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Investigation of Deactivation Mechanisms of ASC Whetlerite Charcoal

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ASC whetlerite, prepared by the impregnation of CWS grade activated charcoal with ammoniacal carbonate solutions of copper(II), chromium(VI), and silver salts, is an effective material for the removal of many low-molecular-weight gases (e.g., cyanogen chloride and hydrogen cyanide) from air streams. Whetlerite loses its effectiveness when exposed to extremes in temperature and/or humidity or by excessive periods of usage. Associated with this deactivation/deterioration process are changes in metal oxidation state(s) and impregnant morphology. This investigation examines the behavior of the metal impregnants on ASC whetlerite when subject to certain extreme conditions and, as a result, develops an understanding of the deactivation mechanism(s) that occur. The deterioration of whetlerite due to thermal deactivating conditions as well as that due to exposure to hydrogen involves the decomposition of the supported $CuOHNH_4CrO_4$ (basic copper ammonium chromate) species. This complex chromate decomposes into a $CuO–CuCr_2O_4$ (copper–chromite) species upon thermal treatments up to 490 K. At temperatures above 490 K the CuO (cupric oxide) sinters away from the chromite and is subsequently reduced to Cu^{1+}-containing and Cu^0 species. When exposed to high humidities for long periods of time (i.e., more than 2 days) it is hypothesized that the whetlerite surface experiences a decrease in pH. This results in the supported $CuOHNH_4CrO_4$ species converting to $Cu_4(OH)_6CrO_4$ (brochantite chromate). The brochantite chromate gradually decomposes into less complex crystalline compounds such as CuO, $Cu_2Cr_2O_4$, and Cr_2O_3 which are not effective for destroying irritating gases. © 1988 Academic Press, Inc.

INTRODUCTION

ASC whetlerite, prepared by the impregnation of CWS grade charcoal with ammoniacal carbonate solutions of copper(II), chromium(VI), and silver salts (*1*), is an effective material for the removal of many low-molecular-weight gases from air streams. Whetlerite functions efficiently under ambient conditions in the hydrolysis of irritating gases (e.g., cyanogen chloride and hydrogen cyanide) to relatively nontoxic products. However, it is well known (*1*) that changes in oxidation state(s) (i.e., reduction of Cr^{6+} species and Cu^{2+} species) and/or impregnant morphology are associated with whetlerite deactivation. The deactivation process is accelerated by exposure to elevated temperatures and/or humidities or by excessive periods of usage. This investigation was undertaken to examine the behavior of the metal impregnants on ASC whetlerite when subjected to these types of extreme conditions and, as a result of this study, to develop an understanding of the deactivation mechanism(s) that occurs.

EXPERIMENTAL

The general experimental approach used was to treat ASC whetlerite so as to simulate deactivating conditions (e.g., thermal and humidity treatments, exposure to gases), followed by characterization of the impregnant layer. The behavior of the supported metal impregnants was then compared to that of model compounds which were treated in a manner similar to that of the ASC whetlerite.

The ASC whetlerite used for most exper-

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iments was lot CAL-1-3 as supplied by Calgon Corp. Percentages by weight of the metals reported in (*1*) and verified by wet-chemistry procedures (*2*) were the following: copper, 8%; chromium, 2.8%; and silver, 0.2%. Charcoal granule size was 12 to 30 mesh (U.S. Standard Sieve) and the BET surface area using a nitrogen adsorbate was 650 m^2/g. Other experiments were done on mechanical mixtures of base (BPL) charcoal (a CWS analog) and basic copper ammonium chromate, $CuOHNH_4$ CrO_4 (a proposed model compound for the major active component on ASC whetlerite), and on $CuOHNH_4CrO_4$-impregnated BPL charcoal. The method presented by Reiner (*3*) was used for the synthesis of $CuOHNH_4CrO_4$. The impregnation procedure involved contacting an ammoniacal solution of $CuOHNH_4CrO_4$ crystals and BPL charcoal for 30 min followed by air drying at 378 K for 3 hr. Solution-to-charcoal ratios were adjusted such that the percentage chromium was approximately equal to that of fresh ASC whetlerite samples (i.e., ~2.8%).

(*a*) *Deterioration/Deactivation Procedures*

Thermal treatments were done on ASC whetlerite samples, $CuOHNH_4CrO_4$-impregnated BPL charcoal, and mechanical mixtures of BPL charcoal and CuOH NH_4CrO_4 to simulate deactivation due to extremes in temperature. Stainless-steel tubes (0.508 cm i.d., 18 cm packed length) were packed with approximately 2.2 g of material and placed in the oven of a gas chromatograph as chromatographic columns for a typical 6-hr heat treatment. Nitrogen at a flow rate of 30 ml/min (NTP) was used as the carrier gas. The range of thermal treatment temperatures investigated was between 303 and 520 K.

To investigate the effect of a reducing gas on the metallic impregnants of charcoal, pure hydrogen (10 ml/min, NTP) was passed through packed columns at temperatures between 303 and 423 K for 1 or 2 hr. This procedure was done following the typical thermal treatment, or, in some cases, instead of thermal treatment.

Whetlerite deterioration studies due to exposure to extremes in humidity were done by placing several grams of fresh ASC whetlerite in a chamber in which the temperature was held at 343 K and the relative humidity held at 100%. Samples were removed daily and dried in air for 3 hr at 378 K. This drying process was shown to be sufficient for removing adsorbed water (*2*). The samples were then stored in a desiccator (dry air atmosphere) for subsequent experimentation and characterization.

(*b*) *Characterization Techniques*

Metal oxidation states on ASC whetlerite and impregnated charcoal samples were determined using wet-chemistry techniques, electron spectroscopy for chemical analysis (ESCA), and H_2 as a surface probe after Hammarstrom and Sacco (*4*). The conventional wet-chemistry procedure involved extracting the samples with either basic or acidic solution (dissolving the Cu^{2+}, Cr^{6+} species and $Cu^{1+,0}$, Cr^{3+} species) and then analyzing the solutions quantitatively by atomic absorption spectrophotometry. The ESCA work was conducted at the Institute of Materials Science at the University of Connecticut. The samples were prepared by pressing powders (<180 μm) into indium foil for introduction into the instrument. A least-squares fitting of Gaussian/Lorentzian peaks was used to identify Cr peak positions for two samples (fresh whetlerite and 490 K-treated whetlerite). Other Cr $2p_{1/2}$, $2p_{3/2}$ peak positions were determined by comparison with the fitted data after correction for the positions of the C1S and O1S peaks. The Cu $2p_{3/2}$Cu L3VV peaks in conjunction with the standard spectrum for CuO were used to monitor the position of the Cu peaks and the chemical state of the copper species. The oxidation states of chromium on thermally treated whetlerites can be correlated with hydrogen uptake from a 0.1-ml (NTP) pulse. The hydrogen molecules are adsorbed and dissociated by a Cr^{3+}-containing species (*4*). This method allows rapid, nondestructive quantification of the Cr^{6+}/Cr^{3+} ratio.

