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Dielectric properties of intrinsic moisture and flotability of coals of various ranks

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Dielectric Properties of Intrinsic Moisture and Flotability of Coals of Various Ranks

A thesis submitted in partial fulfillment of the
requirement for the degree of Master of Science
in Metallurgical Engineering

By

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October 1991

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ABSTRACT

The flotability of Argonne Premium coals varying in rank has been correlated with the intrinsic moisture content and dielectric properties of the intrinsic moisture. The moisture content of Argonne Premium coals varies from 32.24 for lignite to 0.65 for high volatile bituminous coal. These measurements show that as the coal rank increases the intrinsic moisture and dielectric constant of the coal decrease. The nature of intrinsic water present in the coal of different ranks has been characterized using a dielectric mixture equation. The water present in lignite is different from that of sub-bituminous and bituminous coals. The dielectric constant of intrinsic water ranges from 27.4 for lignite to 3.2 for low volatile bituminous coal. The intrinsic water present in lignite is tenaciously bound to the surface and has an oriented dipole structure whereas water present in low volatile bituminous coal has a non oriented and clathrate ice-like structure. It is shown that flotability of coals of various ranks can be explained in terms of the nature and amount of the intrinsic water present in the coal. Thermal treatment can modify some of the structural property of intrinsic water present in the coal and increase the flotability of low rank coals.

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(1.0) INTRODUCTION

More than 80 million tons of clean coal are prepared in the U.S.A by froth flotation(1). Flotation is a physico-chemical process by which one mineral constituent can be separated from another constituent in a cell by selective attachment of air bubble in aqueous phase.

Oil flotation was first used in 1920 for improving the mineral contents of copper and lead-zinc ore pulps. Since then the procedure has been displaced by what is known as froth flotation. Froth flotation is by far the dominant process of mineral dressing in use today and its application includes the treatment of metallic ores that are generally ground finer than 48 to 65 mesh. Some chemical additives such as collectors are added to make the surface hydrophobic and frothers are added to stable froth to hold the hydrophobic particles.

Although coal exhibits natural flotability, its response to flotation varies with ash content. Gaudin(2) observed that the greater the ash content of a coal, the less hydrophobic is the coal. Sulfur content of coal is of considerable importance from an environmental standpoint. The organic sulfur is incorporated structurally in the macro molecular coal polymer as thiophene, sulfur ring structures, which can not be separated by flotation techniques. The inorganic sulfur is present largely in the form of pyrite.

Although coal possesses natural hydrophobicity, its surface also exhibits hydrophilic sites, and usual flotation practice involves the use of frother such as MIBC, pine oil or cresylic acid on the order of 0.2 to 0.5 lb/ton and a promoter such as kerosene or fuel oil of the order of 1 to 3 lb/ton depending on the coal rank. The kerosene promoter usually used in the experiments enhances the contact between the coal particles and the dispersed air bubbles.

(1.1) Coal Flotability:

The flotability of coal is dependent upon its rank, i.e lower-rank coals are hydrophilic and higher rank coals are hydrophobic(3-12). The hydrophilic nature and low flotability of low-rank coals is due to the increasing content of polar groups, low carbon and high ash content. It has been long known that coal minerals possess an inherent flotability. This natural hydrophobicity was shown by Brady and Gauger(13) to be different for coals of different rank, using the contact angle method as a means of evaluation. Subsequent experiments indicated that the contact angle and flotation varied regularly with the dry mineral matter free carbon content of the coal(6,14). Jin et al(12) observed that the contact angle measurements match the flotation response for coals of different rank without collector addition and the bubble attachment times are indicators of the hydrophobic character and can be used to provide an estimate of flotation response.

(1.2) Dielectric Characterization of Bound Water:

The study of the dielectric properties of a substance is essentially the quantitative characterization of its interaction with electromagnetic fields. From the view point of molecular structure, the interaction of molecular systems with electromagnetic fields provides an extremely sensitive tool for the understanding of molecular behavior. The transition of the molecule from the isolated state to the state where intermolecular forces become important is accompanied by alterations in the polarization exhibited by the molecular system that are of two types. In the first type, the polarization terms which exist for the isolated molecule, will, in general, be modified by these intermolecular forces. In the second type, however, polarization terms occur with the system of molecules in strong interaction, rather than in isolated molecule.

Dobson et al(15) reported that water molecules bound to soils (consisting of organic constituents) have an oriented dipole structure and are bound to the soil mineral surfaces probably through hydrogen bonding. Because the water molecules are bound to fixed surface sites, they are not mobile, have a lower dielectric constant than free water, and have a layered structure. The adsorbed water molecules at the hydrophobic soil surfaces have a clathrate ice-like structure and they are not tightly bound to the surface. Instead they are randomly oriented. Similar analyses were made by Drost-Hansen(16), Pauling(17) and Legaly(18) for the structure of water molecules near hydrophobic and hydrophilic materials.

Pauling found that the direct measurement of interaction forces in the interfacial region affirms the concept of disjoining pressure. Moreover, it is quite clear that the structural contribution is present and distinct from electrostatic considerations. Futhermore, the structural contribution is very significant near a solid surface and appears to be the driving force in the flotation process. It is apparent that a layered water structure is present for a hydrophilic surface and has been seen next to a hydrophobic surface, reminiscent of the Drost-Hansen model(16).

Several studies have been made on the dielectric behavior of adsorbed water on materials like TiO_2(20), FeO(21,22), ZnO(23), silica(24-26). McCafferty et al(21,22) measured the dielectric constant of water on FeO as a function of applied frequency (range 70 Hz to 300 kHz) and as a function of water coverage, i.e the number of physically adsorbed layers beyond the underlying hydroxyl layer at 100 Hz and 100 kHz. They found that the first layer of physically adsorbed water does not cause any change in the dielectric constant. They attributed this behavior to the existence of a monolayer in which the adsorbed molecules are firmly bound to the surface at fixed sites. These molecules which may be simulated by dipoles are not able to rotate in an alternating electric field and hence do not contribute to the polarization of the system. The mechanisms for the localization is thought to be hydrogen bonding of a single water molecule to two underlying hydroxyl groups at a hydrophilic oxide surface.

As the coverage of adsorbed water increases, the dielectric constant increases sharply due to the ability of the water molecule to rotate in an alternating electric field This phenomenon indicates that the subsequent layers are more mobile than the first monolayer. Since orientation of polar molecules does not occur instantaneously, the polarization resulting from the presence of such molecules has an associated relaxation time. The force exerted by the field is in competition with forces due to the Brownian movement and only partial orientation results. The speed of orientation depends on size, structure, and shape of polar molecules. The characteristic frequency of the dispersion decreases with an increase in molecular size and weight. For small molecules like water, its value is near 20 GHz; for large molecules like proteins, it is near 1 GHz.

The dielectric constant rises sharply with the start of the second layer. The rise is due to an increased tendency of adsorbed water molecules to respond to the alternating field, so these multilayers are more mobile than a monolayer. Beyond about 3 monolayers of water, the value of the dielectric constant leveled off. The results are all consistent with those observed by Kurosaki(20). He made measurements of dielectric properties of water adsorbed on silica-gel. In the first layer water was firmly bound to the silica gel surface. In the second, the water molecules were more mobile and in the third the adsorbed molecules were more ordered. He concluded the order to be capillary condensed water which has a much more strongly developed hydrogen bonding than liquid water. Examination of the surface of silica gel under an electron microscope revealed the presence of innumerable circular orifices showing that the capillaries of silica gel are mainly of the pinhole type.

Tye et al(28) used dielectric relaxation spectroscopy and immersional type of calorimeter to characterize moisture content and pore structure of low-rank coals. They observed that 80% of the moisture content of lignite is in a loosely-bound form and it freezes to ice below 0° C. The remaining 20% is present as water of hydration, which does not crystallize into ice.

Nelson et al(29) measured dielectric properties of pulverized coal samples at 22° C over the frequency range from 1 MHz to 12 GHz. They found out that the dielectric constants decreased regularly with an increase in frequency from 1 MHz to 12 GHz. Dielectric loss factors of pyrite-bearing fractions of lower sulfur content were high at frequencies below about 50 MHz, and decreased with increasing frequency to low values at microwave frequencies. In contrast, the loss factor of a pyrite-bearing fraction with high sulfur content was low at the lower frequencies and increased with increasing frequency to high levels at microwave frequencies.

(2.0) EXPERIMENTAL TECHNIQUE

(2.1) Coal Sample:

Eight different coal samples of different rank were obtained from Argonne National Laboratory. These samples were not exposed to the atmosphere and can be treated as unoxidized or fresh representative samples. The proximate and elemental analysis of the selected samples along with their ranks and locations of origin are given in Table 1(30). UPL coal was obtained from Emery Mines, Utah, which was sub-bituminous in rank.

(2.2) Dielectric Property Measurements:

The dielectric properties of the as-received coal samples were measured using an Automated Network Analyzer(31) System (consisting of a 8702A Hewlett-Packard Lightwave Component Analyzer and a 85047A Hewlett-Packard S-Parameter Test Set) in the frequency range of 300 kHz to 3 GHz. The sample holder was a GR 874 precision 50 Ω coaxial airline. On the basis of several trial and error measurements it was decided to use a sample length of 1.0-1.2 cm and a packing density of 1.2 gm/cc. Transfer of a sample from the sealed vial to the coaxial airline was conducted in an inert atmosphere in order to avoid unintentional exposure to air.

The coal samples were difficult to transfer from containers into sample holders without losing some of the material. Coal dust remaining in the beakers used to fill the sample holder was

Table I. Proximate (as-received) and elemental (mineral ash free basis) analyses of Argonne Premium Coal samples (30)

	COAL RANK					
	LIG	SUB	HVB1	HVB2	MVB	LVB
Proximate analysis (as-received)						
Moisture (%)	32.24	28.09	2.42	1.65	1.13	0.65
Ash (%)	6.59	6.31	19.46	9.10	13.03	4.74
Volatile (%)	40.45	32.17	29.44	18.48	27.14	18.48
Sulfur (%)	0.54	0.45	0.69	2.15	2.29	0.66
Btu (%)	7454	8426	11524	13404	13315	15024
Elemental analysis						
Carbon (%)	72.9	75.01	82.58	83.2	85.5	91.05
Hydrogen (%)	4.83	5.35	5.25	5.32	4.7	4.4
Nitrogen (%)	1.15	1.12	1.36	1.64	1.55	1.33
Oxygen (%)	20.34	18.02	9.8	1.69	7.51	2.47

LIG: lignite, ND (Beulah Zap)
SUB: sub-bituminous, WY (Wyodak)
HVB1: high vol. bit., WV (Stockton)
HVB2: high vol. bit., PA (Pittsburgh)
MVB: medium vol. bit., PA (Upper Freeport)
LVB: low vol. bit., VA (Pocahontas)

accounted for by weighing the beakers before and after the samples had been transferred to the sample holder.

Coal particle density is highly dependent upon methods of filling containers and upon settling that may occur. Therefore, consistent methods were used in filling the sample holder to achieve uniform settling among the samples of different materials. The coal packing density to be used for each measurement was determined by dividing the weight of the material in the sample holder by the volume of that sample holder. The packing densities of the coal samples were uniformly maintained by continued tapping on a wooden base in a consistent manner.

After the coal sample was packed in the coaxial airline, it was connected to the S-Parameter device which was connected to the Network Analyzer(31) given in figure 1. The S-Parameters were measured using the standard procedure for a two-port network and fed to an American AT PC through a GPIB bus using the scientific language ASYST. The real and imaginary parts of the complex permittivity were calculated and displayed on an HP 1475A plotter. The complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$, where

ε' = Dielectric constant.

ε'' = Dielectric loss factor.

