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The measurements of density, velocity of ultrasonic longitudinal waves at frequency of 2.5 MHz, and dynamic elastic modulus were made for raw and demineralized bituminous coals. The samples were demineralized by treatment with hydrochloric acid. It was confirmed that the demineralization by HCl was not a conservative process because it caused not only the removal of a part of the mineral matter but also changes in elastic properties of pure coal substance.

Introduction

Coal structure studies are often referred to pure coal substance. Therefore, coals are often demineralized before use. The usual demineralization procedure involves treatment with hydrochloric and then hydrofluoric acids. It is important to know whether the demineralization is a conservative process, i.e., whether the removal of the mineral matter disturbs the structure and properties of coal. Any change in matter structure involves a change of elastic properties. Dynamic elastic properties are described by elastic moduli or velocity of ultrasonic waves propagation. Investigations of elastic properties for raw coals have been made by a number of researchers[1–7] (see also ref 8). However, the effect of demineralization has not been analyzed in the above papers. Velocities and elastic moduli were determined by standard methods of solid-state acoustics developed for monolithic specimens (cylinders, cubes, disks, etc.).

Studies of the effect of demineralization procedure on extractability, swelling and macromolecular structure,[9] radical density,[10] porosity, reactivity,[11–15] and dilatometric properties[16] as well as the study of the chemistry of demineralization[17] have been carried out during recent years. Dynamic elastic moduli were not determined in the above papers because standard acoustic or mechanic methods required monolithic samples, while the demineralization procedure was carried out on a ground material. Using a method developed for suspensions of a dispersed phase of one material in a continous second phase seems to be promising for the study of coal after demineralization procedure.

The propagation of sound waves of low and high frequency up to 60 MHz through suspensions was the subject of several studies.[18–34]

One of the earliest applications of the scattering theory for spherical particles was performed by Herzfeld[18] (see also refs 21 and 35) and then by Urick.[19] Herzfeld derived an expression for the adiabatic compressibility of solid in terms of velocity, density of solid and liquid, and compressibility of the liquid. This was based on extensive theoretical considerations of the effect of scattering by numerous small rigid spherical particles in the sound field. Urick[19] derived a simple expression

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Table 1. Elementary Analysis and Maceral Content of Studied Coals

sample no.	C^{daf} (wt %)	VM^{daf} (wt %)	ash (wt %)	V (wt %)	E (wt %)	I (wt %)	MM^a (wt %)	mineral matter (wt %)		
								clay	pyrite	carbonates
2	85.99	20.79	10.93	70.0	3.0	26.0	1.0	0.6	0.2	0.2
17	86.78	20.55	8.07	83.3	1.9	11.6	3.2	3.2	0	0
5	88.20	13.28	4.74	88.5	0	7.7	3.8	3.2	0.2	0.4
13	89.65	6.87	6.73	67.8	0	20.2	12.0	10.8	1.0	0.2

^{a} MM = mineral matter.

for the ultrasonic velocity in a suspension based on the assumption that the velocity of sound in a suspension is the same as it would be in an ideal solution of these two substances. Both methods mentioned above were compared in ref 19. For small volume concentrations of suspensions, both methods give the same results. Differences are important for higher concentrations. Equations of Urick or Herzfeld permit a determination of the elastic moduli of the particles in a suspension from measurements of density and sound velocity.

Further studies of the propagation of sound waves through suspensions discussed the effects of frequency,[20,22−24,26−31] concentration of suspended material,[19,20,22,28,32,33] viscosity,[23,34] and particle size[24,28−32] on the velocity as well as the different models of ultrasound propagation in suspensions, e.g., single or multiple scattering theory,[18−20,23,24,26−29,31,32,34] continuity, momentum and energy equations,[27] and Biot theory developed for a porous solid.[25]

A comprehensive review of theories for ultrasonic propagation in suspensions has been given by Harker and Temple.[27] They have calculated velocities and attenuations of ultrasound in suspensions for several selected samples. The velocities have been calculated using the formulas given by Urick,[19] Ament,[20] Schwartz and Plona,[26] and Biot (1956) (as given in Johnson and Plona[25]) and the expression derived by Harker and Temple.[27] Four cases were considered in which the compression wave velocity and density of the suspended particles were each greater than or less than those of the surrounding fluid. Predicted behavior of materials will be typical for all materials with similar densities and compression wave speeds. There was good agreement between the experimental values for kaolin obtained by Urick[19] and results of phenomenological theories (Urick[19] and Ament[20]) as well as hydrodynamic theory of Harker and Temple[27] for entire range of volume fraction and of fluid saturated porous medium theory[25] for volume fractions of <0.15. At volume fractions up to about 0.15 for particles up to 50 μm radius, multiple scattering can be neglected at frequencies of a few megahertz.[27] For materials (ice and polyethylene in water) having acoustic impedances close to that of the suspending fluid (i.e., water), the velocities calculated by the different formulas agree very closely for all concentrations up to 50% by volume for a frequency of 2 MHz and particle radius of 2 μm.[27]

