

# Carbon-Mineral Adsorbent from Petroleum Pitch and Precipitated Colloidal Silica



Kugatov P.V., Nigmatullin V.F., Zhirnov B.S.

**Abstract:** The carbon-mineral adsorbent was prepared according to a two-stage scheme, which, despite the hydrophilic nature of the surface of colloidal silica, made it possible to prepare pellets with a high specific surface area and compressive strength of up to 70 m<sup>2</sup>/g and 8 MPa, respectively. The proposed method consists in mixing petroleum pitch and colloidal silica in the first stage, followed by granulation and carbonization (at 1000 °C); the resulting carbon-mineral material is crushed and mixed with petroleum pitch in the second stage, after which it is also granulated and carbonized (at 700 °C). Based on the obtained carbon-mineral sorbent, a highly porous carbon adsorbent is produced by etching the silicate base in a concentrated solution of sodium hydroxide during boiling. The total pore volume of the obtained samples reached 3.5 cm<sup>3</sup>/g.

**Key words:** carbon-mineral adsorbent, petroleum pitch, colloidal silica, carbonization, etching.

## I. INTRODUCTION

Among all the porous materials used as adsorbents or catalyst supports, the most widely used are oxide and carbon materials. The first group includes silica gel, active alumina, zeolites, etc.; the second group belongs to various varieties of activated carbons. Representatives of each of these groups have their advantages and disadvantages; therefore, in recent years there has been growing interest in obtaining the so-called carbon-mineral sorbents. In them, high adsorption properties and a customizable pore size of the carbon part are combined with increased oxidation resistance due to the oxide part. An interesting feature of these materials is the fact that the mineral part can be removed by “etching” the carbon-mineral composite with a saturated alkali solution or HF solution, which allows one to obtain a purely carbon material with an increased sorption volume.

Among the described methods and materials for obtaining these sorbents can be identified:

- mixing pitch dissolved in tetrahydrofuran with an aqueous solution of tetraethoxysilane (TEOS) in the presence of HF as a catalyst [1];

- infiltration of a solution of mesophase pitch in benzene through a sample of mesoporous colloidal silica prepared on the basis of TEOS [2];

- sol-gel process using TEOS and furfuryl alcohol as a carbon source in the presence of hydrochloric acid as a catalyst [3];

- cooperative pyrolysis of organosilicon compounds and liquid hydrocarbons, or mechanical mixing of colloidal silica with carbon black, followed by deposition with pyrocarbon and activation with steam, following the example of the family of porous carbon materials Sibunit [4];

- mixing colloidal silicon dioxide with polyvinylidene chloride - the classic Saran carbon precursor [5];

- mixing pitch with ordered mesoporous silica such as SBA-15, MCM-48 [6], or with silica of amorphous structure [7 – 9];

- synthesis of a carbon precursor based on ethylene-propylene and resorcinol polymers in the presence of colloidal silica [10];

- carbon microspheres based on resorcinol and formaldehyde in the presence of ammonia as a catalyst and colloidal silica as a filler [11 – 13].

The main stages of “mixing” of the initial composites are described above, in the subsequent stages of preparation of which carbonization practically always follows - heat treatment in an inert medium at elevated temperatures. The disadvantage of all methods is the high cost of both the mineral part (fumed silica, SBA-15, MCM-48), and the carbon part (mesophase pitch), as well as their precursors (TEOS, polymers, etc.). It should be noted that when the ready-made colloidal silica is used in the above methods, it has a pyrolytic origin, i.e. has a high cost; very rarely, precipitated silica is used for these purposes, although it has the worst dispersion, but is much cheaper.

Therefore, the problem of the development of methods for producing carbon-mineral sorbents based on inexpensive sources of raw materials (both carbon and mineral) is actual. For example, a porous carbon material from carbon black and petroleum pitch was previously obtained [14].