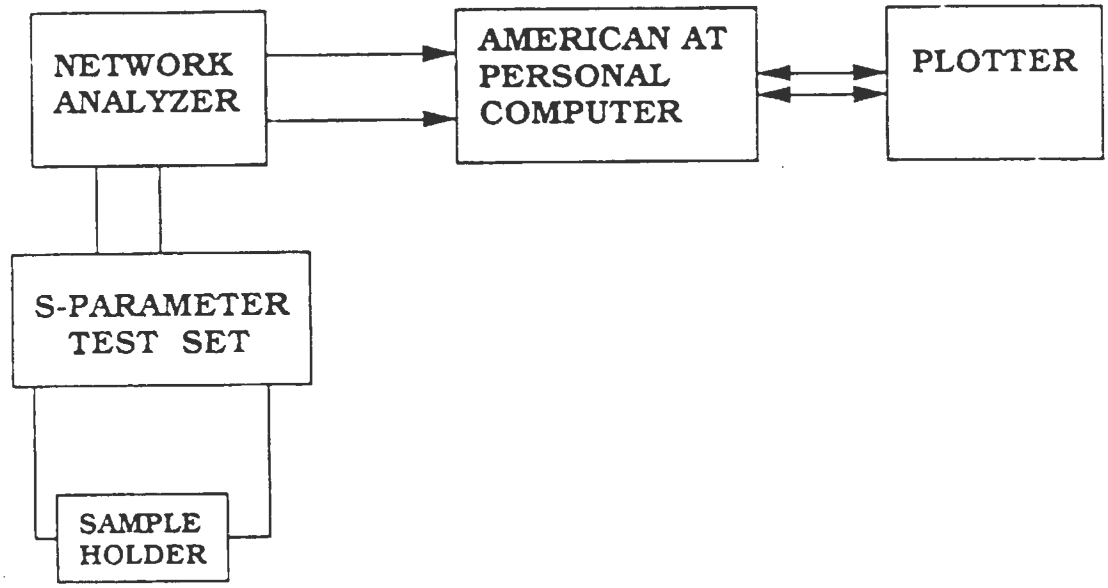

Figure 1. Schematic of the Experimental Set-up for Measurement of Dielectric Properties.

The dielectric constant determines how much electric energy can be stored in a material, while the dielectric loss determines how well a material will absorb microwave energy.

From the loss factor, the conductivities of the coal samples were calculated by the equation given below:

$\sigma = 2\pi f \varepsilon_o \varepsilon''$, where

f = Frequency

ε_o = Permittivity of free space (8.857×10^{-12} farad/m).

The dielectric constant of bound water present in the as-received coal was calculated using the multicomponent mixture model developed by de-Loor(32).

(2.3) **Flotation:**

The flotation of different ranks of coal was conducted with the flotation set-up given in figure 2. One gram (65 x 150 mesh) of coal(LIG, SUB, HVB1, MVB & LVB) was conditioned in 150 cc of water for 15 minutes (at high rpm) or until the coal particles were wetted. This operation is necessary to ensure the complete wetting of the coal surfaces. The experiments were conducted at natural pH with a nitrogen flow rate of 70 cc/min. No frother or promoter was added. Flotation time was one minute. Both concentrate and tailings were filtered, dried and weighed at the end of each experiment to evaluate the percent recovery of coal. Three experimental runs were conducted for the given particle size and the values of percent recovery were noted.

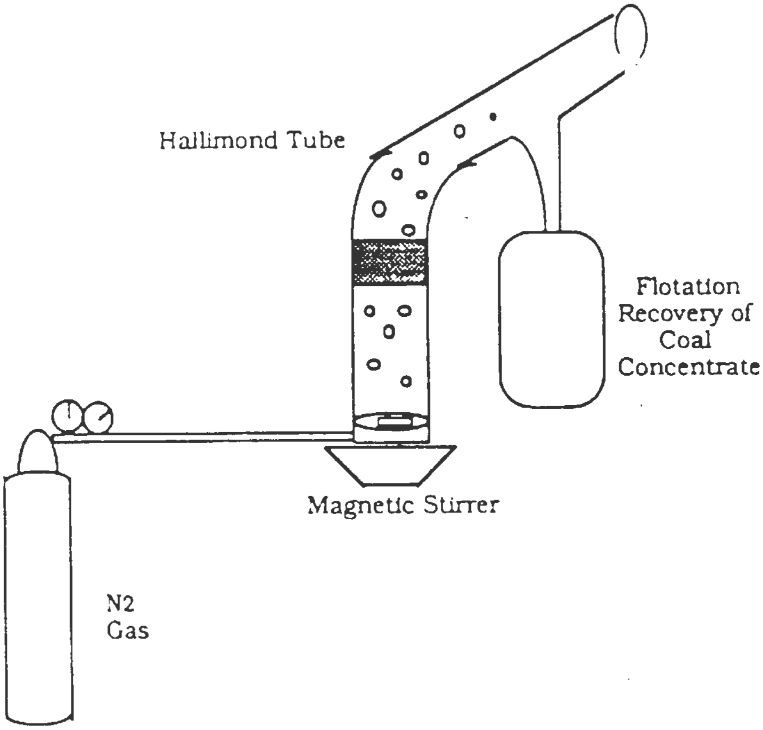

Figure 2. Flotation Set-up.

(3.0) RESULTS & DISCUSSION

(3.1) Dielectric Properties:

The dielectric properties of different ranks of coal as a function of frequency in the range of 300 kHz to 3 GHz were determined with the automated network analyzer system. The measured values of the dielectric constant and dielectric loss vs the frequency of as-received HVB1 (Stockton) and lignite are given in Figure 3. The dielectric constant and dielectric loss of the other coal samples are given in the appendix. The structure of bound water is more predominant in the lower frequency range than in the higher frequency range. Thus all the measurements were taken at 600 MHz. The measured values of the dielectric constant and dielectric loss at 600 MHz for coals of different ranks are given in Figure 4. The dielectric constant and dielectric loss decrease with an increase in the coal rank. The dielectric constant for dry coal (dried at 100 °C) is given in Figure 5. The results show that the dielectric constant of the dried coal is apparently not rank-dependent. This phenomenon implies that the intrinsic moisture present in the coals of different ranks controls the dielectric properties. The relationship between the moisture content and the dielectric properties of coals is given in Figure 6. The dielectric constant decreases with a concomitant decrease in intrinsic water content.

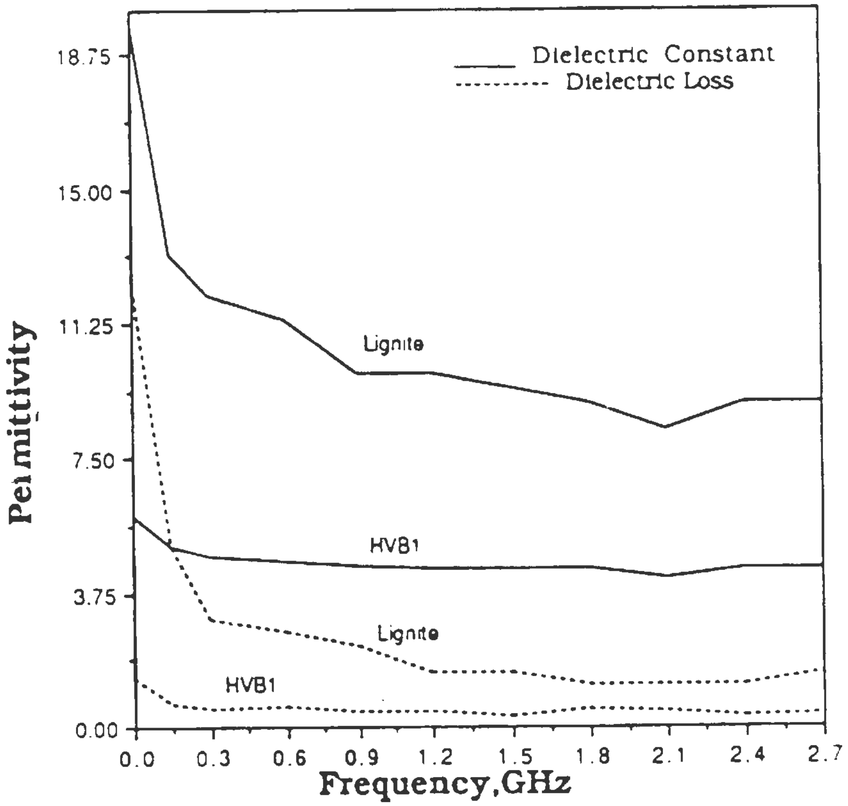

Figure 3. Permittivity of lignite and HVB1(Stockton) as a function of frequency.

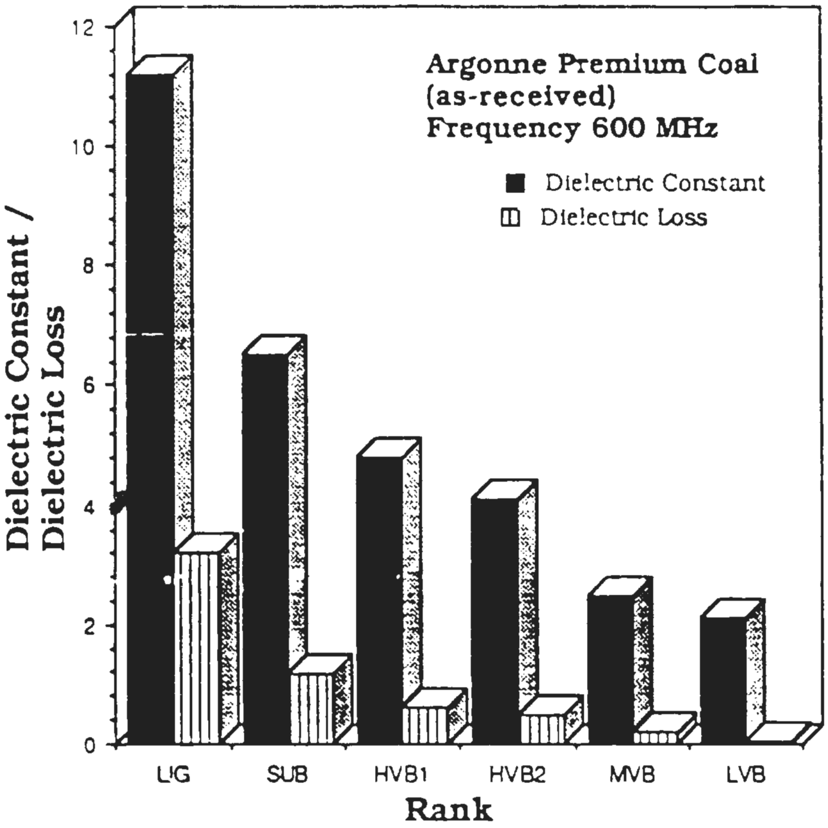

Figure 4. Dielectric constant and dielectric loss of coal of different ranks.

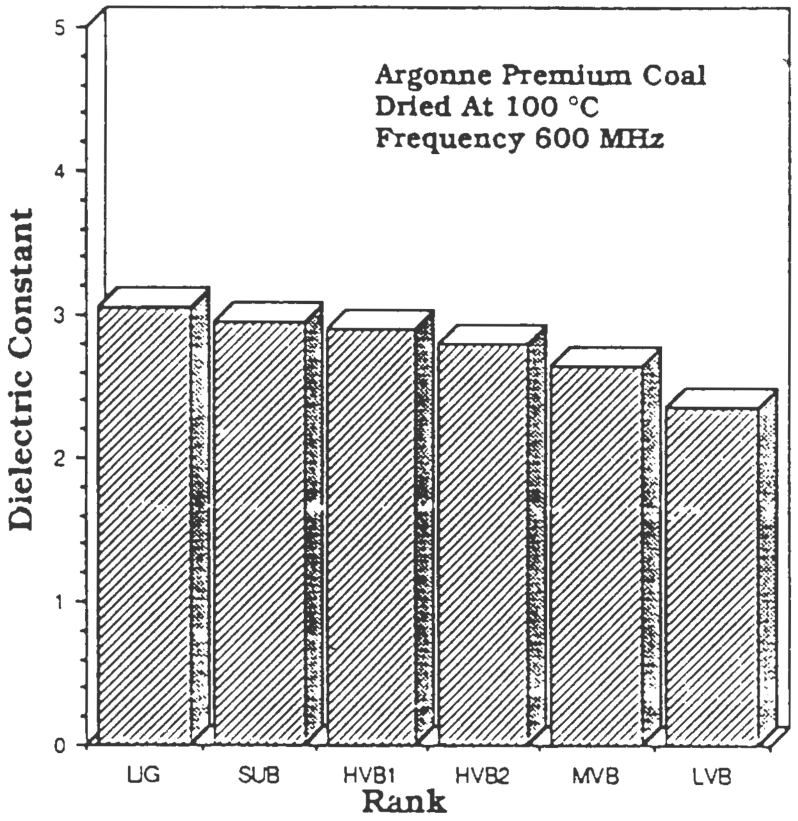

Figure 5. Dielectric constant of dry coal (no moisture).

