

## A STUDY OF POROSITY AND IMPREGNATION OF WHETLERITES

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The apparent and actual densities were measured for a set of seven porous samples with an identical carbon skeleton but differing in the content of inorganic salts. The corresponding values of porosity and density both of the active carbon skeleton and the impregnant of the whetlerites were calculated. In addition, the extractability of inorganic components from the samples was studied. On this basis, the chemical composition of the impregnant and a mechanism of the impregnant decomposition (occurring during its heat treatment) was proposed.

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Active carbon is generally known to be a very efficient sorbent. The purification of gases represents one of its most frequent applications<sup>1</sup>. The activity of carbon is based on physical adsorption, which itself, depends on porosity of the structure and surface properties of the sorbent. In the case of low efficiency of active carbon (*e.g.* with gases which are weakly bound by physical interaction), different types of impregnation were used<sup>2-4</sup>. The active carbon impregnated by a mixture of copper, chromium and silver salts (known as ASC whetlerite<sup>5</sup>) was found to be a generally active sorbent, on which not only the adsorption, but also chemical reactions and catalytic decomposition take place. This type of active carbon is prepared mainly as a protective agent used in the filter packings, against poisonous vapours and gases. In literature, it is usually characterized by its content of copper, chromium and less frequently of silver<sup>6-9</sup>. Very often only a composition of the solution which was used for the sample impregnation is given<sup>10-13</sup>. The extent of impregnation and relative abundance of individual components in the impregnant can be very different. While with the increasing amount of the impregnant, the chemisorption and catalytic activity go up – the physical-adsorption capacity goes down<sup>6</sup>, evidently due to a decrease in porosity.

The active carbon-whetlerite system is, due to its common availability and practical importance, an interesting subject for investigation of the effect of impregnation on the porosity and other properties resulting from treatment of the sample by the impregnating solution. In the previous paper<sup>14</sup>, the composition of the impregnant and its deposition was studied on one whetlerite sample and the comparison with the original, unimpregnated active carbon sample provided new information concerning

the deposition of the impregnant. Also, the approximate composition of the impregnant was suggested on basis of the chemical analysis and density measurements.

In the present paper, this study is extended to a below specified set of samples prepared from the same original active carbon material.

## EXPERIMENTAL

The active carbon used was a commercial product prepared by routine carbonization and subsequent activation by water vapour<sup>4</sup>. This product was granulated to a size between 100–250  $\mu\text{m}$  (sample No 1, denoted as *AC*). The impregnation of the sample *AC* was carried out analogically as in the previous paper<sup>14</sup>, applying the well known procedure<sup>9,10</sup> — using corresponding solutions of salts. In this way, samples with a medium (No 3,  $W_M$ ), lower (No 6,  $W_L$ ) and higher (No 7,  $W_H$ ) impregnant content were obtained. The results found for the samples *AC* and  $W_L$  were already published in paper<sup>14</sup> and they are presented here only for completeness of the evaluated set. In addition, an eight-hour water-extraction carried out in the Soxhlet apparatus (after which no more material was washed-out from the samples), was used for preparation of the samples No 2 ( $AC_E$ ) and No 4 ( $W_{ME}$ ), from *AC* and  $W_M$  respectively. A step-wise extraction of the sample  $W_M$  with water, a 5% acetic acid solution and 2 $\times$  with a 5% ammonium solution, carried out in the Soxhlet apparatus, was used for preparation of the sample No 5 ( $W_{MT}$ ). The results of the sample analysis are presented in Table I and the data are related to samples dried under standard conditions for 2 hours at 105°C. The drying influenced neither the analytically determined content of elements in the samples (related to dry matter) nor the relative amount of Cr(VI) with respect to the total Cr, although one cannot exclude that some redox type reactions proceeded in limited extent in the system. Such reactions become significant at temperatures above 170°C.