Additional information on whetlerite surface species and impregnant morphology was provided by X-ray diffraction analyses (Philips Model 3000, Ni-filtered Cu$K\alpha$ radiation), electron spin resonance (ESR) studies, and electron microscopy. The ESR work was done at Clark University using a Varian E-9 ESR spectrometer. All samples were run at 115 K. A JEOL 100 C transmission electron microscope (STEM) was used for investigating impregnant morphology (100-kV excitation). Samples were prepared by first grinding to a fine powder (<50 μm) and then sprinkling the powder onto holey carbon support grids.

RESULTS AND DISCUSSION

The experimental results indicated that the whetlerite deterioration/deactivation process involved an intricate and complex series of steps. During the deactivation changes in both copper and chromium oxidation states and in impregnant morphology occur. The nature of these changes, as well as the deactivation mechanism itself, varied as a function of the deactivating condition (i.e., high temperature, high humidity, or exposure to gases).

(*a*) *Thermal Decomposition of Whetlerite*

The initial step in the thermal treatment of ASC whetlerite is the reduction of the hexavalent chromate species to the trivalent form (Hammarstrom and Sacco (*4*)). The ratio of chromium in the hexavalent state to the trivalent state was shown to decrease from a value of approximately 48 for fresh whetlerite to a value of about 6 for whetlerite thermally treated at 490 K.

For fresh whetlerite, the ESCA spectra illustrated in Fig. 1 suggest that the important hexavalent chromium species exist as basic copper ammonium chromate, $CuOH\,NH_4CrO_4$. As shown, the Cr $2p_{1/2}$, $2p_{3/2}$ binding energies for pure $CuOHNH_4CrO_4$ (synthesized) were 587.4 and 578.2 eV, respectively, in good agreement with the Cr $2p_{1/2}$, $2p_{3/2}$ (587.3 and 578.2 eV) values measured on a fresh whetlerite sample. In addition, Fig. 1 shows that if one synthesized $CuOHNH_4CrO_4$ and impregnated BPL charcoal (CWS analog) the measured binding energies (587.3 and 578.0 eV) are in good agreement with those of the pure compound and fresh whetlerite. This substantiates the likely existence of basic copper ammonium chromate on whetlerite charcoal.

The $CuOHNH_4CrO_4$ compound was thought to be supported in a highly dispersed form on the charcoal surface since the conditions used for the impregnation of ASC whetlerite (ammoniacal solution of copper and chromium salts) very closely resemble those for the well-documented synthesis of pure $CuOHNH_4CrO_4$ (*3*, *5*). Due to its amorphous nature or perhaps small particle size (i.e., ~5 to 50 Å) it was not possible to positively identify $Cu\,OHNH_4CrO_4$ using conventional X-ray diffraction methods. However, Pytlewski (*6*) in a related study has evaporated an ASC solution to dryness and identified the remaining red–brown solid as $CuOHNH_4\,CrO_4$ in agreement with the ESCA work. Further substantiating its existence on whetlerite is the fact that the pH values for water solutions in which the whetlerite was soaked for 6 hr were on the order of 8.3. These values were in agreement with those reported by Pytlewski (*6*) and well within the range of pH values where $CuOHNH_4\,CrO_4$ is stable (*7*).

The hydrogen probe gas data, X-ray diffraction analyses, and ESCA data suggested that upon thermal treatment the supported $CuOHNH_4CrO_4$ species decomposed into a copper–chromite form, CuO–$CuCr_2O_4$. An X-ray pattern for the synthesized red–brown $CuOHNH_4CrO_4$ is shown in Fig. 2a. Comparing this pattern to the standard pattern in Fig. 2b (*8*) shows the material to be nearly pure and fairly well crystallized. Figure 2c shows the pattern

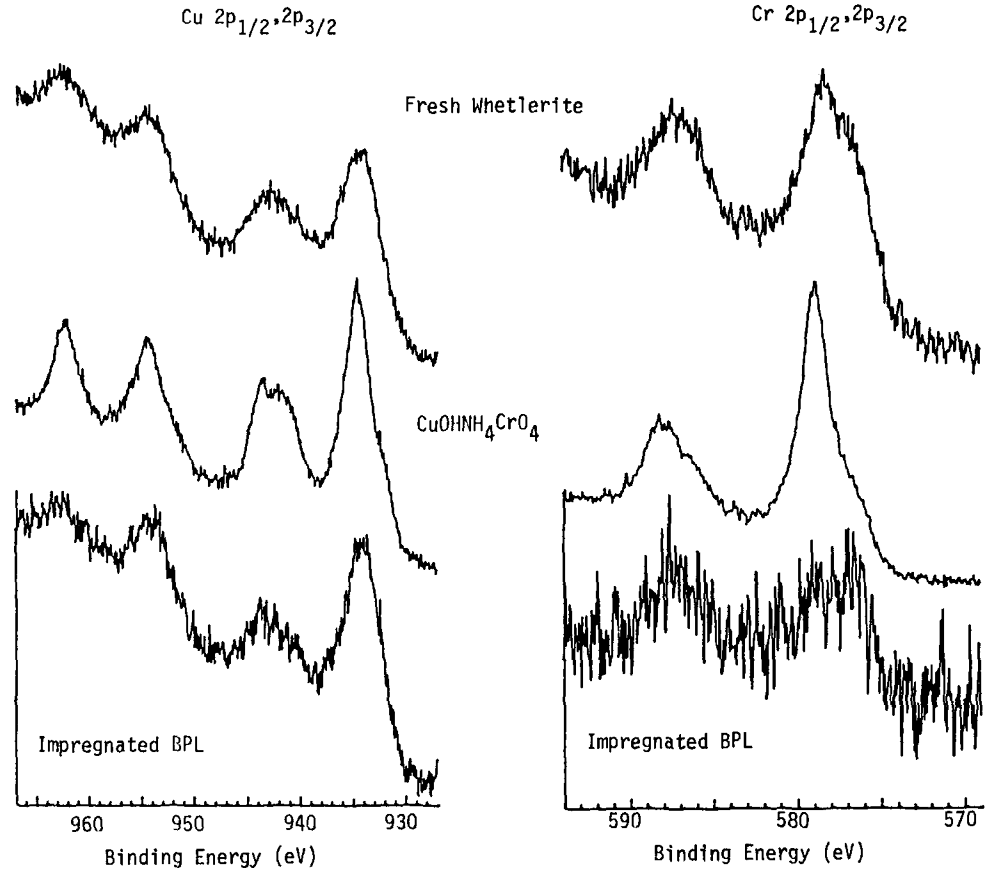


FIG. 1. Comparison of fresh whetlerite to the model compound basic copper ammonium chromate.

