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Sorption of Iodide on Cuprite (Cu₂O)

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The interactions of iodide ions with cuprite (Cu₂O) surfaces were studied by combining batch experiments and surface analyses. The evolution of iodide uptake with pH was investigated. The thermodynamical calculations and surface analyses (X-ray photoelectron spectroscopy, scanning electron microscopy, Raman spectroscopy, and electrochemistry) were used to show that two different pH-dependent mechanisms are responsible for the accumulation of the iodide species on Cu₂O. At pH values lower than 6.5, the precipitation of CuI occurs on the cuprite surface, while in more alkaline medium, the iodide adsorption takes place by substituting the surface hydroxyl groups of Cu₂O. The sorption processes were not affected by a 1000-fold excess of chloride ions, but they were limited to the potential range corresponding to the stability domain of Cu₂O (i.e., between −10 and +190 mV/ENH at pH 8); thus no accumulation was observed either on metallic copper or on CuO.

1. Introduction

Environmental contaminants harmful to the health of present and future generations involve nuclear-fission products, as iodine radioisotopes. ^{129}I is one of the more mobile compounds because of its long half-life ($t_{1/2} = 1.7 \times 10^7$ years) and its ability to diffuse in solution as an anion (most often I$^-$ in natural media) whose migration is not retarded by silicate minerals.[1,2]

The search for solids which present abilities for trapping iodide species is necessary in the nuclear industry, from reprocessing methods of spent nuclear fuel[3] until the design of barriers surrounding waste containers for nuclear fuel disposal in deep geological sites.[4] The uptake of iodide from solutions has been reported to be possible through different pathways. For high iodide concentrations, metal cations M^{n+} as Bi^{3+} or Pb^{2+} are well-known to form precipitates MI$_n$.[5,6] For low concentrations, it has been demonstrated that particular compounds such as silver or mercury[6] react with iodide to form sparingly soluble phases. Finally, adsorption of iodide ions on minerals such as Cu₂O[7] or HgS[8] was proposed for the selective uptake of iodide ions in the domain of very low concentrations.[1] This potentiality led to numerous studies,

reviewed in part in the report by Liu and co-workers.[9] Copper(I) minerals appear to be promising: Cu is cheaper than Ag and less toxic than Pb and Hg, and there is a strong affinity between Cu(I) and iodide. This is the only oxidation state of copper which is suitable, since, by considering the hard and soft acids and bases (HSAB) theory, I$^-$ is a soft Lewis base and Cu$^+$ is a soft Lewis acid, leading to a favorable mutual affinity. Cu^{2+} is a borderline Lewis acid,[10] therefore its interactions with iodide ions are predicted to be weak. The interactions between iodide and cuprous oxides have been reported in two previously published papers.[7,11] In a first study by Haq et al.,[13] copper plates covered with a Cu₂O overlayer(s) have been used as adsorbent for iodide ions. A transient Cu$^+$(OH$^-$)(I$^-$) complex leading to the further crystallization of CuI has been proposed as a possible mechanism. Influence of pH on iodide sorption was tested, but neither the stability of Cu₂O nor the effect of interfering anions was investigated. In a second study, Oscarson et al.[7] showed that iodide uptake by Cu₂O was lower in synthetic groundwater with a high chloride concentration than that obtained in distilled water. This was attributed to an increase of the solubility of CuI in the presence of the anions in the synthetic groundwaters. Influence of the pH of the solution was evoked, but no experimental evidence was provided.

The present paper is dealing with iodide sorption on cuprite, Cu₂O, for iodide concentrations around 10^{-4} M. First of all, the surface of the oxide was thoroughly characterized. The evolution of iodide uptake as a function of pH was then investigated in batch experiments, and for the first time, a diagram of iodide uptake versus pH was drawn. The mechanisms leading to the iodide uptake were investigated using various surface analysis methods, as X-rays photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM), and

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Table 1. XPS Binding Energies and Auger Electron Kinetic Energies for Various Copper-Based Solid Compounds

compound	line	binding energy (eV)	kinetic energy (eV)	ref
$Cu(OH)_2$	$2p_{3/2}$	935.3		a
	$2p_{3/2}$	934.4–935.1		16
Cu_2O	$2p_{3/2}$	932.8		a
	$2p_{3/2}$	932.0–932.7		16
Cu	$2p_{3/2}$	932.2–933.1		16
Cu_2O	$L_3M_{4.5}M_{4.5}$		917.0	a
	$L_3M_{4.5}M_{4.5}$		916.7	15
Cu	$L_3M_{4.5}M_{4.5}$		918.2	a
	$L_3M_{4.5}M_{4.5}$		919.0	15

[a] This study.

electrochemistry with a Cu_2O-modified carbon paste electrode. Finally, it was pointed out how the presence of chloride ions or reducing species in the medium can affect the sorption processes, to mark off the possible use of Cu_2O as an iodide scavenger.

This work deals with the sorption of an inorganic anion on a mineral surface. The system Cu_2O/I^- could be considered as a model system, and the described procedure could be generalized to other systems involving the interaction of anions with solid minerals. This is important since the adsorption of anions represents only a minor part of the previously published works on the sorption of soluble species on minerals, which were mainly devoted to the adsorption of cations.[12,13]

2. Experimental Section

2.1. Reagents. KI (Aldrich), NaCl (OSI), $NaClO_4$ (Fluka), $HClO_4$ (Prolabo), NaOH (Prolabo), CuI (Prolabo), and $NaBH_4$ (Aldrich) were of analytical grade. Solutions were prepared with high-purity water (18 M$\Omega \cdot$cm^{-1}) from a Millipore MilliQ water purification system. Hydrogen with less than $5 \times 10^{-3}\%$ impurities (Airgaz) was used. Cuprous oxide, Cu_2O, from Fluka has been selected for this study. $Cu(OH)_2$ was freshly precipitated by mixing copper nitrate and aqueous sodium hydroxide before use.

2.2. Instrumentation. Surface Analysis. The surface analysis of the solid phases was performed after washing the products with deionized water and drying at room temperature under a nitrogen atmosphere. The powders were pressed onto the adhesive side of a copper adhesive electrical tape (3M). This tape mounted with the powder was then fastened onto a standard sample holder. As the analyzed compounds were highly oxidizable, exposure to air was avoided during transfer to XPS apparatus by flowing nitrogen upon the sample. The absence of any oxidation risk was checked with the surface analysis of a copper powder, previously cleaned with $HClO_4$. The XPS spectra were obtained using an electron energy analyzer (VSW, MCD 5000) and an unmonochromatized magnesium X-rays source (1253.6 eV). The apparatus and the spectra processing were extensively described in a previous paper.[14] Due to the absence of chemical shift observed on copper core levels between metallic copper and cuprous compounds, photon-induced Auger electron spectroscopy was used to distinguish Cu(0) and Cu(I) oxidation states. In fact, the Auger Cu $L_3M_{4.5}M_{4.5}$ line shows a difference between Auger line shape of Cu and Cu_2O[15] (kinetic energies presented in Table 1). The binding energies were corrected on the basis of the standard value of C1s from carbon of contamination at 284.6 eV.[16]

