R. BERG
A. H. GULBRANDSEN
G. A. NEEFJES
Institutt for Atomenergi
Kjeller
NORWAY

THE INFLUENCE OF AGING ON THE CHEMISORPTION CAPACITY OF IMPREGNATED CHARCOAL CATALYSTS

A INFLUÊNCIA DO ENVELHECIMENTO NA CAPACIDADE DE QUIMISORÇÃO DE CATALISADORES OBTIDOS POR IMPREGNAÇÃO DE CARVÃO DE MADEIRA

The effect of aging on the cyanogen chloride capacity of Copper-Chromium-Silver impregnated charcoal has been studied by X-ray powder diffraction, scanning electron microscope and porosimetry techniques. Changes of crystal structures and pore textures have been studied in connection with aging time and aging atmosphere. The results reveal the growth of two types of crystallites. The observed X-rays diffraction patterns strongly indicate the existence of copperoxide and basic copper carbonate crystallites. The growth of these crystallites is accompanied by a reduction of the cyanogen chloride capacity. Reduction of the total pore volume with the aging time as well as changes of pores as a result of the aging process. X-ray diffraction patterns and scanning electron micrographs reveal that the presence of ammonia during the aging process promotes the growth of the cupric oxide crystallites.

1. INTRODUCTION

This paper deals with the aging of copper-, chromium-, silver-impregnated charcoal in relation to their cyanogen chloride capacity. Cyanogen chloride is only weakly bound to activated charcoal by physical adsorption. The most common way to achieve high cyanogen chloride capacity in protection filters is to use copper and chromium oxide impregnants. The exact form of the impregnants is not known in detail, nor is the exact reaction mechanism of the sorbate with the impregnants. It is assumed that cyanogen chloride is decomposed according to the over-all reaction scheme :

$$\mathrm{ClCN} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{NH_4Cl} + \mathrm{CO_2}$$

It is well established that the cyanogen chloride capacity is strongly dependent on the moisture content of the charcoal (1). A problem frequently encountered in protection filters using commercial charcoal exposed to humid atmosphere for some time is the loss in cyanogen chloride capacity even after desorption of the water. This phenomenon is usually called aging and must be distinguished from the loss of capacity due to poisoning of the impregnants. The mechanism of the irreversible inactivation of the charcoal's impregnation is not understood, and attempts to correlate the loss in chemisorption capacity with the results from chemical analysis of the water soluble part of the impregnation, have failed (1). The effect of aging on commercial charcoals of different origins and impregnated with copper, chromium and silver salts has been demonstrated by X-ray diffraction technique (2). The diffraction pattern technique reveals crystallite growth on the charcoal. In this preliminary study we try to understand the nature of the aging process in terms of changes in the physical-chemical properties occuring on the charcoal surface.

The techniques used were scanning electron microscopy (SEM), X-ray diffraction, Hg-porosimetry, N_2 isotherms (BET) measurements.

In view of the complexity of this subject, the results must be interpreted as qualitative effects limited to the case being investigated.

2. EXPERIMENTAL

2.1. MATERIALS

2.1.1. COPPER-CHROMIUM-SILVER IMPREGNATED CARBON

Commercially impregnated carbon of the type Pittsburgh ASC 12 x 30 was used for the artificial aging experiments. The physical properties and chemical analysis of the charcoal samples used in these experiments are shown in table 1.

Table 1

Physical properties and chemical analysis of the impregnated charcoal samples

Type of charcoal	Pittsburgh ASC 12 x 30
Impregnation	Cu–Cr–Ag compounds,
Composition W %	Cu 6,0, Cr 2,5; Ag 0,05
Surface area m^2/g	911
Pore volume cm^3/g pore size 15 – 200 Å	0,50
Pore volume cm^3/g pore size 200–75000 Å	0,21
Bulk density g/cm^3	0,45
Water content* %	2,5

** Weight loss after 24 hr at 115 °C*

2.1.2. THE ARTIFICIAL AGING PROCEDURE

5 g of charcoal were placed in a open glas crucible. The crucible was transferred to a special designed aging chamber of 50 cm^3 volume, where the carbon was equilibrated in a saturated water vapour atmosphere at 72 °C over a period of 2 – 20 days. Before the cyanogen chloride test, the charcoal was evacuated overnight at room temperature.