The analysis was carried out in the usual way, after previous decomposition of the ash by oxidizing fusion. After having been transferred into a solution, the copper content was determined electrolytically. The total chromium content was obtained, after addition of Mohr's salt by titration with a dichromate in the acid medium, using diphenylamine as an indicator. The content of Cr(VI) was determined by titration of the extract which was obtained by treatment of the sample with a 2% NaOH solution. Previous removal of copper on a silicagel column<sup>15</sup> was needed for the silver content determination. More details concerning the analysis of silver in the whetlerites are described in the other paper<sup>16</sup>. The organic carbon content was obtained from the elementary analysis.

The apparent (mercury) density ( $\rho_{Hg}$ ) and actual (helium) density ( $\rho_{He}$ ) were measured — after previous removal of moisture in the vacuum for 2 hours at  $10^{-2}$  Pa and 105°C — in the earlier described way<sup>17</sup>, enabling to determine both types of densities on one sample in the same apparatus. The filled volume was determined from the weight of mercury. The amount of sample introduced into the apparatus was recalculated with respect to the weight of standard dry-matter.

## RESULTS AND DISCUSSION

### *Extraction of the Samples*

The extraction with water does not remove all inorganic compounds from *AC*,

as is evident in Table I on the amount of ashes obtained by combustion of the sample  $AC_E$ . This ash contained approximately 19%  $SiO_2$  (as follows from the weight-deficit observed after treatment with HF); in addition, a presence of iron was proved qualitatively but no further analysis, in detail, was carried out (for the ash-content and its composition in various samples of active carbon — see ref.<sup>18</sup>). The alkali carbonates, which were extracted into the solution, were determined by conductometric titration — using the characteristic dependence of conductivity on the amount of added hydrochloric acid.

For evaluation of the extraction of  $W_M$ , the results of the analyses in Table I were recalculated (applying the apparent density) to the contents in  $1\text{ cm}^3$  of sample. This is because the content of elements given in weight % of the sample cannot be compared in a simple way, due to different sample densities. In this way it was found that only 8% of Cu and 45% of Cr (in the form of Cr(VI)) were extracted with the water from the total amount present in  $W_M$ . In the sample thus remained 11% of Cr(VI) which was extracted with a solution of 2% NaOH and then titrated. The sample still contained 44% of Cr, probably in the form of insoluble chromium(III) compounds. In addition to the mentioned elements, a part of more closely unidentified ashes was extracted with water, however, the silver present in the sample remained undissolved.

The analysis showed that during the extraction of  $W_M$  with a 5% ammonia solution — 65% of Cu, 63% of Cr and 77% of Ag was transferred from the total amount into the extract. When compared with the above extractions with water and a 2% NaOH solution, the increased amount of extractable chromium indicates that a part of Cr(III), forms soluble complexes with  $NH_3$ . In the extraction of  $W_M$  with

TABLE I  
Sample composition

Sample		Content, %				
Number	Description	Cu	Cr	$NH_3$	ashes	organic carbon
1	$AC$	—	—	—	5.33	89.66
2	$AC_E$	—	—	—	3.56	91.39
3	$W_M$	9.46	3.22	0.79	22.29	67.52
4	$W_{ME}$	9.44	1.93	—	18.84	71.44
5	$W_{MT}$	0.16	0.68	—	3.05	90.40
6	$W_L$	8.76	3.14	0.87	20.64	71.82
7	$W_H$	11.33	3.63	0.98	24.46	67.09

a 5% acetic acid solution — 94% of Cu, 54% of Cr and 19% of Ag is dissolved. After the last two mentioned extractions, the samples were not further investigated. To this purpose, a "totally extracted sample  $W_{MT}$ " was prepared for further investigation. After gradual extraction with water, acetic acid and ammonium solutions, the sample still contained — 1% of Cu, 16% of Cr and 8% of Ag. The lesser non-extractable remainder of elements indicated that the forms in which the followed elements are extracted by the acetic acid and ammonium solutions, are different. It may be assumed that the extractions of  $W_L$  and  $W_H$  samples would lead to similar results and they were therefore not carried out.

