

TASK II

Project II.4

ESR and ENDOR INVESTIGATION FOR COAL LIQUEFACTION UNDER MILD CONDITIONS

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INTRODUCTION

This annual report summarizes our research activities and accomplishments during May 1, 1992 through April 30, 1993. This period constituted the concluding year of our project, wherein our goal has been to obtain an enhanced understanding of the fundamental steps in the chemistry of coal liquefaction under mild conditions---low reaction temperature and pressure. Our working hypothesis has been that free organic free radicals (i.e., chemical entities bearing unshared electrons, therefore high chemical reactivity) play a key role in the mechanism of coal liquefaction, especially under homogeneous catalysis conditions. A strong support for our hypothesis has been provided by the pioneering studies of Farcasiu and coworkers¹. From their results on model compounds such as 1,2-di-1-naphthylethane (DNM), compound I here, these authors have suggested that radical cation species play the key roles in the mechanism of intramolecular bonds in such compounds¹. However, Farcasiu's evidence in support of this hypothesis was only indirect, since no direct spectroscopic data were cited¹. Since ESR and ENDOR spectroscopies are known to be the most direct techniques for characterizing free radical species, we proposed that such studies be carried out on compounds such as DNM, and related model compounds.

II. Experimental Techniques

A. ESR/ENDOR Measurements

All ESR and ENDOR measurements were made at the X-band (9.5 GHz) microwave frequencies utilizing the modified Bruker ER300D ESR/ENDOR spectrometer system. Over the years we have developed accessories for carrying out in-situ ESR investigations at

temperatures up to 800 °C, and ENDOR measurements up to 250 °C. In our system, the microwave frequency is measured with a Hewlett-Packard digital frequency counter, model 5430A, whereas the magnetic field is calibrated with an NMR gaussmeter. For liquid samples, the radicals are produced via reaction with triflic acid or a sodium/potassium reduction procedure. A methodology was developed for radical generation and ESR/ENDOR measurements under various gaseous atmospheres, including under a vacuum or an argon atmosphere.

B. Photochemical / Product Analysis Measurements

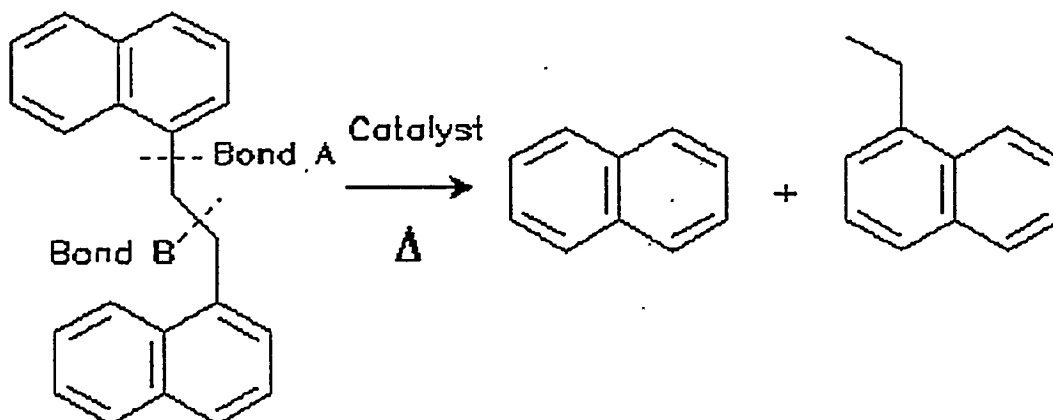
Photochemical reactions were carried out utilizing a mercury lamp-based reactor developed in our laboratory. Excitation was obtained at preselected wavelengths utilizing various cut-off filters. Product identification was carried out by gas chromatography, NMR, and mass spectrometry, utilizing laboratory-synthesized model compounds.

III. RESULTS AND DISCUSSION

During the past few months, we have investigated the bond cleavage mechanisms of polycyclic aromatic model compounds in order to better understand catalyst functions. Our approach towards understanding the bond cleavage mechanisms of polycyclic aromatic compounds has involved a dual pathway to elaborate the desired information. In the first pathway, independent generation of important reactive intermediates has been attempted in order to accurately assess their reactivity. A second approach has been to characterize the proposed radical intermediates by ESR techniques.

The mechanistic problem arises from the products isolated from a series of naphthylated model compounds which were subjected to coal liquefaction conditions with various catalysts which have been prepared elsewhere in the Consortium. Model compound I (i.e., 1,2-di-1-naphthylethane (DNM)) is shown in Figure 1 and is representative of the reactivity of this set of model compounds in that bond A cleavage is always observed. Bond A is the bond connecting the naphthyl group to the alkyl side chain. The bond A cleavage has been rationalized as originating from a radical cation, based on the observation of catalytic activity, the appearance of a surface charge on the catalyst at the same temperature as the onset of catalytic activity,¹ and theoretical calculations which indicate the least electron density in

Figure (1)

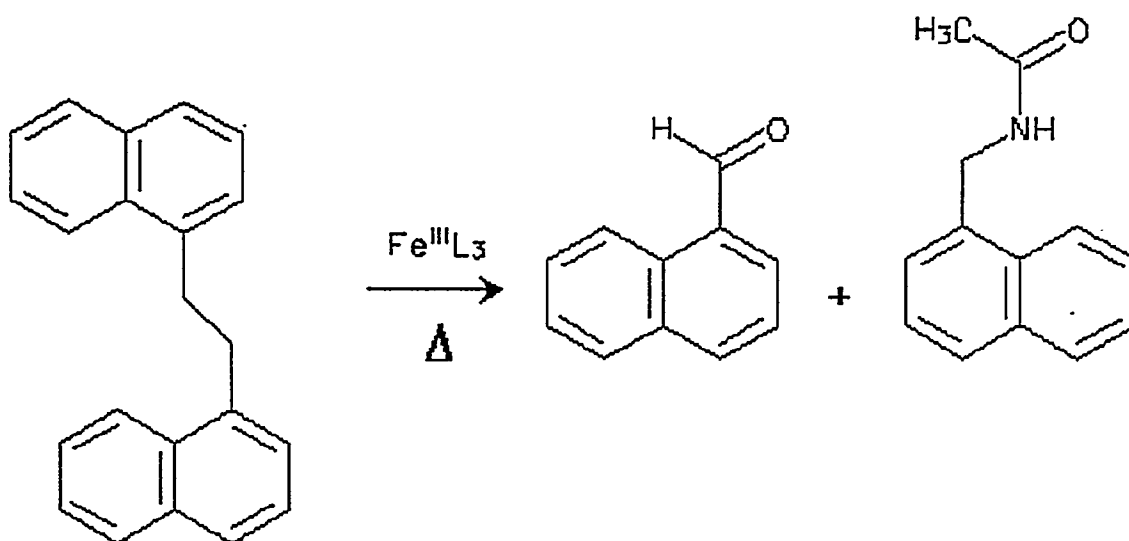


catalytic conditions. 1,2-di-1-naphthylethane is representative in that bond A is the predominate bond being cleaved under catalytic conditions. This result is shown in Figure (1). While the radical cation explanation of catalyst reactivity is attractive, the results of these naphthylated compounds are in apparent contradiction to the known reactivity of monoaryl systems. We report here results from the bond cleavage reactions of the radical cation of 1,2-di-1-naphthylethane (DNM) which appear to contradict the reactivity pattern postulated above.