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The advantage of this material over other porous carbon materials is the relative cheapness and availability of the binder – petroleum pitch. By analogy with this material, when mixing and granulating the initial mixture, precipitated colloidal silica can be used as filler, which is hydrated silica obtained by precipitation from a solution of sodium silicate (water glass) with acid, most often sulfuric, followed by filtration, washing and drying. Also, the finished material can be etched to obtain a highly porous carbon material.

## II. EXPERIMENTAL

### 2.1 Raw materials and preparation methods

In this work, we used precipitated colloidal silica of grades BS-100, BS-120, BS-50, U-333 produced by Soda OJSC. Colloidal silica is a powder and fragile lumps of white. Table 1 presents the main physicochemical parameters of the silica samples. As a carbon precursor and a binder, petroleum pitch was used with a yield of 52.2% volatility and 38.3% fraction insoluble in toluene.

Table 1 – Characteristics of colloidal silica

Наименование показателя	Grades			
	U-333	BS-50	BS-100	BS-120
1 Average particle size, nm	-	50 – 77	23 – 34	19 – 27
2 Mass fraction of silica, %, not less	88	76	86	87
3 Moisture, %, no more	6.5	6.0	6.5	6.5
4 Loss in mass on calcination, %	-	7.0 – 10.0	5.0 – 7.0	3.5 – 7.0
5 Bulk density, g/dm <sup>3</sup>	180 – 200	200 – 230	170 – 220	180 – 230
6 Specific surface area by phenol adsorption, m <sup>2</sup> /g	30 – 60	35 – 55	80 – 120	100 – 140

The aim of this work is to obtain two types of products: carbon-mineral sorbent and carbon sorbent by etching silica in the composite obtained in the previous stages. The scheme for obtaining all samples is shown in Figure 1.

At the first stage (Figure 1a), samples of the carbon-mineral adsorbent were prepared by mixing the crushed petroleum adsorbent and colloidal silica in different proportions in the presence of a solvent, extruding the resulting mixture through 2 mm diameter nozzles and carbonizing the pellets in a stream of nitrogen at temperatures of 700 – 1000 °C for 1 hour followed by cooling.

Due to the fact that the pellets prepared in the first stage were fragile, the final samples of the carbon-mineral adsorbent were obtained in the second stage (Figure 1b) by a similar procedure, but the powder obtained by grinding the samples obtained in the first stage was used as filler.

To obtain a carbon sorbent (Figure 1c) from the prepared carbon-mineral composite, it was boiled in 50 ml of a 3M sodium hydroxide solution for 15 min. To complete etching, the procedure was performed five times. Next, the sample was washed with distilled water until neutral, the samples were dried at a temperature of 140 – 150 °C for 5 hours.