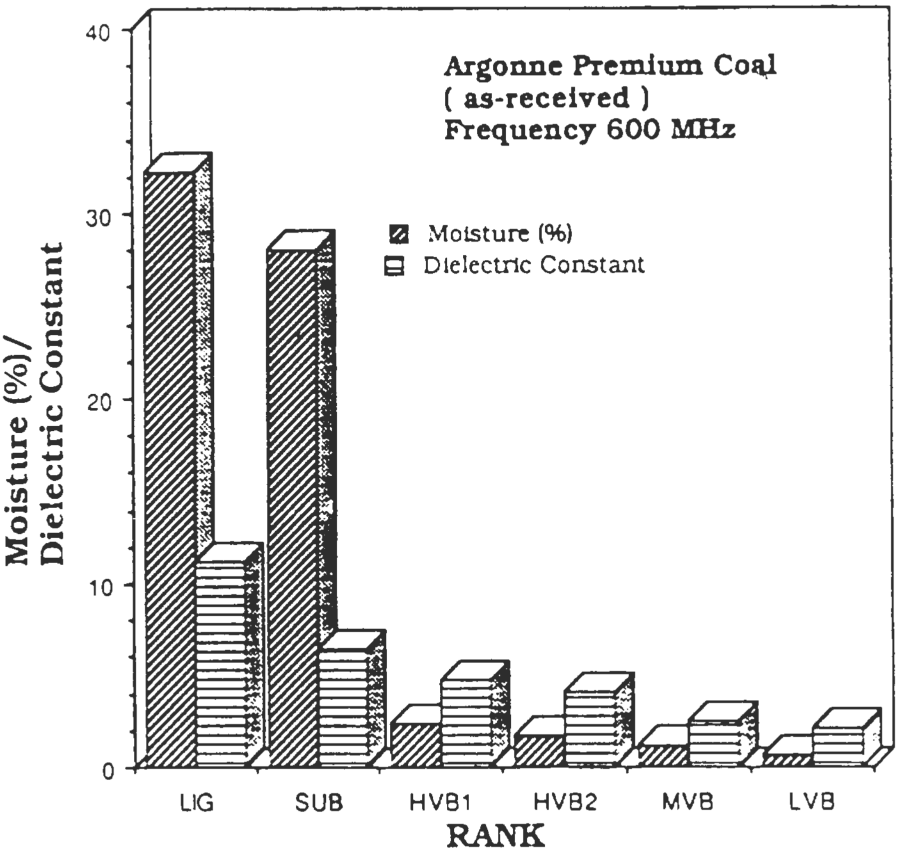

Figure 6: Dielectric constant and moisture content of as-received coal samples.

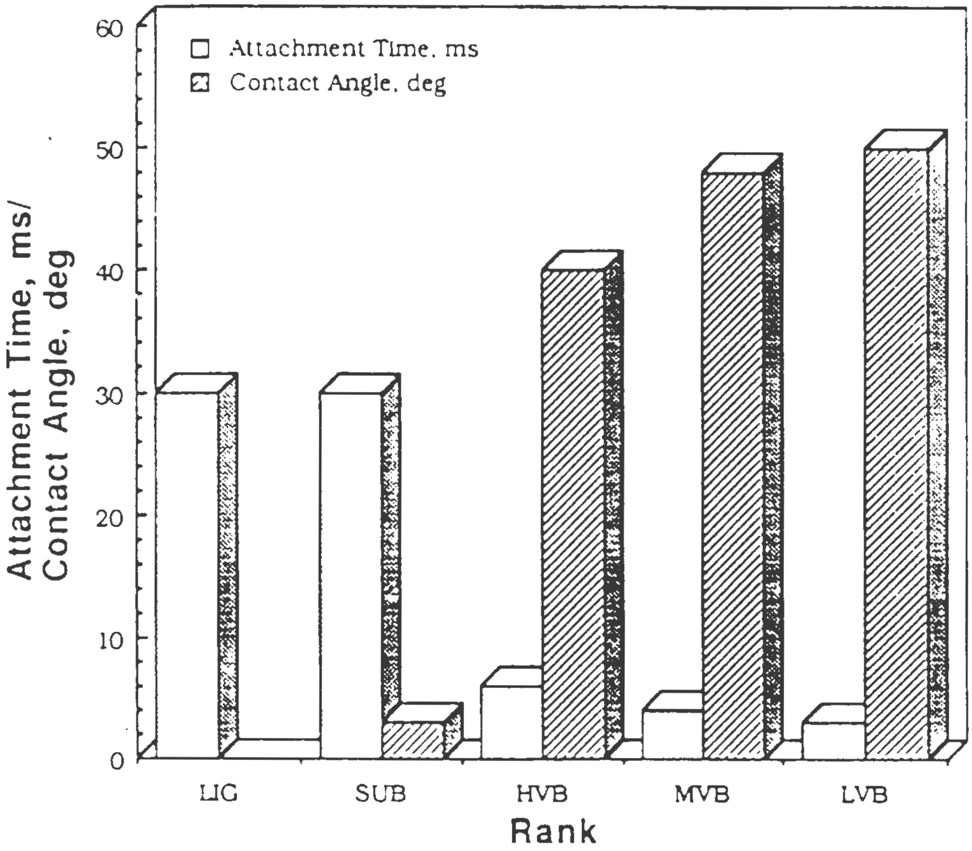

Figure 7. Contact angle and attachment time vs the rank for different ranks of as-received coal samples(Jin et al).

For lignite the dielectric constant is 11.2 at a moisture content of 32.2%, whereas for LVB the dielectric constant is 2.1 at a moisture content of 0.65%. This suggests that the amount of water present initially plays an important role in the prediction of dielectric properties of coal.

(3.2) Flotability of Coals of Different Ranks:

The coal literature is replete with information regarding the hydrophilicity and hydrophobicity of coals of different ranks. Diagnostic tests such as contact angle and attachment time have been used to confirm that the hydrophilicity decreases with an increase in coal rank (Figure 7)(12). Hallimond tube flotation tests conducted in the laboratory with coals of different ranks confirm such observations (Figure 8). No flotation was obtained with lignite. For sub-bituminous coal, only 5% flotation was obtained. However, flotation recovery steadily increased with an increase in rank. It was noted that there was a sudden increase in flotation response going from sub-bituminous to high-volatile bituminous coal A similar observation was made by Jin et al(12). Figure 9 gives the flotation recovery as a function of controlled thermal treatment for different ranks of coal. So flotability of coal can be altered to some extent by simple thermal treatment .

The flotability of coals of different ranks along with their intrinsic moisture content and dielectric constant are given in Figure 10. Lignite and sub-bituminous coals, which have high

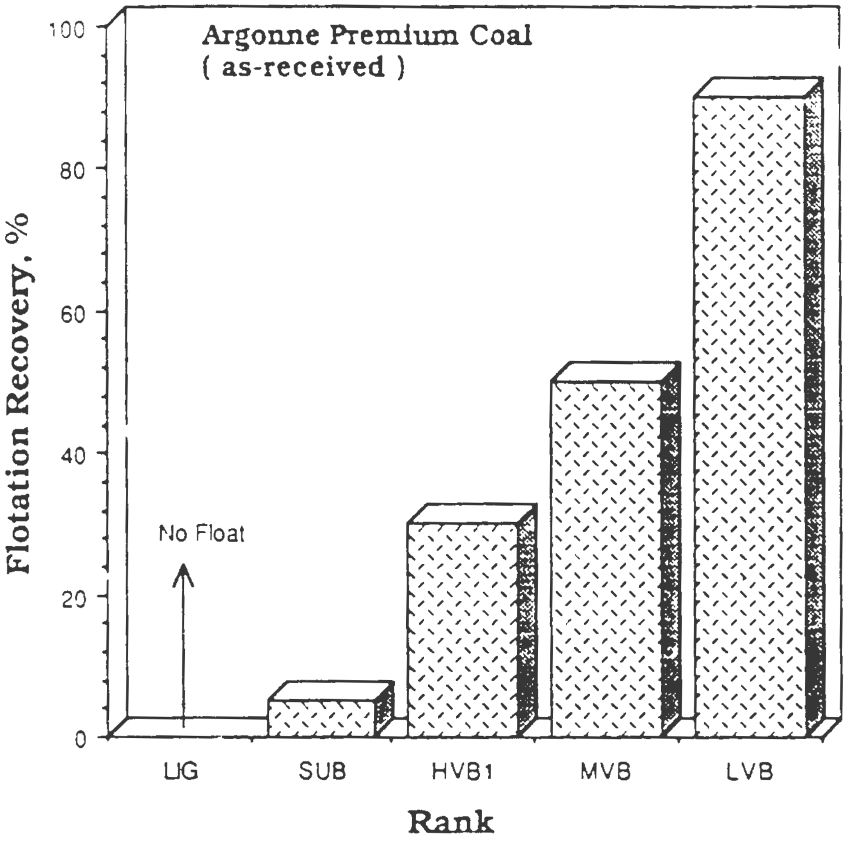

Figure 8. Flotation recovery of coals of different ranks (65x150 mesh).

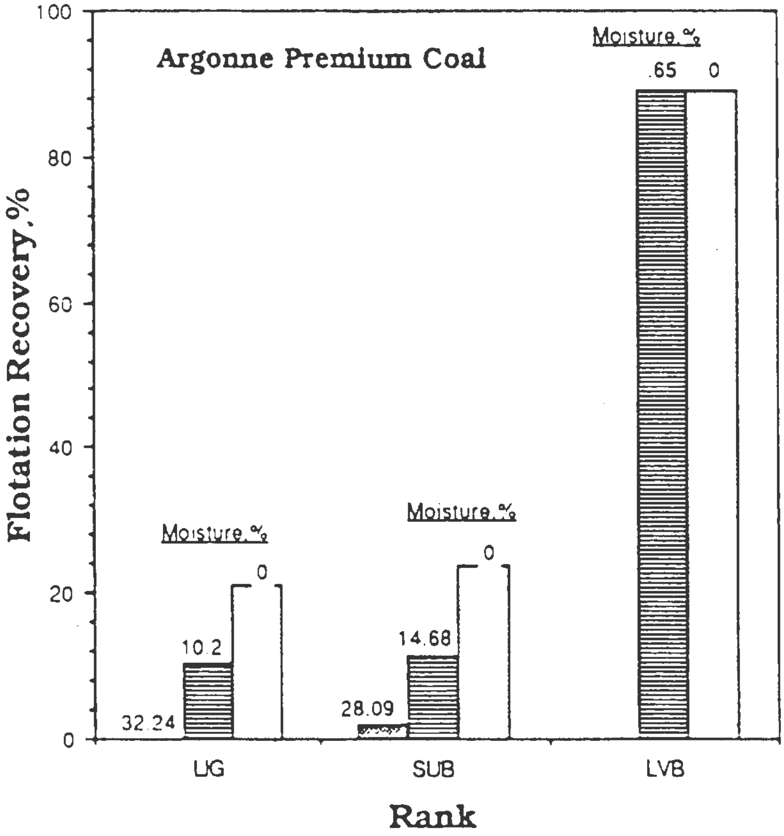

Figure 9. Flotation recovery as a function of controlled thermal treatment.

