

# Uptake of Iodide by a Mixture of Metallic Copper and Cupric Compounds

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Ability of copper/cupric compound mixtures to remove iodide from solution was investigated to predict sorption of radioactive iodine in the environment and to assess their use in a nuclear reprocessing method. Thermodynamic calculations were performed to study the stability of such mixtures in solution and to obtain equilibrium constants of  $\text{Cu(0)/Cu(II)/I}^-$  and  $\text{Cu(0)/Cu(II)/Cl}^-$  systems. Both calculations and experimental results showed that a  $\text{Cu(0)/Cu}_3(\text{OH})_2(\text{CO}_3)_2$  (azurite) mixture selectively uptakes iodide ions (initial concentrations:  $10^{-2}$  and  $10^{-1}$  M) in the presence of  $10^{-1}$  M chloride ions. Reaction of iodide with copper powder and azurite crystal or copper plate and azurite powder have also been investigated, leading to precipitation of  $\text{CuI}$  onto massive copper phase. The different solids were separately analyzed by XPS and MEB-EDX, giving some insight in the uptake mechanism. It is proposed that soluble copper released by the cupric compound is reduced at the surface of metallic copper, leading to a preferential precipitation of  $\text{CuI}$  on copper surface.

## Introduction

Environmental contaminants harmful to the health of present and future generations involve nuclear fission products as iodine radioisotopes.  $^{129}\text{I}$  is potentially one of the more mobile products because of its long half-life ( $t_{1/2} = 1.7 \times 10^7$  yr) and its tendency to go into solution as an anion that is not retarded with silicate minerals. The specific activity of these iodine radioisotopes is their ability to concentrate in the thyroid and cause cancers (1). The biosphere contamination with radioiodine may have numerous sources such as nuclear power plants (2), reprocessing plants (2), waste disposal (2), atmospheric explosions (2), accidents (1), and nuclear fuel waste geological disposal (3, 4). Thus, predicting sorption and remobilization of iodine in environment is useful and requires explicit interactions between iodine and natural or artificial materials of the environment on contact with surface waters and groundwaters.

Numerous studies dealt with materials that could form a barrier surrounding the waste containers in the vault to prevent iodide from reaching the biosphere. The ability of compounds of Bi (5), Pb (6, 7), Hg (8–10), Ag (11, 12), and Cu (8, 9, 13–15) to form sparingly soluble phases with iodide have been documented. With copper, iodide uptake can only take place with cuprous compounds because cupric ones do not interact with iodide ions (13, 14). Thus, iodide sorption

experiments were carried out on  $\text{Cu}_2\text{O}$  (13–15) and  $\text{Cu}_2\text{S}$  (9), and a significant decrease of iodide concentration is observed for initial concentrations less or equal to  $10^{-4}$  M.

Bringing into contact iodide with  $\text{Cu(I)}$  can be achieved by using a mixture of metallic copper with insoluble  $\text{Cu(II)}$  compounds, which amphoterize and lead to  $\text{Cu(I)}$ . This is the first published study dealing with the ability of such a system to remove iodide from solution. This mixture is commonly found in the environment since a copper surface is usually oxidized, as observed on water pipes by Adeloju and Duan (16, 17). Moreover, current reprocessing methods to remove radioiodine from aqueous nuclear waste involve mercury (18), lead (18), or silver (18, 19); thus, it is useful to assess new materials as inorganic anion exchangers (20) or copper compounds, less toxic or less expensive than the current ones and compatible with the preferred waste immobilization options since they do not cause long-term problems within a underground repository (20).

For a  $\text{Cu/Cu(II)}$  mixture, we focused on copper carbonates (malachite and azurite) because of their large occurrence as corrosion products of copper in freshwater (16).

This paper presents the results of thermodynamic calculations on reactions between a  $\text{Cu/Cu(II)}$  mixture and iodide ions. Then iodide concentration in the presence of a copper/azurite system was experimentally monitored, and the influence of chloride ions was observed. Analysis of solids by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) allowed us to have a better insight in the mechanism of iodide uptake and to show that iodide is preferentially precipitated on a copper surface.