for $CuOHNH_4CrO_4$ which was mechanically mixed with BPL charcoal and thermally treated at 490 K. The pattern of Fig. 2d is that of pure $CuOHNH_4CrO_4$ decomposed in a crucible over an open flame according to the method of Connor *et al.* (*9*). Although the patterns are noisy due to the charcoal, if one compares the patterns of Figs. 2c and 2d to that of Fig. 2a it appears that thermal treatment brings about a pronounced change from a well-crystallized material to a more amorphous material. This observation is consistent with the work of Adkins *et al.* (*10*) and Stroupe (*11*) who reported that the crystallinity and stoichiometry of copper–chromite-type catalysts, formed by the thermal decomposition of $CuOHNH_4CrO_4$, depended upon the decomposition conditions. For example, Stroupe described an amorphous $Cr_2O_3 \cdot 2CuO$ "copper–chromium oxide" catalyst formed by controlled low-temperature $CuOHNH_4CrO_4$ decomposition. He reported, however, that the exothermic nature of the decomposition reaction made temperature control difficult and that the normal catalyst batch was usually a mixture of crystalline and amorphous compounds. In addition, Adkins *et al.* (*10*) reported that the catalyst contained copper oxide and copper chromite, but that it was neither a simple copper chromite nor a mechanical mixture of copper oxide and copper chromite. The data of Figs. 2c and 2d show peaks indicative of residual $CuOHNH_4CrO_4$, as well as peaks for CuO and $CuCr_2O_4$ species. The powder

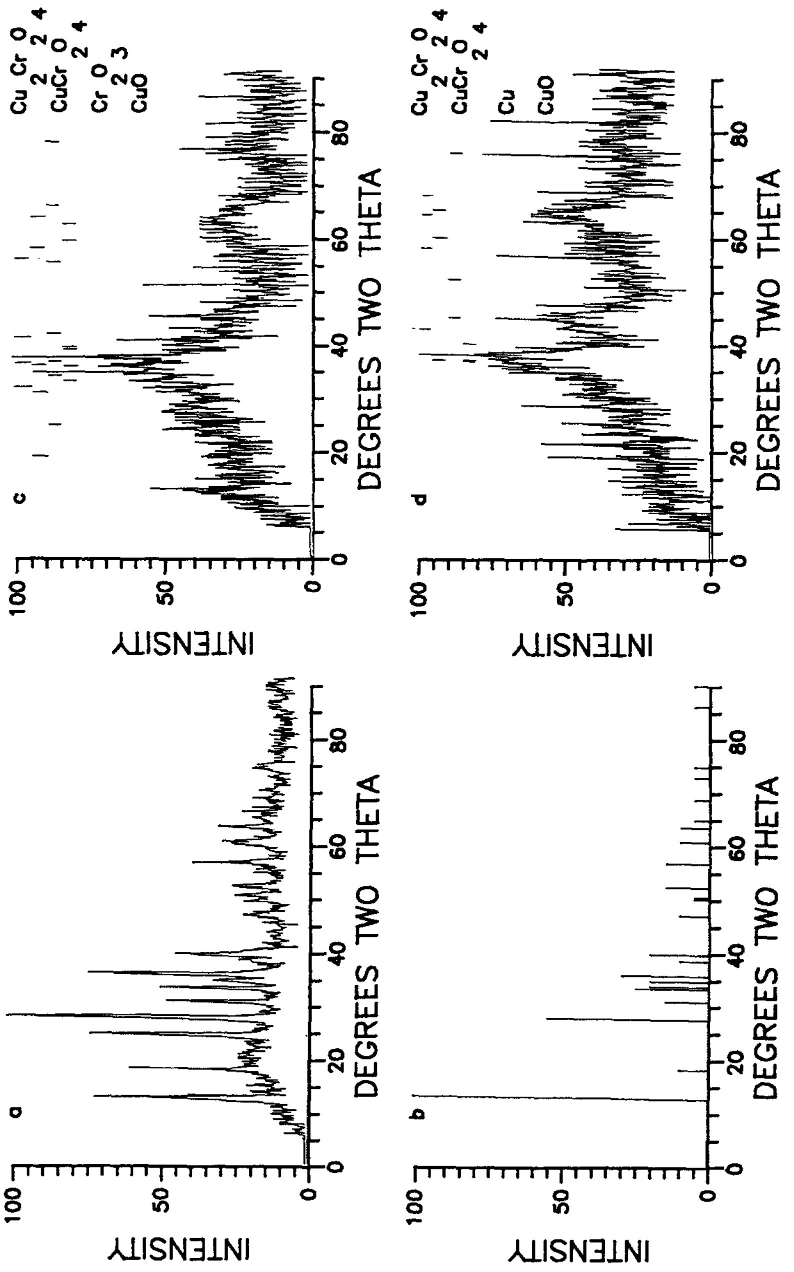


FIG. 2. X-ray diffraction patterns for $CuOHNH_4CrO_4$ and its decomposition products.

from the mechanically mixed $CuOHNH_4CrO_4$–BPL charcoal after heat treatment was brown–black in color indicating partial decomposition (the completely decomposed product is reported by Connor *et al.* (*9*) to be jet black). The powder of Fig. 2d was dark black, indicative of more complete decomposition of $CuOHNH_4CrO_4$. There are also peaks indicating that $Cu_2Cr_2O_4$ and Cu may be present. This result suggested that some of the $CuOHNH_4CrO_4$ species was severely decomposed (i.e., the Cu^{2+} species suffered some degree of reduction). Adkins *et al.* (*10*) and Stroupe (*11*) have reported that reduction of the divalent copper species occurs if the thermal decomposition process is too harsh; thus the data of Figs. 2c and 2d are again consistent with these observations.