The extractability values of the samples can be of importance not only in further applications and treatment of the samples but they can serve also as an interesting characteristics both of the impregnants and ashes. In our case, obtaining the fundamental carbon skeleton was the main purpose of the extraction procedure which made it possible to study in which way the impregnant is deposited in the pores<sup>19</sup>. Even after gradual extraction of  $W_M$ , relatively large amount of chromium is found in  $W_{MT}$ , yet, the total amounts of ashes and organic carbon show that a reasonably purified carbon skeleton — comparable to  $AC_E$ , is obtained. While with pure water only small amounts of copper salts are extracted, the diluted acetic acid solution removes copper nearly quantitatively. On the other hand, the diluted ammonium solution extracts preferentially the chromium and silver salts. The interpretation of the water-extraction results, with respect to elucidation of the chemical composition of the impregnant, will be discussed later.

### *Water in the Samples*

From Table I (in which the results are presented in a conventional way, *i.e.* in %, related to standard dry-matter) a quantitative relation is evident between the amount of the impregnant and the content of the ashes — regardless whether the impregnated or extracted samples are concerned. Similarly, a dependence exists between the content of the organic carbon and the ashes. The quantitative evaluation of this dependence will be presented further in this paper. The sum of the ashes and organic carbon does not equal 100%. The difference corresponds to the hydrogen and oxygen from the carbon skeleton,  $CO_2$  from the carbonate,  $NH_3$  and water — crystalline or chemically-bound in the ashes. A part, however, consists also of water condensed in the micropores which cannot be removed under the used, standard conditions of drying. On the other hand, the drying of a sample is connected with a loss of  $NH_3$ . The carbon content, recalculated on the ash-free sample, is not constant: for the non-impregnated samples, including  $W_{MT}$ , it is equal  $94.24 \pm 0.86$ ; for the impregnated samples 3, 4, 6, 7 it equals  $88.56 \pm 1.52\%$ . This difference, most probably, is caused by the water bound by the impregnant.

The standard conditions of drying give reliably reproducible results. With the sample *AC*, good agreement was observed between the loss of weight after 3 hours of drying at 200°C in the air drier on one hand and drying in the vacuum at  $10^{-2}$  Pa and 105°C on the other hand. If it is assumed that under these conditions all the condensed and physically adsorbed water was removed from the examined samples, then the error in the dry-matter determination (under standard conditions) is approximately constant for all studied samples. In this study, the error may be neglected because it makes, *e.g.*, in determination of the ash content — 0.38% for  $W_M$  and 0.07 for *AC*, only. Table II shows the differences in the weight-deficit, obtained

TABLE II

The difference in water content in the samples dried by a standard procedure and in the vacuum

Sample		Loss of weight mg/g <sup>a</sup>	Water residuum % <sup>b</sup>
Number	Description		
1	<i>AC</i>	11.38	1.21
3	$W_M$	15.66	1.67
6	$W_L$	16.11	1.69
7	$W_H$	14.57	1.52

<sup>a</sup> The difference between loss of weight after drying under standard conditions and drying in the vacuum (for 2 hours, 105°C and  $10^{-2}$  Pa) — related to 1 g of undried sample; <sup>b</sup> water content in standard dry-matter (in %), under assumption that all water is removed by drying in the vacuum.

TABLE III

Density (in g/cm<sup>3</sup>) and porosity of the samples

Number	Description	$\rho_{Hg}$	$\rho_{He}$	$V_p$
1	<i>AC</i>	0.659	1.922	0.682
2	$AC_E$	0.651	2.092	0.685
3	$W_M$	0.864	2.075	0.621
4	$W_{ME}$	0.794	2.433	0.643
5	$W_{MT}$	0.660	2.211	0.681
6	$W_L$	0.829	2.208	0.632
7	$W_H$	0.881	2.460	0.615

after the standard and "in vacuum" drying; in addition it gives the water-residuum values determined in the standard dry-matter.