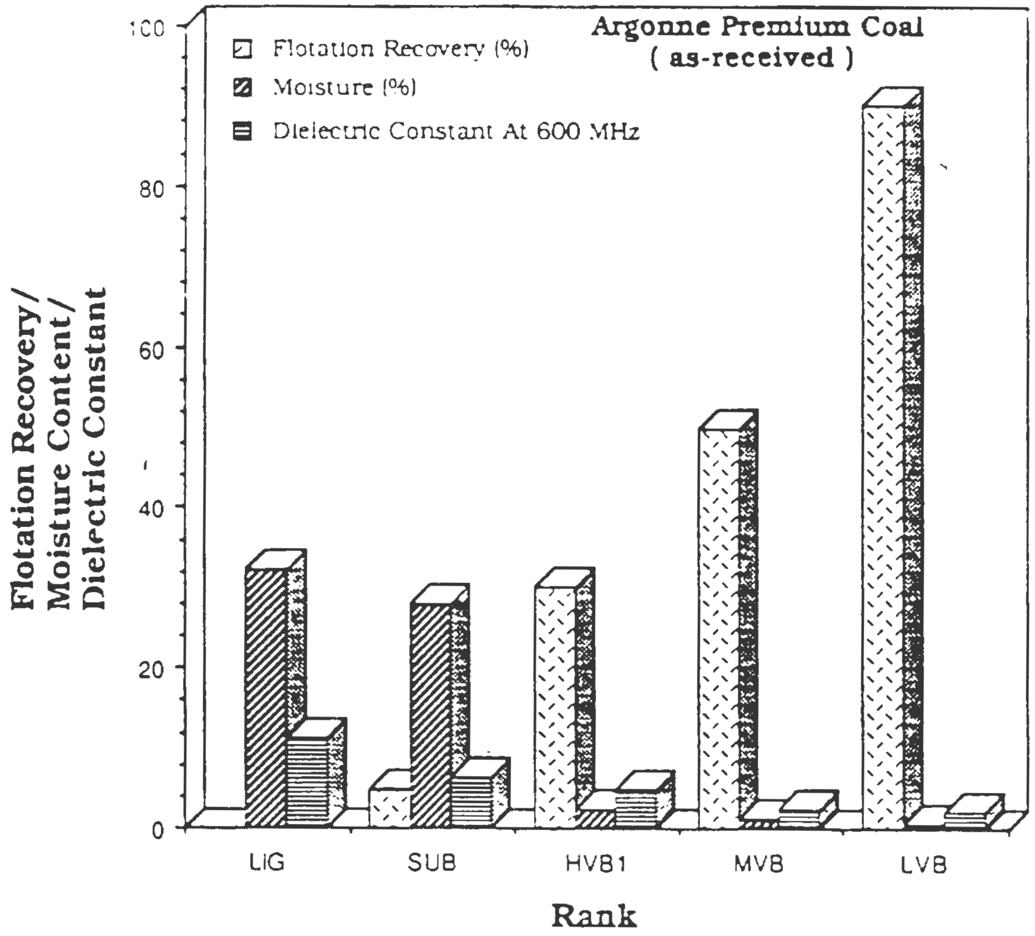

Figure 10. Flotation recovery, moisture content and dielectric constant of coals of various ranks.

moisture, exhibit low flotability. Low volatile bituminous coal, which has a low amount of moisture, exhibits good flotability. These results suggest that in addition to other reported factors, the intrinsic moisture content in coals of different ranks can be used as a criteria for the flotability of coals. Figure 11 gives the correlation between flotation recovery and intrinsic moisture content in coals of different ranks. The role of intrinsic moisture in controlling the flotability is not yet clear. However, it can be imagined that the structural nature of the intrinsic water at low rank coal surfaces is such that the air bubble/particle attachment and subsequent flotation is inhibited. A dielectric spectroscopic technique in conjunction with a dielectric mixture model was used to characterize the intrinsic water.

(3.3) Characterization of Intrinsic Water:

The direct characterization and analysis of the intrinsic water at the coal (or any other material) surface is extremely complicated. There are several dielectric models which have been developed to obtain the permittivity of mixtures from the known dielectric constants and the volume or weight fractions of the constituents. One such model is the de-Loor mixture model(32). This model has been successfully used by Dobson et al(15) to calculate the dielectric properties of bound water present in soil. It is shown that the water bound to soil absorbs microwave energy very well and has a real part of the permittivity in the range of 20-40.

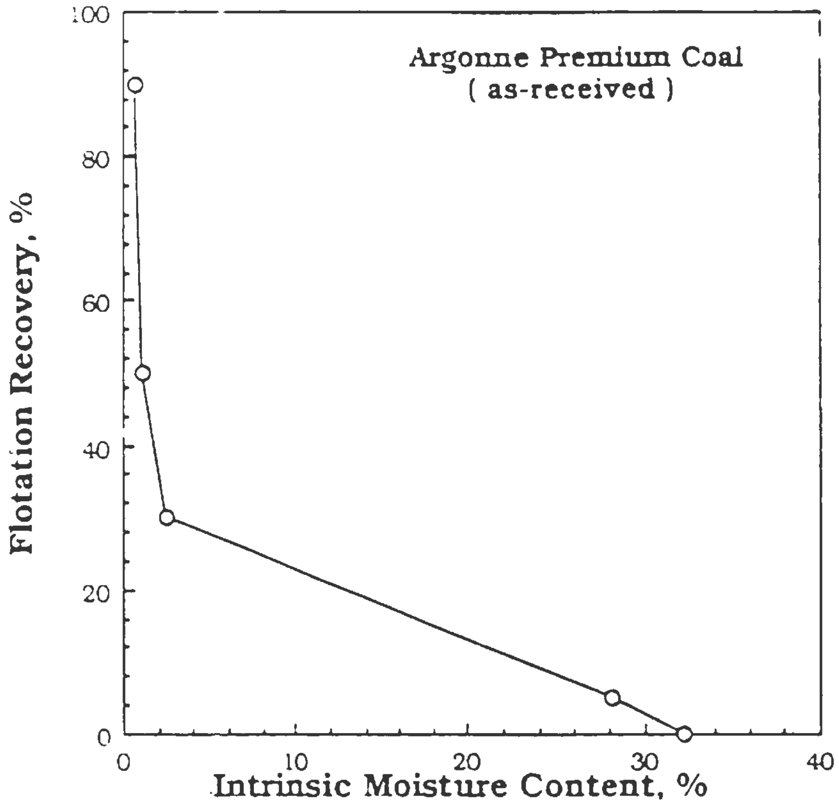

Figure 11. Correlation between flotation recovery and intrinsic moisture content of coals of different rank.

The general form of the de-Loor's mixture equation is given by (1):

$$\varepsilon = \varepsilon_c + \sum_{i=1}^{3} \frac{V_i}{3}(\varepsilon_i - \varepsilon_c) \sum_{j=1}^{3} \frac{1}{\left[1 + A_j\left(\frac{\varepsilon_i}{\varepsilon^*_e} - 1\right)\right]} \qquad (1)$$

where

ε_c, ε_i = dielectric constant of the host (coal) and the inclusions (bound water, ash and pyrite), respectively;

ε^*_e = an effective internal dielectric constant near the boundaries of the dispersed granules and with the potential range $\varepsilon_c \leq \varepsilon^*_e \leq \varepsilon$;

A_1, A_2, A_3 = depolarization factors along the main axes of the ellipsoid (where the inclusions can in general be assumed to be ellipsoids).

$A_1 + A_2 + A_3 = 1$

V_i = volume fractions of the inclusions.

It is assumed that $\varepsilon^*_e = \varepsilon$. If a four component mixture model is considered to be made up of dry coal, pyrite, ash, and bound water (excluding free or bulk water which is not present in this case), the above equation (1) reduces to the form given in equation (2) :

$$\varepsilon_m = \frac{(3\varepsilon_{coal} + 2V_{py}(\varepsilon_{py} - \varepsilon_{coal}) + 2V_{ash}(\varepsilon_{ash} - \varepsilon_{coal}) + 2V_{bw}(\varepsilon_{bw} - \varepsilon_{coal}))}{(3 + V_{py}((\varepsilon_{coal}/\varepsilon_{py}) - 1) + V_{ash}((\varepsilon_{coal}/\varepsilon_{ash}) - 1) + V_{bw}((\varepsilon_{coal}/\varepsilon_{bw}) - 1))} \qquad (2)$$

Where ε_{coal} = dielectric constant of dry coal

V_{py} = volume percent of pyrite

ε_{py} = dielectric constant of pyrite

V_{ash} = volume percent of ash

ε_{ash} = dielectric constant of ash

V_{bw} = volume percent of bound water

ε_{bw} = dielectric constant of bound water

ε_m = dielectric constant of the heterogeneous mixture

From equation (2), the dielectric constant of the bound water can be calculated by substituting the measured dielectric properties of the mixture components. For a sample calculation of SUB coal:

ε_{coal} = dielectric constant of dry coal = 3.0

V_{py} = volume percent of pyrite = 0.01

ε_{py} = dielectric constant of pyrite = 7.0

V_{ash} = volume percent of ash = 0.06

ε_{ash} = dielectric constant of ash = 4.6

V_{bw} = volume percent of bound water = 0.3

ε_{bw} = dielectric constant of bound water

ε_m = dielectric constant of the heterogeneous mixture = 6.5

The value for the dielectric constant of bound water is obtained by substituting all the above values in equation 2. Table 2 illustrates the calculated dielectric constant of bound water present in the different ranks of coal.

As can be seen in Table 2, the dielectric constant of the intrinsic water present in lignite is 27.4, which is much lower than that for free water. Similarly, the dielectric constant of intrinsic water in sub-bituminous coal is 20.6. These numbers indicate that the water molecules have an oriented dipole structure and are bound to the lignite and sub-bituminous coal surface probably through hydrogen bonding. Because the water molecules are bound to fixed surface sites, they are not mobile, have a lower dielectric constant than free water, and have a layered structure. Similar conclusions were reached by Dobson et al.(15) for water bound to soil.

The dielectric constant of water in high-, medium-, low-, volatile bituminous coals is about 3. Interestingly, the dielectric constant of adsorbed water is much less for high volatile bituminous coal. The change in the dielectric properties of the bound water can be correlated with the flotation results where it was noted that flotation recovery is much greater for high volatile bituminous coals. The low dielectric constant of

Table 2: Dielectric constant of as-received coal (ε_m), dielectric constant of intrinsic water (ε_{bw}), and flotation recovery of coals of different ranks.

COAL RANK	ε_m	ε_{bw}	FLOTATION RECOVERY (%)
LIG	11.2	27.4	0.00
SUB	6.5	20.6	5.00
HVB1	4.8	3.2	30.00
MVB	2.5	3.2	50.00
LVB	2.1	3.2	90.00
$\varepsilon_{\text{free water}} = 78$ at 2.45 GHz.			

bound water in high volatile bituminous coal indicates that the structure of near surface water molecules is different from that of lignite and sub-bituminous coals. The adsorbed water molecules at the hydrophobic coal surfaces have a clathrate ice-like structure. Rather than being tightly bound to the surface, they are randomly oriented. Similar analyses were made by Drost-Hansen(16), Pauling(17) and Legaly(18) for the structure of water molecules near hydrophobic and hydrophilic materials.

(3.4) Effect of Added Water vs Bound Water on Dielectric and Flotability:

As shown before, the dielectric properties decrease with an increase in coal rank and moisture content. It is also established that the structural arrangement of bound water varies with rank, i.e for low-rank coal, water molecules are oriented and bound to the surface. For high rank coals the water molecules are not bound to the surface and have a clathrate ice-like structure. It is believed that the structure of bound water plays an important role in determining the flotability of low and high rank coals. In order to substantiate this concept, a series of experiments were conducted with lignite, sub-bituminous and high volatile bituminous coals.