The ESCA data also support the hypothesis that the supported $CuOHNH_4CrO_4$ on the charcoal surface decomposes into a $CuO–CuCr_2O_4$-type species. Figure 3 shows the copper and chromium spectra for a series of thermally treated whetlerites. The Cr $2p_{3/2}$ binding energies for these heat-treated samples are all equal to about 576.0 eV which is somewhat lower than the value reported for the Cr_2O_3 compound, 576.6 eV (*12*), originally proposed by Hammarstrom and Sacco (*4*), as the major thermal decomposition product. This result would suggest that chromium has gained electron density (i.e., its oxidation state is

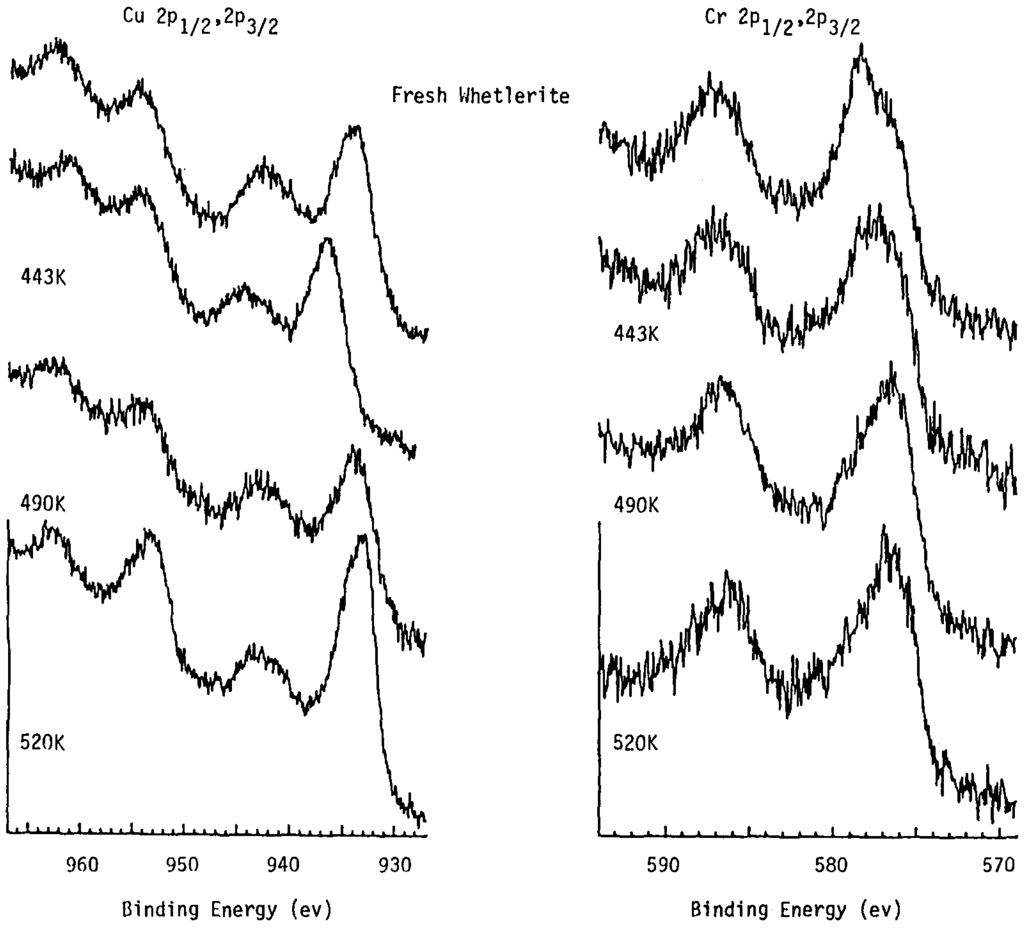


FIG. 3. XPS spectra for thermally treated whetlerites.

less than 3+) as would occur if it existed in a $CuCr_2O_4$, copper–chromite-type compound. Cimino *et al.* (*13*) reported a Cr $2p_{3/2}$ binding energy of 575.6 eV for a magnesium chromite species. The value obtained in this investigation was ~576.0 eV which, although not as low as the value reported by Cimino *et al.*, reflects the shift to lower binding energies when a chromite species is formed. The copper spectra for these compounds illustrate that the binding energies and separation of the $2p_{1/2}$, $2p_{3/2}$ peaks for each of the samples closely match those of pure CuO (20.0 eV). This suggests that a large percentage of copper exists in this form on whetlerite. A material balance on the total Cu and Cr using the measured Cr^{6+}/Cr^{3+} and $Cu^{2+}/Cu^{1+,0}$ ratios indicates that only a very small amount of the copper (<5%) exists in the original $CuOHNH_4CrO_4$ species.

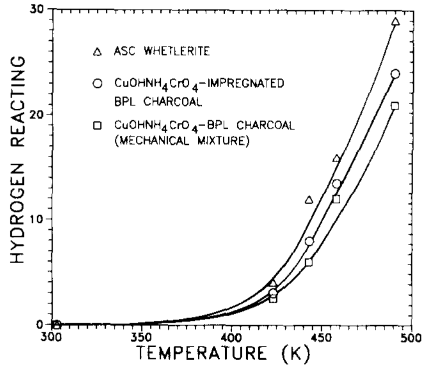


FIG. 4. Comparison of hydrogen reactivity as a function of thermal treatment temperature for whetlerite and model compounds.

The hydrogen pulse reaction data provided additional support that the $CuOHNH_4CrO_4$ species on whetlerite decomposed into a copper–chromite species upon thermal treatment. Figure 4 shows hydrogen pulse reactor data for thermally treated ASC whetlerite, thermally treated impregnated BPL charcoal, and mechanical mixtures of $CuOHNH_4CrO_4$ with BPL charcoal that were subject to heat treatment. The hydrogen reactivity on $CuOHNH_4CrO_4$-impregnated BPL charcoal and mechanical mixtures of $CuOHNH_4CrO_4$ with BPL charcoal show the same trends as the reactivity on thermally treated ASC whetlerite samples suggesting that the type of reaction occurring on these model compounds was the same as that taking place on ASC whetlerite. Hammarstrom and Sacco (*4*) have determined activation energies for the hydrogen–whetlerite reaction and have shown that the mechanism of hydrogen reactivity is adsorption–dissociation of H_2 (followed by H-atom spillover to the charcoal support) by Cr^{3+}-containing species. The actual H_2 reactivity values for the impregnated and mechanically mixed samples are approximately two-thirds and one-half, respectively, of the values reported for ASC whetlerite. These values are not unreasonable considering the fact that the $CuOHNH_4CrO_4$ compound was synthesized prior to impregnation on the charcoal support; thus the impregnant dispersion would not be expected to be as high as for commercially prepared whetlerites; also, for the mechanically mixed samples, the spillover of hydrogen atoms to the charcoal support would be somewhat hindered, resulting in lower H_2 reactivity values.

It is proposed, then, that the hydrogen reactivity observed on these compounds is due to the presence of $CuO–CuCr_2O_4$ species. These types of copper–chromium oxides, often used as hydrogenation catalysts, are routinely formed when $CuOHNH_4CrO_4$ is thermally decomposed (*3, 5, 10, 14, 15*). Thus, the initial step in whetlerite decomposition is thought to be the reduction of hexavalent chromium, mainly in the $CuOHNH_4CrO_4$ form, to the $CuO–CuCr_2O_4$ (chromite form), characterizable by the ability of whetlerite to adsorb and dissociate hydrogen molecules.