Independent generation of the radical cation of DNM has been attempted by several routes. The first method for generating the radical cation utilized a well-known and accepted photochemical procedure in which an oxidant is created by photochemical excitation. This reactivity has been included in previous reports from this group and shows conclusively that the radical cation of 1,1,2,2-tetraphenylethane (TPE) cleaves only bond B. Following the same procedure that was used for TPE, 9,10-dicyanoanthracene was irradiated in a solution containing DNM. In analogy to reactions of 1,2-diphenylethane, no bond cleavage was observed which could be attributed exclusively to the radical cation of DNM, indicating that the bond dissociation energy of the radical cation must be somewhat high. An alternative method of generating the radical cation of DNM utilized the reaction of feroin (i.e., $\text{Fe(III)(1,10-phenanthroline)}_3^{+3}$) with DNM in acetonitrile at 130°C. Only preliminary data are available on mass balance at the current time. Gas Chromatography results of the reaction shown in Figure (2) have been presented at the 1993 Annual Technical Meeting.

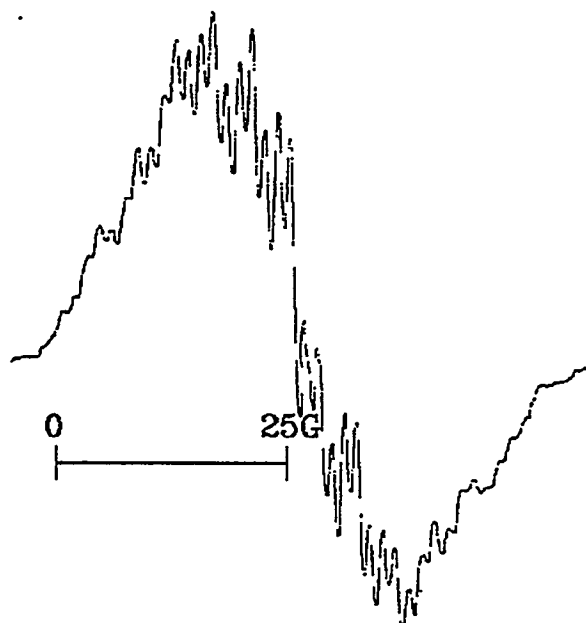
Since 74% of the reaction mixture resulting in two products which can only arise via Bond B cleavage were quantified, we conclude that a minimum of 37% of the radical cation reactivity at 130°C proceeds via bond B cleavage. Extensive efforts have been made to obtain an HPLC separation of the products, but so far our efforts have failed. A third method of examining the reactivity of the radical cation is to examine the mass spectral splitting pattern. From the ratio of the bond B cleavage products to the bond A products, a minimum ratio of 300:2 could be obtained for the reactivity of the gas phase radical cation of DNM.

Figure (2)



Since the quantification of the reaction did not proceed as desired, we have synthesized 1,1,2,2-tetranaphthylethane (TNE). Both photochemical and Fe based methods for radical cation generation proceed smoothly to yield products which can be easily characterized. The products are 1,1-dinaphthylmethane and 1,1-dinaphthyl-1-methoxy-methane, exactly analogous to those produced in corresponding reactions of TPE. Thus, there are no *a priori* differences in reactivity of the radical cations which lead us to believe that naphthyl containing polycyclic aromatic radical cations react differently than their phenyl counterparts. We are still attempting to get good mass balances from these reactions in order to make definitive statements.

Our second approach to understanding the reactions of radical cations is to identify them by ESR spectroscopy. In order to identify the radicals, appropriate methods of generation must be determined and the structures of easily identifiable intermediates must be conclusively identified. Representative of our efforts in this area is the spectrum of 1-methylnaphthalene shown below. It is apparent that sufficient fine structure exists to enable us to conclusively identify the radical when the resolution is optimized. However, the large number of nonequivalent hydrogens in this compound make an exact identity uncertain at the present time. (Other possible species in solution are the 1-methylnaphthalene radical or a dimeric radical cation species.) We have attempted to reduce the number of nonequivalent hydrogens by introducing symmetry into the molecule (e.g., 2,6-dimethylnaphthalene, 1,8-dimethylnaphthalene). However, producing spectra at this resolution has not yielded to our hands yet. Another approach for obtaining higher resolution was through ENDOR measurements. Strong ENDOR signals were easily obtained from radical cations and anions of the unsubstituted, symmetric model compounds naphthalene, anthracene and tetracene. However similar measurements were not successful on radicals obtained from compounds such as 4-(1-naphthylmethyl)-bibenzyl even in the powdered lattice, possibly because of the low ESR spectral intensity and/or fast electronic spin-lattice relaxation times. Efforts will be continued to complete these studies in the near future provided funding will be obtained.



References

1. a) Farcasiu, M.; Smith, C. *Energy Fuels*, 1991, 5(1), 83-7.
b) Farcasiu, M.; Smith, C. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, 1990, 35(2), 404-13.

2. a) Ades, Harriet F.; Companion, Audrey L.; Subbaswamy, K.R. *J. Phys. Chem.*, 1991, 95(17), 6502-7. b) Ades, Harriet F.; Companion, Audrey L.; Subbaswamy, K.R. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, 1991, 36(1), 420-4. c) Ades, Harriet F.; Companion, Audrey L.; Subbaswamy, K.R. *J. Phys. Chem.*, 1991, 95(6), 2226-31.
3. Farcasiu, M. private communication.
4. Mattes, S.L.; Farid, S. *Organic Photochemistry*, 1983, 6, 233.
5. Okamoto, A.; Snow, M.S.; Arnold, D.R. *Tetrahedron*, 1986, 42, 6175.

TASK II

Project II.5

XPS STUDIES OF RAW, CATION EXCHANGED AND LIQUEFIED CATION EXCHANGED LIGNITE COALS

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Introduction

X-ray photoelectron spectroscopy (XPS) has been used to investigate the surface characteristics of lignite coals and lignites that contain cation-exchanged iron. Cation exchanged lignite residues that have been processed in a coal liquefaction reactor have also been investigated. Beulah and Hagel lignite coals were used for this purpose. It has been reported that the liquefaction oil yield of lignites that undergo a cation-exchange process in which iron is exchanged primarily for calcium, was significantly increased.¹ The oil yield from the ion exchanged lignites was increased by 25% (for Beulah) and 10% (for Hagel) compared to the yield obtained by physically mixing 30Å ultrafine iron catalyst particles in the oxyhydroxide form with the coal samples. XPS studies of the two lignites confirm that the Fe and O concentration was generally increased after the ion exchange process. The increase of oxygen concentration in the ion-exchanged lignite is due to the majority of the iron particles being present in the oxyhydroxide form (FeOOH) after the ion exchange process. Sputtering with Ar⁺ ions followed by XPS depth profiling analysis has also been carried out to determine the distribution of the major elements in the surface and bulk regions of the coal particles. The elemental composition of each of the raw, cation-exchanged and liquefied lignite residues was found to change as the time of Ar⁺ sputtering increased. A systematic trend towards higher atomic concentrations of C and Fe was observed for the raw coals, the ion exchanged coals and the liquefied coal residues as the sputtering time increased. However, the surface concentrations of O and Si decreased consistently for all the coal samples as the sputtering time

increased.