Back diffusion scanning micrographs were obtained by scanning electron microscopy (SEM) with a Philips XL30 scanning electron microscope. Raman spectra were recorded using a Jobin

Yvon T 64000 Raman spectrometer in backscattering ($\lambda_{exc} = 514.56$ nm of an argon laser Spectra Physics Stabilité 2017, 4 mW power at the sample) fitted out with a microprobe ($\times 50$ magnification). Thus, a spatial resolution of 2 μm was reached, and the detection (triple subtractive) allowed a spectral resolution of 2.5 cm^{-1} and a precision of ca. 1 cm^{-1}. The microprobe allowed analysis of an area of around 5 μm². A model 283 EG&G Princeton Applied Research (PAR) potentiostat/galvanostat, monitored by M270 electrochemical research software (EG&G PAR), was used for the electrochemical experiments. Cyclic voltammetry measurements were performed at room temperature in an undivided three-electrode cell containing the supporting electrolyte (0.1 M $NaNO_3$). The working electrode was a homemade Cu_2O-modified carbon paste electrode (Cu_2O-MCPE) prepared as described elsewhere.[17] The counter-electrode was made of a platinum wire, and a saturated calomel electrode (SCE) was used as the reference.

2.3. Procedure. Batch experiments were carried out in stoppered polyethylene centrifuge tubes (Nalgene), on suspensions of Cu_2O (between 1 and 4 g) in 30 mL of potassium iodide. Since the concentration of iodide released by nuclear fuel waste is foreseen to be below 3×10^{-4} M,[4] sorption experiments were carried out with an initial iodide concentration of 10^{-4} M (unless specified otherwise). $NaClO_4$ (0.1 M) was used to keep a constant ionic strength, and the initial pH was fixed by addition of strong acid ($HClO_4$) or base (NaOH). When required, pH was modified by adding 1 mL of 10^{-3} M acid or base in the suspensions, which were then allowed to reach another equilibrium state. At this time, the concentration of iodide in solution was determined by UV spectrometry (Beckmann DU 7500) at 228 nm, on the supernatant after centrifugation. Iodide concentration was then corrected by a dilution factor coming from acid or base additions. The error on the uptake of iodide is estimated to be about 10%. To make the figures clearer, the uncertainty bars were not shown. The operation (acid or base addition, equilibration, and analysis) was repeated twice with the same suspensions. This allowed obtaining numerous experimental data, and checking the reversibility of the iodide uptake.

Experiments under hydrogen atmosphere were carried out in an apparatus designed for kinetics studies. Hydrogen was bubbled into the Cu_2O suspension (40 mg of Cu_2O in 4 mL of solution at pH 8) in a closed circuit, and the pressure (initially 10^5 Pa) was recorded throughout the experiment. The reactor could be heated to 90 °C by an external circulation of water.

3. Results and Discussion

3.1. Adsorption of Iodide Ions. "Activation" of Commercial Cu_2O. The commercial Cu_2O powder we used was visibly hydrophobic, which is thought to result in a limitation of the interactions with the ions present in aqueous solution. Its surface was oxidized as attested by the comparison between XPS $Cu2p_{3/2}$ spectra for synthesized $Cu(OH)_2$ and commercial Cu_2O, which are presented in Figure 1 (curves A and B, respectively). The binding energy of the $Cu2p_{3/2}$ line of $Cu(OH)_2$ is pointed out at 935.3 eV, and strong satellites are observed around 940–945 eV. These satellites, whose origin has been extensively discussed in the literature,[18–20] are observed with most of the Cu(II) compounds (CuO,[16] azurite,[21] ...) but never exist with Cu(I) compounds or metallic copper. The spectrum of the commercial Cu_2O powder presents two peaks pointed out at close energies (932.8 and 935.3 eV) and a weak satellite structure at 940–945 eV. The $Cu2p_{3/2}$ line at 935.3 eV and the satellite structure were attributed to $Cu(OH)_2$, and the main peak, pointed out at 932.8 eV, is consistent with Cu(I) compounds or metallic

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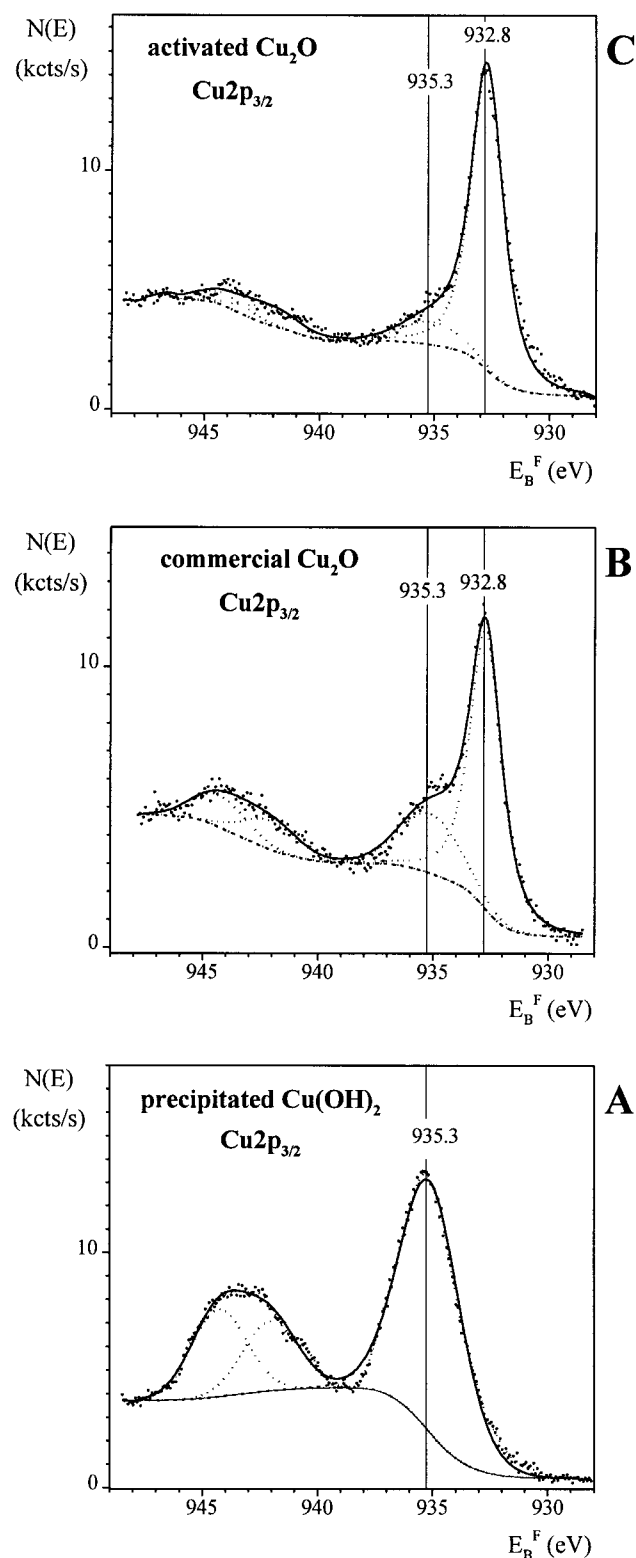
Figure 1. Mg Kα XPS spectra of the Cu2p$_{3/2}$ line on (a) a freshly precipitated Cu(OH)$_2$, (b) a commercial Cu$_2$O powder and (c) an "activated" Cu$_2$O powder.