As received coals were dried at 100° C in a controlled manner. After careful drying, the dielectric properties of dried lignite were measured. Following these experiments, an equivalent (originally present water) amount of water was added to the lignite. An equilibration time of 24 hrs was used and the

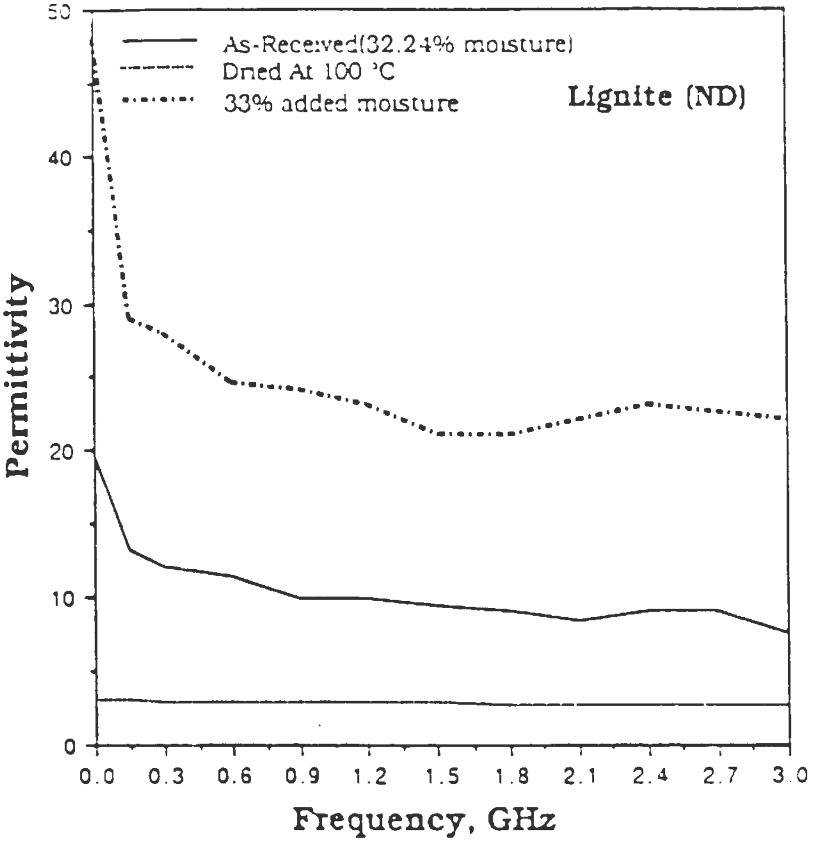

Figure 12. Permittivity of lignite as-received, dried and with added moisture.

dielectric properties were measured as a function of frequency. Results for as-received, dry lignite, and lignite to which water was added are given in Figure 12. The dielectric constants of lignites with added moisture are almost twice that of the as-received coal even though the moisture content of both samples are identical. This simple experiment illustrates the fact that there is an inherent difference in the nature of bound water in the as-received coal.

The inherent water present in the lignite has significantly different physical, structural and electrical properties. Indeed, the mixture theory calculations show that the dielectric constant of inherent water at microwave frequencies is 20.6-27.4 (Table 2) whereas the dielectric constant of added water is 78, the value for bulk water. In the latter case the water is not bound to the coal surface. If that is the case then the flotation response for dried coal (with added moisture) should be different. More importantly, it will be more significantly than that of as-received lignite.

The flotability of lignite, sub bituminous and low volatile bituminous coal with and without controlled thermal drying is given in Figure 9. By removing the bound water through thermal treatment, a flotation recovery of 22% can be obtained as opposed to no flotation with as-received coal. A similar improvement was noticed for sub bituminous coal. These results are consistent with the observation made by Ye et al(10) for thermal treatment of low rank coals. Figure 13 shows the variation of moisture percentage

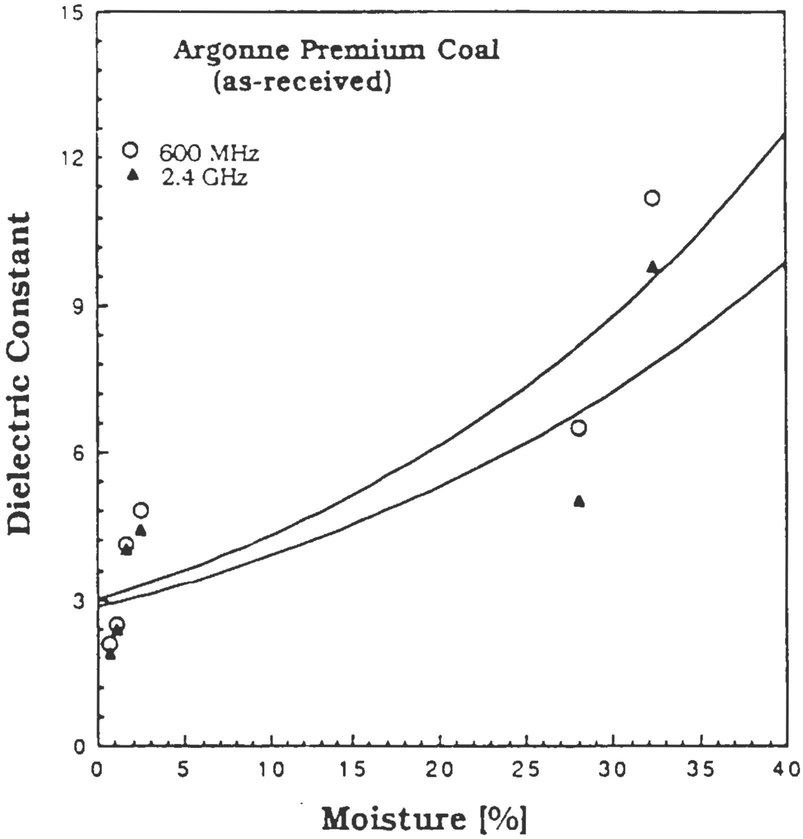

Figure 13. moisture percentage vs dielectric constant of Argonne Premium coals at 600 MHz and 2.4 GHz.

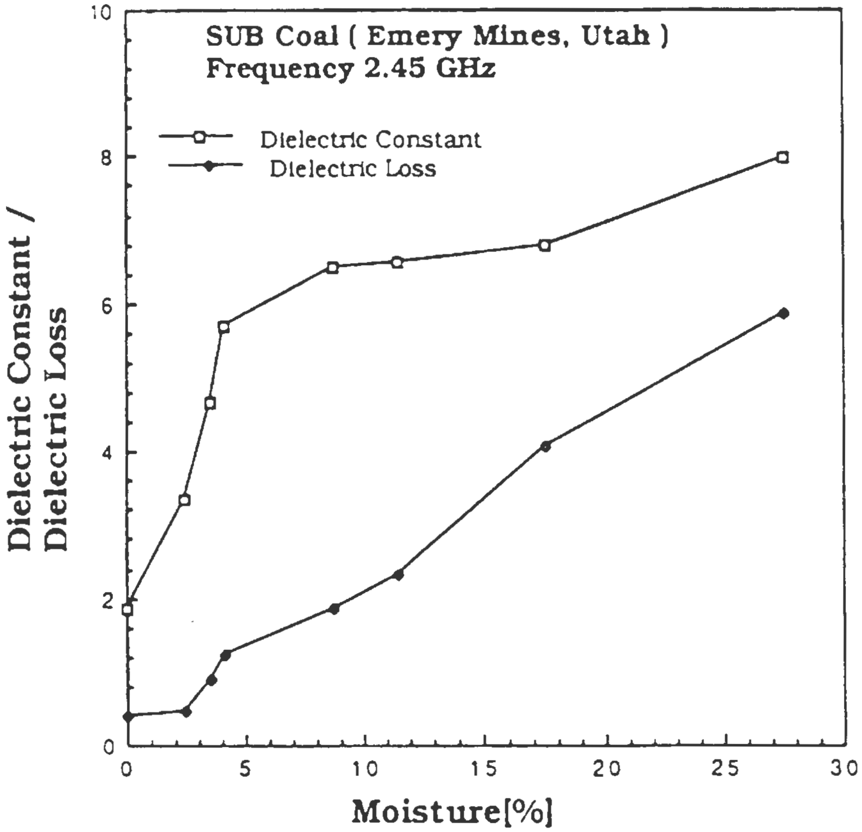

Figure 14. Measured dielectric constant and dielectric loss factor as a function of added moisture.

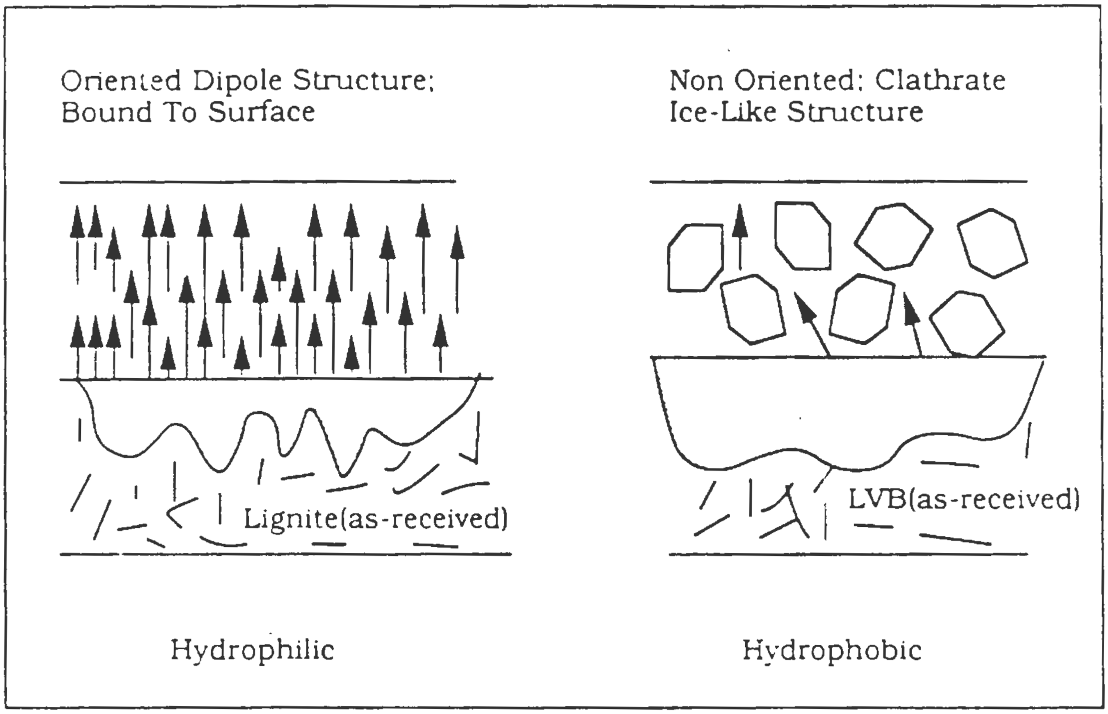

Figure 15. Schematic representation of the structure of water molecules at hydrophilic and hydrophobic coal surfaces.

vs dielectric constant of Argonne Premium coal at 600 MHz and 2.4 GHz. Figure 14 gives the variation of the dielectri constant and the dielectric loss factor with added moisture for the SUB (Utah) coal sample. Thermal treatment apparently has no effect on low volatile coal. This is because the water present at the surface of low volatile bituminous coal has a clathrate ice-like structure and is not bound to the surface. Flotation response together with dielectric properties reinforces the notion that the hydrophilicity of low rank coal is due to the presence of moisture and also due to the structural nature of bound water present in the coal. A schematic representation for the structure of water molecules at a hydrophilic coal surface (lignite) and a hydrophobic coal surface (LVB) is depicted in Figure 15.

