Inorganic Species in Coals and Their Potential Catatytic Effects on Liquefaction Processes

by

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It may as well be admitted at the start that there is very little factual evidence available demonstrating the effect of inorganic species in coals on their behavior in liquefaction processes. The nature of the suites of minerals found in coals is well understood [1-3], and there is a certain amount of information about the concentrations of minor and trace elements in coals[3-15]. It is a theme of this paper that a great deal of more precise information is needed, which identifies the associations of a number of elements. On the basis of this information, significant experiments can be planned that will establish the role of inorganic species in their various forms of combination in coal conversion.

A small amount of data bearing on the problem has been obtained by the author and his colleagues, most of which is included in two publications whose preparation is nearing completion[16] (pre-publication copies will be available). This work is referred to below where appropriate.

Modes of Occurrence of Inorganic Matter in Coals

The principal minerals in coals are clays, together with (usually) smaller amounts of quartz, various carbonates (Ca, Mg, Fe, Mn), hematite and rutile (occasionally), and sulfides (almost entirely pyrite). Minor and trace elements may be present in clays on ion exchange sites and in other minerals by isomorphous substitution.

Metal ions can also be held by organic matter, and in two quite distinct ways. The organic structure of lignites, and to a minor extent subbituminous coals, contain carbonyl groups, -COOH, which are fairly weak acids (pK about 4-6). These can pick up ions from ground waters (e.g. Na, K, Ca, Mg), and the effect of acid extraction on the carbonyl vibration in the infrared spectra of lignites shows that a fairly high proportion (>50%?) of the carboxyl groups are in the salt form in the raw coals[17] (see also[18]).

Cations can also be held as chelate complexes, in which at least two functional groups in the coal structure bind the ion by a combination of electron transfer, electron sharing and electron donation. In coals of all ranks up to low volatile bituminous, phenolic OH groups certainly, and aromatic C=O groups probably, are available for chelation. In low rank coals, carbonyl groups are available also for this type of bonding. In general chelated ions are not removed readily by ion exchange.

Clay Minerals and Their Significance

In most coals the quantitatively most important minerals in coals are the clays, kaolinite, illite, chlorite and montmorillonites, and occasionally muscovite. The relative amounts of these can vary widely. It is known that some clays at elevated temperatures catalyze organic reactions, particularly those that proceed by carbonium ion mechanisms, such as the catalytic cracking of hydrocarbons. Indeed the first catalytic cracking carried out by the oil industry used clays, particularly montmorillonite. The catalytic sites are the structural -OH groups, which are quite strongly acidic. They are capable of exchanging protons for metal cations, with a drop in catalytic activity.

The ion exchange capacity is a factor that makes it difficult to predict the catalytic effects of clays in coals. It seems probably that during the history of a coal, ions from ground waters will to a greater or less extent replace protons or other cations and alter catalytic activity.

In current work by Dr. Mahmoud Abdel-Baset in the author's laboratory, the effect of a number of variables on behavior of coals in liquefaction are being roughly assessed in a simple way, by heating samples of coals in a steel vessel with tetralin. No catalyst is added, and the vessel is not pressurized with hydrogen so that it need not be a special high pressure autoclave.

Sufficient hydrogen can be transferred from the tetralin to the coal to liquefy it. It has been observed with a number of coals ranging in rank from lignite to high volatile bituminous that the conversion to liquid product is usually increased by some 10% if the coal is first extracted at 60°C with 2N hydrochloric acid and then washed with deionized water. The effect is apparently not due to strongly bound HCl that could not be washed out, since exposure of a coal for 24 hours in a closed vessel to the vapor of concentrated HCl did not change conversion to oil. A possible explanation of the effect is that the acid treatment removes metal cations from the exchange sites of clays and increases their catalytic activity, perhaps for hydrocracking. It must be borne in mind that treatment of some clays with acid changes the mineral structure as interlayer cations are removed and replaced by protons.

It must be admitted that catalysis by clay minerals need not necessarily involve carbonium ion mechanisms. Jurg and Eisma[19] heated a pure straight chain fatty acid, $C_{21}H_{43}COOH$, with water and bentonite clay to 200°C in a pressure vessel for several days. They found that a number of hydrocarbons and fatty acids with both more and fewer carbon atoms per molecule were produced. The distribution of products indicated that the reactions proceeded by a free radical mechanism, not a carbonium ion process. It can be inferred that the acid OH groups in the clay are not the catalytic sites for a free radical reaction and therefore that exchange of protons for metal cations would not be toxic.

Previous identifications of clay minerals in coals do not demonstrate the extent to which active hydrogen is replaced by metals. This should be determined by analysis of acid extracts of coals, and by X-ray diffraction studies of the mineral matter of coals isolated by ashing at low temperatures with the aid of an oxygen plasma.