copper, in comparison with reference values given in Table 1. Thus, this compound is basically composed of Cu$_2$O, whose surface is partially oxidized into Cu(OH)$_2$. As cupric compounds are not expected to react with iodide ions,[1,7,11] the interactions between aqueous solutions of iodide and untreated commercial Cu$_2$O are therefore thought to be limited for both these reasons (hydrophobicity and surface oxidation).
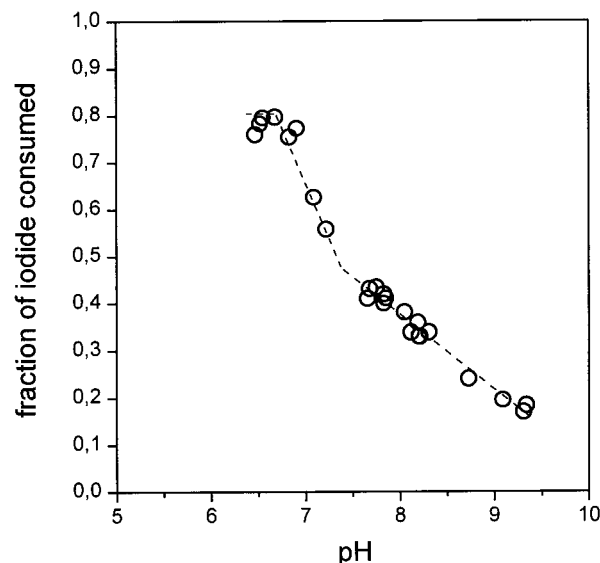

Figure 2. Iodide uptake by Cu$_2$O observed as a function of pH in a 30 mL solution ($[KI]_0 = 10^{-4}$ M) with 1.5 g of Cu$_2$O (○), fitted by linear segments (dashed lines).

This is confirmed by a preliminary experiment with a commercial Cu$_2$O powder used as received. A 0.5 g Cu$_2$O sample was allowed to react with a 20 mL solution containing 10^{-4} M KI (pH 6) over a 12 h period of time. No consumption of the solution-phase iodide species was observed. This is consistent with the fact that during this period of time, the hydrophobic character of Cu$_2$O particles prevented their dispersion into the solution; it was necessary to continuously stir the suspension during typically 2 weeks to ensure a proper dispersion of solid particles. A significant decrease in the iodide concentration in the solution was observed only after several months, in agreement with what was observed by Oscarson et al.[7] Similarly, time-consuming experiments for iodide sorption onto oxidized copper plates were reported by Haq et al.[11]

The above results claim for a pretreatment of the commercial Cu$_2$O before use in sorption experiments, which would make this material less hydrophobic by removing the oxidized layer on their surface. This was achieved by a so-called "activation" procedure consisting in the immersion of Cu$_2$O in slightly acidic medium (pH around 4) during 12 h. After this treatment, Cu$_2$O particles were easily dispersed in aqueous solutions and their surface reveals only a weak remaining oxidation, as checked by XPS (Figure 1, curve C) where the peak pointed out at 935.3 eV and the satellite structure significantly decreased. The above adsorption experiments (0.5 g of Cu$_2$O in 20 mL of 10^{-4} M KI) were then repeated using the "activated" Cu$_2$O, exhibiting a substantial iodide uptake after only 12 h. As a consequence, all the further adsorption experiments were performed using commercial Cu$_2$O powder previously treated in HClO$_4$ medium.

3.2. Adsorption Isotherm for I$^-$ on Cu$_2$O as a Function of pH. The iodide uptake was studied at various pH values on activated Cu$_2$O. Results of these experiments are shown in Figure 2. Iodide uptake takes place in the whole range of pH values studied here, i.e., between 6.5 and 9.5. The uptake efficiency was found to decrease by decreasing pH as expected for an anion sorption isotherm, in agreement with previous work.[11] The shape of this isotherm is apparently fitted with two linear evolutions with different slopes for pH values between pH 6.7 and 7.4 and between 7.4 and 9.5, with a saturation observed for pH values lower than 6.7. Such data suggest a nonunique mechanism for I$^-$ sorption on Cu$_2$O.

Table 2. Evolution of pH and Iodide Uptake with Acid and Base Addition (1 μmol) for Selected Suspensions of Iodide[a]

initial equilibrium data			final equilibrium data	
pH	fraction of iodide consumed	added ion	pH	fraction of iodide consumed
6.70	0.80	OH$^-$	7.20	0.56
7.75	0.43	OH$^-$	8.75	0.24
8.05	0.38	OH$^-$	9.10	0.19
9.35	0.18	H$^+$	8.10	0.34
8.10	0.34	H$^+$	7.65	0.41
7.70	0.43	H$^+$	6.85	0.75

[a] Experimental conditions: $[KI]_0 = 10^{-4}$ M (in 0.1 M NaClO$_4$), 1.5 g of Cu$_2$O in 30 mL solution.

Since equilibrium data were intended, evolution of both the iodide uptake and pH was measured as a function of time, to estimate the time necessary to reach the equilibrium. Experiment times ranging from a few minutes to 90 days were applied. During the first days, and especially the first one, the changes were significant, but the variations during the following 3 months were close to the experimental errors of the analytical method. It was thus estimated that equilibrium was achieved within 5 days.

Finally, it was checked that the isotherm presented in Figure 2 was fully reversible. Typical results are shown in Table 2 where several equilibrium states were deliberately disturbed by addition of either acid or base in the medium and I$^-$ concentration was checked after reaching a new equilibrium state. As expected, the iodide uptake was decreasing when pH was rising (first three lines) and increasing in the presence of additional protons (three last lines). But most importantly, the same fraction of iodide was always sorbed at a given pH, whatever the way used to reach this pH. This demonstrates the reversible character of the uptake phenomenon.

3.3. Sorption Mechanisms. This adsorption isotherm is mainly divided in two parts so that it cannot be rationalized by considering only a unique mechanism, contrary to what was previously proposed by Haq et al.[11] Indeed, in our study, we took into account the influence of pH, not only on the amount of adsorbed species but also on the stability and surface state of Cu$_2$O. This allows distinguishing different cases as a function of the pH range, according to the Pourbaix diagram for copper oxides:[22]

For high pH values, Cu$_2$O is oxidized into Cu(OH)$_2$ or CuO, as further confirmed by XPS analysis. At this "+2" redox state, copper compounds do not exhibit affinity for iodide and its uptake is predicted to be negligible. This was ascertained by both experiments on Cu(OH)$_2$ and CuO solutions, where no I$^-$ accumulation was observed.