Nevertheless, the results related to the unit weight of samples cannot be used for their direct comparison. All studied samples were prepared from the same original sample (AC) and they have therefore identical carbon atom skeleton but different content of inorganic components. They could be therefore, *e.g.*, compared on the basis of the unit content of organic carbon. However, it was found that the most suitable for purposes of comparison are the values related to the "apparent" ( $1/\rho_{\text{Hg}}$ ) volume of samples, which remains constant independently on the content of the impregnant. In this way, the error caused by a water residuum in the standard dry-matter is eliminated, since both the determined values and the apparent (mercury) density are related to it.

### The Porosity

The determined values of the apparent ( $\rho_{\text{Hg}}$ ) and actual ( $\rho_{\text{He}}$ ) density are presented in Table III. In next step, the values were evaluated by linear regression

$$Y = a + bX \quad (I)$$

by means of the least-squares analysis and the constants obtained for equation (I) are presented in Table IV. In the case, where  $X$  signifies the % of ashes in the sample dried by a standard procedure and  $Y$  is  $\rho_{\text{Hg}}$ , reasonable results were obtained. On the other hand, the results using  $\rho_{\text{He}}$  are not sufficiently accurate for mutual comparison of the samples within the evaluated set, as can be seen on the unreasonable increase of the  $\rho_{\text{He}}$  values in the extracted samples 2 and 4 (compared with the original samples 1 and 3, respectively). The washed-out fraction of inorganic salts has actually a higher

TABLE IV  
Values of the constants in equation (I)

$Y$	$X$	$a$	$b$	$s$	$r_k$
$\rho_{\text{Hg}}$	% of ashes	0.6131	0.0107	0.0110	0.9923
$\rho_{\text{He}}$	% of ashes	2.0399	0.0114	0.1391	0.5628
$\rho_{\text{Hg}}$	100/% C	0.0415	0.5560	0.0111	0.9923
$V_p$	% of ashes	0.6972	-0.0033	0.0037	0.9898
% C	% of ashes	95.0706	-1.1834	0.9801	0.9950

$s$  Signifies the standard deviation;  $r_k$  is the coefficient of correlation.

density than the carbon skeleton and the  $\varrho_{\text{He}}$  values must therefore drop after the extraction. The standard deviation in  $\varrho_{\text{He}}$  determination for one sample equaled  $0.068 \text{ g/cm}^3$ , while for  $\varrho_{\text{Hg}}$  it was only  $0.004 \text{ g/cm}^3$ . The higher scatter of the determined  $\varrho_{\text{He}}$  values (which can be observed also in evaluation of the dependence of  $\varrho_{\text{He}}$  on the content of ashes — see Table IV) results also in unreliability of the porosity values of  $V_p$ , which are calculated from the experimental values by means of a well-known equation

$$V_p = (\varrho_{\text{He}} - \varrho_{\text{Hg}})/\varrho_{\text{He}} \quad (2)$$

The values of  $V_p$  according to equation (2) are therefore not given in Table III.

The apparent density of the ash-free sample  $\varrho_0$  equals, according to the dependence of  $\varrho_{\text{Hg}}$  on the ash-content (equation (1), Table IV),  $a = \varrho_0 = 0.6131 \text{ g/cm}^3$ . Similarly, according to the empirically found linear dependence of  $\varrho_{\text{Hg}}$  on the reciprocal value of relative organic carbon content (100/% C), we get, (using the value 96.5% C in equation (1) — in agreement with the estimation of the non-carbon groups in the skeleton) the value  $\varrho_0 = 0.6177 \text{ g/cm}^3$ . In further considerations, only the  $\varrho_0 = 0.6131 \text{ g/cm}^3$  value will be used.