(4.0) SUMMARY

It is observed that the flotability of coals of different ranks show good correlation with the intrinsic water content and dielectric properties of the coal. It is the nature of bound water that plays a critical role in the flotability of coals. The structure of bound water can be characterized from its dielectric constant which is calculated using a mixture equation. The intrinsic or adsorbed water present in low rank coals (lignite and sub-bituminous) is tenaciously bound to the surface and has a dielectric constant in the range of 20-27. It is due to the existence of a monolayer in which the adsorbed molecules are firmly bound to the surface at fixed sites. The molecules which may be simulated by dipoles are not able to rotate in an alternating electric field and hence do not contribute to the polarization of the system. The mechanism for the localization is due to hydrogen bonding of a single water molecule to two underlying hydroxyl groups at a hydrophilic surface.

The intrinsic water molecules present in high rank coals are randomly oriented, loosely bound to the surface, and have a clathrate ice-like structure. As a result the dielectric constant of intrinsic water near the surface of high rank coals is about 3 which is close to that of ice. Such low dielectric constants are due to the much more strongly developed hydrogen bonding (approaching that of ice) than for liquid water. Also the water molecules here are more mobile than the monolayer; thus they respond differently to the alternating field with the resulting low dielectric constant.

It is observed that low rank coals do not have good flotability properties. But by thermal treatment flotation recovery is increased. This is observed in the case of lignite and sub-bituminous rank of coals. Therefore by thermal treatment it is possible to change some of the structural properties of the intrinsic water present in coal, whereas it is not true in the case of high rank coal.

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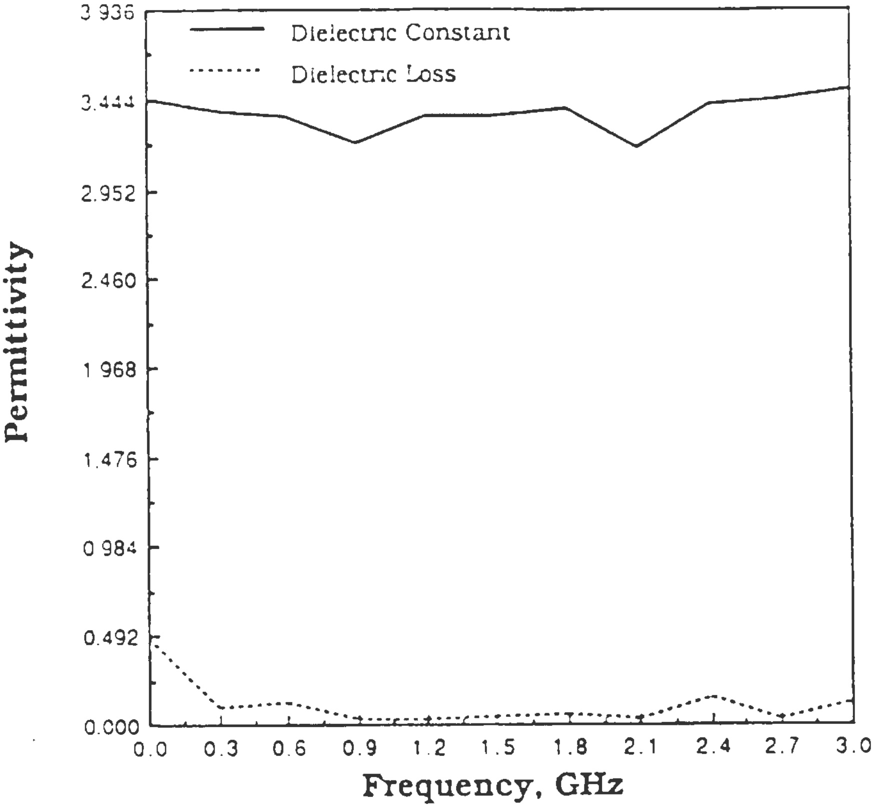

Figure 1. Permittivity of as-received Blind Canyon (HVB) coal as a function of frequency.

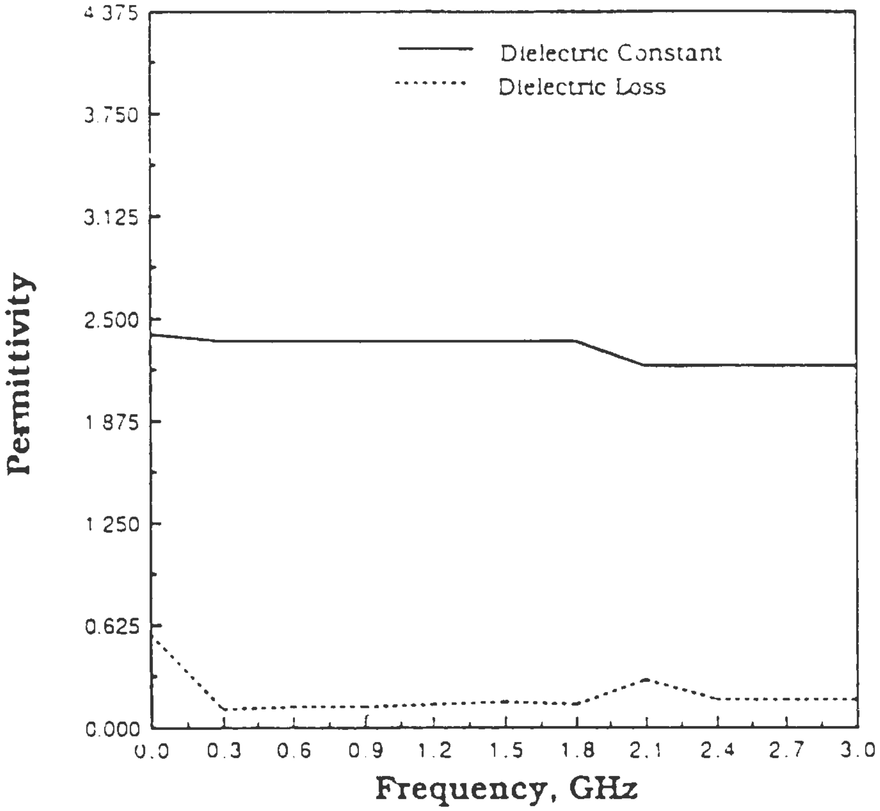

Figure ii. Permittivity of Blind Canyon (HVB) coal dried at 100° C as a function of frequency.

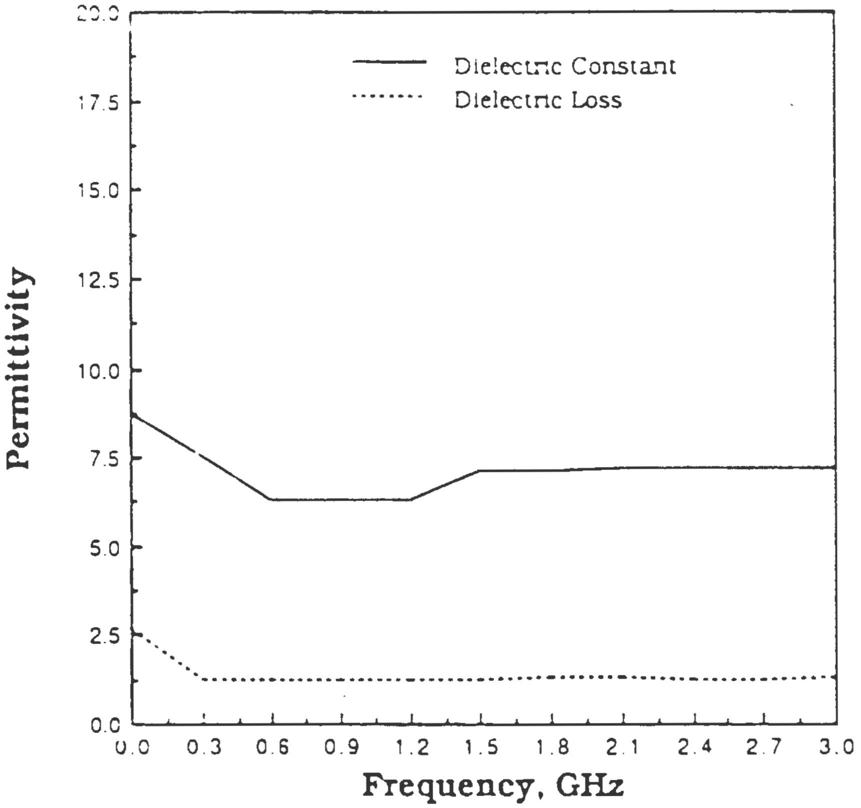

Figure iii. Permittivity of as-received Wyoming (SUB) coal as a function of frequency.

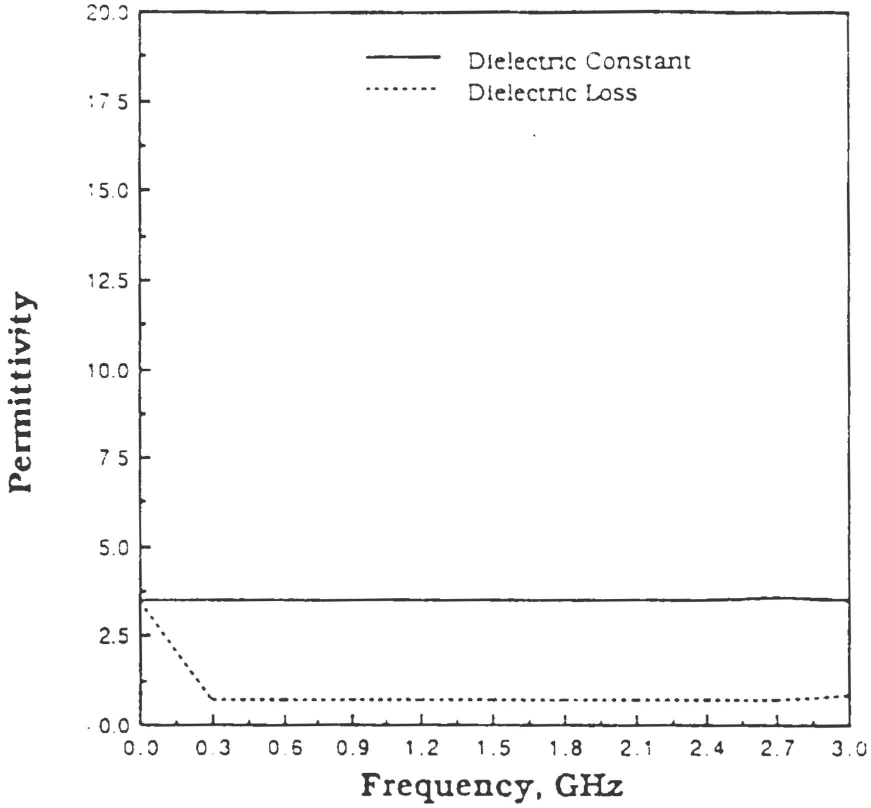

Figure iv. Permittivity of Wyoming (SUB) coal dried at 100° C as a function of frequency.

