exhibited less significant mobility included Cd, Cr, Cu, Dy, Ga, Hf, La, Li, Pb, Sb, Sc, Sm, U, and Y. Those elements that generally exhibited no mobility during pyrolysis included Si, Al, K, V, Mg, Ca, Fe, Na, Ti, Ba, Ce, Co, Cs, Eu, Lu, Mn, Ni, Rb, Sr, Ta, Tb, and Th. Because of their extremely low concentrations, elements such as Ag, Au, In, Mo, W, and Sn were generally not detected at levels where any reasonable conclusions could be drawn.

Correlation of element mobility and organic association showed that elements associated with the organic material were the same elements that showed losses during pyrolysis. Two exceptions to this general rule were: (1) The alkali and alkaline earth elements generally were not lost during pyrolysis. These same elements were usually present to some extent in an exchangeable ion form and often showed a very high organic association. (2) The group of primarily sulfide elements, which include Pb, Zn and As, normally showed little or no organic association. The mechanism for mobility probably involved a thermal breakdown of the mineral itself. Iron usually occurred as the predominant sulfide mineral, but it was immobile.

The dissociation of pyrite when heated in a reducing atmosphere is well known. In coal, however, this reduction of pyrite to pyrrhotite takes place at relatively low temperatures, occurring at less than 450°C. During this process, two types of pyrrhotite were produced, one of which had magnetic properties. The material formed was susceptible to either chemical or magnetic cleaning. Mössbauer spectroscopy was used to identify four species of Fe^{+2} in the chars, only two species have been identified similarly in the raw coal.

The condensed volatile components from the pyrolysis of the coal were analyzed further to determine the organic composition of the products. Separation of the condensed organics into acid, base, and neutral fractions indicated that the components in the acid fraction predominated at the lower pyrolysis temperatures, and the components contained in the base fraction predominated at the higher temperatures. The distribution of constituents making up the organic fractions were shown to be strongly influenced by the temperature at which the pyrolysis was conducted. Furthermore, removal of virtually all of the mineral phases from the coal prior to heating significantly altered the proportion of tar to light fractions in the product; much less tar was produced when mineral phases were absent.

Correlations of mineral-phase content and the distribution of organic fractions at a given temperature indicated that the temperature at which the process was operated had a dominant effect on the product composition; nevertheless, the composition also was affected significantly by the kinds of mineral phases present. Individual effects of minerals on the distribution of organic constituents in condensed pyrolysis products are still being studied, but it is evident that knowledge of the organic associations and mineral phases present in an individual coal is necessary before a satisfactory evaluation of coal performance during utilization can be made.