CHARACTERIZATION OF SHUNGITE BY PHYSICAL ADSORPTION OF GASES

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Abstract

Shungite is a natural carbonaceous mineral, abundant in Russia. Their properties are currently under study and their applications are continuously growing. In this work the surface properties for a sample of shungite were characterized using physical adsorption of N_2, Ar, O_2 and CO_2. Pore size distribution and pore volume were calculated. Real and apparent densities were determined and the adsorption energy distribution was calculated for N_2, Ar and CO_2. The sample of shungite shows a mesoporous surface with a narrow size pore distribution. Their specific surface is relatively low and the surface seems to be rather homogeneous.

Resumen

Shungita es un mineral natural carbonoso que se encuentra en yacimientos en Rusia. Sus propiedades y aplicaciones se encuentran actualmente en pleno desarrollo. En este trabajo se presentan resultados, obtenidos a partir del estudio de la adsorción comparada de N_2, Ar, O_2 y CO_2, que contribuyen a la caracterización del mineral. Se informa la distribución de tamaños de poro, el volumen total de poro, la densidad real y aparente y la distribución de energías de adsorción. La muestra ha resultado mesoporosa, con una distribución de radios de poro bastante estrecha y presenta una superficie específica relativamente baja. A pesar de su composición y los tratamientos a los que ha sido sometida, la superficie aparece como bastante homogénea desde el punto de vista energético.

Introduction

Shungite (schungite) is elementary carbon with amorphous structure, although X-Rays studies show the existence of fragments with graphitic structures with an interlayer distance of 3.4 and 3.5 Å. Recently it has been stated that the mineral has important amounts of fullerenes, mainly C_{60} [1].

Shungite rocks have a peculiar structure. They are characterized by highly dispersed silicate mineral grains evenly distributed in the shungite carbon matrix. It determines their numerous practical applications. Shungite rocks have high electric conductivity and considerable mechanical strength.

Shungite possesses an extra-molecule structure detectable by electron microscopy. Round or elongated globules of a fraction of an angstrom in size are the elements of the

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extra-molecule structure. The globules in shungite are mutually oriented. Probably this explains the anisotropy of physical properties of shungite [1].

The real density of shungite carbon can vary from 1.9 to 2.1 g/cm^3 and depends on its structure and the conditions of its formation. Shungite is characterized by a high elasticity. The ratio of compression strength to dynamic modulus of elasticity for shungite is the highest among carbon materials, including graphite and glassy carbon. With respect to its reactivity with oxygen, shungite is more active than coke. At the same time, shungite is more resistant to oxidation, in oxygen-free aggressive media, than even graphite.

The surface of shungite carbon is partially oxidized. This can be attributed to its peculiar physical and physico-chemical properties. The shungite surface is more water-receptive than graphite. Water infusion of shungite has an acid reaction (pH = 4).

Shungite possesses properties adsorption, catalytic and bactericidal which depend on the specific area of the carbon. Shungite rocks are characterized by a wide range of carbon content and by the diversity in the composition of the silica component [1, 2].

The mineral has low specific surface area (6 to 11 m^2/g), when it is treated with alkali in an autoclave the specific surface area could be raised to about 26 m^2/g.

Some of their applications can be summarized as follows:

Shungite can replace coke, graphite, carbon black or glassy carbon, it can serve as a complex raw material in thermal processes, it can be used to replace graphite in mold paints, it mix well with all known binders, it can screen high frequency electromagnetic emissions when included in construction materials, it can be used to produce fire-safe ecologically clean heating units, it can play a valuable role in the production of rubber and plastics, it is useful in the treatment of skin aliments and besides, it has proven to be quite effective in water treatment processes.

The sample of shungite was provided by the Wynterwade Company. It is a mineral from Zazhoginskoye (Russia) and according to specifications by the provider has the following composition: 30% C, 40% quartz and 25% of silicates [1].

This work shows the results obtained in the characterization of a shungite sample using N_2, Ar, O_2 and CO_2 adsorption.

The specific surface area, pore size distribution and adsorption energies distribution are reported. For comparison, N_2 and Ar adsorption energies distribution were calculated employing two different methods.