The actual density of carbon skeleton for  $X = 0$  equals, according to the dependence of  $\varrho_{\text{He}}$  on the ash-content (equation (1), Table IV),  $a = \varrho_c = 2.0399 \text{ g/cm}^3$  — in agreement with the value reported for amorphous carbon in literature<sup>20</sup> (1.8 to  $2.1 \text{ g/cm}^3$ ). It seems, therefore, that the non-carbon groups of the skeleton influence its density only in a negligible extent. According to the same linear dependence, the actual density of the inorganic component for  $X = 100$  is  $\varrho_A = 3.1799 \text{ g/cm}^3$ .

A justification for extrapolation of the values by means of equation (1) follows from the following relations. For  $\varrho_{\text{Hg}}$  it holds that

$$\varrho_{\text{Hg}}V'' = \varrho_0V'' + \varrho_A V'_A, \quad (3)$$

where  $V''$  is the "apparent" volume of the sample and  $V'_A$  the actual volume of the inorganic components in the pores of the sample. Equation (3) can be rewritten in the form

$$\varrho_{\text{Hg}} = \varrho_0 + \varrho_A(V'_A/V'') \quad (4)$$

which after comparison with equation (1) gives  $a = \varrho_0$ ,  $b = k\varrho_A$  and  $kA = V'_A/V''$ , where  $A$  stands for % of ashes. For  $A = 0$  it follows that  $V'_A = 0$  and  $\varrho_{\text{Hg}} = \varrho_0$ . The upper limit of applicability of the equation (3) is given by the relation  $V_p = V'_A$ .

For  $\varrho_{\text{He}}$  it holds that

$$\varrho_{\text{He}}V' = \varrho_C V'_C + \varrho_A V'_A, \quad (5)$$

where  $V'$  is the actual volume of the sample and  $V'_C$  the actual volume of the carbon skeleton. Since

$$V' = V'_C + V'_A \quad (6)$$

we can write

$$\varrho_{\text{He}} = \varrho_C + (\varrho_A - \varrho_C) V'_A/V' \quad (7)$$

Equation (7) can be compared with equation (1). In this case  $a = \varrho_C$ ,  $b = k'(\varrho_A - \varrho_C)$  and  $k'A = V'_A/V'$ . In the case of  $A = 0$ , also  $V'_A = 0$  and  $\varrho_{\text{He}} = \varrho_C$ . For the case of  $A = 100$ ,  $V'_A = V'$  and  $\varrho_{\text{He}} = \varrho_A$ .

The porosity of ash-free sample,  $V_0 = 0.6994$ , was calculated from the relation

$$V_0 = (\varrho_C - \varrho_0)/\varrho_C \quad (8)$$

Finally, the porosity of individual samples was determined from the experimental values of  $\varrho_{\text{Hg}}$  and the volume  $V'_A$ , calculated by means of the relation

$$\varrho_A V'_A = \varrho_{\text{Hg}} - \varrho_C V'_C \quad (9)$$

where the carbon-skeleton volume is

$$V'_C = 1 - V_0 \quad (10)$$

The porosity of individual samples is then given by a relation

$$V_p = 1 - (V'_C + V'_A) \quad (11)$$

The above given value of  $\varrho_A$  was used with the impregnated samples  $W_M$ ,  $W_{ME}$ ,  $W_L$  and  $W_H$ . For the samples  $AC$ ,  $AC_E$  and  $W_{MT}$ , a different composition of the inorganic component with lower density had to be considered. Taking into account the known densities of the alkali metals carbonates and  $\text{SiO}_2$  (ref.<sup>21</sup>), the value of  $\varrho'_A = 2.6$  was used, which seems to be justified for  $AC_E$ . One has to mention that the differences in the obtained values  $V_p$  (using  $\varrho'_A$  instead of  $\varrho_A$ ) are very small in the three above mentioned samples, due to the low content of ashes. The deviation from linearity of the  $\varrho_{\text{He}}$  dependence on  $A$ , caused by a change of  $\varrho_A$ , must be according to equation (7) partially eliminated by the deviation of  $k'$  in the opposite sense.