For such cases the expressions of Urick are the most convenient to use. The great advantage of the Urick equation is its simplicity, requiring the knowledge of only two parameters for each phase and both are easily measurable.

The purpose of the research reported in the present paper was to obtain experimental results of density and ultrasonic velocity as well as elastic modulus for samples of raw coal and coal after treatment with hydrochloric
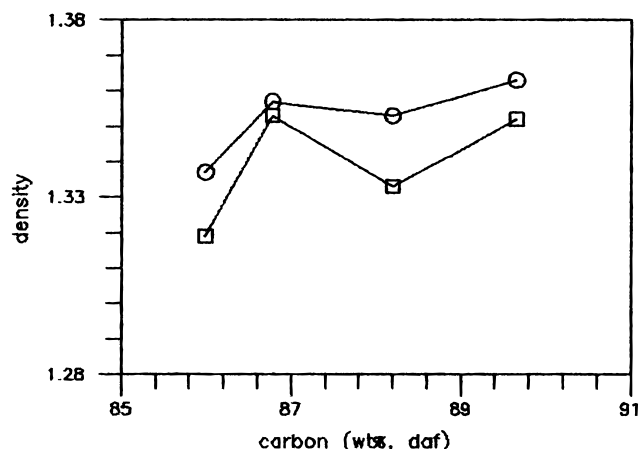

Figure 1. Plot of density in (g/cm³) of raw (○) and demineralized (□) coals versus carbon content C (wt %, daf).

Table 2. Densities in (g/cm³) of Raw and Demineralized Coals Measured Using Helium Pycnometer and Densities of Raw Coal Corrected for Ash, Mineral Matter, and Carbonates

sample	measured density		corrected density of raw coal		
	raw	demineralized	ash	MM	carbonates
17	1.357	1.353	1.298	1.334	1.357
2	1.337	1.319	1.256	1.330	1.336
5	1.353	1.333	1.319	1.326	1.350
13	1.363	1.352	1.314	1.274	1.362

acid in order to check whether the demineralization procedure altered the coal structure.

Experimental Section

Four samples of bituminous coals from Polish mines: Nowa Ruda (no. 2), Thorez (no. 17), Wałbrzych (no. 5), and Victoria (no. 13) with carbon contents of about 86−90 wt % daf were used in the study. Results for selected parameters of elementary analysis and petrographic content of the samples studied are presented in Table 1.

The samples were demineralized by treatment with concentrated hydrochloric acid. Densities were measured for raw and demineralized coals using a helium pycnometer "Micromeritics" (U.S.). Results are presented in Table 2 and Figure 1.

The velocities of ultrasonic longitudinal waves at frequency equal to 2.5 MHz were determined for raw and demineralized samples by suspension method developed by Herzfeld[18] and Urick.[19] Coal suspensions of the same concentration, 3 wt % (volume concentration 2.5%), were prepared in glycol using an ultrasonic desintegrator. The measurements of the ultrasonic velocities in pure liquid and suspensions were performed in the temperature range 15−40 °C with SW-08 apparatus based on the "sing-around" pulse method. This ultrasonic technique used for investigations of liquid coal products has been described in our previous papers.[35−39] The ultrasonic

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Table 3. Material Properties Used (Ratios Calculated Versus Glycol Except for Data from Ref 27)

material	density (10^3 kg m^{-3})	ρ/ρ_l ratio	compression wave speed (m s^{-1})	acoustic impedance ratio to liquid $\rho v/\rho_l v_l$
no. 17 coal^{raw}	1.357	1.2	1955.7	1.41
no. 17 coal^{dem}	1.353	1.2	2122.5	1.53
glycol	1.1135	1.0	1690.0	1.0
polyethylene[a]	0.9	0.9	1950	1.2
ice[a]	0.963	0.963	3608	2.3
kaolin[a]	2.6	2.6	4100	7.2
water[a]	1.0	1.0	1500	1.0