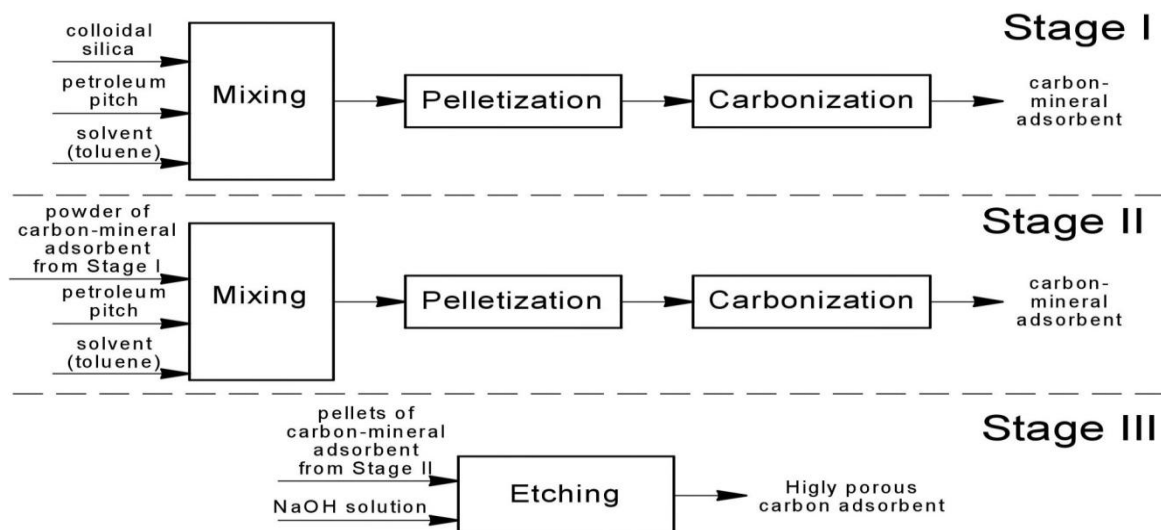


Figure 1 – Scheme of preparation of carbon-mineral adsorbent

### 2.2 Characterization

For the studied samples, the benzene adsorption isotherm was measured at 20 °C using the dynamic method. It was shown in [15] that the isotherms obtained by this method are

in good agreement with the isotherms measured on static vacuum units.

Before direct measurements, the samples were dried in a stream of nitrogen at a temperature of 300 °C for 1 h. By treating the isotherms using the BET equation [16], the specific surface area of the samples was calculated. To determine the surface area of mesopores and the volume of micropores, we used the  $\alpha_s$ -method proposed by Singh [16], which consists in comparing the adsorption isotherm of the test sample with the isotherm of the standard sample. In this work, we used data on the adsorption of benzene on graphitized carbon black [17] as a standard.

Also, for all the studied samples, compressive strength of the pellets was determined on the device "Prochnomer PK-1", total pore volume according to procedure [18] and ash content according to procedure [19]. The structure of the obtained granules was studied by electron microscopy on a JEOL JSM-6610LV instrument.

The first part of the work was the preparation of carbon-mineral adsorbent pellets by directly mixing the pitch with colloidal silica (stage I). The pitch content in the initial mixture was varied in the range of 10 – 50 % by weight, the heat treatment temperature was 700 °C. The obtained calcined pellets had a specific surface area of 40 – 70 m<sup>2</sup>/g, and it decreased slightly with increasing amount of binder. Electron microscopic images (Figure 2) show spherical formations ranging in size from 10 to 250 microns, which indicates incomplete mixing of silica and petroleum pitch. You can also observe heterogeneous areas, which, apparently, directly comprise a combination of particles of silica and pitch coke. Pores of 4 – 300 microns in size are also present. In general, similar results are obtained with increasing heat treatment temperature and the use of silica of different grades.