Experimental

The two lignites used were Beulah (obtained from Department of Energy Coal Samples, DECS-11) and Hagel (obtained from Penn. State Office of Coal, PSOC-1482). These lignites were cation exchanged by stirring a slurry mixture of the lignite and ferric acetate [$\text{Fe}(\text{OOCCH}_3)_3$] in a 10 liter fermenter wherein iron was exchanged mainly for calcium. The lignites were then subjected to liquefaction experiments. These liquefaction experiments were aimed at investigating the effect of ion exchanged iron catalysts on the total yield and product distribution in the liquefaction process.

Three samples each from Beulah and Hagel lignites were studied. They were raw Beulah and Hagel coal, ion exchanged coal and residue from liquefaction (for both Beulah and Hagel lignites). The particle sizes of the powdered samples were less than 200 mesh. The powdered samples were mounted on the spectrometer probe tip by means of a double sided adhesive tape. The samples were pressed with the help of a metallic spatula (cleaned thoroughly with acetone and distilled water) so that the coal powders stuck to the adhesive tape. The excess powder was carefully tapped off. To exclude the possibility of getting unwanted photoionization signals from the tape, a separate XPS analysis was carried out for the tape alone and it was found that the constituents of the tape were not detected by XPS. After heat treating at 65 °C for 10 hours in a pretreatment chamber to remove remaining volatile materials from the coal residues, the samples were inserted into an ultrahigh vacuum chamber for surface analysis.

The samples were examined by XPS using a Kratos XSAM 800 spectrometer. Mg K α (1253.6 eV) radiation was used and a fixed retarding ratio (FRR) mode at a pass energy of 12 kV and 13 mA was employed. Under these conditions, the full width at half maximum (FWHM) of the Ag (3d_{5/2}) peak is 1.1 eV. The system pressure was normally maintained below 3×10^{-8} torr using a 300 1/sec ion pump and Ti sublimators to minimize contributions from the vacuum contaminants.

To compensate for sample charging, carbon 1s at 285 eV were taken as a

reference. Elemental concentrations were obtained from peak areas and corrected for atomic sensitivity factors. Also radiation damage to the samples due to the long time exposure to the X-ray beam was not observed.

In situ Ar⁺ ion sputtering of the residue samples was carried out using a differentially pumped and computer controlled 3M mini-beam ion gun. The incident ion gun was operated at 3.5 keV and sample currents were kept around 3 μ A across a sample area of about 5x5 mm². The estimated etching rate of ca. 50 Å/min was determined from a SiO₂ standard film. The pressure in the main chamber was kept below 4x10⁻⁶ torr during ion sputtering. After ion sputtering, a consistent increase in the FWHM for all elements was found with increasing ion dose. No compensation was made for charging of the sample after Ar⁺ sputtering.

Results and Discussion

Surface Characterization of Hagel Lignites

The individual XPS surface scans were carried out on the raw, ion exchanged and liquefied Hagel residue coal samples. The surface XPS spectra showed a distinct peak for each of the major elements, carbon, oxygen, and silicon as well as the minor components, sulfur, iron and calcium in each sample. The binding energies of these elements showed the expected values for the most stable oxidation states. The raw and ion exchanged samples showed a S 2p peak split into two small background photolines at 170 eV and 164 eV, respectively. The higher binding energy photoline can be ascribed to the oxidized form of sulfur (sulfate) and the peak at 164 eV corresponds to the inorganic sulfide and other sulfidic forms. The surface of the Hagel samples seemed to be oxidized to a significant extent as the sulfate peak was more predominant. The iron concentration increased sharply in the ion exchanged sample (compared to the raw sample), indicating that iron has been exchanged primarily for calcium, whose concentration drops in the ion exchanged sample compared to the raw coal. It has been reported that the liquefaction oil yield of lignites that undergo a cation-exchange process in which iron is exchanged primarily for calcium, is significantly increased¹ and this was confirmed by XPS studies. Oxygen concentration also increased in the ion exchanged samples, due to the iron being present primarily

in the oxyhydroxide form (Fe(OOH)). Silicon concentration dropped remarkably in the liquefied samples. Also noticeable was the decrease in iron concentration in the liquefied residue sample. This can be related to the fact that most of the iron becomes encapsulated by organic materials from the coal, as discussed in a later section of this report. The initial surface XPS elemental concentrations of the coal samples are given in Table 1. The Fe 2p peak shows the characteristic 13.6 ± 0.05 eV splitting between the $2p_{1/2}$ and $2p_{3/2}$ peaks in the ion exchanged sample. The observed splitting corresponds well with the Fe 2p peaks of Fe_2O_3 and/or FeOOH (Goethite) in model compound studies. The Fe compound on the surface of the catalyst samples can thus be ascribed to FeOOH.

Surface Characterization of Beulah Lignites

Similar surface XPS scans were carried out on the Beulah samples. The results were also quite similar to those of the Hagel samples. However the carbon concentration in the Beulah samples (except the liquefied residue sample) was higher than that of the Hagel samples. This is in accordance with the bulk analysis data. Also the surface concentration of iron in the Beulah ion exchanged sample was higher than that of the ion exchanged Hagel coal. Silicon also showed a higher surface elemental concentration for the raw and ion exchanged coal samples. A sharp drop in silicon concentration was observed in the case of the liquefied coal residue samples. This tendency corresponds well with the Fe element result. Further analysis is needed to characterize the mineral element effect on the oil yield. The initial surface XPS elemental concentrations of coal samples are given in Table 2.

Depth Profile Characterization of Hagel Lignites

In order to delineate the differences in the distribution of the elements and chemical changes between the surface and bulk, the samples were analyzed by combining Ar^+ ion sputtering with XPS measurement. For all the three Hagel samples, it was observed that a sharp drop in the oxygen concentration occurred, after the first sputtering, attributable to the air oxidation. The oxidized layer was estimated to be *approx.* 40-50 nm in thickness. An increase in Fe concentration was

observed with further Ar⁺ sputtering time. This can be explained in terms of the surface iron particles being covered with an oxide layer. It can also be concluded that the iron particles are most likely encapsulated by organic materials from the coal. The silicon concentration also decreases with sputtering time. This is associated with silicon being preferentially etched over other elements. Figures 1, 2, 3 show depth elemental concentrations, as a function of etching time, of the Hagel raw, ion exchanged and liquefied coal residue samples, respectively. The Fe/S ratio was generally greater than 1 in the case of raw and ion exchanged coal but the ion exchanged coal showed much higher values than this as the time of Ar⁺ ion sputtering was increased. The result is given in Figure 4. In coal liquefaction, the main role of the sulfate anion is to stabilize fine particles by retarding agglomeration and sintering of iron oxide particles. It has been reported that the oil yield from ion exchanged lignites is increased by 10 % for Hagel and 25 % for Beulah compared to the yield obtained by physically mixing 30 Å ultrafine iron catalyst particles in the oxyhydroxide form with the coal samples. This is due to lack of agglomeration during liquefaction and can be attributed to either S present in the liquefied samples (detected by XPS) or to the coal matrix, which appears to act as a substrate in preventing catalyst agglomeration.