[a] Data from ref 27.

velocities in glycol and suspensions at $t = 20$ °C were calculated from experimental dependences of velocity on temperature. The values mentioned above as well as coal and glycol densities were applied to determine the ultrasonic wave velocities in coal particles v according to eq 1:[21,40]

$$v_s = \frac{v_l}{\{[1 + k(\rho/\rho_l - 1)][1 - k(1 - \rho_l v_l^2/\rho v^2)]\}^{1/2}} \qquad (1)$$

where v_s is the velocity of ultrasonic wave propagation in suspension, ρ_l and ρ are the densities of pure liquid and suspended matter, respectively, v_l and v are the velocities of ultrasonic wave in pure liquid and in particles of suspended matter, respectively, and k is the volumetric concentration of particles of suspended matter.

Equation 1 was derived from $v_s = (\rho_{eff}K_{eff})^{-1/2}$ with effective density ρ_{eff} and effective compressibility K_{eff} defined by Herzfeld in a first approximation of his theory and then by Urick.[19] Equation 1 is valid under the following assumptions:[18] (1) Adiabatic and isothermal compression are indistinguishable (in solids, i.e., also in coal the difference between them is small); (2) Any influence of a change in temperature which might occur in the suspension through conduction from the liquid subjected to adiabatic compression may be neglected; (3) The particles are small spheres, which we can treat as isotropic solids (this is a consequence of averaging the random orientation of anisotropic particles); (4) The difference in density of solids and liquids is small; (5) All shearing and frictional effects may be neglected; (6) Only the longitudinal waves are taken into account since the transversal waves in the liquid die out rapidly; (7) The mutual influence of the suspended particles may be neglected.

Table 3 presents the comparison of the material properties for the suspensions of coal no. 17 with the data from ref 27. The coal data are similar to those for polyethylene and ice, for which there is complete overlap of the results of theoretical calculations by means of the simple and more sophisticated theories mentioned in ref 27.

Coal particles used in this study were small (diameters less than 10 μm) and almost spherical. Density ratios equal to 1.2 (Table 3) demonstrated that the difference in density of particles and liquid was small. The acoustic impedance ratio for coal and glycol were closer to unity than those for ice, kaolin, and water. Volume concentrations used in our experiments were small (equal 0.025), so mutual interactions between suspended particles were negligible. Biot theory and scattering theory predict that the viscous effects diminish at high frequencies for spherical obstacles.[28] The small density difference between the two phases in suspensions[30] is also responsible for the fact that the contribution of viscoinertial

mechanisms to the acoustic velocity behavior is small. In relation to the above the frictional effects were negligible for frequency of 2.5 MHz and similar densities of suspension components. Thus, eq 1 was sufficiently correct for determination of velocity in coal particles.

The ultrasonic velocity measurements in coal suspensions were described by us for the first time in ref 41 and later in ref 42.

In the general case, the relationship between the velocity of propagation v, the absorption of sound waves α, and the components of the complex modulus of elasticity $E^* = E' + iE''$ is determined by the following equations:[43]

$$E = \rho v^2 \frac{[1 - (\alpha v/\omega)^2]}{[1 + (\alpha v/\omega)^2]^2} \cong \rho v^2 \qquad (2a)$$

$$E'' = 2\rho v^2 \frac{\alpha v}{\omega} \frac{1}{[1 + (\alpha v/\omega)^2]^2} \cong 2\rho v^3 \frac{\alpha}{\omega} \qquad (2b)$$

where E' is called the dynamic modulus of elasticity, E'' the loss modulus, and ω the angular frequency ($\omega = 2\pi f$, in which f is the frequency of the oscillations). When the attenuation per wavelength is small, $E \cong \rho v^2$, and such an expression was used in our study to determine elastic properties of coal.

All samples were ground in an agate ball mill to obtain the size of particles of about 10 μm. This granulation is required to fulfill the condition of "small particles". For the wave frequency of $f = 2.5$ MHz, the size of particles is considerably smaller than the wavelength. This condition is required to neglect the higher-order coefficients (quadrupole, etc.) in the complex propagation constant in suspension. All of the measurements and the HCl-demineralization procedure were performed for coals with the same granulation (10 μm).

All measurements were made for one frequency. Thus, we were not able to study the effect of frequency, i.e., dispersion.

Hampton[22] showed that the measured velocity dispersion in the laboratory-prepared sediments is approximately 2% over the frequency range 4–200 kHz. Velocity increases with frequency.