Experimental

N_2, O_2 and Ar adsorption isotherm were obtained at 80.2 K (liquid air temperature) and CO_2 isotherm at 273.2 K. Data were obtained employing conventional adsorption volumetry. Pressure measurements were determined by using an absolute capacitance manometer and temperature was measured with a digital thermometer with a Pt-100 (DIN) sensor head previously calibrated against an oxygen vapor pressure thermometer. The maximum experimental error, determined according to standard methods, was 0.3% in the adsorbed volume; more details concerning the experimental technique have been published elsewhere [3,4].

The adsorbed volume was calculate assuming ideal behavior of all gases in the experimental conditions. All gases were of high purity and the corresponding liquids have been distilled under vacuum before use to ensure a maximum degree of purity [5].

The adsorption – desorption isotherms are shown in figures 1 to 4. The specific surface area of the shungite sample is 25.09 m^2g^{-1}. It was calculated using the BET method from N_2 isotherms, assuming a value of 0.162 nm^2 for nitrogen cross-sectional area and using the standard range of relative pressures [6]. Similar calculations have been performed using Ar, O_2 and CO_2 adsorption isotherms. Results are summarized in Table 1.

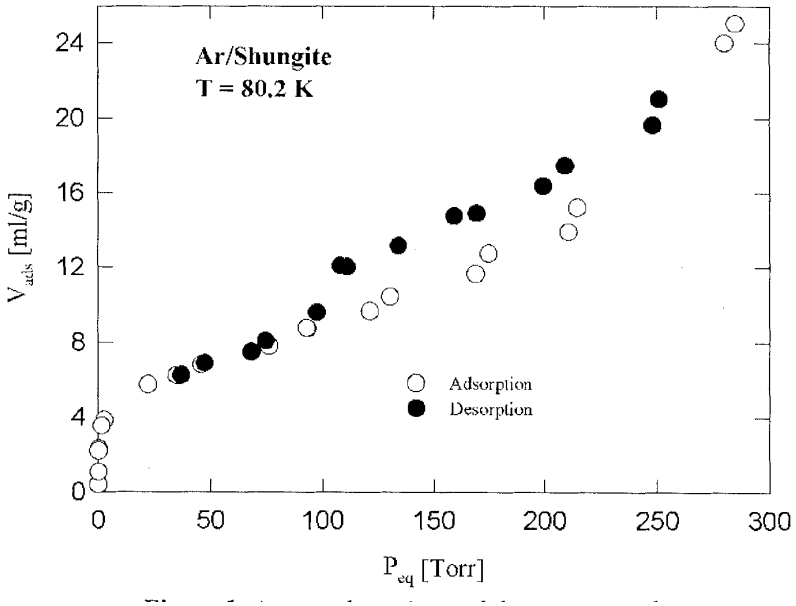

***Figure 1**: Argon adsorption and desorption isotherms*

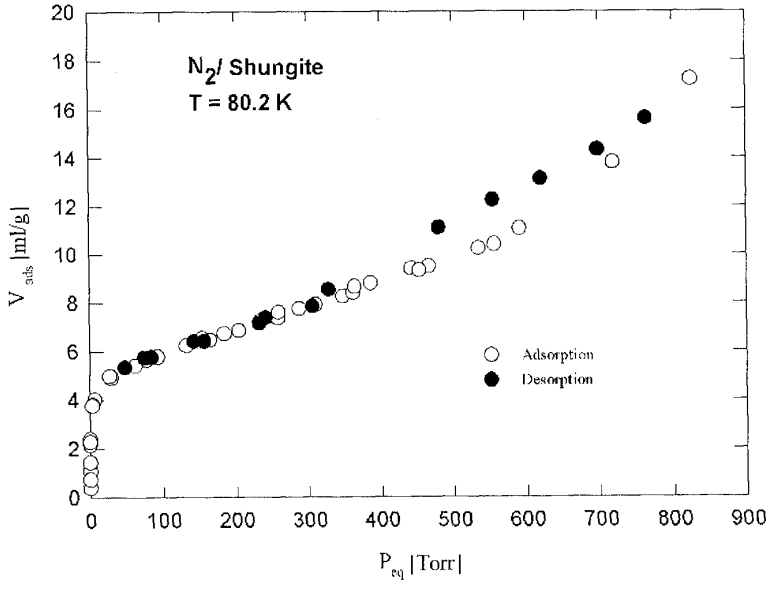

***Figure 2**: Nitrogen adsorption and desorption isotherms*

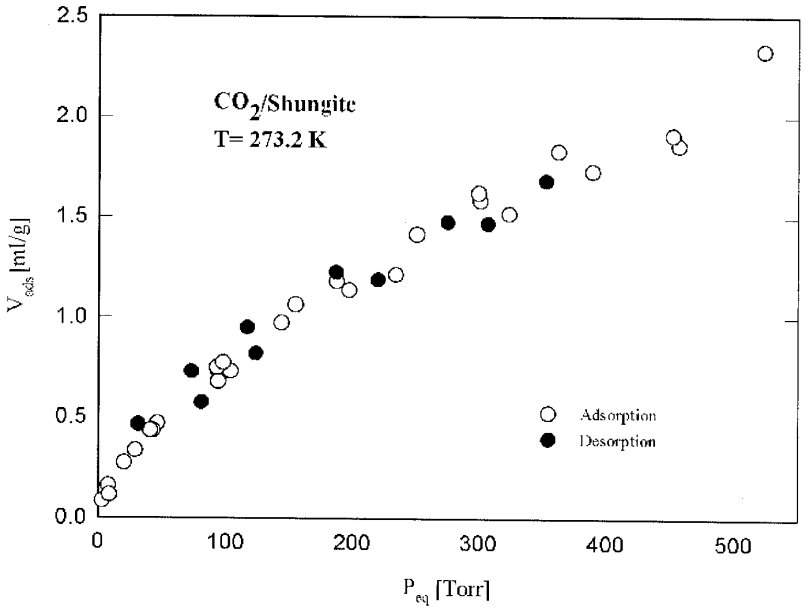

***Figure 3**: Oxygen adsorption and desorption isotherms*

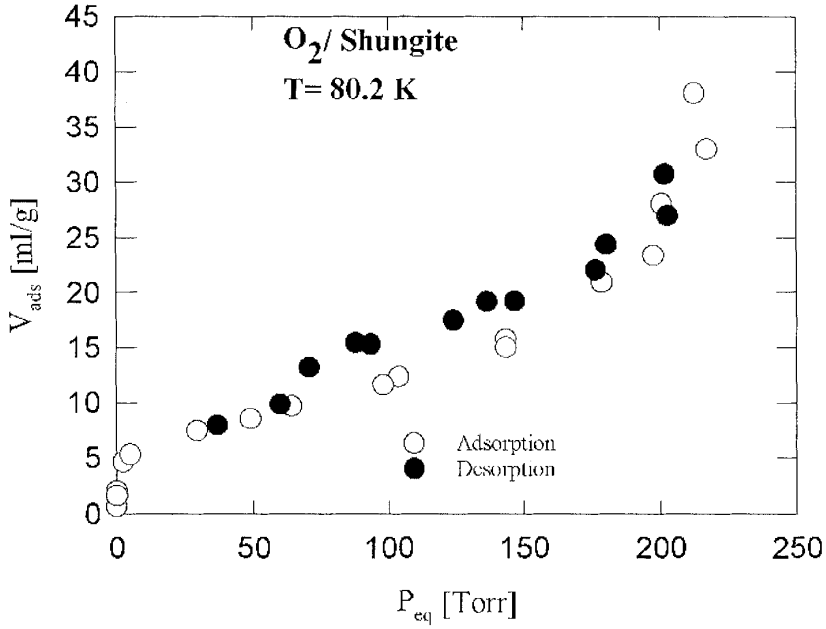

***Figure 4**: Carbon dioxide adsorption and desorption isotherms*

***Table 1:** Surface area calculated from experimental isotherms*

Gas	N_2	O_2	Ar	CO_2
Cross Sectional Area (nm^2)	0.162	0.135	0.136	0.164
S BET (m^2/g)	25.09	25.68	24.84	22.54

The real and apparent densities were determined using Helium gas volumetry and CCl_4 picnometry respectively.