After decomposition of supported $CuOHNH_4CrO_4$ species, the whetlerite thermal decomposition process continues with the separation of CuO from the Cr^{3+} species followed by the reduction of the Cu^{2+} into

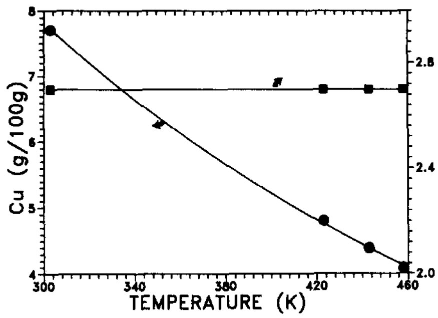


FIG. 5. Copper and chromium surface "concentrations" as a function of thermal treatment temperature.

Cu^{1+} species and Cu^0. Figure 5 is a plot of copper and chromium surface concentration determined by ESCA as a function of thermal treatment temperature. The data clearly show a decrease in intensity of the detected copper signal as the thermal treatment temperature was increased. This phenomenon is due to segregation of copper from chromium and its sintering into larger crystallites. As the CuO becomes isolated from $CuCr_2O_4$ the species become very unstable and as reported by Stroupe (*11*) and Adkins *et al.* (*10*) are subsequently reduced to $Cu_2Cr_2O_4$ (Cu^{1+}) and Cu^0. It was previously shown in Fig. 2d that $Cu_2Cr_2O_4$ and Cu have been identified on decomposed $CuOHNH_4CrO_4$. In addition, the spectra presented in Fig. 3 indicate the tendency of the Cu^{2+} to suffer reduction when thermally treated above 490 K. The Cu $2p_{3/2}$ binding energy shows a decrease for whetlerite treated at 520 K consistent with the wet-chemistry data and indicative of Cu^{2+} reduction. These results are in agreement with the study of Ehrburger *et al.* (*16*) who showed that reduction of carbon-supported CuO to Cu_2O and Cu begins at 513 K. However, the thermal reduction of copper begins only after the hexavalent chromium species has been substantially reduced (the major deactivation step), and coincides with the severe oxidation of the carbon support as shown by our thermal gravimetric analyses (*17*). Therefore, under the extreme condition of thermal deactivation (i.e., temperature >520 K) the loss of carbon support due to oxidation (10% weight loss at 580 K) becomes a more serious practical problem than the reduction of copper.

(*b*) *Deterioration due to Hydrogen Exposure*

Exposure of whetlerite to pure hydrogen at relatively low temperatures (i.e., 303 to 323 K) for 2 hr does not appear to cause any degree of deterioration. Table 1 shows that when thermally treated whetlerite samples

TABLE 1

Hydrogen Reactivity, Cr^{6+}/Cr^{3+} and $Cu^{2+}/Cu^{1+,0}$ Ratios for Whetlerites Exposed at Low Temperatures to Hydrogen for Extended Times

Thermal treatment	% Hydrogen reacting	Cr^{6+}/Cr^{3+}	$Cu^{2+}/Cu^{1+,0}$
423 K-treated	0	48	6.3
	(0)[a]	(48)	(6.3)
443 K-treated	2.5	35.6	6.0
	(2.6)	(36.0)	(6.2)
458 K-treated	12.6	19.2	6.0
	(12.8)	(18.0)	(5.9)
490 K-treated	33.0	6.5	6.1
	(30.0)	(6.0)	(5.9)

[a] Values in parentheses are obtained from 0.1-ml (NTP) hydrogen pulses prior to extended hydrogen exposure.

TABLE 2

Effect of High-Temperature (423 K) Hydrogen Exposure on Metal Oxidation States and Hydrogen Pulse Reactivities

Sample treatment	H_2 treatment/time	Cr^{6+}/Cr^{3+}	$Cu^{2+}/Cu^{1+,0}$	% H_2 reacting
Fresh whetlerite	423 K/2 hr	2.0 (48.0)[a]	5.6 (6.3)	13.0 (0)
423 K treated	423 K/2 hr	2.0 (35.0)	5.6 (6.0)	13.2 (2.5)
458 K treated	423 K/2 hr	1.5 (19.0)	5.5 (5.8)	13.2 (12.6)
490 K treated	423 K/2 hr	1.5 (6.0)	5.6 (6.0)	30.0 (33.0)
$CuOHNH_4CrO_4$-BPL charcoal (mechanical mix.)	423 K/2 hr	3.0 (40.0)	NA	2.0 (0)
Decomposed $CuOHNH_4CrO_4$-BPL charcoal (mechanical mix.)	423 K/2 hr	3.0 (6.0)	NA	6.5 (4.0)

[a] Values in parentheses are metal oxidation states and hydrogen reactivities prior to high-temperature exposure.

were exposed to hydrogen, copper and chromium oxidation states and impregnant morphology did not appear any different from those of the unexposed samples. For the thermally treated whetlerites the percentage of the hydrogen pulse reacting after prolonged hydrogen exposure was the same as that of the unexposed samples. Thus, the results of Table 1 suggested that the low-temperature hydrogen exposure did not affect either impregnant oxidation state or the ability of the $CuO-CuCr_2O_4$ to adsorb and dissociate hydrogen.

ASC whetlerite exposed to pure hydrogen at 423 K, however, undergoes some degree of deactivation. The mechanism of the deactivation very closely parallels the thermal deactivation process in that the hexavalent chromium is reduced, hydrogen dissociation sites are formed, and eventually the divalent copper species is reduced. Table 2 lists relative metal oxidation states and hydrogen pulse reactivities for a series of samples exposed to hydrogen for 2 hr at 423 K and compares these values to samples which were not treated with hydrogen at 423 K. The data of Table 2 show three major results due to high-temperature hydrogen exposure: (i) substantial reduction in the Cr^{6+}/Cr^{3+} ratio in whetlerite, (ii) generation of hydrogen dissociation sites, and (iii) initiation of Cu^{2+} reduction. High-temperature exposure to hydrogen reduced the Cr^{6+}/Cr^{3+} ratio to a value of about 2.0 for all samples examined. Following hydrogen exposure, the percentage hydrogen reacting can no longer be correlated with the thermal treatment temperature as it was shown to be in Fig. 4. This finding suggests that during the hydrogen treatment process a certain amount of the hexavalent chromate species is reduced to the trivalent form but the Cr^{3+} exists in a species different from the copper chromite ($CuO-CuCr_2O_4$) form. It is hypothesized that the Cr^{3+} exists as small (undetectable by X-ray diffraction) Cr_2O_3 crystallites. Miya *et al.* (*18*) reported the complete reduction of $CuO-CuCr_2O_4$ catalysts to Cu and Cr_2O_3 following exposure to hydrogen at temperatures of 500 K. Although it was not possible to detect Cr_2O_3, our X-ray diffraction patterns for a series of hydrogen-exposed whetlerites and model compounds do show Cu^{2+} reduction as indicated by the presence of copper metal as well as $Cu_2Cr_2O_4$ (Cu^{1+}).