It was found[28] for water–polystyrene and oil–polystyrene suspensions that the velocity was essentially constant with frequency (within 100 kHz to 1 MHz). This was because the densities of the fluids and polystyrene were almost the same (ρ/ρ_l was equal 1.1 for water and 1.2 for oil) and the relative motion that usually has a significant effect on velocity dispersion was minimized here. Therefore, the change in relative motion with frequency, which will occur in a suspension of components of highly contrasting densities, will be negligible, and the velocity will not vary with frequency.

Similarly, for a suspension of blood[24] for which $\rho/\rho_l \cong 1.05$, the influences of frequency, as well as particle shape, and orientation were negligible. When differences in densities between suspension components are large, the velocity of sound varies significantly with ultrasound frequency, and with particle shape and orientation, especially for suspensions containing spheroidal particles. This fact was observed for dilute suspensions. For the dilute suspensions of coals studied here (volume fraction 0.025), ρ/ρ_l was equal to 1.2, similar to suspensions of polystyrene in oil as well as in water and for blood. In relation to the statements in refs 22, 24 and 28, it can be assumed that substantial effects of particle shape, orientation, and ultrasonic frequency on the velocity of sound through the coal suspensions may be negligible in our study.

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Results and Discussion

Table 2 presents experimental and recalculated (to eliminate the effect of mineral matter on densities) data of raw coal densities for pure coal substance. Relation from ref 8 was applied here. Three corrections were calculated: for ash, for mineral matter, and for carbonate content. The following value was assumed for ash and mineral matter densities, 2.8 g/cm^3, and for carbonates, 3.0 g/cm^3. It can be seen from Table 2 that coal densities after HCl treatment considerably decrease in comparison with raw state except for sample no. 17, which does not contain carbonates. Since hydrochloric acid removes mainly carbonates, this result is not surprising. If hydrochloric acid removes only carbonates, the density of demineralized coal is equal to the values presented in the last column of Table 2. It was shown that the measured densities of the demineralized coals are lower than those corrected for carbonates but generally higher than those corrected for the mineral matter densities of raw coals. It means that either HCl removed also other components of mineral matter or caused physical structural changes resulted in decrease of density. Considerable decrease of density for sample no. 2 can demonstrate that the changes of structure occurred independently of the mineral removal. One can see from Figure 1 that correlation between changes of density and coal rank does not exist.

Mineral matter affects also the velocity of ultrasonic waves. Mineral matter inclusions in small coal particles (<10 μm) change their average density and therefore change the ultrasonic velocity. Larger mineral grains with diameters about 20 μm and greater occurred in small amounts, except from pure coal and polluted particles. They possessed different shapes than spherical coal particles (visible in electron miscroscope). It is well-known from the work of Ahuja[23] that the particle shapes have an effect on the velocity potential of the disturbance of the sound wave caused by the particle, when the density difference between the particle and the suspending medium is significant. Mineral matter is characterized by higher density, considerably different than glycol, and its shape is different than spherical shapes of coal. They will influence the ultrasonic velocity. More detailed calculations are difficult, but we think that this effect is negligible. The velocity of raw and demineralized coals were determined using respective densities for raw and demineralized samples.

Figure 2 shows the plot of the longitudinal ultrasonic (f = 2.5 MHz) wave velocity versus rank for raw and demineralized coals. Velocity of ultrasounds in samples after demineralization increases for lower-rank coals, but for the highest-rank coal, it is almost the same. Acoustic resistance, defined as the product of density and velocity, also increases for coals after demineralization procedure except for the highest-rank sample no. 13. Thus, it can be stated that, for lower-rank coals, elasticity increases after hydrochloric acid treatment.

The dependence of the dynamic modulus of elasticity on rank is characterized by a plot similar to that of v vs coal rank presented in Figure 2. Figure 3 shows the plot of the difference of the modulus between raw and demineralized coals versus rank. The highest increase of elasticity is observed for coals with carbon content of $\cong$87%. The plot is similar in the shape to the plot of M_c (carbon %), which illustrates average molecular
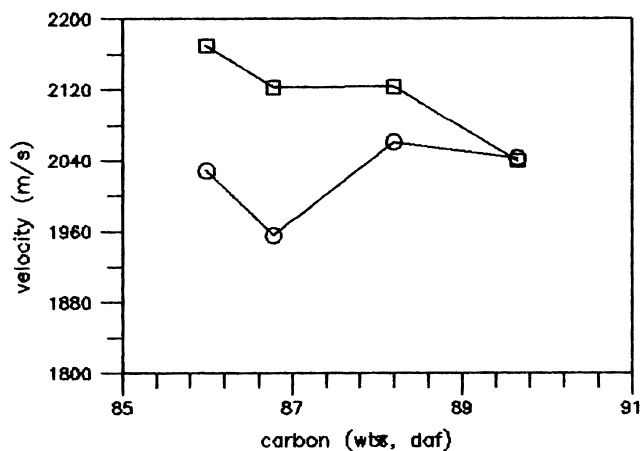