Depth Profile Characterization of Beulah Coal

Most of the elements have the same trend in the Beulah samples as in the Hagel coal. With sputtering time, oxygen and silicon tended to decrease in concentration while carbon, iron, calcium and sulfur increased in concentration. The increase in calcium concentration was less in the beginning of the etching but with increased sputtering time (more than 30 minutes) the calcium concentration increased at a greater pace. Thus it can be said that the calcium distribution was less near the surface and was present in higher concentrations at a depth of 150nm (taking the sputtering rate to be 5 nm/min). There was a drop in oxygen concentration after the first sputtering period indicating that the surface oxides had been sputtered away. Figures 5, 6, 7 show depth elemental concentrations, as a function of etching time, of the Beulah raw, ion exchanged and liquefied coal residue

samples, respectively. The Fe/S ratio was always greater than 1 in the case of the ion exchanged coal as shown in Figure 8. EXAFS and Mossbauer studies have shown that under liquefaction conditions with dimethyl disulfide being added to catalyst/coal residue mixtures, the iron catalyst was converted to iron sulfide (pyrrhotite) within a few minutes of starting the reaction.²

Summary and Conclusion

It is apparent from this study that XPS and Depth Profiling can be used to delineate the elemental concentration distributions on a depth scale. XPS studies of the two lignites showed that the Fe and O concentrations generally increased after the ion exchange process. The increase of oxygen concentration in the ion exchanged lignites is due to the majority of the iron particles being present in the oxyhydroxide form (FeOOH) after the ion exchange process. With Ar⁺ sputtering a systematic trend towards higher atomic concentrations of C and Fe was observed for raw coals, ion exchanged coals and liquefied coal residues. However, the surface concentration of O and Si decreased consistently for all the coal samples as the sputtering time increased. The Fe/S (catalyst element) ratio was always greater than 1 in the case of ion exchanged coal samples but became less than 1 in the liquefied coal residue samples (after a sulfiding treatment).

References

1. M. Taghiei, F. Huggins, B. Ganguly, and G. Huffman, *Energy & Fuels* 1993 7, 399.
2. M. Taghiei, Private communications.

Table 1. XPS analysis (at. %) of Hagel coal samples

| Sample | C | O | Fe | S | Ca | Si |
|----------------------|------|------|-----|-----|-----|-----|
| Raw Coal | 67.1 | 25.8 | 0.1 | 0.2 | 0.2 | 6.6 |
| Ion Exchange Coal | 64.1 | 27.8 | 1.1 | 0.2 | - | 6.8 |
| Liquefied Coal | 87.9 | 10.0 | 0.1 | 0.1 | - | 1.9 |

Table 2. XPS analysis of Beulah Coal Samples

| Sample | C | O | Fe | S | Ca | Si |
|----------------------|------|------|-----|-----|-----|-----|
| Raw Coal | 76.9 | 18.6 | - | - | 0.2 | 4.3 |
| Ion Exchange Coal | 69.9 | 25.0 | 1.4 | 0.3 | - | 3.4 |
| Liquefied Coal | 85.8 | 11.3 | 0.2 | - | - | 2.7 |