For low pH values, Cu$_2$O is partially dissolved and Cu$^+$ species are released in solution. In the presence of iodide, thermodynamic calculations predict the possible formation of CuI precipitates. In the absence of any complexing ligand for Cu$^+$, this leaching process results in the disproportionation of Cu$^+$ to give corresponding amounts of metallic copper (Cu^0) and Cu^{2+}. This was checked by monitoring solution phase Cu^{2+} species upon addition of protons to an aqueous suspension of Cu$_2$O.[17]

For intermediate pH values, Cu$_2$O is stable and contains surface hydroxyl groups able to react with solution species and to undergo adsorption processes. This situation corresponds to what was observed by Haq et al.[11] and

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attributed to I$^-$ adsorption on Cu$_2$O via the formation of a surface complex.

It appears therefore that two mechanisms can lead to iodide uptake by Cu$_2$O, iodide ions being either *precipitated* as CuI or simply *adsorbed* on Cu$_2$O surface. Further evidence will be given hereafter for both cases.

Formation of CuI. Let us first consider the case of Cu$_2$O in acidic medium which leads to the leaching of transient Cu$^+$ species from cuprite surfaces into solution. In the absence of iodide, Cu$_2$O is dissolved according to eqs 1 and 2

$$Cu_2O_{(S)} + 2H^+ \rightarrow 2Cu^+ + H_2O \qquad (1)$$

$$2Cu^+ \rightarrow Cu^0 + Cu^{2+} \qquad (2)$$
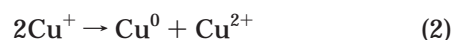
where subscript (S) refers to the solid phase, leading to the following total reaction:

$$Cu_2O_{(S)} + 2H^+ \rightarrow Cu^0 + Cu^{2+} + H_2O \qquad (3)$$
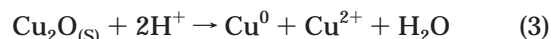
In the presence of iodide, disproportionation of Cu$^+$ species (eq 2) is prevented by stabilizing Cu(I) in the form of a solid precipitate, CuI (eq 4), which leads to an overall reaction for the action of I$^-$ on Cu$_2$O in acidic medium described by eq 5

$$Cu^+ + I^- \rightarrow CuI_{(S)} \qquad (4)$$

$$Cu_2O_{(S)} + 2H^+ + 2I^- \rightarrow 2CuI_{(S)} + H_2O \qquad (5)$$
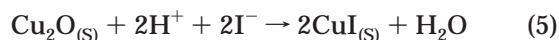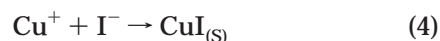
which is characterized by an equilibrium constant of 7.9 $\times 10^{-6}$. Equation 5 indicates that the amount of precipitated CuI is pH-dependent. The theoretical fraction of precipitated iodide, f_{ppt}, can be described by eq 6

$$f_{ppt} = 1 - 10^{(pH - 7.5)} \quad \text{for} \quad pH \leq 7.5$$

$$f_{ppt} = 0 \quad \text{for} \quad pH > 7.5 \qquad (6)$$

As will be seen below, the first part of the isotherm (Figure 3) agrees with the theoretical evolution of eq 6. For pH values lower than 6.7, however, the experimental fraction of consumed iodide is slightly above the calculated fraction. This could be due to the disproportionation of a small fraction of Cu(I), which would be not totally negligible.

To show the effect of an addition of protons on the amount of precipitated iodide, increasing quantities of acid were added to a suspension of 1 g of Cu$_2$O in 30 mL of 10^{-3} M KI, and the uptake of iodide was monitored after reaching the equilibrium. Results are shown in Table 3 (third line). Theoretical values of iodide uptake were calculated (second line) with the assumption that the entire reaction was only characterized by eq 5. In this experiment, pH was initially at 7.8 and a small uptake of iodide was observed. Then, this iodide uptake increased linearly with the amount of added protons, indicating a significant role of protons in the accumulation process. It should be mention, however, that values of the experimentally observed uptake were lower than those expected on the basis of eq 5. It appears therefore that whole Cu$^+$ species released during the attack of Cu$_2$O by protons (eq 1) did not react with iodide according to eq 4, a small portion being most probably disproportionated (eq 2). A back diffusion scanning electron micrograph of this sample (Figure 4) shows 0.2$-$0.6 μm pale (light) particles. This is indicative of the presence of CuI clusters, the presence of iodide being confirmed by energy-dispersive X-ray (EDX)
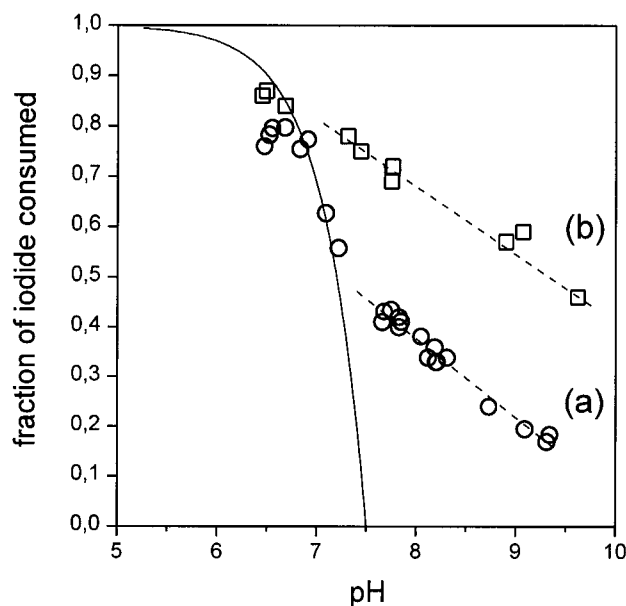
Figure 3. Iodide uptake by Cu_2O observed as a function of pH (30 mL solution, $[KI]_0 = 10^{-4}$ M). Mass of Cu_2O was (a) 1.5 g ($\bigcirc$) or (b) 3 g ($\square$). Solid line represents the theoretical fraction of precipitated iodide (eq 5 in text).

Table 3. Evolution of Iodide Uptake as a Function of the Addition of Protons (as HClO$_4$)^a

amount of added protons (μmol)	0	12	24	30	36
theoretical fraction of iodide consumed	0	0.4	0.8	1	1
experimental fraction of iodide consumed	0.07	0.30	0.63	0.77	0.93
pH at the equilibrium	7.8	6.8	6.8	6.8	6.8

^{a} Measurements were made after the medium reached the pH values of 6.8. Experimental conditions: $[KI]_0 = 10^{-3}$ M (in 0.1 M NaClO$_4$), 1.0 g of Cu_2O in 30 mL of solution.

analysis (comparison of curves C and D in Figure 4). An XPS analysis of the solid revealed only a weak intensity of the *I*3*d* line which, associated with results of SEM-EDX, allows the conclusion that CuI is not spread out on the whole Cu_2O surface but it has rather grown as microcrystallites. By comparison, no CuI clusters were observed for a Cu_2O sample treated in iodide solution at pH equal to or higher than 8; in this case, the presence of iodide was not detected by EDX.