### III. RESULTS AND DISCUSSION

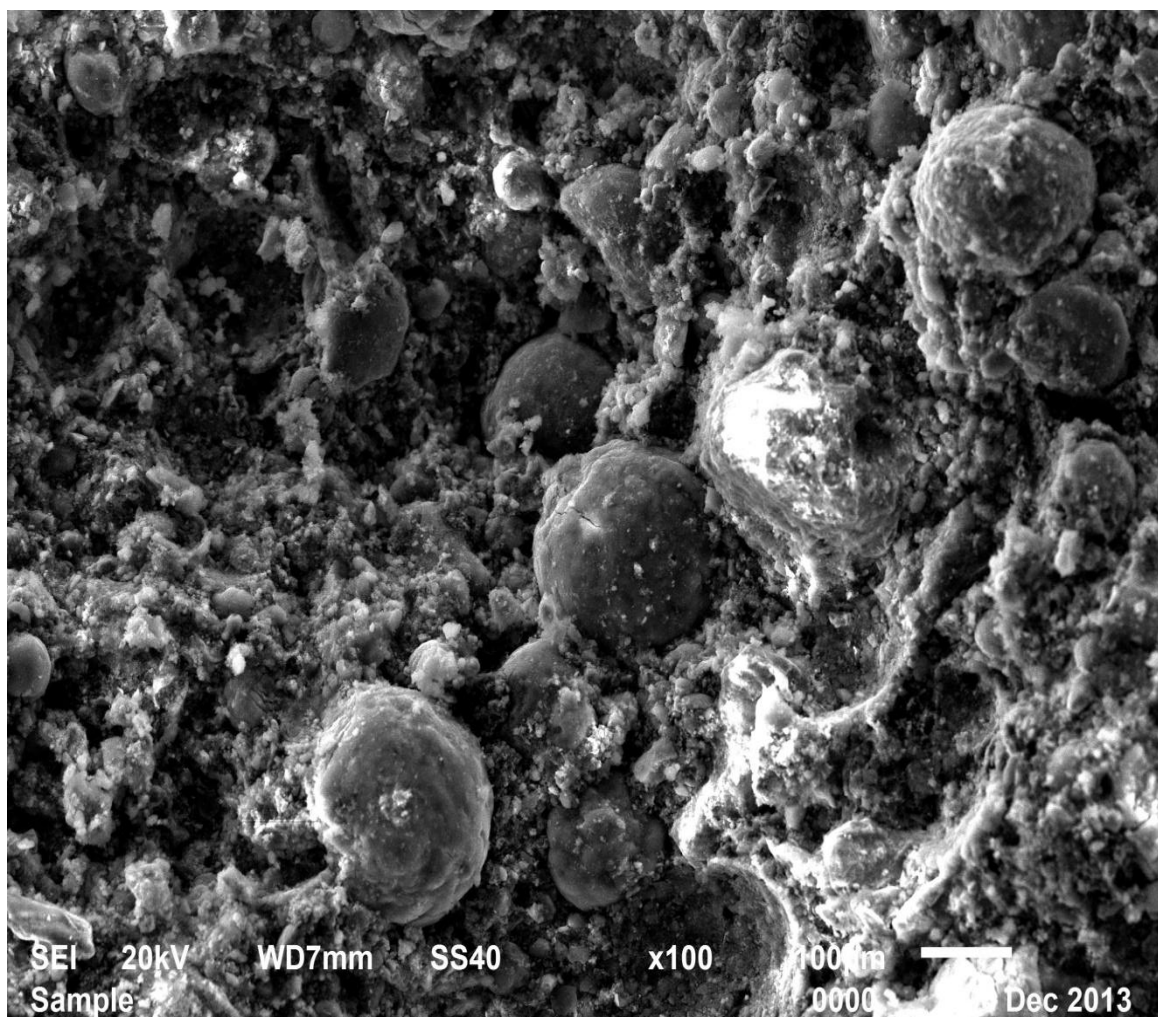


Figure 2 – Micrograph of cleaved granules with a pitch content of 30 %

Samples of carbon-mineral material obtained by the above methodology were relatively fragile. Apparently, the reason for this is the hydrophilic nature of the particle's surface of colloidal silica and the hydrophobic nature of the petroleum pitch and the coke formed from pitch. At the same time, it is known from the literature [20] that when calcining silica at temperatures up to 1000 °C, the surface of silica becomes hydrophobic. Therefore, the study calcined the initial colloidal silica at temperatures of 200 – 1000 °C

before directly mixing it with pitch. The results show that the main mass loss occurs at temperatures up to 200 °C (6 % wt.). And the total weight loss at 1000 °C is less than 10 % wt. However, after mixing the pitch with calcined silica (up to 1000 °C) and further according to the method of stage I, the final granules had an insignificant specific surface (less than 1 m<sup>2</sup>/g), while the compressive strength increased to 3.5 MPa.