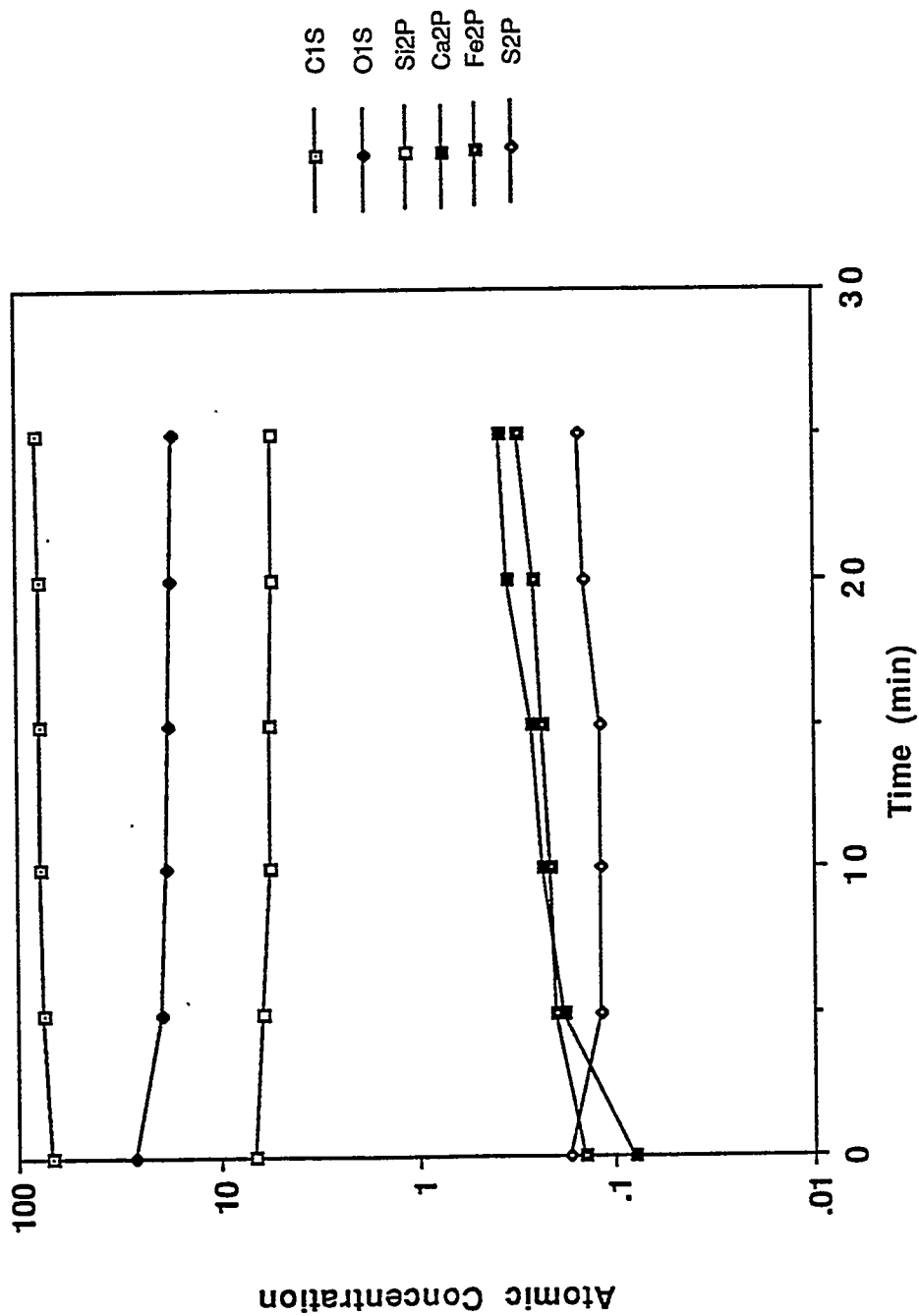


Figure 1. Depth Profile of Element Concentrations of Hagel Raw Coal

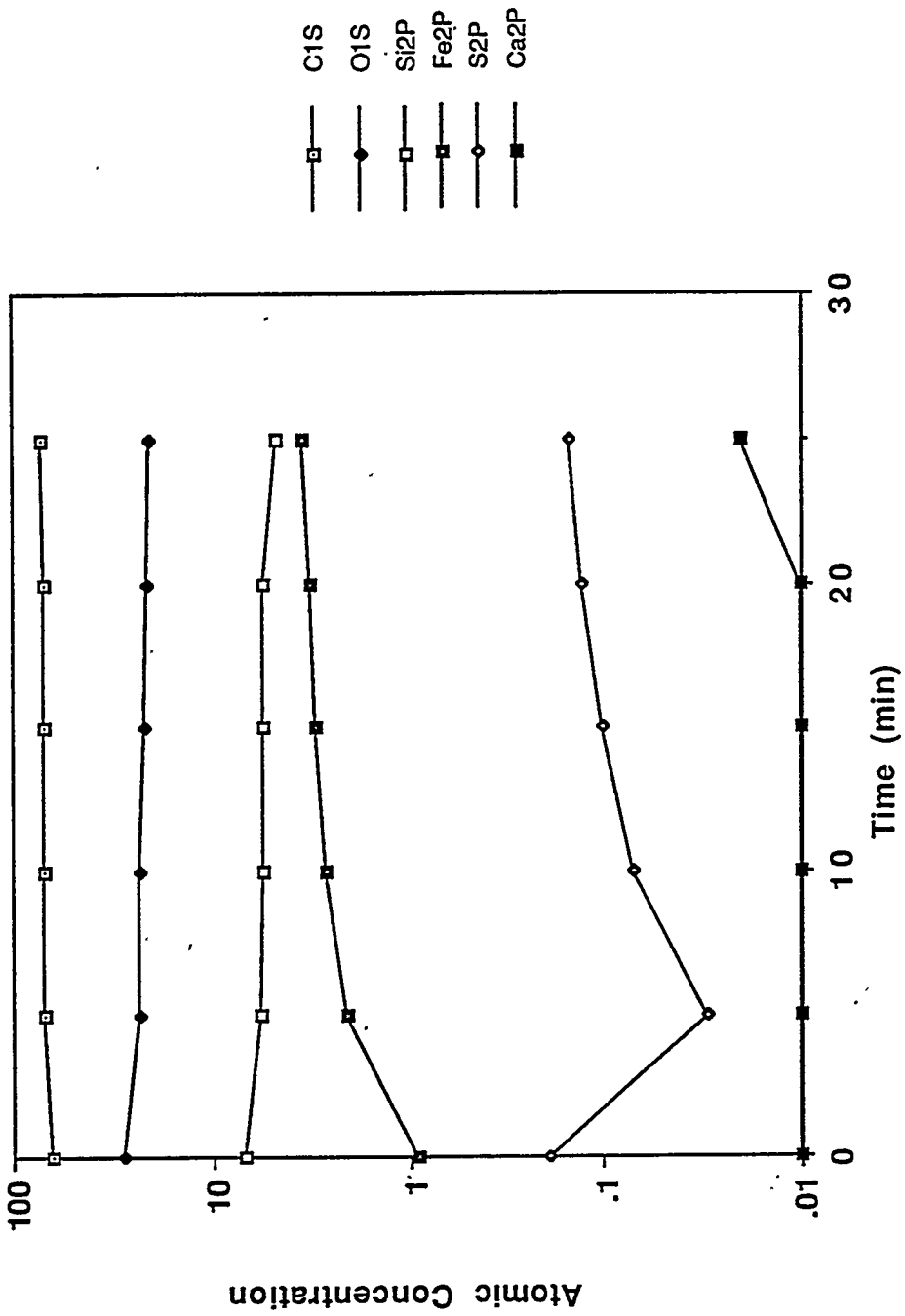


Figure 2. Depth Profile of Element Concentrations of Hugel Ion Exchanged Coal