2.1.3. THE BREAK THROUGH TEST

The sorption capacity of the different charcoal samples for cyanogen chloride was measured according to the test parameters specified in table 2. The cyanogen chloride capacity was reported in terms of break-through time, which is the time from the start of the test to the time when the concentration of the cyanogen chloride in the effluent is reaching a preset value of 1 ppm.

Table 2

Test – parameters

Carrier gas	air
CNCl concentration, mg/ml	2,4
Moisture content of the influent %	∼0
Bed height, cm	3
Bed area, cm^2	2,4
Linear velocity, m/min	10
Filter temperature, °C	18
Break through criterion, ppm	1

2.1.4. SCANNING ELECTRON MICROSCOPY (SEM)

The SEM used in this work is a Siemens U-1 Autoscan with an energy dispersive spectrometer with Si(Li) crystal. The acceleration potential was max. 30 keV and the resolution of the microscope, 100 Å. The resolution of the energy analyzer was 143 eV (at 5,9 keV) and the detector area 10 mm^2.

The carbon granules were fixed to the sample-holder by means of aluminium paint. A gold layer (∼200 Å) was evaporated on the charcoal samples before transferring them to the microscope. In the case of ED analysis, pure carbon layer was brought on to the impregnation by means of a sputtering device.

2.1.5. X-RAY DIFFRACTION

The X-ray diffraction powder patterns were obtained by means of standard technique. The instrument used was a Philips X-ray diffractometer.

The radiation was the K(α)-doublets of copper (1,54 Å). The corresponding compounds were identified by means of the 1970 Inorganic Index to the Powder Diffraction File (3).

2.1.6. PORE VOLUME, SURFACE AREA

The total specific area (BET surface) was determined by uptake of the N_2 isotherm at 77 °K. The pore size and pore size distributions were calculated from the desorption isotherm using the classical BET sorption method. For this purpose a conventional glass type apparatus was employed. The larger transition and macropores were measured by using Hg-porosimetry technique covering the pore range 117 – 75000 Å. The porosimeter used was a Carlo Erba of the serie 800, operating in the pressure range 1 – 640 kg/cm^2. The pore size distribution was calculated according to the method of Ritter and Drake (4).

3. RESULTS AND DISCUSSION

3.1. AGING IN HUMID AIR

3.1.1. SEM

The result of the aging process on the cyanogen chloride capacity are shown in figure 1 A. The change of the capacity with the aging time is expressed as percent of the original capacity (16,1 mg CNCl/cm^3 carbon). The capacity decrease is pronounced after 5 days aging.