The investigation of pH lower than 6.5 is rather complex due to the low stability of Cu_2O in acidic medium. The equilibrium is therefore reached after a long time, when most of the protons, which were initially present in solution, were consumed in the dissolution of Cu_2O (eq 3). As a consequence, sorption studies at pH < 6.5 must be performed under transient conditions, far from the equilibrium state. Electrochemistry at carbon paste electrodes modified with Cu_2O particles (Cu_2O-MCPE) was found to be an elegant way to overcome this problem. The general procedures involves a two-step procedure: (i) the accumulation at open circuit from a medium containing iodide ions at a selected pH, followed by (ii) a voltammetric detection of these previously accumulated species after transfer to an appropriate electrolyte solution. A unique advantage of modified carbon paste electrodes with respect to sorption studies is that neither the accumulation step nor the electrochemical detection affect macroscopically the solution composition.[23] Only the species located in the

close vicinity of the electrode surface (i.e., in the diffusion layer) are involved in the mass transfer reaction. Because of the very low solid-to-liquid ratio, the concentrations in solution remain unchanged. Furthermore, a constant concentration gradient can be maintained within the diffusion layer by a continuous and constant stirring of the solution during the accumulation step. Figure 5 shows cyclic voltammograms obtained after iodide accumulation from solutions at various pH values, ranging from 4.4 to 6.4. Peak currents correspond to the oxidation of CuI,[17] as ascertained by cyclic voltammetry using a CuI-modified carbon paste electrode in the same medium. Peak areas are proportional to the amount of accumulated species (I$^-$). A linear evolution was found between the voltammetric response and the proton concentration in the accumulation medium. This indicates that the amount of iodide accumulated at the electrode surface (and therefore the area of the oxidation peak, *A*) after a selected preconcentration duration can be related to pH according to eq 7

$$\log A = -0.8\text{pH} - 0.41 \tag{7}$$

in agreement with eq 5. The investigation of such acidic media was only possible by transient measurements, allowed by electrochemistry at Cu_2O-MCPE.

Further characterization was achieved by Raman spectrometry on two Cu_2O samples previously treated in 10^{-4} M KI at pH 6.1 and pH 8.1. Results are shown in Figure 6, along with spectra of pure reference compounds CuI and Cu_2O. The only signal for CuI (curve a) is pointed out around 123 cm^{-1} (fundamental TO mode[24]) and that of Cu_2O (curve b) is located at about 219 cm^{-1}. The spectrum of sample treated at pH 6.1 (curve c) reveals the presence of these signals with maxima pointed out at 121 and 218 cm^{-1}, arguing for the presence of CuI at the Cu_2O surface. Alternatively, no CuI was detected for the Cu_2O sample treated in an iodide solution at pH 8.1. At the same time, calculations predict that CuI precipitation does not take place for pH values greater than 7.5. In conclusion, at pH < 7.5, iodide sorption occurs via the formation of a CuI precipitate on the cuprite surface, while for higher pH values iodide adsorption must take place according to another mechanism. With respect to previous works,[11] this should occur by the substitution of surface hydroxyl groups by iodide ions.

Adsorption of Iodide. This mechanism is common for the accumulation of numerous anions and cations on oxides.[12,13] For the iodide/cuprite system, it can be expressed as follows:

$$(Cu_2O)\text{-OH}_{(S)} + I^- \rightarrow (Cu_2O)\text{-I}_{(S)} + OH^- \tag{8}$$
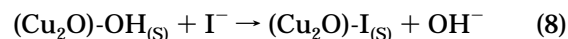
This reaction involves an increased adsorption yield by decreasing pH, which agrees well with the evolution of the iodide uptake between pH 7.4 and 9.5 (see Figures 2 and 3). The evolution of the adsorbed fraction of iodide at various pH values can be connected to the I/Cu ratio at the mineral surface, determined by XPS measurements. This is shown in Figure 7A. The corresponding XPS spectra are presented in insets B (*I*3*d*) and C (Cu2p$_{3/2}$). Despite a poor signal to noise (S/N) ratio in the spectra of iodine, the area of *I*3*d* peak can be safely measured. In Figure 7C, the Cu2p$_{3/2}$ spectrum is consistent with a Cu(I) signal for pH $\leq$ 8.1. A Cu(II) contribution appears on the spectrum at higher pH (pH 11.2 in the figure): the shoulder at the highest energies for the main peak and the satellite

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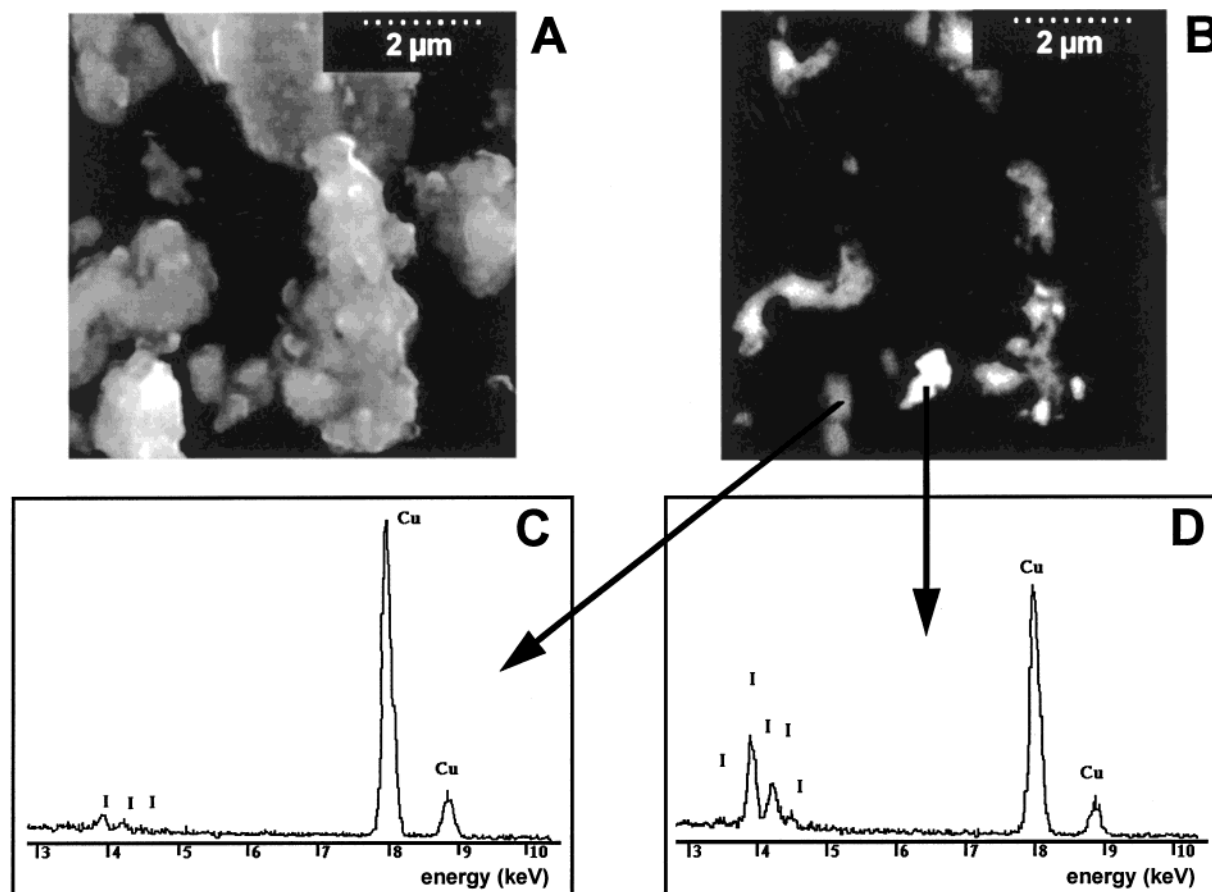
Figure 4. (A) Scanning electron micrograph and (B) back diffusion scanning electron micrograph of Cu_2O after reaction with 30 mL of 10^{-3} M iodide and 1.2×10^{-3} M $HClO_4$. Heavy elements (like iodine) appear to be pale. EDX analyses of a Cu_2O particle (C) and a CuI particle (D) gave atomic ratios, I/Cu, equal to 0.016 and 0.13, respectively.
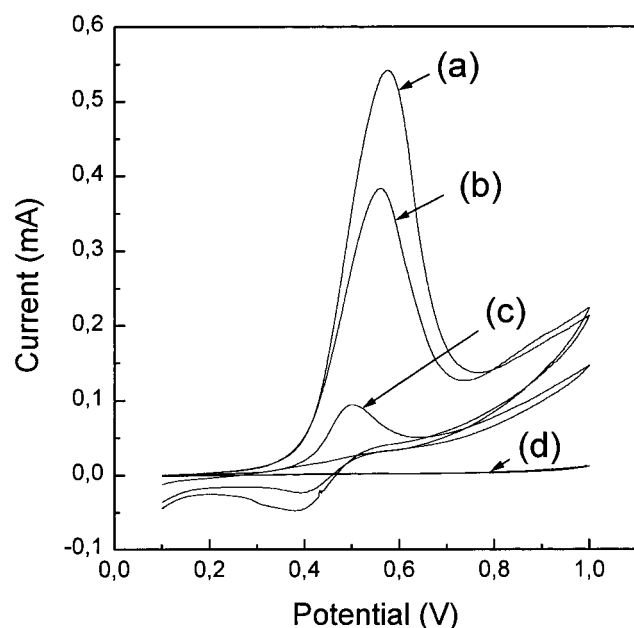