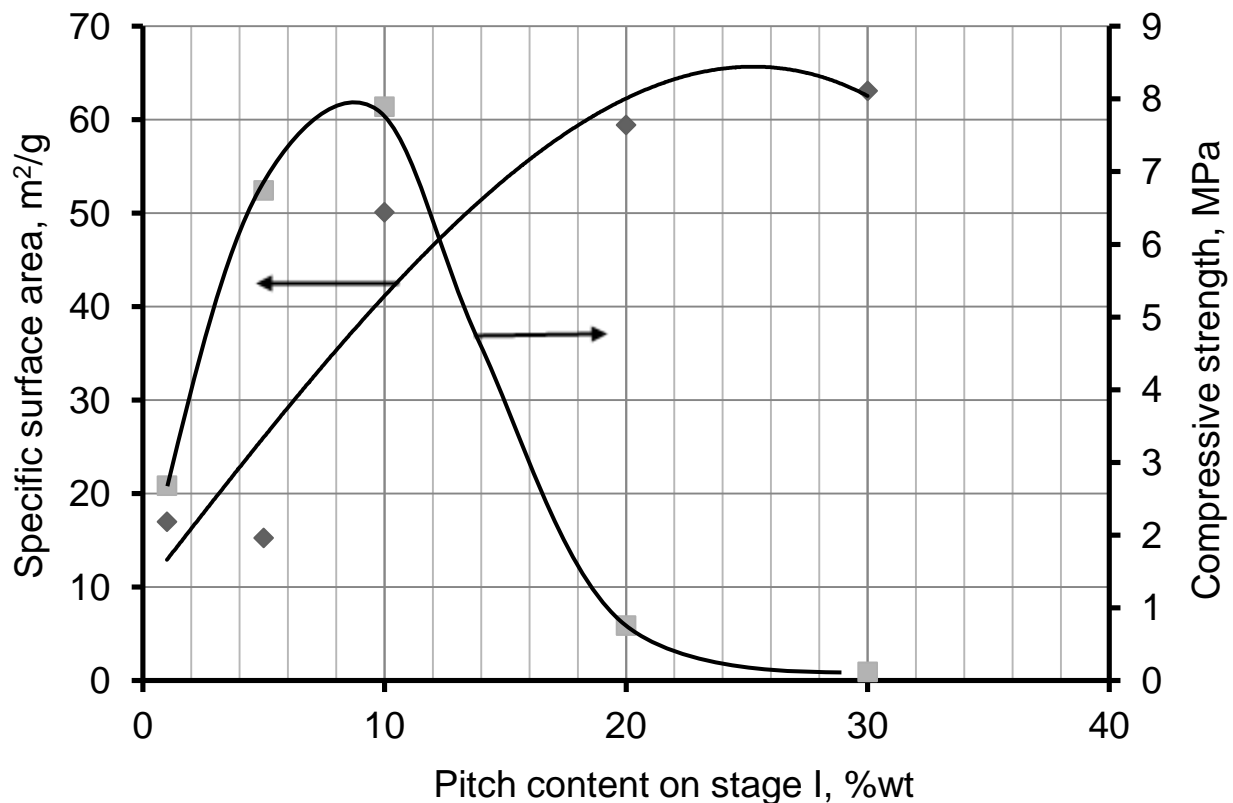


## Carbon-Mineral Adsorbent from Petroleum Pitch and Precipitated Colloidal Silica

This can be explained by an increase in the adhesion of pitch coke to silica particles. In general, we can say that this method of increasing strength is ineffective due to a significant decrease in the specific surface area of the pellets. Another way to increase the strength of the finished pellets without reducing the specific surface area was to obtain samples according to a two-stage scheme (Figure 1b). For this purpose, in stage I, the pitch was mixed with silica in various proportions (from 1 to 30 % wt.).

After granulation and carbonization, the finished granules were crushed and a filler was obtained for stage II. This filler is essentially a powdery carbon-mineral adsorbent. The effect of preserving the specific surface area can be expected from the fact that particles of pitch coke, which were formed from the initial pitch, wedge between the particles of colloidal silica and prevent them from agglomerating, thereby stabilizing the system.

In the second stage, the obtained filler was again mixed with pitch, which in all experiments was taken in an amount of 30 % wt. The results of the finished pellets in terms of specific surface area and strength are shown in Figure 3.