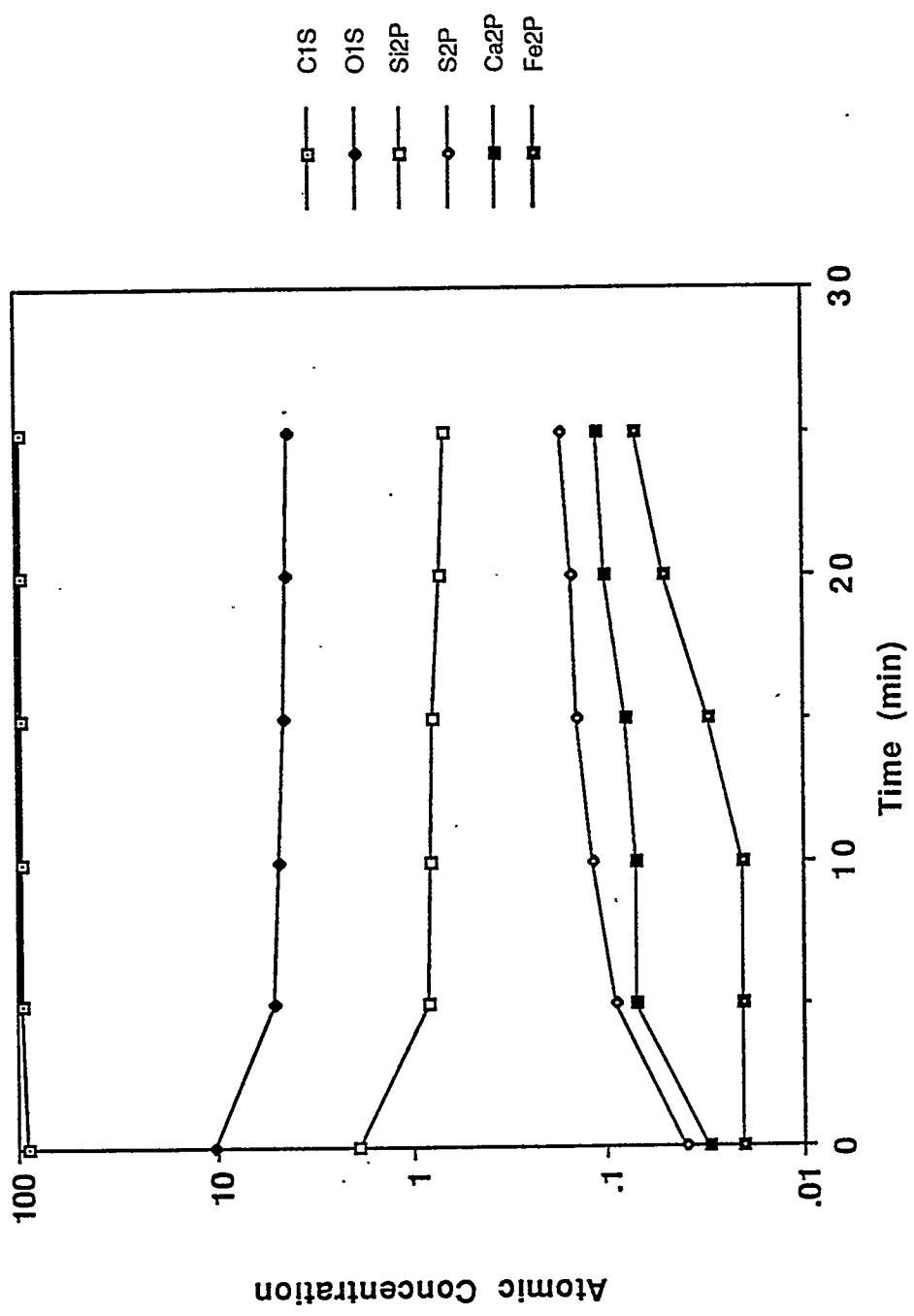


Figure 3. Depth Profile of Element Concentrations of Hugel Liquefied Coal Residue

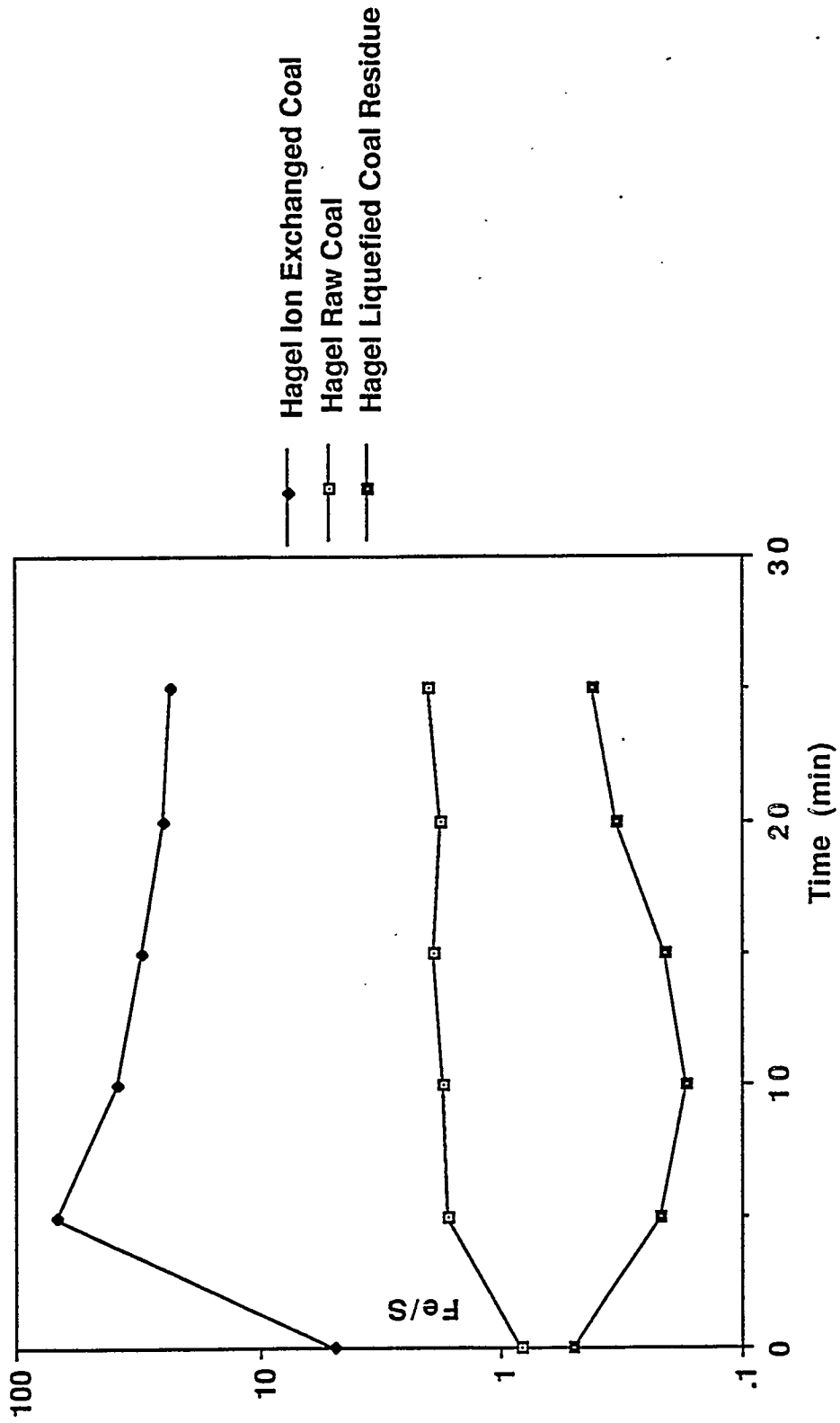


Figure 4. Fe/S Ratio for Hagel Raw Coal, Ion Exchanged Coal and Liquefied Coal Residue.