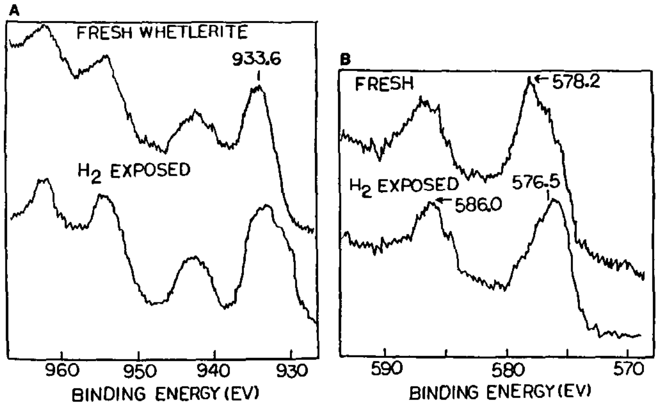


FIG. 6. ESCA spectra for hydrogen-exposed (423 K) whetlerite compared to fresh whetlerite. (A) copper; (B) chromium.

The chromium and copper $2p_{1/2}$, $2p_{3/2}$ peaks for a H_2-exposed sample are shown in Fig. 6. These data indicate that the binding energies decrease for fresh whetlerite exposed to H_2 at 423 K, and were ~586.0 and 576.5 eV, respectively, which are reasonably close to the values of 586.2 and 576.6 eV reported for Cr_2O_3 in (*12*).

The hydrogen pulse reactivity data for fresh whetlerite, 423 K-treated whetlerite, $CuOHNH_4CrO_4$ mechanically mixed with BPL charcoal, and decomposed $CuOHNH_4$ CrO_4 mechanically mixed with BPL charcoal show that hydrogen dissociation sites are created after high-temperature hydrogen exposure. The X-ray patterns suggest the existence of the $CuO–CuCr_2O_4$ species that adsorbs and dissociates hydrogen. Thus, it is apparent that exposure of whetlerite to hydrogen at 423 K does induce decomposition of $CuOHNH_4CrO_4$ into "copper–chromite"-type species. Then, similar to decomposition due only to thermal treatment in an inert nitrogen gas stream, the final step of Cu^{2+} reduction to Cu^{1+}-containing species and Cu^0 occurs. The $Cu^{2+}/Cu^{1+,0}$ ratios listed in Table 2 reflect this trend as the values obtained are somewhat lower than the values observed before hydrogen treatment. The shoulder on the lower binding energy side of the Cu $2p_{3/2}$ peak for the fresh whetlerite exposed to hydrogen at 423 K (Fig. 6) also suggests the initiation of Cu^{2+} reduction. These data are consistent with Miya *et al.* (*18*) and Stroupe (*11*) who showed that the copper species can be reduced to $Cu_2Cr_2O_4$ and/or segregate away from the chromite and be reduced to Cu^0 following the use of copper–chromite catalysts in hydrogenation reactions.

(*c*) *Deterioration due to Humid Aging*

The focal point for the humid aging of ASC whetlerite again centers on the supported $CuOHNH_4CrO_4$ species. As discussed previously, the pH of water solutions in which fresh whetlerite was soaked were on the order of 8.3 which are favorable for the existence of the $CuOHNH_4CrO_4$ species. Figure 7 illustrates the pH values as a function of humid aging time. These data show that upon exposure and adsorption of moisture, the pH of whetlerite solution are gradually reduced. Figure 8 compares an X-ray pattern for the pure $CuOHNH_4CrO_4$ compound exposed to 100% RH at 343 K for 1 week to the pure $CuOHNH_4CrO_4$ compound and shows peaks for both the $CuOHNH_4CrO_4$ compound and the Cu_4 $(OH)_6CrO_4$ compound (brochantite chromate) indicating the slow conversion of the $CuOHNH_4CrO_4$ species into the crystalline brochantite chromate form. The Cu_4

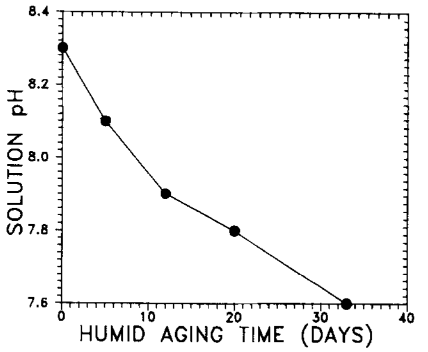


FIG. 7. Whetlerite solution pH as a function of humid aging.

(OH)$_6$CrO$_4$ species was also detected on whetlerite samples humid aged for 15 and 33 days. These observations are in agreement with the studies of Pytlewski (*6*). He suggested that the gradual decrease in basicity over a period of time promoted the conversion of the CuOHNH$_4$CrO$_4$ compound into a yellowish-green brochantite chromate species, Cu$_4$(OH)$_6$CrO$_4$. This brochantite chromate species was reported to exist in an amorphous state on the charcoal but did convert to a more crystalline form over a period of time (e.g., 2 weeks exposure of whetlerite to humid air).