**Figure 3 – Influence of pitch content on stage I on the specific surface area and compressive strength of the pellets obtained in stage II**

Therefore, to obtain a highly porous carbon adsorbent according to stage III (Figure 1c), the pitch content at stage I was taken to be 10 wt.%, and at stage II this parameter was varied within 30 – 50 % wt. Figures 4 and 5 show that, after the etching process, both the specific surface area and the total pore volume for all samples increase significantly (2 – 8 times) and reach 170 m<sup>2</sup>/g and 3.5 cm<sup>3</sup>/g, respectively. As for the specific surface area, the achieved values cannot be considered sufficient to use the resulting carbon material as an adsorbent (traditionally, for activated carbons, the specific surface area is several hundred square meters per

It can be seen from the figure that the specific surface area increases with increasing pitch content up to 60 m<sup>2</sup>/g. However, this is caused by the presence of micropores in pitch coke [21], and an increase in its content in the composite. To understand whether the two-stage scheme for producing a carbon-mineral adsorbent allows maintaining a relatively high specific surface area, it is necessary to pay attention to the sample with the minimum amount of pitch added in stage II. And already for this sample, the specific surface area is about 15 m<sup>2</sup>/g, which significantly exceeds the surface of the calcined samples in stage I.

It is interesting to note that the dependence of the strength of the pellets on the amount of pitch added in stage II is more complex. With an increase in pitch content, strength first increases (this can be explained by an increase in binder content), reaches a maximum at 10%, and then decreases to very low values. The fall of this curve remains incomprehensible, but in any case, one can note a sample with the best combination of specific surface area and strength.

gram). However, this material presents good prospects for its use as a support for the production of composite adsorbents. An example of such adsorbents is salt-in-porous matrix sorbents [22].

These sorbents are obtained by impregnating the support with various drying agents, or rather, their solutions, for example, calcium chloride. As you know, this salt has good water absorption, however, the difficulty of its use in industry is due to the impossibility of obtaining in the form of granules.

If the salt is in the pores of the support, this disadvantage is eliminated. It is obvious that the efficiency of the drying process in this case will be determined by the specific pore volume of the carrier used. In the patent [22], the specific pore volume of the support was 0.9 cm<sup>3</sup>/g, which is less than that obtained in our work. It is possible to obtain samples

with a larger specific surface area by varying the parameters of the preparation of pellets. For example, we obtained a sample with a pitch content of 10 % in the first stage, the specific surface of which was 200 m<sup>2</sup>/g (pore volume about 3.0 cm<sup>3</sup>/g).

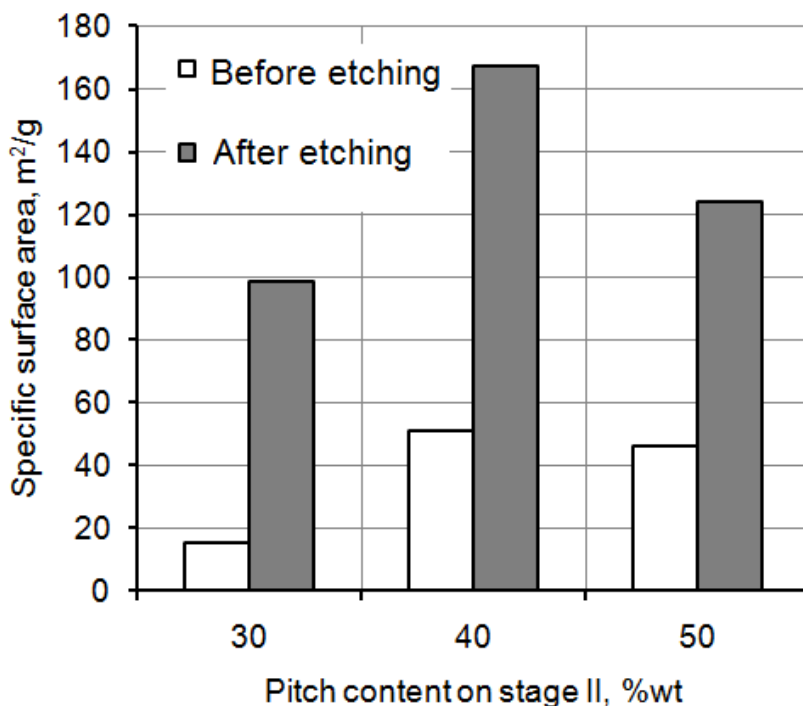


Figure 4 – Diagram of changes in the specific surface area of the pellets before and after etching