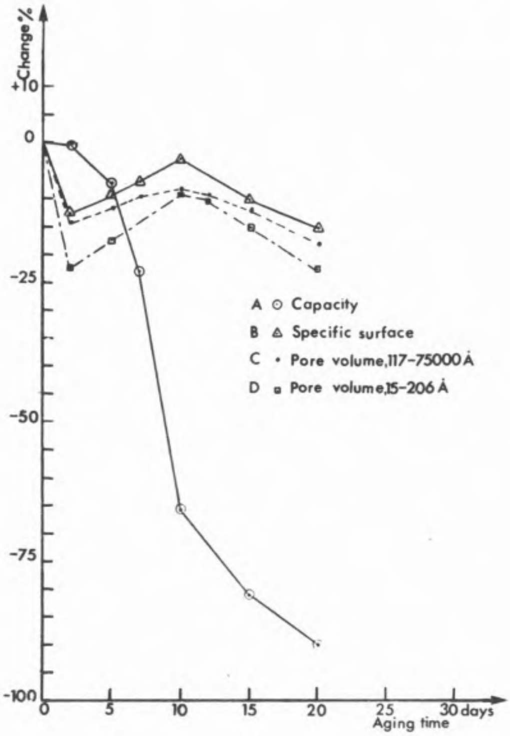


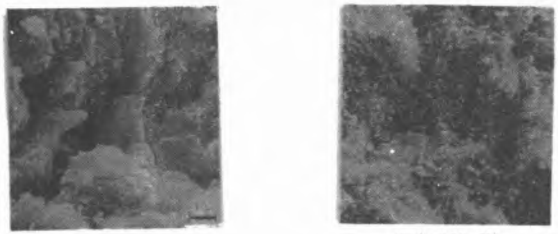
Fig. 1

Percentage change of cyanogen chloride capacity, specific surface and pore volume of Cu-Cr-Ag impregnated charcoal in dependence of the aging time in humid air at 72 °C

The cause of this capacity decay is partly revealed by the SEM pictures of figure 2 A-D. Figure 2 A demonstrate a typical fresh copper and chromium impregnated carbon having a high cyanogen chloride capacity. The crystallites of the impregnants are too small to be observed on the micrograph even at magnifications of the order of 40000 X. The resolution of the microscope is 100 Å, the crystallite dimension is consequently smaller than this size. The same charcoal samples as shown in figure 2 A on being aged for 2 and 10 days in humid air reveal growth of at least two types of crystallites which can be observed from figures 2 B and 2 C.

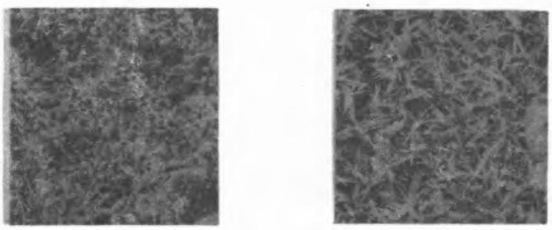
A qualitative observation from the micrograph of the number of the «spheroidal» shaped crystallites indicates a maximum after 10 days of aging. A simultaneous growth of both needle shaped and spheroidal shaped crystallites occurs in the aging period 2 – 10 days. Figure 2 D indicates the domination of the needle shaped crystals after 20 days of aging. The main element occuring in both types of crystallites was revealed by energy dispersive analysis of X-rays. Figure 3 A shows a typical magnified picture of those crystallites. Figure 3 B and 3 C demonstrate the results of the energy dispersive analysis of the X-rays emmitted by the elements of the impregnants. The distribution map of copper, figure 3 B, reveals that this element is the dominant one in both types of crystallites. The distribution of chromium in figure 3 C shows no concentration tendency on the crystallites regarding this element. A qualitative comparison of the corresponding energy dispersive spectra is shown in fig. 4 A, B, C.

The spectra reveal that the $K(\alpha)$ intensities of copper in the two cases, 4 B and 4 C, corresponding to the crystallites of fig. 3 B and 3 C, is higher than the average peak heights refering to the whole area of fig. 3 A. The $K(\alpha)$ peak of chromium suffers a loss of intensity when comparing the same cases as for copper. This indicates that chromium is not embodied in the crystallites as a main element. The chromium peaks obtained in case 4 B and 4 C could, however, result from small amounts of chromium distributed on the crystal surface or near the crystallites, refer fig. 3 C.



A (1300 X)
FRESH

B (1300 X)
AGED 2 DAYS



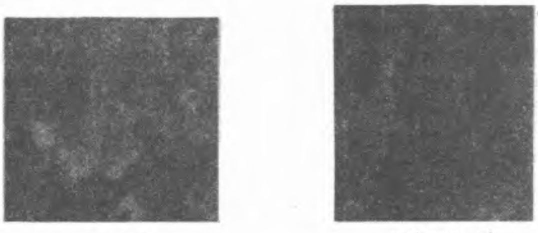
C (1300 X)
AGED 10 DAYS

D (1300 X)
AGED 20 DAYS

Fig. 2

Scanning electron micrograph of Cu-Cr-Ag impregnated charcoal, artificially aged in humid air at 72 °C