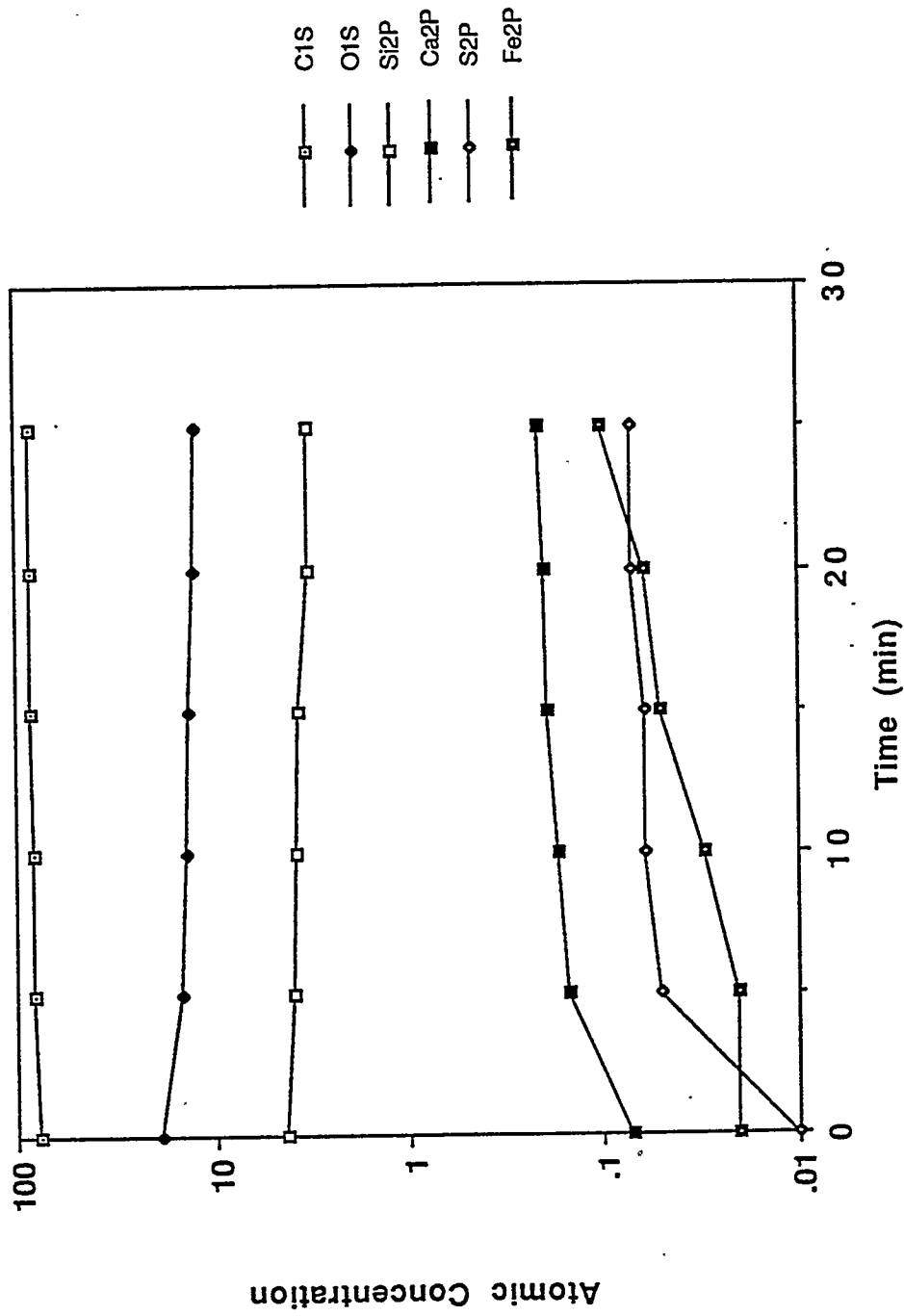


Figure 5. Depth Profile of Element Concentrations of Beulah Raw Coal

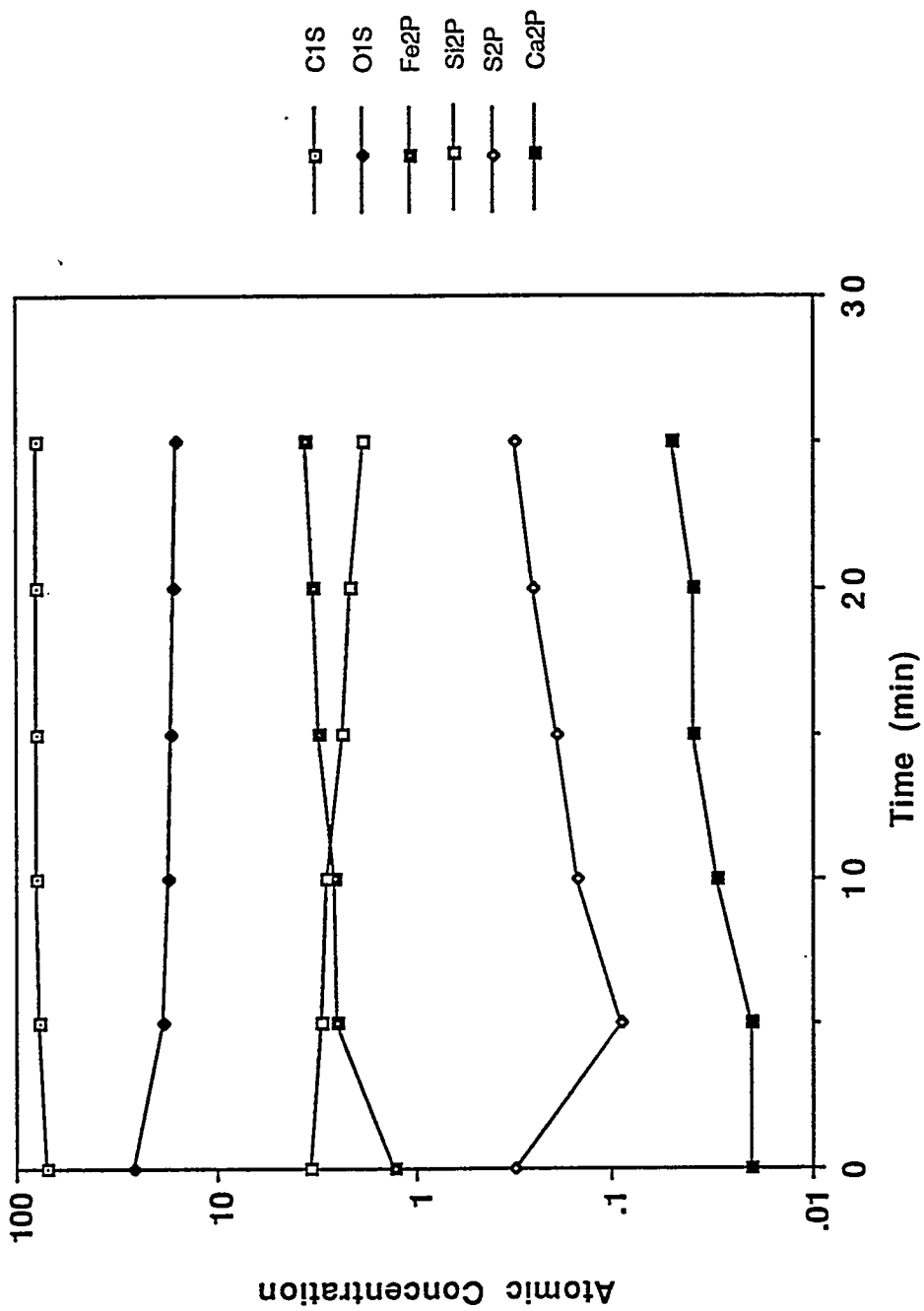


Figure 6. Depth Profile of Element Concentrations of Beulah Ion Exchanged Coal