The calculated values  $V_p$  (equation (11), Table III) decrease, with the increasing  $\varrho_{\text{Hg}}$  values — *i.e.* (in agreement with the impregnant content and the effect of extraction), in a sequence  $AC_E$ ,  $AC$ ,  $W_{MT}$ ,  $W_{ME}$ ,  $W_L$ ,  $W_M$ ,  $W_H$ . This sequence of decreasing  $V_p$  values also agrees with the increasing content of ashes — with the exception



of sample  $W_{MT}$  (Table I). This dependence is quantitatively evaluated in Table IV and shows a very good linearity. Finally, a very good linear dependence between the content of organic carbon and the ashes can be also seen in Table IV. According to this latter dependence, the organic carbon content does not equal 100% for the zero content of ashes. The non-carbon remainder equals (even after subtraction of the water which was not removed by the standard procedure of drying - c. 1.5% according to Table II) approximately 3.5%, which represents most probably the content of the hydrogen and oxidic groups, chemically bound on the carbon skeleton. For  $Y = \varrho_C = 0.6131$  in equation (1), the content of non-carbon groups would equal, according to the dependence of  $\varrho_{Hg}$  on 100% C, 2.7%.

#### Characterization of the Impregnant

In the previous work<sup>14</sup>, the density of the impregnant  $\varrho_{im}$  in the sample  $W_L$  was determined by means of relations

$$G_{im} = \varrho_{Hg}(W) - \varrho_{Hg}(AC), \quad (12)$$

$$\Delta V_p = V_p(AC) - V_p(W) \quad (13)$$

and

$$\varrho_{im} = G_{im}/\Delta V_p. \quad (14)$$

In the given equations,  $G_{im}$  and  $V_p$  are the weight of the impregnant and its volume in 1 cm<sup>3</sup> of the "apparent" volume of the sample. Similar calculations were carried out also for the presented set of samples and the results are given in Table V. Unlike with samples 3, 6 and 7 - for the samples 4 and 5 (which were obtained by extraction of  $W_M$ ) the above equations were modified:

$$G_{im} = \varrho_{Hg}(W) - \varrho_{Hg}(AC_E), \quad (15)$$

$$\Delta V_p = V_p(AC_E) - V_p(W) \quad (16)$$

since for a comparison it is necessary to use also the extracted sample  $AC_E$ . Finally, for the sample 1 we have

$$G_{im} = \varrho_{Hg}(AC) - \varrho_{Hg}(AC_E), \quad (17)$$

$$\Delta V_p = V_p(AC_E) - V_p(AC). \quad (18)$$

In the last case,  $G_{im}$  and  $\varrho_{im}$  is not related to the impregnant but to the content of inorganic salts extractable with water. Because of low values of  $G_{im}$  and  $V_p$ , the value  $\varrho_{im}$

in equation (14) is in very good agreement with the density of alkali carbonates ( $\rho = 2.43$  and  $2.53$  g/ml for  $K_2CO_3$  and  $Na_2CO_3$ , respectively) which were found in the water-extract (see the part concerning the extraction of the samples). Also the value  $\rho_{im}$  in this case agrees well with the chosen value of  $\rho'_A$ . Striking is the low density of the inorganic residuum in  $W_{MT}$ . One has, however, to take into account the possibility of a large error, caused by using  $\rho'_A$  in the calculation of  $V_p$ . For the original value  $\rho_A$ , the value of  $V_p$  would be 0.685 and thus  $\Delta V_p = 0$ . For this sample, therefore, the given value  $\rho_{im}$  is unreasonable and its true value must be higher.

Table V shows further the molar ratio Cu/Cr (according to the analysis in Table I) and the ratio  $G_M/G_R$  (where  $G_M = G_{Cu} + G_{Cr}$  is the sum of the weights of copper and chromium in  $1\text{ cm}^3$  of the „apparent” volume of the sample and  $G_R = G_{im} - G_M$  gives the weight of the rest of the impregnant without the both mentioned elements, determined analytically in  $1\text{ cm}^3$  of the “apparent” volume of the sample).