A (3000 X)
SEM MICROGRAPH OF Cu-Cr-Ag
IMPREGNATED CHARCOAL



B (3000X)
DISTRIBUTION MAP OF Cu-K_α
8,0 keV, SAME AREA AS A

C (3000 X)
DISTRIBUTION MAP OF Cr-K_α
5,4 keV, SAME AREA AS A

Fig. 3

Energy dispersive analysis (X-ray) of artificially aged charcoal. Aging time 10 days

3.1.2. X-RAY DIFFRACTION PATTERN

Figure 5 A-D demonstrates examples of X-ray powder pattern of fresh and artificially aged charcoals. Figure 5 A shows broad bands but no other reflection, which is typical for fresh Cu-Cr-Ag impregnated charcoal of this type. The lack of reflections is consistent with fig. 2 A.

The influence of the aging atmosphere is shown in fig. 5 B-D. As can be observed, the presence of humidity is a necessary condition in order to obtain reflections and indicate that the copper and chromium impregnation is amorphous, non crystalline, to X-rays. They still might be present in the form of small crystallites less than 100 Å, fig. 2 A. X-ray reflections, fig. 5 C, observed as crystallites, are obtained on the same samples as those shown in fig. 2 B, C.

X-ray diffraction examination regarding the influence of artificial aging on impregnated charcoal exposed to humid air, is compiled in fig. 6 A-E. The relative widths of the reflections are indicated on the diagram as lines with different broadness.

The observed X-ray pattern consists partly of narrow reflections and partly of diffuse bands. Some of the reflection's maxima cannot be exactly identified due to the diffuse appearance (broadening) and low intensity. However, repeated diffraction runs confirmed the existence of the low intensity reflections. The patterns are characterized by two or more strong lines and some small and diffuse lines, mainly concentrated in the high angle part of the diffraction diagram. The intensity of the main reflections $d = 2,52$ and $d = 2,31$ increase during the aging time 2-10 days, fig. 6 A-C. They indicate the existence of CuO belonging to the monoclinic system with the unit cell $a_0 = 4,68$ Å, $b_0 = 3,42$ Å, $c_0 = 5,12$ Å, $\beta = 99°28'$.