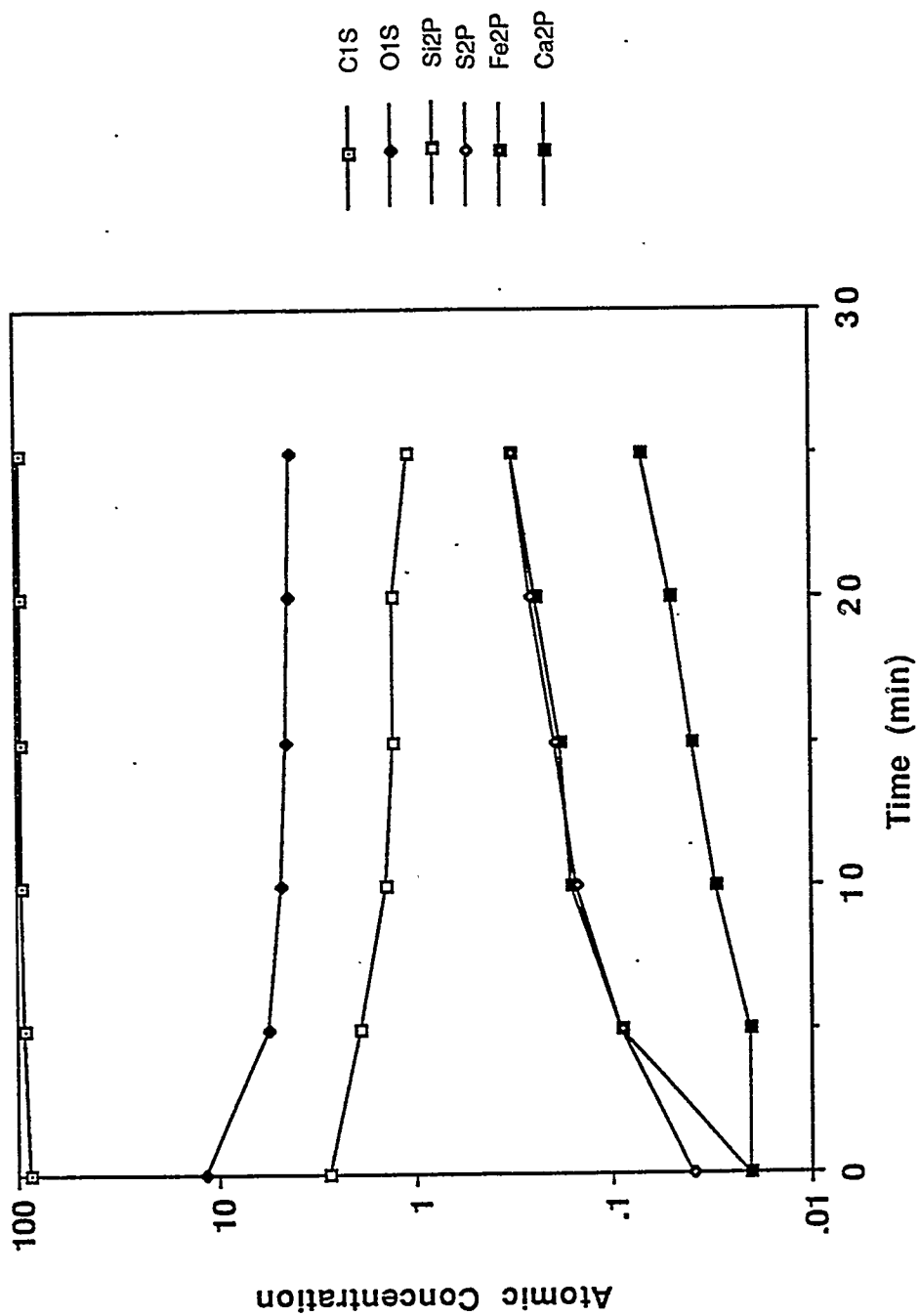


Figure 7. Depth Profile of Element Concentrations of Beulah Liquefied Coal Residue

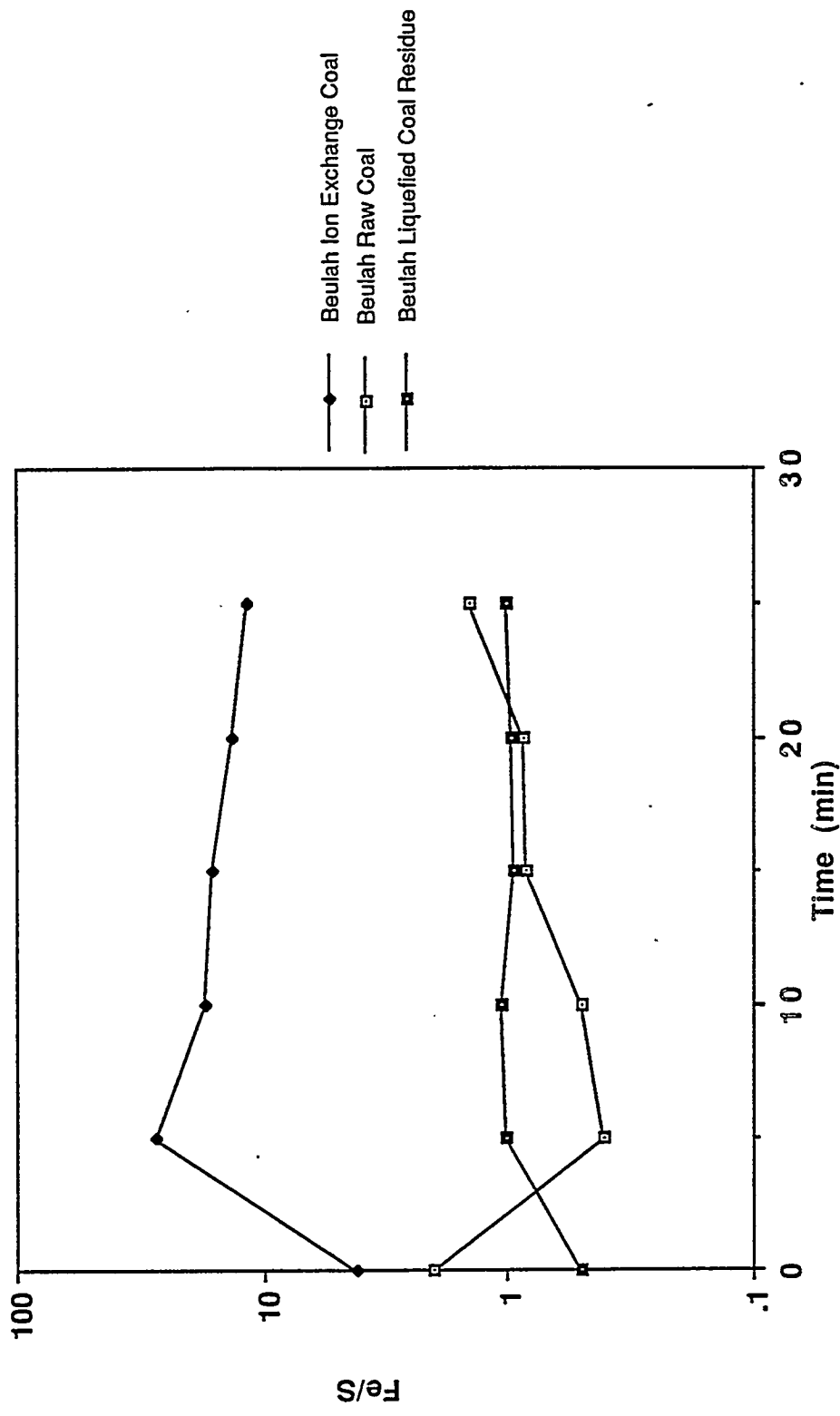


Figure 8. Fe/S Ratio For Beulah Raw Coal, Ion Exchanged Coal and Liquefied Coal Residue