After the formation of crystalline brochantite chromate-type species continued

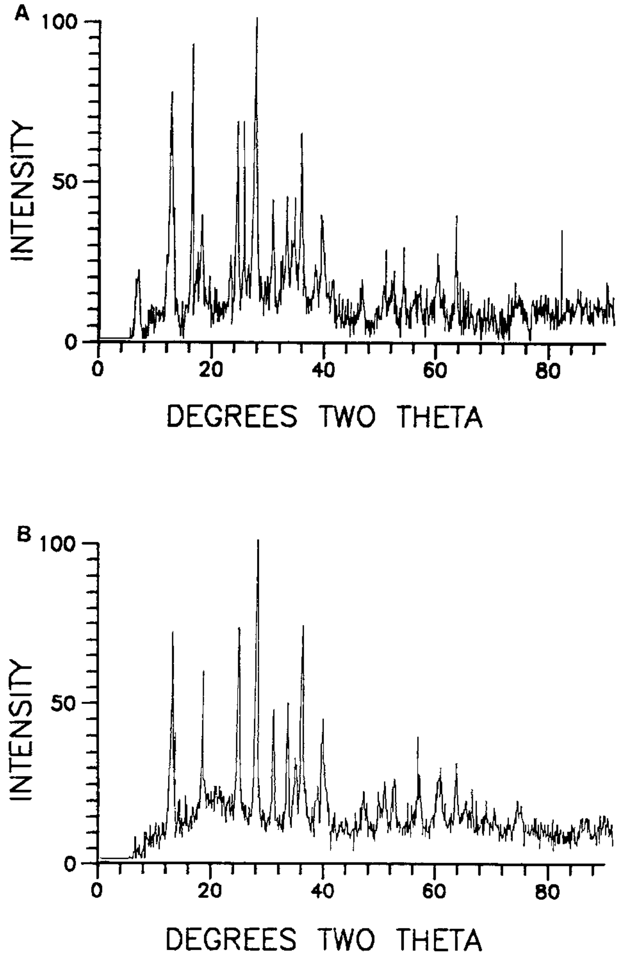


FIG. 8. X-ray diffraction pattern for humid aged CuOHNH$_4$CrO$_4$. (A) 100% RH, 343 K, 7 days; (B) pure.

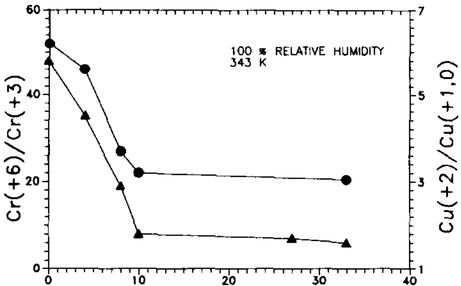
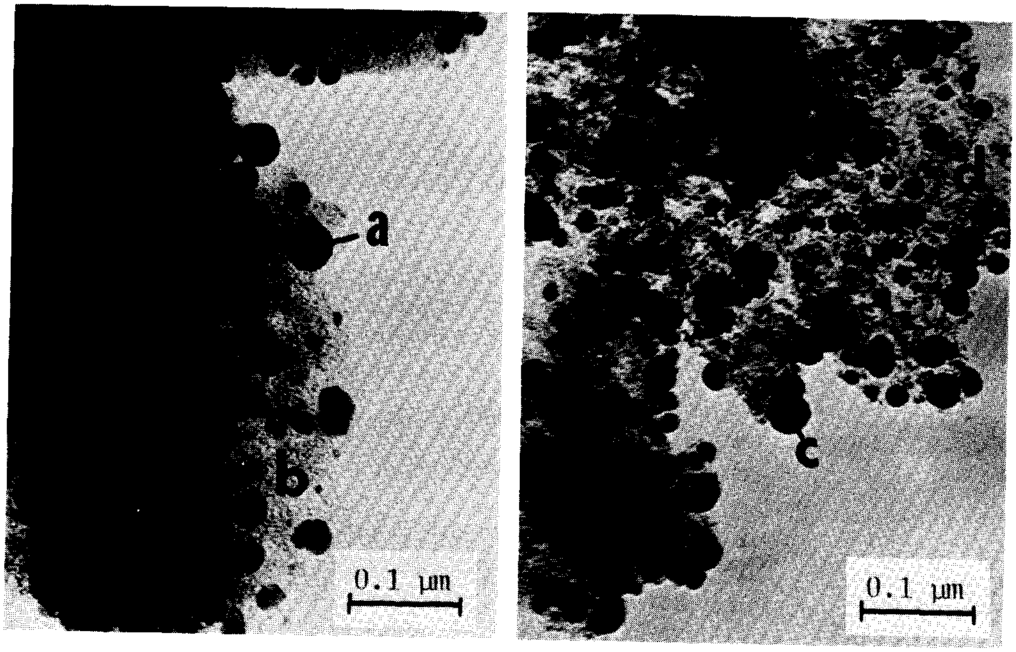


FIG. 9. Reduction of Cr^{6+} and Cu^{2+} as a function of humid aging.

exposure to moisture causes reduction of both the Cr^{6+} and Cu^{2+} species. Figure 9 shows the Cr^{6+}/Cr^{3+} and $Cu^{2+}/Cu^{1+,0}$ ratio in whetlerite as a function of humid aging time and indicates that the Cr^{6+}/Cr^{3+} ratio decreases from a value of about 48 for the fresh sample to a value of about 6 for samples humid aged for 10 days. This behavior is similar to that reported for the thermal treatment of whetlerite (*4*); however, none of the humid aged samples exhibited any ability to dissociate hydrogen, the reason being that the supported



4 days humid aged

33 days humid aged

EDX ANALYSIS

region	%Cu	%Cr
a	100	—
b	65	35
c	100	—
d	59	41

FIG. 10. TEM micrographs of humid aged samples and EDX results.

$CuOHNH_4CrO_4$ converted to $Cu_4(OH)_6CrO_4$ during the adsorption of moisture and not to the "copper–chromite" species that is formed under thermal decomposition. No evidence for the existence of the CuO–$CuCr_2O_4$ was seen in any X-ray patterns for the humid aged samples. The reduction of the Cu^{2+} species is more gradual than the reduction of Cr^{6+} but becomes quite significant after about 8 days of himid aging. During this humid aging process, the X-ray diffraction data, microscopy work, and electron spin resonance spectra show that the copper species undergoes substantial chemical and morphological changes.

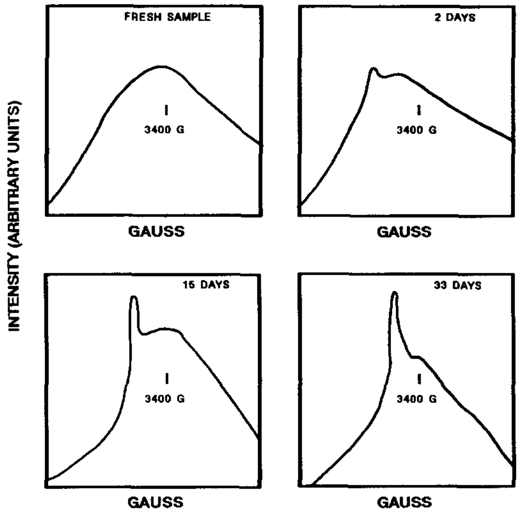
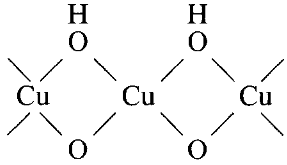
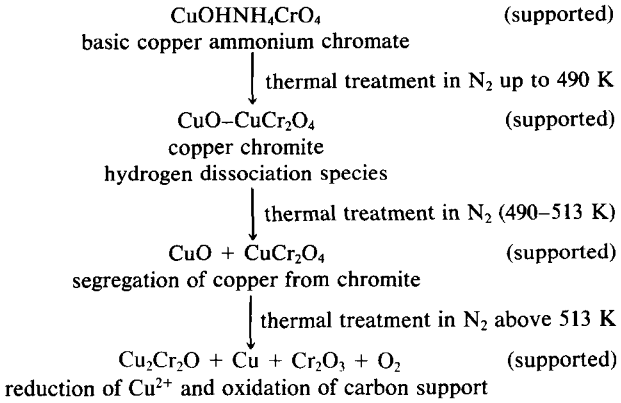


FIG. 11. ESR spectra of humid aged whetlerites (Varian E-9 spectrometer).