Figure 5. Cyclic voltammograms recorded using a Cu_2O-MCPE in an electrolyte solution (0.1 M $NaNO_3$) after a 30 min accumulation from 10^{-3} M KI at pH (a) 4.4, (b) 4.8, (c) 5.5, and (d) 6.4. Sweep rate was 50 mV s^{-1}.

Figure 6. Raman spectra of (a) commercial CuI powder, (b) activated Cu_2O, (c) Cu_2O after reaction with iodide at pH 6.1, and (d) Cu_2O after reaction with iodide at pH 8.1.

structure at $940-945$ eV are consistent with a cupric oxyhydroxide.[16]

A way to distinguish between precipitation and adsorption consists of the investigation of the influence of the Cu_2O mass used in sorption experiments. It should have
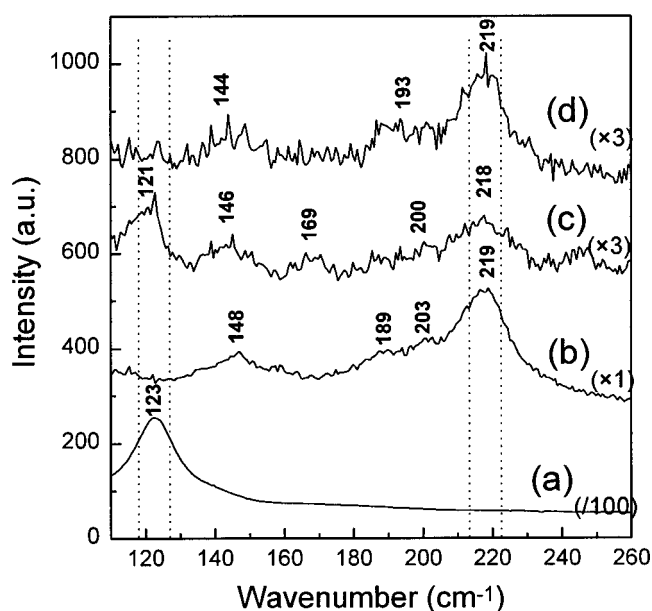
no influence on the amount of precipitated CuI (as far as the molar concentration of Cu_2O is in excess as compared to that of protons), whereas I^- adsorption would be favored when increasing the amount of Cu_2O in the suspension because it leads to more available hydroxyl groups to be exchanged for iodide species. To check this hypothesis,
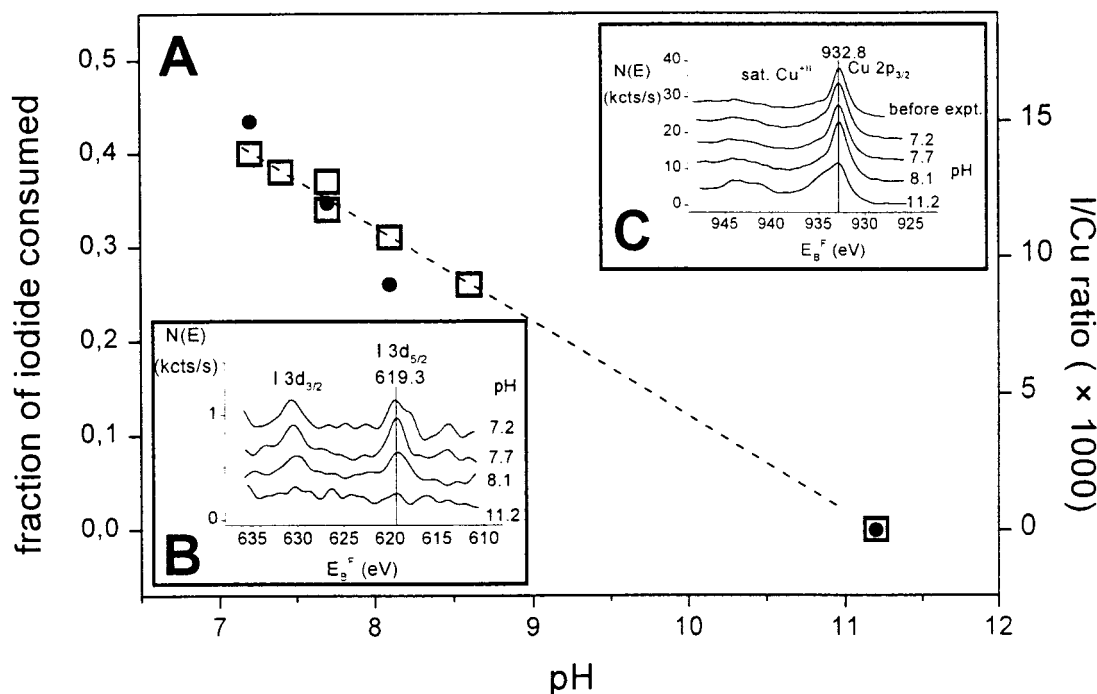
Figure 7. (A) Comparison between solution and surface analysis of iodide sorption on Cu_2O: (□) adsorbed fraction of iodide ($[KI]_0$ = 10^{-4} M, 1.5 g of Cu_2O in 30 mL) and (●) atomic I/Cu ratio and XPS spectra of (B) iodine and (C) copper samples.
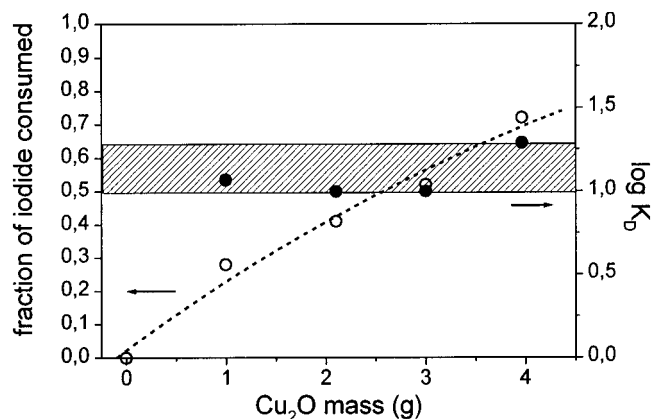