Results and Discussion

The distribution function of adsorption energies has been calculated solving the general adsorption equation:

$$V_{ad}(p) = V_m \int_{U_{min}}^{U_{max}} \theta^l(p,U)\, f(U)\, dU$$

where $V_{ad}(p)$ is the volume of gas adsorbed at equilibrium pressure p, V_m is the monolayer volume, $\theta^l(p,U)$ is a local isotherm and $f(U)$ is the distribution function of adsorption energies. This equation is a Fredholm 1st kind integral equation that cannot be analytically solved for these systems. In order to calculate $f(U)$, numerical methods are needed [7, 8, 9].

The choice of the local isoterm $\theta^l(p,U)$, the distribution function $f(U)$ and the integral resolution by the least square method has been widely described in previous papers [8, 9]. For N_2 and Ar this integral has been solved also using the CONTIN method [10].

Both Ar and N_2 distribution functions of adsorption energies suggest a relatively homogeneous surface with maxima at very similar potentials, while CO_2 distribution shows two different adsorption sites and a less homogeneous surface (figures 5 - 7).

The N_2 distribution function obtained using CONTIN method is rather similar to those obtained by the least square method even when the maximum lies at potentials somewhat lower. However for the Ar distribution function the difference between both methods is very important, showing the CONTIN method a very broad distribution.

The pore size distribution, $\frac{dV}{d(r_K)}(r_K)$ was calculated using the Kelvin equation for cylindrical pores, assuming a contact angle of zero. The results for N_2, Ar and O_2 are shown in figure 8.

The pore size distributions for Ar and O_2 show a maximum for a radii of about 17 *Å*, that corresponds to a mesoporous surface according to the Brunauer classification, and a narrow distribution. For N_2 the distribution is less defined. This can be due to the form of the lower end of the hysteresis loop (figure 2).

The absence of pores with radii between 3 and 4 *Å* confirm that the graphitic fraction of the surface is rather low.

The total pore volume was determined from N_2 adsorption – desorption isotherms following the usual method described in Gregg y Sing [11]. A value of 0.019 ml g^{-1} was obtained, in good agreement with the one obtained from real density (1.995 ml g^{-1}) and apparent density (1.925 ml g^{-1}).