Further careful study of the role of clay minerals in coal liquefaction processes is necessary. It must be determined whether the tendency to increased conversion on HCl extraction is reversed on removal of siliceous substances by subsequent HF extraction (present indications are that it is). It is also necessary to know what changes in mineral structure accompany HCl treatment. The effect of adding well characterized pure clay minerals should then be determined. While the hydrogen-donor technique described above is useful for initial rapid scanning of phenomena, any important conclusions should obviously be verified in a continuous reactor with added catalyst and hydrogen.

Lignites and Carboxylate Salts

A single experiment has been carried out in which a lignite was treated with dilute HCl to remove all exchangeable cations and any soluble salts.[16] A portion of the product was then treated with sodium chloride and enough sodium hydroxide to give a final pH of 8.3; the sodium ion introduced was about 3% by weight of dry coal. On catalytic hydrogenation of the two products, cation-free and sodium-rich, it was found that the conversions to oil were almost equal but the viscosity of the oil from the sodium-rich sample was about one quarter of that of the oil from the other sample. Moreover, the aromaticity of the asphaltenes from the two samples was markedly different.

These observations suggest exciting possibilities of controlling the character of the oil obtained from lignites, and raise important issues relating to the catalytic effects of cations in metal carboxylates. An extensive investigation is called for here, in which similar experiments are made with other lignites and other cations.

It has been found with many lignites that the loss in weight on extraction with dilute HCl is in the range 4-8%, and is equivalent in weight to at least 50% of the total mineral matter. It seems unlikely that the loss in weight could be due entirely to exchangeable cations, and so the presence of soluble salts has been suspected. Clearly the extract from a number of lignites and subbituminous coals should be analyzed for major cations and ions, and for trace elements.

Other Minerals

At first sight it would appear that carbonate minerals would play no significant part in the liquefaction process, except that manganese might be of interest. Some trace transition metals could be present in carbonates by isomorphous substitution; it might be possible to determine if this is so by carefully leaching bituminous coals with a weak acid, such as acetic, hoping that the concentration of protons would be low enough to minimize ion exchange reactions with the clay minerals.

Hematite is not a common mineral in coals, but when it occurs it is likely to be reduced at least to ferrous oxide and perhaps to iron. Hematite is known to adsorb trace metals strongly, and if present in this way in coals, they would be released during hydrogenation.

The almost universal presence of pyrite in coals raised some interesting questions. The known chemistry of pyrite[20] indicates that it would be reduced to metallic iron during coal liquefaction. However, such evidence as is available suggest that it is not, but gives a ferrous sulfide that may by pyrrhotite, $Fe_{1-x}S$. Some observations relative to the reduction produce of pyrite have been made recently.

Since the various petrographic components (macerals) and minerals in coals have different hardnesses, some degree of fractionation occurs if a coarse sample is crushed and a number of sieve fractions taken. Further fractionation occurs if the size fractions are separated in liquids of different density. A lignite was separated into seven fractions in this way by Dr. H.L. Lovell, and the fractions were hydrogenated in a batch autoclave by D.C. Cronauer (Gulf Research and Dev. Co., Pittsburgh). Six of the fractions gave closely similar, poor conversions to oil, 48% ± 2% while the seventh gave about 70% conversion.[16]

The seventh fraction had a high concentration of fusinite (30%), which is considered an inert maceral. On the other hand, it was the fraction of highest density, and had over double the mineral matter content of the other fractions. Moreover almost all the pyrite in the coal had accumulated in this one fraction, so that pyritic iron represented about 2.5% of the whole coal. It was suspected that this iron, perhaps as pyrrhotite, had a significant catalytic effect. As against this, Illinois coals naturally having high pyrite contents did not give noteably higher conversion than other coals of similar rank but lower pyrite content.

There are other facts that may be relevant. Those minor and trace elements that are associated with organic matter will tend to concentrate in the fractions of lower density; these include titanium (see below). Also, it was noticed that the SiO_2/Al_2O_3 ratios and the Ca content varied widely in the ashes of the various fractions, indicating that a considerable fractionation of the minerals had accompanied the separation processes. Further data are needed.

The possible formation of pyrrhotite in coal liquefaction raises some complex issues. Pyrrhotite minerals have a range of compositions, and therefore the concentration of defects in the crystal structure will vary. The presence of defects in a crystal structure is often associated with catalytic activity, and this activity will vary with the nature and concentration of the defects. Some pyrrhotite minerals are strongly ferromagnetic, as is smythite, another non-stoichiometric iron sulfide; greigite, yet another, is not.

It will be important to isolate the iron compound(s) from the residues after hydrogenation of a number of coals, identify it/them, and investigate catalytic and magnetic properties.