Figure 2. Plot of velocity of longitudinal ultrasonic wave in raw (○) and demineralized (□) coals versus carbon content C (wt %, daf).
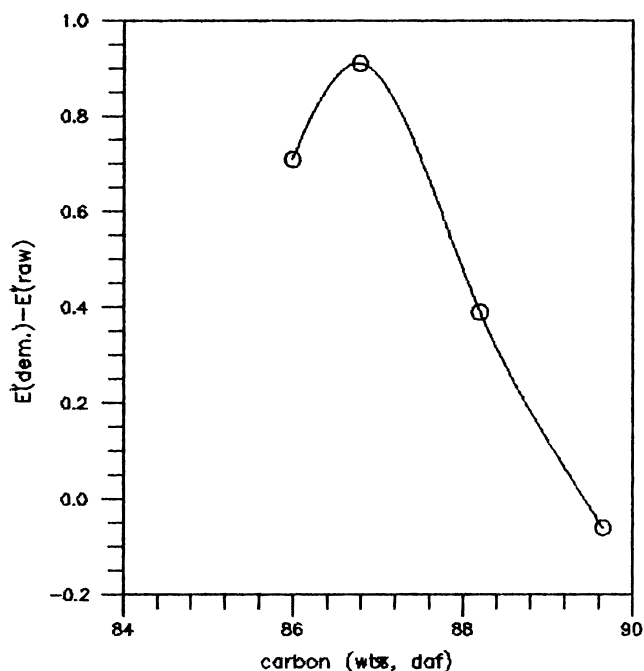

Figure 3. Plot of the difference: E' (demineralized coal) − E' (raw coal) in ($\times 10^9$ N/m^2) versus carbon content C (wt %, daf).

weight between cross-links versus carbon content.[44] The coals with the minimum in cross-link density are most effectively altered by the HCl treatment. The most cross-linked coal sample no. 13 with carbon content of $\cong$90% exhibits a slight decrease of value E'.

Sample no. 17 did not contain carbonates, which would be washed out in HCl demineralization procedure. This sample ought to exhibit the smallest changes of measured values. In fact, density remains almost the same after acid treatment. On the other hand, values of v and E' differ considerably before and after HCl treatment. It means that the hydrochloric acid demineralization is not a conservative process. HCl has an effect on the physical structure of coal and resulted in changes of its elastic properties.

We discussed the changes of density and ultrasonic velocity and consequently changes in the elastic modu-

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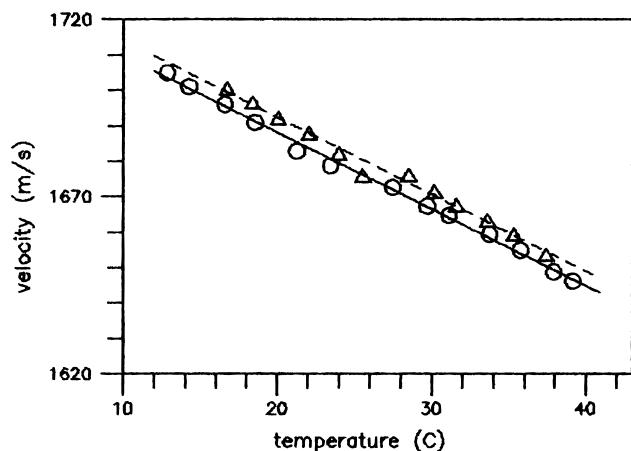
Figure 4. Temperature dependences of ultrasonic velocity in glycol suspensions of coal no. 17 in raw state: not subjected to EtDa action (○) and after EtDa action (△).
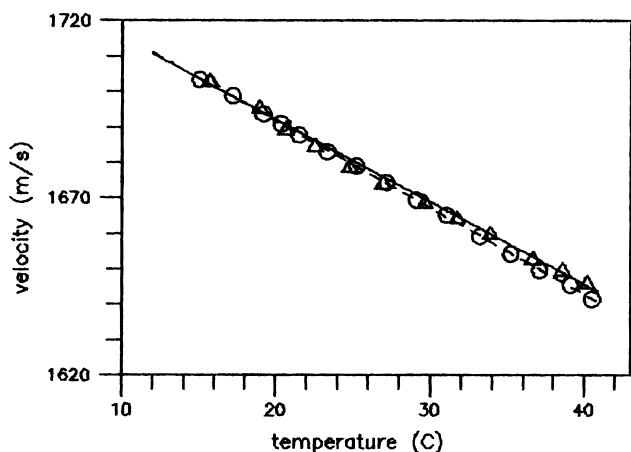