X-ray patterns suggest the formation of crystalline copper species during humid aging for periods between 2 and 33 days. The patterns show the growth of CuO, $Cu_2Cr_2O_4$, and possibly Cr_2O_3 compounds during the humid aging process. Figure 10 shows transmission electron micrographs of moisture-treated samples. The impregnant morphology has changed significantly compared to fresh whetlerite; the crystallite size is much larger and ranges from 100 to 500 Å. The corresponding energy dispersive X-ray analysis on several of the crystallites signified that copper was the dominant species. The ESR spectra in Fig. 11 also show the isolation and crystallization of the copper species. The signal is fairly broad (FWHM $\approx$ 1800 G) and not well defined for the fresh (or thermally treated) ASC whetlerite samples. However, as the time of humid aging increases, a sharper, well-pronounced signal due to the Cu^{2+} species appears. The shape of the spectra is indicative of axially symmetric copper in a tetragonal arrangement. The fact that the signal becomes sharper with time of aging suggests that copper is in a more "isolated" environment and that the ligands around it are more symmetric. For our humid aged whetlerite samples these effects are most likely due to copper sintering and segregating away from other paramagnetic species (e.g., Cr^{3+}-containing species and other Cu^{2+} species) and the surrounding of Cu^{2+} by ligands such as $OH^-(Cu(OH)_2)$, O^{2-} (CuO), or water. This hypothesis is consistent with the results reported by Poziomek *et al.* (*19*) for whetlerites challenged with H_2O and $CNCl$. They suggest that when a "polymeric"-type copper species, for example,



exists on the whetlerite surface, no ESR signal is observed. If $CNCl$ and water are present, however, the hydroxy bridges are broken resulting in the conversion of the polymeric species into monomeric hydrated Cu^{2+} complexes and the appearance of the ESR signal, the intensity of which can be correlated with the exposure to $CNCl$ (MacKay *et al.* (*20*)). Thus, the ESR spectra in Fig. 11 suggest that complex copper chromate species (e.g., $Cu_4(OH)_6CrO_4$ and $CuOHNH_4CrO_4$) are attacked by water molecules and subsequently broken up into crystalline cop-

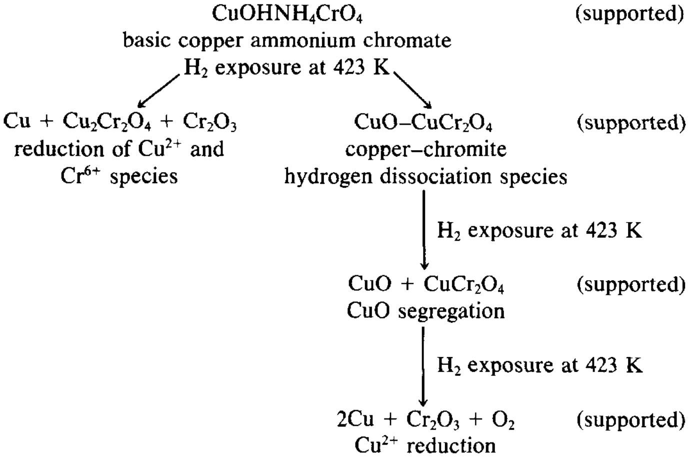


SCHEME 1. Thermal deactivation mechanism.

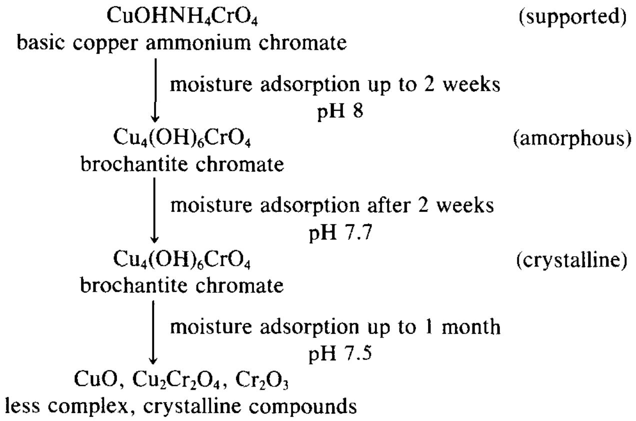
per compounds such as CuO and $CuCO_3 \cdot Cu(OH)_2$. This "breakup" and formation of crystalline copper compounds is the final and most damaging step in the whetlerite deterioration process.

CONCLUSION

The deactivation/deterioration of ASC whetlerite involves a complex series of steps depending on the deactivating condition (i.e., high temperature, high humidity, or exposure to reactive gases). The deterioration process is associated with changes in whetlerite surface conditions, reduction of chromium and copper oxidation states, and variations in impregnant morphology. Under thermal deactivating conditions, the supported $CuOHNH_4CrO_4$ compound first decomposes into a "copper–chromite"-type species (i.e., $CuO–CuCr_2O_4$). Continued high-temperature exposure causes sintering of the copper species, its separation from the chromite, and eventual reduction to $Cu_2Cr_2O_4$ and Cu, as well as severe oxidation of the carbon support. Whetlerite deterioration due to high-temperature (i.e., 423 K) hydrogen exposure follows the same pathway except that reduction of Cr^{6+} and Cu^{2+} is more substantial. Schemes 1 and 2



SCHEME 2. Hydrogen deactivation mechanism.



SCHEME 3. Moisture deactivation mechanism.

summarize the series of steps in these deactivation/deterioration processes.

The deterioration of whetlerite due to humid aging first involves the adsorption of moisture with the subsequent decrease in basicity at the whetlerite surface causing the $CuOHNH_4CrO_4$ species to convert into a brochantite chromate form, $Cu_4(OH)_6CrO_4$. As time passes the moisture and more acidic condition prommote the decomposition of brochantite chromate into less complex crystalline compounds such as CuO, $Cu_2Cr_2O_4$, and Cr_2O_3. This mechanism is shown in Scheme 3.

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