Gluskoter[3] has noted that the concentrations of the chalcophile (sulfide forming) trace elements in a set of Illinois coals showed correlations with each other; these elements were As, Sb, Hg, Pb, Ni, Cu, and Co. Zn is not included in this list although the same author has detected sphalerite, ZnS, in some coals. Some of the elements named may be present in pyrite by isomorphous substitution, and so would be released on hydrogenation of the pyrite, at least partly.

Minor and Trace Elements

The elements that cause catalyst poisoning in the hydrodesulfurization of residual fuel oils are all present in coals. The vanadium content of crude oils is highly variable, and can be well over 1000 ppm. or as low as 1-3 ppm. The elements V, Ni, Cu are present in oils mostly, though not entirely, as porphyrin complexes, which are soluble in the oil. It appears that the metal ions are extracted from the complexes and deposited on the catalyst surface.

Coals are largely derived from the higher plants, the leaves of which contain oxidative enzymes that tend to destroy chlorophyll during senescence of the leaf. One would not, therefore, expect to find much porphyrins formed from chlorophyll in coals, and so far as they have been studied the porphyrin content is indeed extremely low. The contents of V, Ni, and Cu are also low; V is typically 10-50 ppm of whole coal, though a few coals with contents over 10 ppm have been noted by Zubovic.[10] Chelating groups that coals do contain are mostly oxygen functional groups, though nitrogen, presumed to be present in pyridine rings, may be involved also. Thus the situation in regard to trace elements is very different as between coal and oil. Algae, from which oils are believed to be chiefly derived, do not contain lipoxidase enzymes, and their chlorophyll is not destroyed as their cells die.

Zubovic[9] has considered the tendency of trace elements to be present in coals as organometallic complexes rather than in mineral phases. This tendency should increase with increasing values of the ratio, ionic charge/ionic radius. Ge, Ga, Ti, and V are among the elements expected to have a high tendency to form organic complexes. This tendency could be overridden if formation of a highly insoluble oxide or sulfide can occur, so that the partition of such an element between organic and mineral association will depend, inter alia, on the relation between the stability constant of available complexes and the solubility product of feasible insoluble compounds. Copper, for example, forms a highly insoluble sulfide, and is unlikely to form organic complexes if H_2S was present in the environment of deposition of the coal. Hence the distribution of some metals between the two modes of occurrence will differ for saline and fresh water conditions in the original peat swamp.

The distribution of minor and trace elements between the two modes of occurrence is very important in considering possible catalytic effects. It is difficult to imagine an element poisoning an added (synthetic) catalyst unless it is present as an organometallic complex that is soluble in the vehicle. On the other hand any positive catalytic effect of inorganic species of coals is likely to be on the surfaces of distinct solid phases.

Yet few studies have been made that attempt to distinguish experimentally between the two modes of occurrence of inorganic species.

Such attempts as have been made have relied on determination of whether an element tends to be concentrated in the high density fraction of a coal.[4,6,9] The data of Alpern and Morel[6] show that the ratio of concentrations of an element in light and heavy fractions of a coal can be highly variable as between different coals.

It is known that there may be different mineral associations with the different macerals in a coal.[21,22] It is also likely that trace element associations will differ also. Separation of fractions of a coal according to density effects some maceral separations as well as mineral, and therefore the interpretation of trace element concentrations in density fractions may be difficult. Nevertheless, coals should be fractionated on the basis of differing hardness and density of components, as described above, and attempts made to understand the trace element distribution in the fractions in the light of their petrographic analysis.

The one element known already to have a (negative) catalytic effect on coal liquefaction is titanium. Wet chemical analysis usually reports TiO_2 as 0.5-3% of the ash, so that it is a minor element in coal rather than a trace element. It does occur as TiO_2, rutile, in some coals, but apparently is common in organometallic form in many coals. In Zubovic's scale of affinity for organic matter, titanium ranks fourth below Ge, Be and Ga, elements that are much less abundant in coals than titanium. Perhaps the most significant fact about titanium in coals, vis â vis such trace elements as vanadium, is that it is present in much higher concentrations.

Little information is available about the distribution of titanium between organic and mineral associations, and none about its association with the various macerals. It is important that such data should be developed.

The study of Alpern and Morel[6] showed that there are often considerable lateral variations in trace element concentrations within a single seam. Humic acids in soils and peats are known to bind strongly a variety of metals;[8] yet the concentrations of trace elements in peats are often below the average abundances in the earth's crust.[23]

A number of investigations (reviewed by Given and Dickinson[23]) have shown that trace elements tend to accumulate around the margins of peat swamps, where they are efficiently trapped from inflowing waters so that areas remote from the source have little opportunity to become enriched in trace elements. It is easy to see that in these circumstances a coal seam formed from the peat is likely to have very variable trace metal concentrations over its lateral extent and possibly also in vertical profiles. The various macerals arise from different types of plant debris in peat swamps and from various processes of degradation. One would predict, therefore, that the different macerals in a sample of coal from one location in a coal seam will have different trace element distributions.