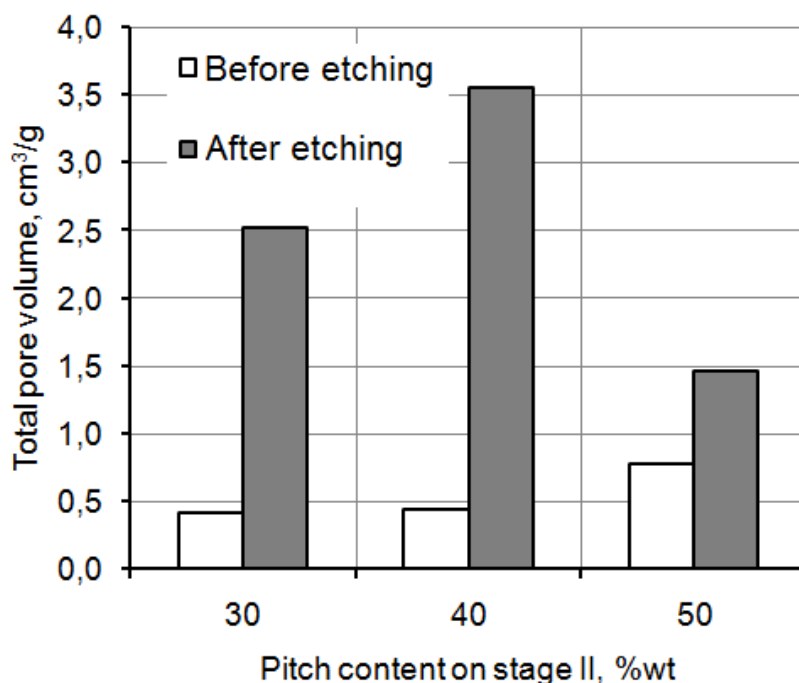


Figure 5 – Diagram of changes in the total pore volume of the pellets before and after etching

IV. CONCLUSIONS

In the course of the research, a carbon-mineral adsorbent was obtained, where petroleum pitch was used as a binder, and precipitated colloidal silica was used as a filler. It was

found that with an increase in the pitch content, the specific surface area decreases, and the strength increases. The samples had a relatively low strength (up to 2 MPa) and a specific surface area (up to 80 m<sup>2</sup>/g).

Pictures taken with an electron microscope made it possible to evaluate the structure of these carbon-mineral materials.

To increase the mechanical strength of the pellets, pre-calcined silica to 1000 °C (this method was ineffective). The carbonization temperature was also increased to 1000 °C – it was possible to obtain pellets with greater mechanical strength (up to 3 MPa), but a lower specific surface (up to 1 m<sup>2</sup>/g).

Materials were also obtained from different grades of silica. The specific surface area and strength values of these samples are comparable (15 – 30 m<sup>2</sup>/g and 2.5 – 3.5 MPa, respectively).

In carrying out the previous methods, it was not possible to obtain a durable carbon-mineral material, therefore, a two-stage production scheme was used with carbonization of pellets at the first stage of 1000 °C, and at the second – 700 °C, respectively. It was possible to obtain samples with strength up to 8 MPa, total pore volume up to 1.2 cm<sup>3</sup>/g, specific surface area up to 70 m<sup>2</sup>/g. This material can be used as supports for catalysts.

To increase the specific surface area of the material obtained by the two-stage method, the etching process was used. The specific surface area and total pore volume increased by 2 – 8 times (up to 170 m<sup>2</sup>/g and up to 3.5 cm<sup>3</sup>/g, respectively). This material can be used as a support for the preparation of composite adsorbents of the "salt in a porous matrix" type.

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