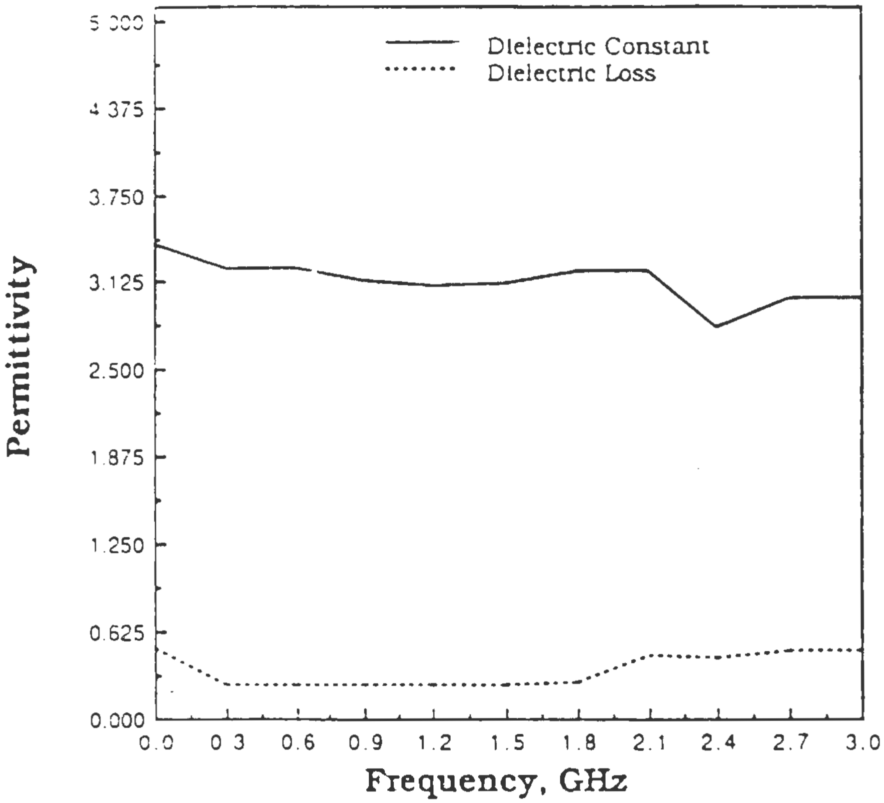

Figure v. Permittivity of Wyoming (SUB) coal twice dried at 100° C as a function of frequency.

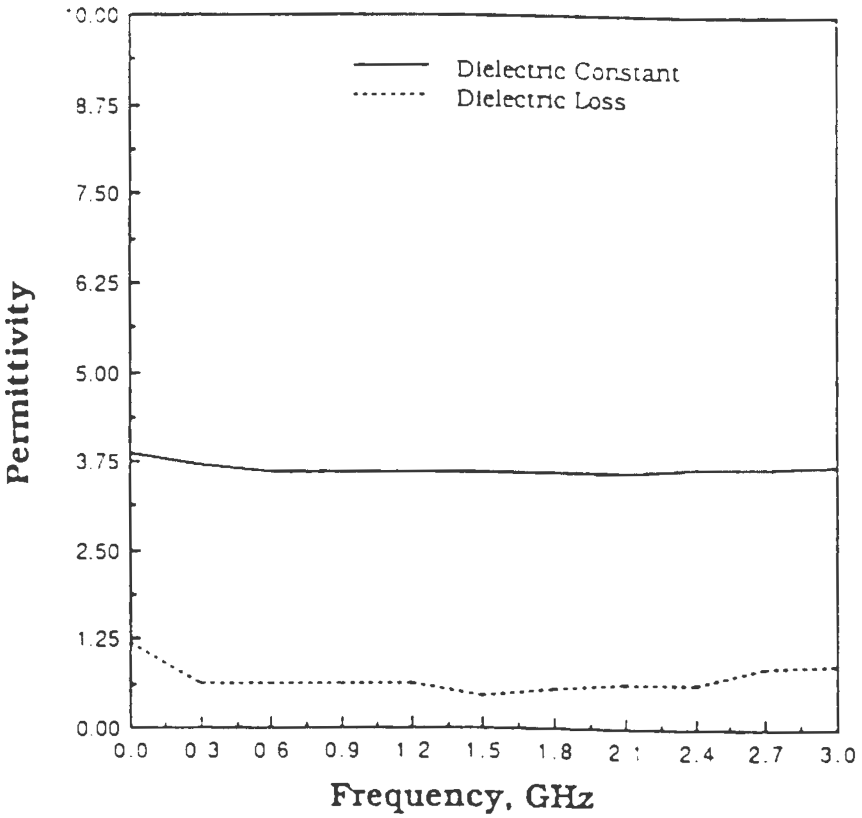

Figure vi. Permittivity of as-received Illinois #6 (HVB) coal as a function of frequency.

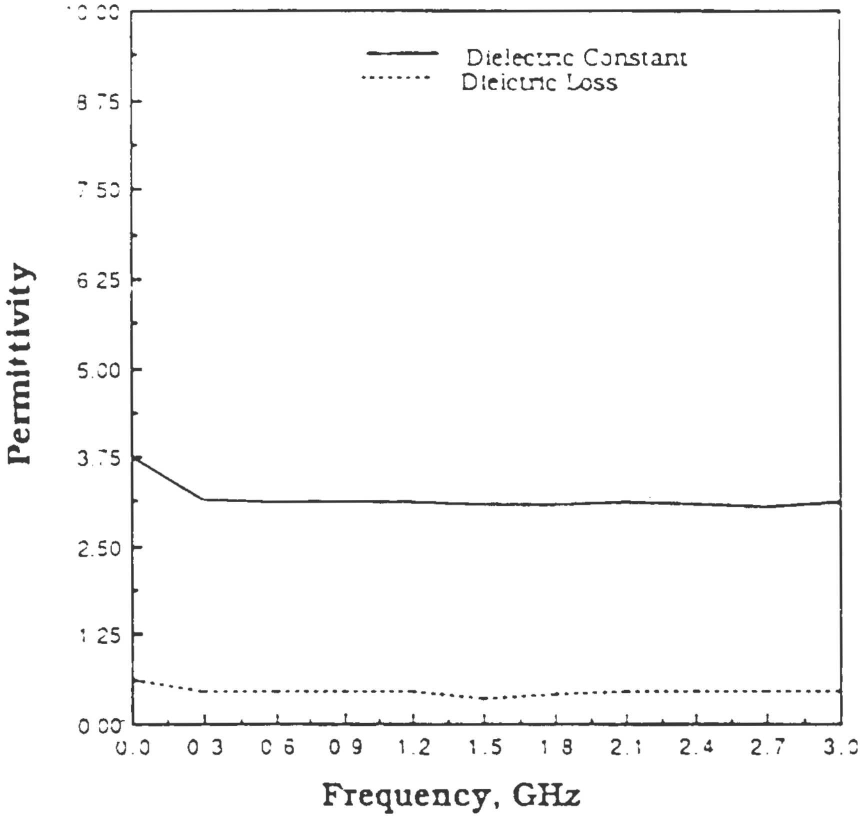

Figure vii. Permittivity of Illinois #6 (HVB) coal at 100° C as a function of frequency.

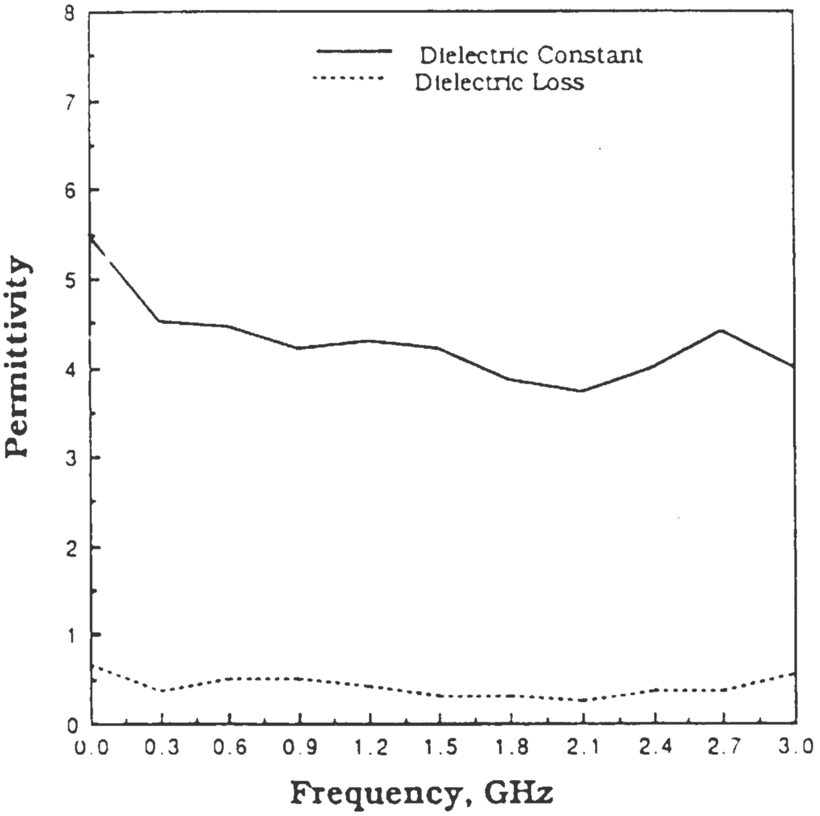

Figure viii. Permittivity of as-received Pittsburgh #8 (HVB) coal as a function of frequency.

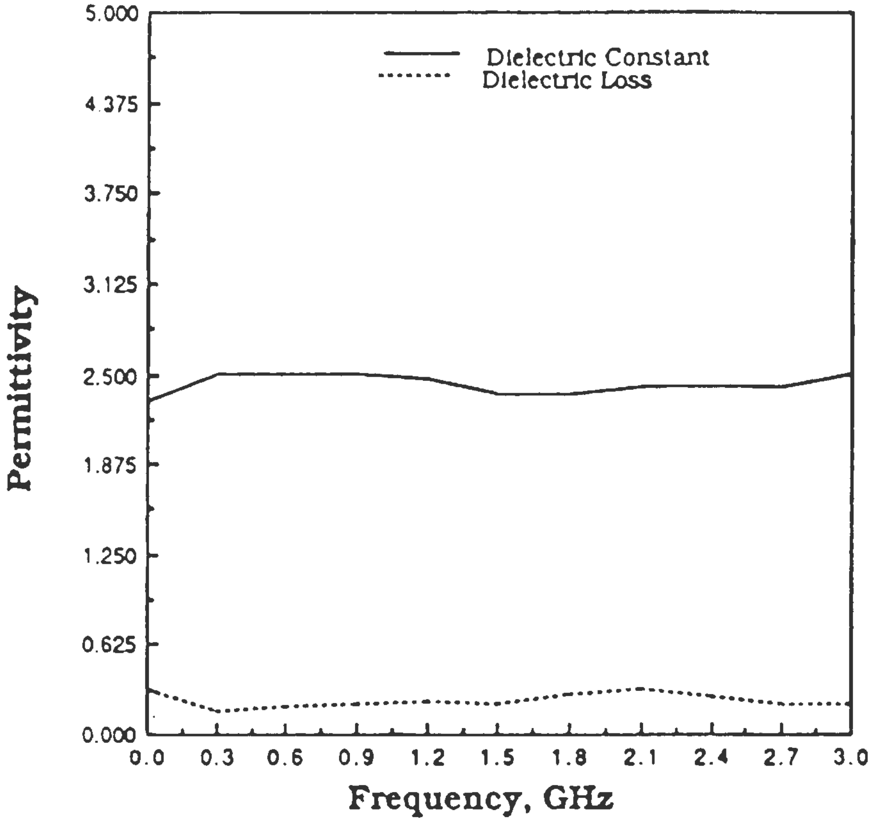

Figure lx. Permittivity of Pittsburgh #8 (HVB) coal dried at 100° C as a function of frequency.