Figure 8. Evolution of iodide consumption (open circles) and K_D (solid circles) from 30 mL solutions containing KI at an initial concentration of 10^{-4} M, in contact with increasing amounts of Cu_2O (pH 7.8).

various Cu_2O quantities (1, 2, and 4 g) were added to 30 mL of a 10^{-4} M KI solution. Final pH was 8.3 ± 0.1 for the three samples. Iodide concentration was measured after equilibration, and results are represented in Figure 8 where the amount of adsorbed species is plotted versus the Cu_2O content in the suspension. Distribution coefficients, K_D, were calculated (eq 9)[13] and also presented on the same figure

$$K_D = \frac{f}{(1-f)}\frac{V}{m} \qquad (9)$$

where f represents the fraction of iodide consumed, V is the solution volume, and m is the mass of solid in the suspension. Figure 8 shows that f increases and K_D remains at the same order of magnitude when increasing the mass of Cu_2O, as expected for an adsorption mechanism.

Overall Isotherm. Finally, experiments with 3 g of Cu_2O at various pH values have also been reported in Figure 3 and compared with experiments performed with

1.5 g. The range where each of the two above-mentioned mechanisms takes place can be clearly distinguished: the uptake of iodide increases with the mass of Cu_2O in the pH range corresponding to adsorption (pH > 7.4), while being quite independent of the Cu_2O mass in the pH range allowing CuI precipitation (pH ≤ 7.4).

3.4. Effects of Composition and Redox Properties of the Medium. Beside pH, two other parameters could hinder or even prevent the uptake of iodide species on Cu_2O: the presence of competitive anions in the medium and the potential. The competitive anions can either react with Cu^+ species produced in acidic medium or compete for the adsorption on surface hydroxyl sites in alkaline medium. The potential defines the existence domains of the various chemical forms of copper: metallic Cu (E_{NHE} < −10 mV at pH 8), Cu_2O (−10 mV < E_{NHE} < 190 mV), or CuO (E_{NHE} > 190 mV at pH 8).[22] This concern is linked to the specific application as scavenger for iodide species in natural media. For example, possible French disposal sites for nuclear waste disposal in deep soil are characterized by typical groundwater properties. The pH was found to be between 7 and 8, and chloride concentrations ranged from 0.01 to 0.5 M,[25] with potentials around −250 mV.[26] With respect to possible applications to waste disposal in surface or in shallow soil, the pH range is wider and potentials are less negative.

Iodide Uptake in the Presence of Chloride Ions. First of all, stability of Cu_2O in chloride media must be checked. Calculations of the equilibrium constant for reaction between Cu_2O and Cl^- (eq 10), derived from thermodynamic data involving CuCl and Cu_2O,[27] gave a value of 2.5 × 10^{-14}. This allows the deduction of the relationship between chloride concentration in solution and pH (eq 11), and therefore prediction of the stability of Cu_2O in the presence of Cl^- at different pH.

$$Cu_2O_{(S)} + 2H^+ + 2Cl^- \rightarrow 2CuCl_{(S)} + H_2O \qquad (10)$$
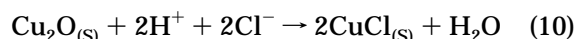
$$\log [Cl^-] = -6.2 + pH \qquad (11)$$

This indicates that for pH greater than 6.2, Cu_2O is stable

Table 4. Influence of Chloride Concentration and Cu$_2$O Mass on Iodide Uptake (consumed fraction and distribution coefficient) from 30 mL Solutions of Iodide[a]

chloride concentration (mol L^{-1})	0	1×10^{-3}	1×10^{-2}	5×10^{-2}	1×10^{-1}
fraction of iodide consumed by 1 g of Cu$_2$O	0.30	0.26	0.21	0.11	0.10
log K_D (mL g^{-1}), for 1 g of Cu$_2$O	1.1	1.0	0.9	0.6	0.5
fraction of iodide consumed by 3 g of Cu$_2$O	0.52	n.e.	n.e.	0.37	n.e.
log K_D (mL g^{-1}), for 3 g of Cu$_2$O	1.0	n.e.	n.e.	0.8	n.e.

[a] Initial iodide concentration: 10^{-4} M. n.e., *n*o *e*xperiment was performed in the conditions described in the table.

in the presence of chloride at concentrations as high as 1 M. Thus, Cu$_2$O is expected to be unaffected by chloride species in most of continental waters.

In more extreme conditions, where pH and chloride concentration would allow the formation of CuCl (i.e., upon the release of Cu$^+$ from the acidic degradation of Cu$_2$O, eq 1), this would not prevent the trapping iodide since CuI is more stable than CuCl, resulting in the following reaction (eq 12)

$$CuCl_{(S)} + I^- \rightarrow CuI_{(S)} + Cl^- \tag{12}$$
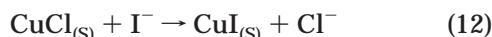
with a ratio [Cl$^-$]/[I$^-$] = $10^{5.3}$ at the equilibrium. Thus, the uptake of iodide by Cu$_2$O according to the precipitation mechanism would not be hindered by the presence of chloride providing [Cl$^-$] does not exceed that of [I$^-$] by more than 5 orders of magnitude.

On the other hand, adsorption of iodide by surface complexation of Cu$_2$O could be hindered or even prevented by the presence of interfering ions.[7] The chemical properties of chloride toward Cu(I) are similar enough to those of iodide to allow a possible competition for the available sites. This was checked by carrying out competitive experiments in conditions leading to the adsorption process (i.e., in alkaline medium). Results are presented in Table 4 for several Cu$_2$O masses and various chloride concentrations. They show that the iodide uptake efficiency decreases with rising the chloride concentration but always exists even for a 1000-fold excess of chloride over iodide. It can be also seen that, with pH around 8.7 ± 0.4, the fraction of consumed iodide increases with Cu$_2$O mass, whereas K_D varies lightly. Thus, iodide uptake at a given pH can be tuned by varying both these parameters: Cu$_2$O mass and Cl$^-$ concentration.