Figure 5. Temperature dependences of ultrasonic velocity in glycol suspensions of coal no. 17 in demineralized state; not subjected to EtDa action (○) and after EtDa action (△).

lus caused by hydrochloric acid during the demineralization process. It is interesting how the demineralization influences the solvent action on coal and whether it is observable by means of the ultrasonic velocity measurements. It was checked for pyridine (PY) and ethylenediamine (EtDa). Coal no. 17 was selected for the study, due to the maximum difference E'(dem) − E'(raw).

The raw sample no. 17 and after demineralization was then placed in pyridine to measure its swelling ratio. It appeared that, after demineralization by HCl, swelling was reduced from 2.0 for raw to 1.2 for demineralized sample. In the report of Larsen et al.,[9] it was confirmed that there is a tendency toward greater swelling (pyridine also) of the demineralized coal, but the differences were small. This result refers to low-rank coals and full demineralization procedure, i.e., HCl/HF treatment. It is not possible to compare those results with ours.

Some portions of both raw and demineralized sample no. 17 were flooded with ethylenediamine and remained

up for near 2 weeks. Then they were filtered and dried. Suspensions of raw coal, raw coal after EtDa action, demineralized coal, and demineralized coal subjected to EtDa action were prepared in glycol. Figure 4 shows the dependences of $v(t)$ for suspensions of raw coal and raw coal after EtDa action. The distinct difference between the plots of $v(t)$ indicates that ethylenediamine caused an observable change in coal, which is reflected in the separation of two straight lines in Figure 4. If not, the straight lines would overlap (within the range of experimental errors).

Figure 5 shows the dependences of $v(t)$ for suspensions of demineralized coal and the demineralized coal after EtDa action. Straight lines are almost overlapped. Thus, ethylenediamine did not cause changes of elastic properties in the sample after HCl treatment. It is possible that HCl demineralization reduces the action of solvent on coal. A comparison of the data obtained for the same coal sample (see Figures 4 and 5) results in the confirmation of the influence of HCl demineralization on elastic properties of coal.

Results reported in this paper were compared qualitatively with data from refs 13 and 16. Calahorro et al.[13] performed the measurements of densities and compressibilities of Spanish bituminous coal (carbon 80.9 (wt %, daf), mineral matter 58.7 (wt %), and ash 53.9 (wt %, dry)) before and after HCl treatment. He observed that, after demineralization in hydrochloric acid, density increased from 1.41 to 1.51 g/cm^3 and compressibility decreased from 1.93×10^{-10} to 1.47×10^{-10} m^2 N^{-1}. Density data quoted in ref 13 are inconsistent with our results. It is difficult to compare them because Calahorro et al. reported densities corrected for large mineral matter content also for demineralized coals in contrast to the data of the present paper. Whereas a decrease in compressibility due to HCl demineralization is consistent with our results.

Wachowska et al.[16] performed the dilation measurements for two coals with carbon content of 84.5% and 85.4%. The hydrochloric acid treatment of these samples resulted in reduction of dilation from 68% to 20% (sample I) and from 155% up to 23% (sample II). In this case, the effect of HCl on increase of elasticity was also observed. Greater changes in the case of sample II of higher rank compared to lower-rank sample I are qualitatively consistent with the tendency reported in Figure 3.

It is shown that the first step of demineralization procedure, i.e., treatment by hydrochloric acid causes the following: decrease of density, increase of the dynamic modulus of elasticity for coals with the low cross-link density, reduction of swelling or more general, action of solvents.

The investigations presented in this paper ought to be repeated for the second step of the demineralization procedure, i.e., treatment by hydrofluoric acid, which will be performed in the future.