In the last paper<sup>14</sup> it was shown that in  $W_L$ , according to the values of  $\rho_{im}$ , Cu/Cr and  $G_M/G_R$ , the chemical composition of the impregnant is close to the formula  $2[CuCO_3 \cdot Cu(OH)_2] + CuCr_2O_7 \cdot 2H_2O$ . The values corresponding to this formula would be  $\rho_{im} = 3.04$  g/cm<sup>3</sup>, Cu/Cr = 2.50 and  $G_M/G_R = 1.25$ . The major part of the chromium present can be, however, reduced to  $Cr_2O_3$ , which together with other reaction products increases the value of  $\rho_{im}$ . Similarly, also the values for samples  $W_M$  and  $W_H$  are close to the given formula, as shown in Table V. The average values of all three impregnated samples are  $\rho_{im} = 3.6$  g/cm<sup>3</sup>, Cu/Cr = 2.41 and  $G_M/G_R = 1.32$ . The deviations are naturally caused also by a non-stoichiometric content of corresponding elements in the whetlerites. The composition of the impregnant of the extracted sample  $W_{ME}$  differs completely in the Cu/Cr ratio.

It can be assumed that a treatment of the sample during the impregnation process (with a heating up to  $150^\circ\text{C}$ ) leads to a partial decomposition of the impregnant, e.g.

TABLE V

The characteristic values calculated for the impregnant

Sample		$G_{im}$ g/cm <sup>3</sup>	$\Delta V_p$	$\rho_{im}$ g/cm <sup>3</sup>	Cu/Cr	$G_M/G_R$
Number	description					
1	AC	0.008	0.003	2.67	—	—
3	$W_M$	0.205	0.061	3.36	2.41	1.15
4	$W_{ME}$	0.143	0.042	3.40	4.00	1.71
5	$W_{MT}$	0.009	0.004	2.25	0.20	1.60
6	$W_L$	0.170	0.050	3.40	2.28	1.38
7	$W_H$	0.222	0.067	3.31	2.55	1.46

according to the following scheme



where Cr(VI) from the released  $\text{CrO}_3$  is reduced, on the account of carbon compounds from the skeleton, to Cr(III). The last one is, as  $\text{Cr}_2\text{O}_3$ , not extracted with water or a diluted solution of NaOH. During a storage of the samples, the components of the impregnant are rehydrated. The sample  $W_M$  contains, according to the analysis, 44% of unextractable chromium. Under the assumption that it is in the form of Cr(III), the sample contains 56% of Cr(VI); according to the above mentioned scheme, a proportion  $44/5$  — i.e. approximately 9% of Cr(VI), would be in the form of  $\text{CuCrO}_4 \cdot 2 \text{CuO} \cdot 2 \text{H}_2\text{O}$  (unsoluble in water) and the rest — i.e. 47% Cr(VI) ( $56-9$ ), as  $\text{CuCr}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$  (extractable with water). Since from the total amount, according to the given formula, only 20% of Cu is in the form of chromate, then from the rest of  $\text{CuCr}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$  (remaining after the decomposition), only the amount  $47 \times 0.2$ , i.e. 9% of the total copper content should be extracted with water into a solution. These values are in good agreement with the results of water-extraction and they support the assumed composition and decomposition scheme of the impregnant.

The above mentioned considerations were not verified in experiments with specially prepared compounds, since their behaviour in the porous system of active carbon could be different. One has also to consider that the presented system is rather complicated, and includes many parallel reactions. The suggested formula and decomposition scheme are therefore a large simplification and only a rough approximation of the real situation. In spite of that, they can be helpful as initial hypothesis for extended studies of the impregnants of the whetlerites and of the reactions proceeding on them.

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