These complexities are unfortunate for the investigator and the process engineer, but are a fact of life to be reckoned with. However, even though the total concentrations of trace elements may vary within a seam, the distribution between the different modes of combination may be more regular.

Conclusions: Needed Research

It is clearly of importance not only to understand the distribution of the various inorganic species in coals and their associations but also their fate during conversion processes. The latter aspect must be studied by analyses performed on the catalyst, the solid residue and the liquid products from the process, including the aqueous phase, and for a few elements perhaps also the gaseous products.

The fate of inorganic species during conversion is also relevant to the environmental impact of coal liquefaction, and this should be borne in mind during studies related to catalytic effects. Some elements may be more or less easily leached by weathering from the solid residue than would be predicted from their mode of occurrence in the original coal. Other elements may appear in the aqueous discharge or as contaminants in the recovered sulfur. If the oils produced by coal liquefaction are to be used for combined cycle power generation, they must not only have low contents of particulate mineral matter, but must also have contents of certain elements (e.g. Na, K,V) at levels of 1 ppm or less. This provides a further reason for determining inorganic species in the product oils.

Accordingly, it is submitted that the following questions with regard to inorganic species in coals need to be answered:

1. What cations of the elements abundant in the earth's crust are associated with the clay minerals? in what amounts? with what effects on catalysis?

2. What cations occur in carboxylate salts in lignites and subbituminous coals?

3. What is the distribution of the more significant minor and trace elements between clay minerals, carbonates, sulfides, carboxylate salts (for low rank coals) and organometallic structures?

4. What changes, other than removal of the cations referred to in question 2, are brought about by extraction with dilute acid?

Clues to part of the answer to question 3 can be obtained from correlations between the concentrations of certain elements in a series of coals. For example, there appears to be a tendency in the data of O'Gorman and Walker[3] for the concentrations of Pb and Zn, but not Cu, to be high in coals high in pyrite. There is an unsurprising tendency for Sr and Ba to be high in lignites from North Dakota, Montana and Wyoming, in which Ca is also high, but in addition the concentration of Mn is usually relatively high in the same samples and some Texas lignites, implying that a considerable part of the Mn is present as manganous carboxylates.

An adequate data base is probably available now for it to be worth getting trace element concentrations and coal characterization data on to magnetic tape and making computer tests for correlations like those indicated above.

It is difficult to make any firm statement as to how many coals will need to be studied to establish reasonably generalized answers to questions 1-4 above; more samples will, of course, be needed in answering some questions than others. The total number will inevitably be large, in view of the number of variables, and the widely differing geological setting, geological history, petrography and rank of the coals in the major coal basins of the United States. Perhaps the best policy would be to work initially with a carefully selected suite of 50 samples, and then assess what further should be done.

It has been shown that the petrographic compositon of a coal can have a considerable influence on its liquefaction behavior.[16] Some degree of management of coal composition can be achieved by selection of coal and by adapting coal preparation plants to perform the kind of particle size and density fractionation described above. Accordingly, it would be desirable to know what fractionations of minerals and trace elements accompany this process. It is known already that pyrite and the larger grains of other minerals accumulate in the higher density fractions, but more detailed information is needed than this. A pilot study should be performed on four or five coals to see to what extent data capable of being interpreted and generalized are likely to be obtained. As indicated earlier, interpretation may be difficult, but the approach should be explored, and further work planned in the light of the results.

For such minor elements as Na, K, Ti, Cl, it should be possible to determine maceral and/or mineral associations by means of computer-automated scanning electron microscope/electron microprobe instrumentation; it is understood that a proposal embodying this approach is shortly to be submitted to EPRI. Unfortunately it is unlikely that the associations of trace elements can be obtained in this way.

A feasible means of determining organometallic associations should be the extraction of coals with phenanthrene, followed by determination of the relevant trace elements in extract and residue.

There are a number of lines of experimentation that should be followed in attempts to determine directly the effect of inorganic species on liquefaction behavior. Correlations between behavior and the analyses proposed above should, of course, be sought. In addition, the effects of demineralization, spiking demineralized or low mineral matter coals with pure minerals, isolating the mineral matter from one sample by low temperature ashing and adding it to others, etc. should be investigated.

It will be important to determine by X-ray methods what sulfide(s) are produced by reduction of pyrite, and establish their magnetic and catalytic properties. This by itself will be a substantial project. With lignites, the role of cation-carboxylate associations in determining yields and properties of oil must be established. Finally, petrographic, chemical and mineralogical analyses of the solid residue from liquefaction (spent from the iron sulfides) are needed, as is identification of elements other than titanium deposited on the catalyst.

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