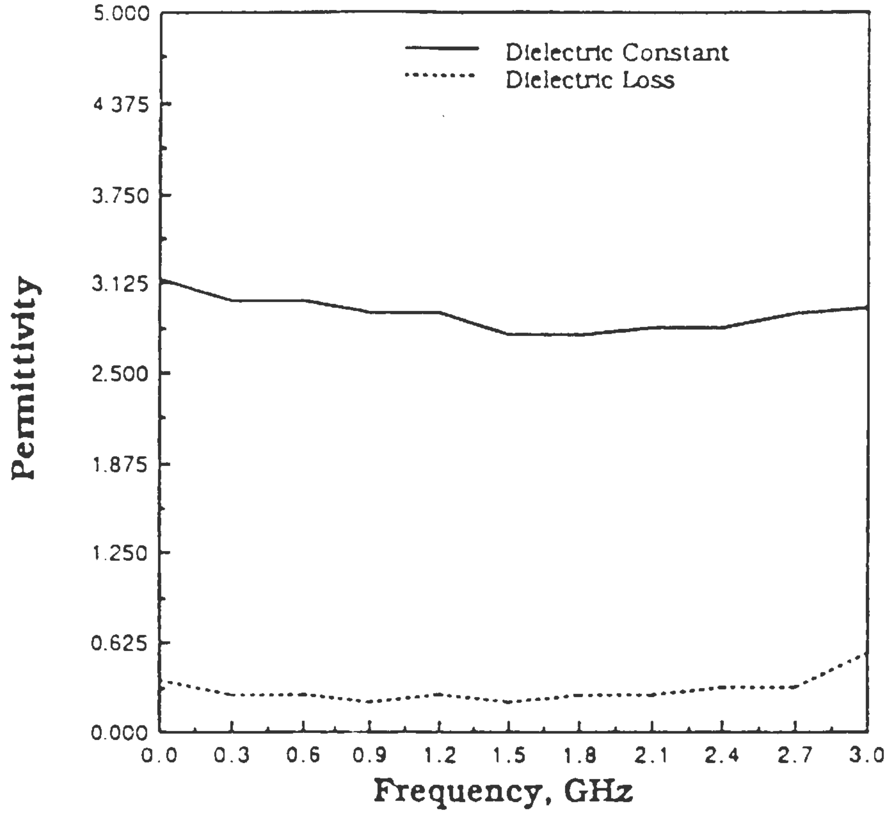

Figure x. Permittivity of Pittsburgh #8 (HVB) coal twice dried at 100° C as a function of frequency.

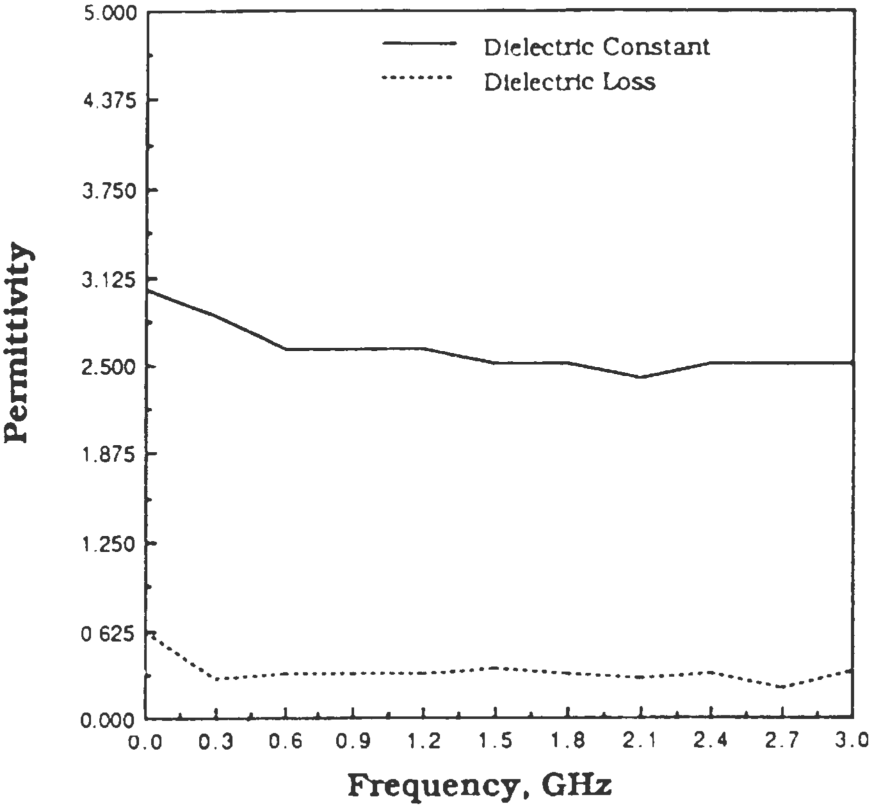

Figure xi. Permittivity of as-received Upper Freeport (MVB) coal as a function of frequency.

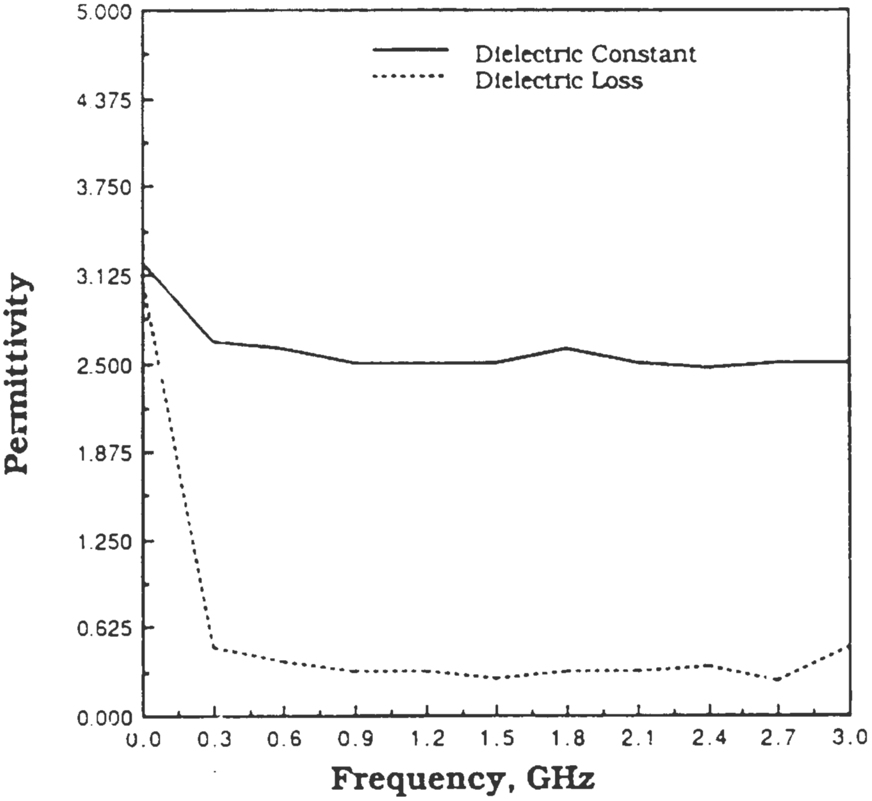

Figure xii. Permittivity of Upper Freeport (MVB) coal dried at 100° C as a function of frequency.

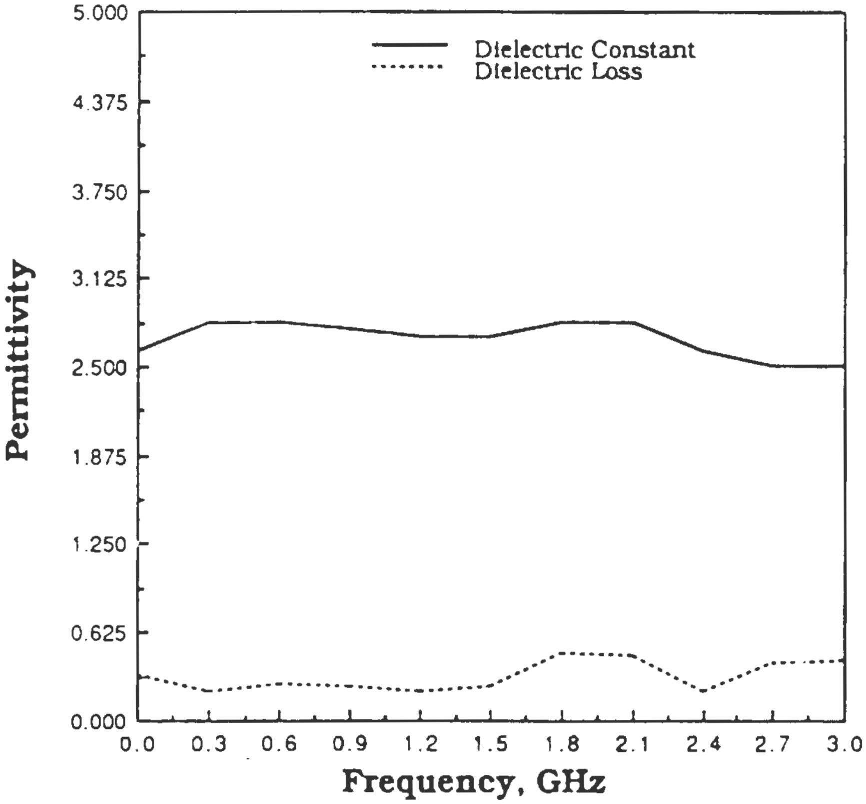

Figure xiii. Permittivity of Upper Freeport (MVB) coal twice dried at 100° C as a function of frequency.

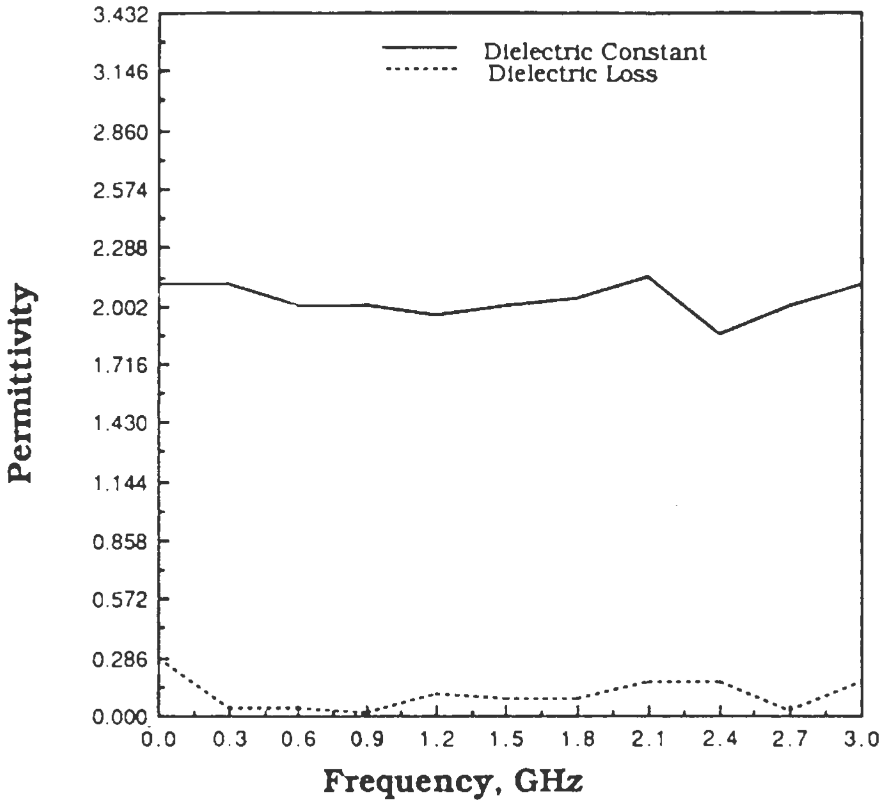

Figure xiv. Permittivity of as-received Pochahontas (LVB) coal as a function of frequency.

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C***************************************************************
*     THIS PROGRAM CALCULATES THE DIELECTRIC CONSTANT          *
*                                                              *
*     OF BOUND WATER GIVEN VOLUME AND DIELECTRIC CONSTANT      *
*                                                              *
*     OF PYRITE, ASH, HETEROGENEOUS MIXTURE AND DRY COAL.      *
*                                                              *
*                                                              *
****************************************************************

      Real Ec, Vp, Ep, Va, Ea, Vb, Em, Eb

      Ec = 3.0
      Vp = 0.01
      Ep = 7.0
      Va = 0.06
      Ea = 4.6
      Vb = 0.3
      Em = 6.5
      Eb = 9.9033+SQRT(117.5346)
      Print *, Eb
      End
```