Effect of Reducing Potentials on Iodide Uptake. By use of Nernst's law applied to the Cu$^+$/Cu couple and solubility product of CuI,[27,28] it can be calculated that CuI is in equilibrium with 10^{-4} M I$^-$ at a potential of +50 mV. Thus, it is deduced that the uptake of iodide (for an initial concentration of 10^{-4} M) by Cu(I) compounds would not take place at more negative potentials. This is true for iodide ions precipitated as CuI. For adsorbed iodide species, however, the characteristics of the Cu$_2$O surface are expected to be different from those of free Cu(I), and the reduction of Cu(I) bound to iodide, at the surface of a Cu(I) containing solid such Cu$_2$O could require a lower potential than that corresponding to the reduction of bulk CuI. On the other hand, Cu$_2$O reduction would prevent a subsequent iodide uptake (at pH 8, Cu$_2$O is reduced into metallic copper below −10 mV[22]) since metallic copper does not adsorb iodide species. This was ascertained by monitoring the concentration of iodide in solution (50 mL, 8×10^{-4} M initial concentration) in the presence of a

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(26) Gras, J. M. Report EDF−HT-40/96/002/A, Electricité de France, Restricted diffusion, 1996.

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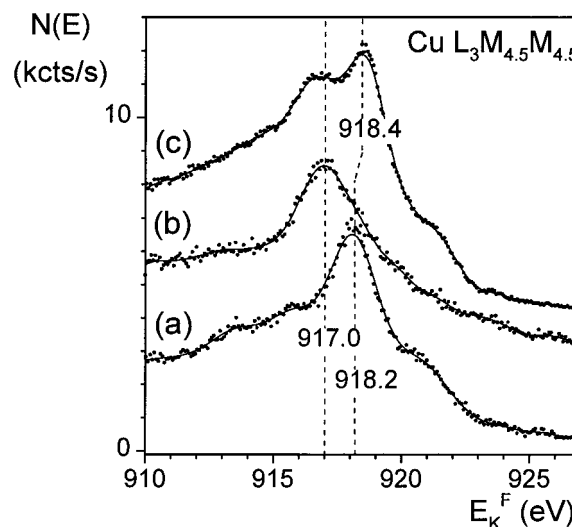
Figure 9. Cu L$_3$M$_{4.5}$M$_{4.5}$ Auger line produced by X-ray (Mg Kα) experiments on (a) copper after etching by acid, (b) "activated" Cu$_2$O, and (c) Cu$_2$O after reaction with NaBH$_4$.

reducing agent (0.1 M NaBH$_4$): the iodide concentration was found to remain constant upon the addition of 1 g of metallic copper. When air was allowed to bubble in the solution, to rase the potential toward more anodic values, iodide concentration was found to decrease as a result of its uptake by oxidized copper (namely Cu$_2$O).

Effect of Reducing Potentials on the Stability of Cu$_2$O. Since metallic copper cannot sorb iodide, experiments were performed to study the effect of two strong reducing agents (H$_2$ and NaBH$_4$) on Cu$_2$O. Indeed, the reduction of this copper oxide into metallic copper would be a limiting factor with respect to the use of Cu$_2$O as a scavenger in a barrier for iodide species in deep geological sites.

The first experiment consisted in flowing hydrogen in a suspension of Cu$_2$O (see details in the Experimental Section). A linear decrease of the pressure was observed, 40 Torr for the experiment at 70 °C or 60 Torr at 84 °C, after 200 min of stirring. We assumed that this consumption indicates a reduction of Cu$_2$O, whereas its slow rate did not allow evidence of metallic copper phase in the sample.

NaBH$_4$ was then used to achieve a more quantitative reduction of Cu$_2$O. After reaction, Cu L$_3$M$_{4.5}$M$_{4.5}$ Auger spectra induced by X-rays were recorded on the solid phase (Figure 9, curve c). For comparison purposes, the spectrum of pure copper powder, cleaned with HClO$_4$, is also represented in Figure 9 (curve a). The main peak is pointed out at a kinetic energy of 918.2 eV. The metallic copper spectrum was in good agreement with that of previous published data,[15] indicating that the sample has not been oxidized during the transfer to the measurement chamber. It must be noticed that such an experiment performed without great care toward the oxidation by air led to the formation of a thick Cu$_2$O overlayer onto copper, preventing the detection of Cu^0 by XPS.[13] The spectrum of Cu$_2$O is also presented in Figure 9 (curve b) where a ca. 1 eV

shift of the Auger line maximum is observed. The spectrum of Cu_2O after reaction with $NaBH_4$ presents two peaks, at binding energies close to those of Cu^0 and Cu_2O. It is thus concluded from these surface analyses that Cu_2O was only partially reduced into copper by $NaBH_4$, confirming that the use of Cu_2O as an adsorbent for iodide species is rather limited in reducing media.

Effect of Oxidizing Potentials. Under oxidizing conditions, Cu_2O is likely to transform into CuO or Cu-$(OH)_2$.[22] These compounds are expected to be unable to sorb iodide, because Cu(II) species exhibits a weak affinity for iodide species. This was demonstrated experimentally by suspending 0.5 g of CuO in a solution of 20 mL of 10^{-4} M KI stirred in the presence of CuO or $Cu(OH)_2$ where no significant decrease in the iodide concentration was observed after 12 h. The low affinity of Cu(II)-containing compounds for iodide was also related by other published data.[1,7,11]

4. Conclusions

Cu_2O was found to be an efficient compound for the uptake of iodide ions from aqueous solutions, depending on pH, potential, and presence of chloride species.

The uptake of iodide ions takes place when contacting Cu_2O in the pH range corresponding to the stability of this solid (6.5–9.5). For acidic solutions, surface analysis showed that iodide is trapped as CuI, according to thermodynamic calculations. In alkaline solutions, the sorption phenomenon has been explained by a substitution of surface hydroxyl groups of Cu_2O by iodide ions. In the presence of chloride ions, the uptake of iodide still took place, whereas the iodide concentration remaining in solution increased. Therefore, the iodide uptake by Cu_2O can be stated to be selective. The ability for copper to adsorb iodide from aqueous solutions is limited to the range of potentials keeping Cu_2O stable, where it was not reduced into metallic copper or oxidized into CuO. The application of these findings to environmental problems indicates that Cu_2O could not act as an efficient scavenger for iodide ions released by radioactive waste containers in natural underground environments, since the potentials induced by these media are very cathodic. However it could be useful in a less-reducing medium, as would be the case if an external oxic intrusion takes place in the disposal sites. This study also indicates a possible uptake of iodide from surface waters by copper(I) oxides available in the environment (copper pipes, copper minerals, etc.).