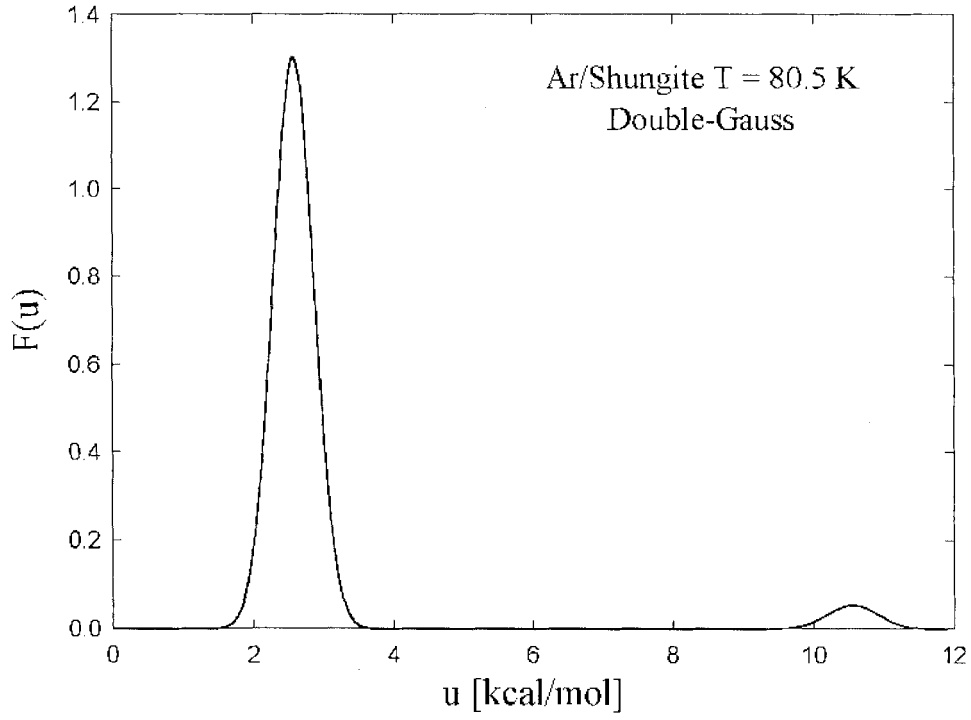

***Figure 5**: Argon adsorption energy distribution function (Using a Double Gaussian model)*

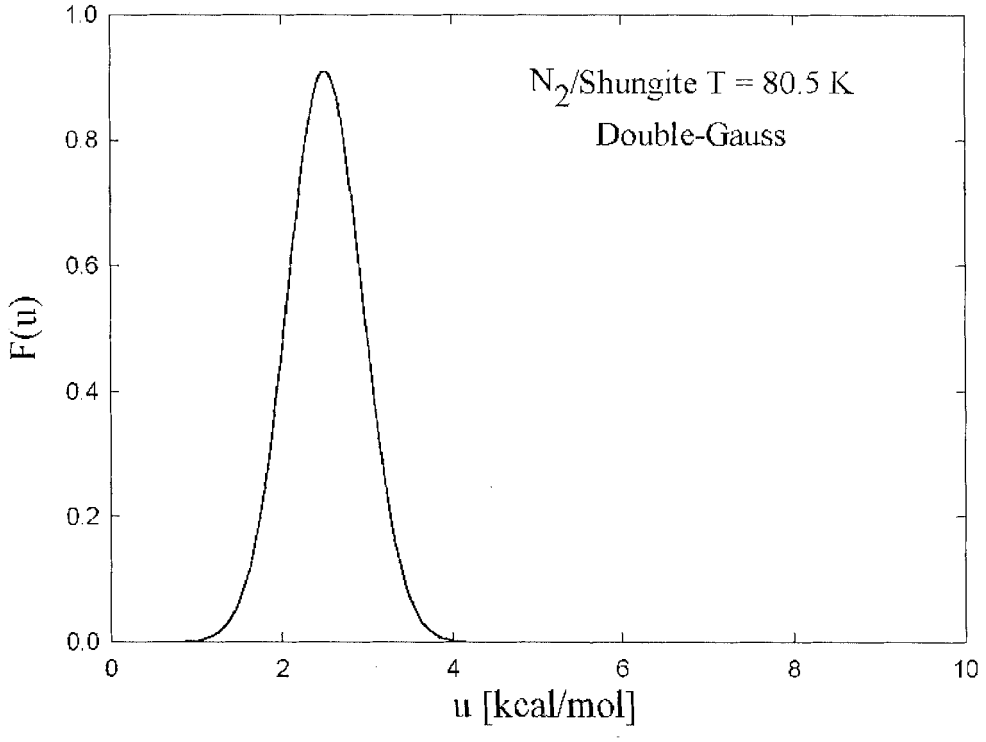

***Figure 6**: Nitrogen adsorption energy distribution function (Using a Double Gaussian model)*

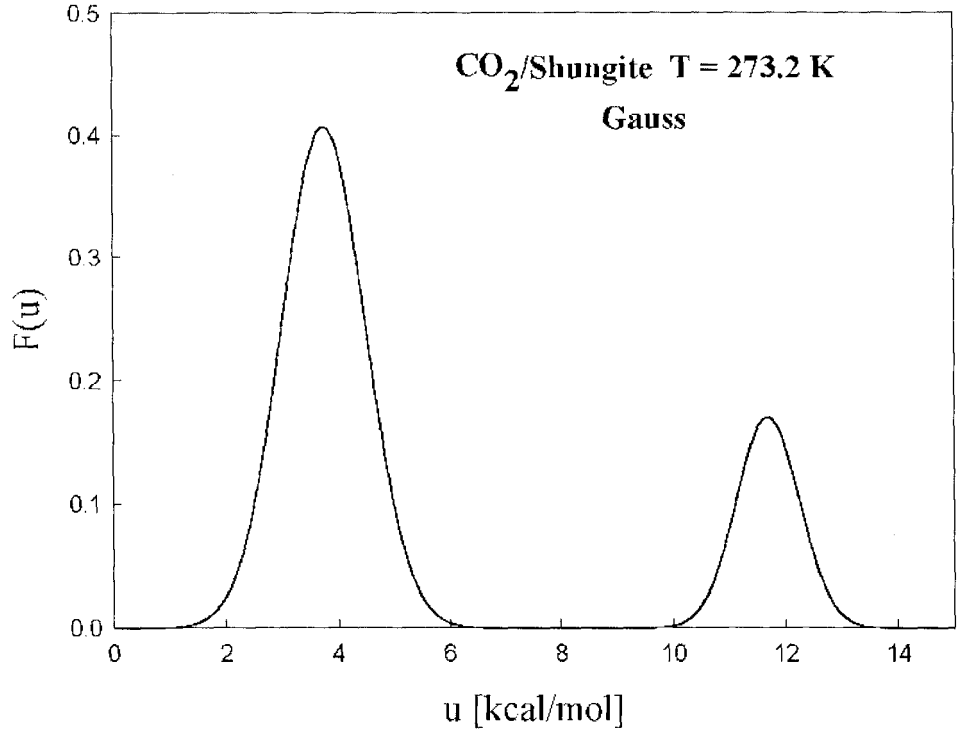

***Figure** 7: Carbon dioxide adsorption energy distribution function (Using a Gaussian model)*

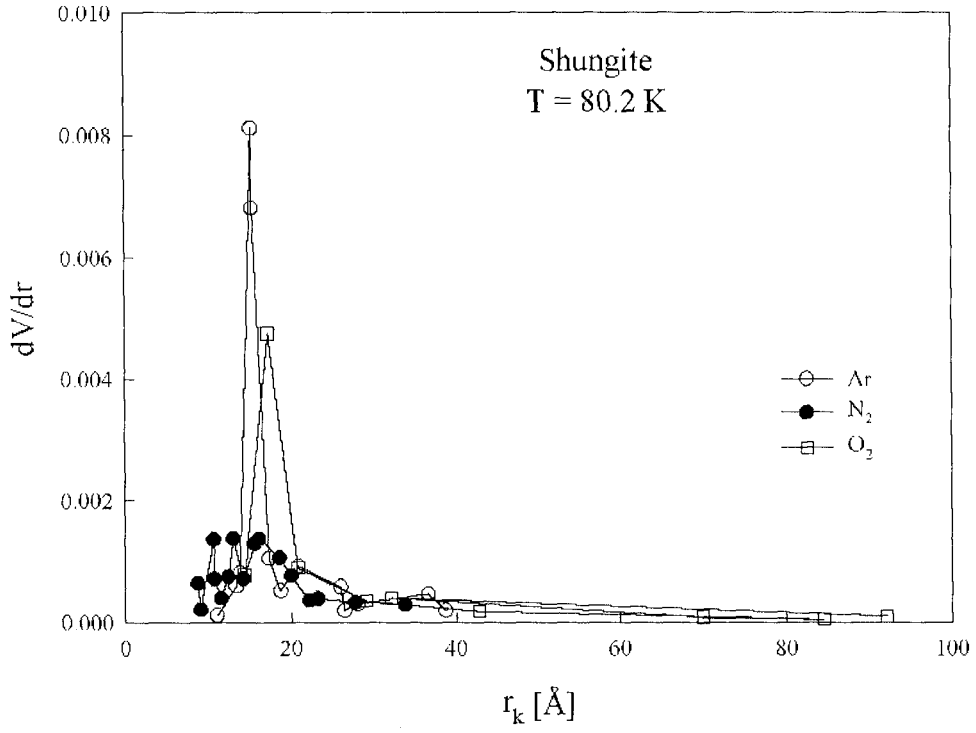

***Figure 8**: Porous size distribution*

The total pore volume was not determined for the others gases because the calculation implies to correct the Kelvin pore radius by the thickness of the layer of gas adsorbed over the pore wall (thickness *t*) [12] and the *t* values obtained for these gases show an important dispersion.

Conclusions

The shungite studied is a mesoporous material with a narrow porous radii distribution and a small porous volume. The specific surface area is relatively low. Notwithstanding its origin and treatment, the gas–solid potential distribution suggests a rather homogeneous surface.

The lack of agreement between the least square and CONTIN distributions for Ar is still under study. The use of the CONTIN method must be carefully evaluated.

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