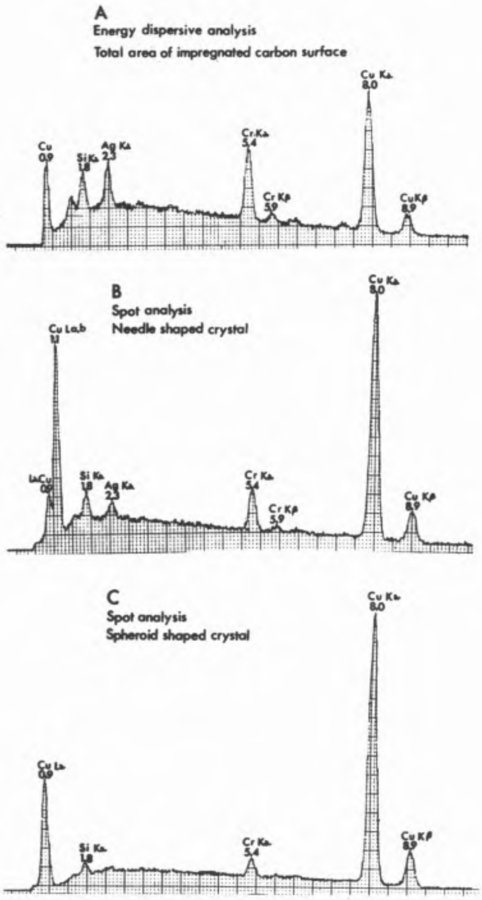


Fig. 4

Energy dispersive spectra of the sample shown in figure 3

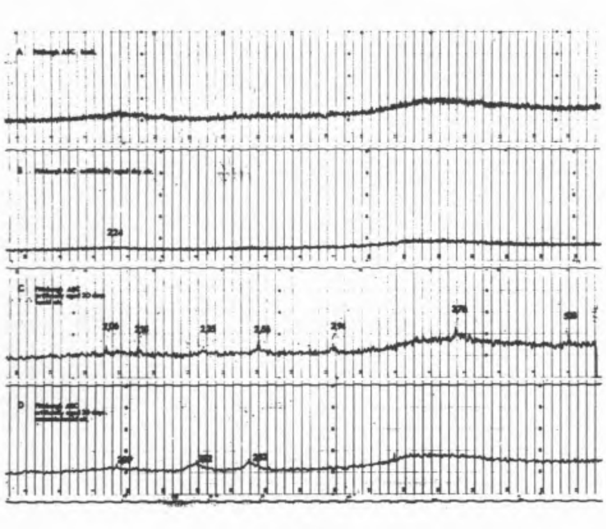


Fig. 5

X-ray diffraction patterns of unaged and artificially aged charcoal in dependence of different aging atmosphere

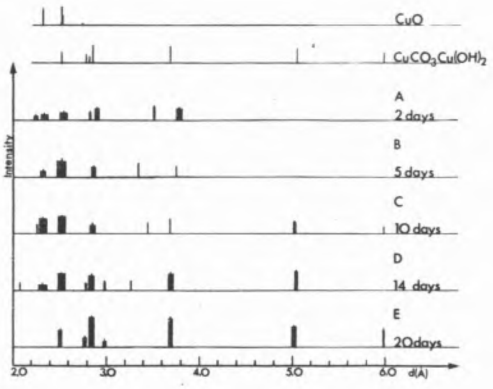


Fig. 6

X-ray diffraction pattern of Cu-Cr-Ag impregnated charcoal in dependence of the aging time in humid air at 72 °C

The growth of the crystals in the directions of the three axes would be expected to result in a crystallite body having an appearance which does not favour any of these directions. This is confirmed by the «spheroidal» shaped crystallites shown on the SEM picture, figure 2 B-C. Further aging up to 20 days results in the disappearance of the line d = 2,31 which coincides with the increase of the reflections d = 5,99, 5,02, 3,69, 2,86, 2,52, fig. 6 C-E. These lines were identified as the main reflections of $CuCo_3\,(CuOH)_2$ with the unit cell a = 5,61 Å, b = 14,03 Å, c = 5,40 Å, β = 98° in the monoclinic system. By regarding the b-axes it is expected that the crystallite growth will be pronounced in one of the crystallographic directions compared with the two others. This assumption is confirmed in fig. 2 C-D where needle shaped crystallites are observed. Figure 2 D also confirms the disappearance of the spheroidal shaped crystallites which is in accordance with the disappearance of the CuO line 2,31, fig. 6 E. The growth of $CuCO_3\,Cu(OH)_2$ seems to occur at the expenses of the copper oxide crystallites. The change of cyanogen chloride capacity, fig. 1 A, coincides with the growth of both types of crystallites. During the first aging period of 7 days, the remaining capacity is more than 75 %. In this period the presence and growth of CuO crystallites are dominant.

In the aging period, where the concentration of the needle shaped crystals dominates, the capacity is drastically reduced. This indicates that these crystallites do not have any chemisorption effect regarding cyanogen chloride. Reflections from crystallites of silver compounds were not detected, probably due to the low concentration of silver salts, table 1.

3.1.3. PORE VOLUME, SURFACE AREA

The influence of the aging on the pore volume and on the specific surface is shown in fig. 1 B-C. A loss of pore volume as well as specific surface is observed after 20 days of aging. There exists, however, no correlation between the capacity loss and the pore volume change. The remarkable increase of pore volume and specific surface in the 2 – 10 days aging period, fig. 1 B-C, indicates the opening of blocked pores. This phenomenon is explained by the following hypothesis :

As a result of the impregnation process, part of the pore volume is supposed to be blocked by impregnants. Charcoal posesses a large