## Materials and Methods

For all experiments, the chemicals KI (Aldrich), KCl (Rhone Poulenc), and  $\text{AgNO}_3$  (Cerac) were of analytical grade. Solutions were prepared with deionized water. The used copper metal was Cerac powder (grain size  $100\text{ }\mu\text{m}$ , specific area measured by BET (Kr):  $0.18\text{ m}^2/\text{g}$ ) or mechanically polished polycrystalline copper plates purchased from Goodfellow (purity 99.5%, dimensions:  $12.7 \times 12.7 \times 0.5\text{ mm}$ ). The azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ) was obtained from Rhone Poulenc (grain size  $10\text{ }\mu\text{m}$ , specific area:  $0.33\text{ m}^2/\text{g}$ ) or was a natural crystal, embedded in epoxy resin, with a polished face of  $5 \times 7\text{ mm}$ . Freshly precipitated  $\text{Cu(OH)}_2$  was prepared by mixing copper nitrate and aqueous sodium hydroxide.

The analysis of the aqueous phase was performed after centrifuging (for experiments with powders) or after sedimentation (for experiments where a massive compound was present). Iodide concentration was determined by UV spectrometry (Beckman DU 7500) at 228 nm after dilution of test parts. For a simultaneous determination of iodide and chloride concentration, the potential at an Ag electrode was recorded during  $\text{Ag}^+$  addition, as described by Charlot (21).

The surface analysis of solid phase was performed after washing with deionized water and drying at room temperature. The XPS spectra were obtained using an electron energy analyzer (VSW, MCD 5000) and an unmonochromatized magnesium X-ray source (1253.6 eV). The apparatus and the spectra processing were extensively presented in a previous paper (22). 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. The binding energies were corrected on the basis of the standard value of C1s from contaminants at 284.6 eV (23). The samples were also examined by SEM (Philips XL30)

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TABLE 1. Experimental Conditions for Iodide Sorption on Cu(0)/Cu(II) Mixtures<sup>a</sup>

experiment	copper	azurite	solution	remarks
CuAz-1	2 g of powder	0.8 g of powder	30 mL of [KI] <sub>0</sub> 10 <sup>-1</sup> M	mixtures of two powders
CuAz-1Cl			30 mL of [KI] <sub>0</sub> 10 <sup>-1</sup> M and [KCl] 10 <sup>-1</sup> M	
CuAz-2			30 mL of [KI] <sub>0</sub> 10 <sup>-2</sup> M	
CuAz-2Cl			30 mL of [KI] <sub>0</sub> 10 <sup>-2</sup> M and [KCl] 10 <sup>-1</sup> M	
(Cu)Az	one plate of 3.2 cm <sup>2</sup>	0.8 g of powder	70 mL of [KI] <sub>0</sub> 10 <sup>-2</sup> M	mixtures with a massive compound
Cu(Az)	2 g of powder	natural crystal of 0.35 cm <sup>2</sup>		

<sup>a</sup> The temperature was kept around 20 °C in all experiments.

TABLE 2. Thermodynamical Constants of Equilibria Involving Cu(0)/Cu(II) Mixture

equilibrium	constant
2H <sub>2</sub> O + Cu <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ↓ + 3Cu <sup>0</sup> + 6I <sup>-</sup> = 6CuI↓ + 2HCO <sub>3</sub> <sup>-</sup> + 4OH <sup>-</sup>	10 <sup>1.5</sup>
H <sub>2</sub> O + Cu <sub>2</sub> (OH) <sub>2</sub> (CO <sub>3</sub> )↓ + 2Cu <sup>0</sup> + 4I <sup>-</sup> = 4CuI↓ + HCO <sub>3</sub> <sup>-</sup> + 3OH <sup>-</sup>	10 <sup>-0.7</sup>
2H <sub>2</sub> O + Cu <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ↓ + 3Cu <sup>0</sup> + 6Cl <sup>-</sup> = 6CuCl↓ + 2HCO <sub>3</sub> <sup>-</sup> + 4OH <sup>-</sup>	10 <sup>-30.1</sup>
H <sub>2</sub> O + Cu <sub>2</sub> (OH) <sub>2</sub> (CO <sub>3</sub> )↓ + 2Cu <sup>0</sup> + 4Cl <sup>-</sup> = 4CuCl↓ + HCO <sub>3</sub> <sup>-</sup> + 3OH <sup>-</sup>	10 <sup>-24.3</sup>

TABLE 3. Calculated Halides Concentrations in Presence of Cu(0)/Cu(II) Mixture with Azurite or Malachite as Cu(II) Compounds ([HCO<sub>3</sub><sup>-</sup>] = 10<sup>-3</sup> M, pH 8)

solids	halogen in solution	concn at the equilibrium
copper + azurite	iodide	[I <sup>-</sup> ] = 10 <sup>-5.2</sup> M
copper + malachite	iodide	[I <sup>-</sup> ] = 10 <sup>-5.1</sup> M
copper + azurite	chloride	[Cl <sup>-</sup> ] = 1 M
copper + malachite	chloride	[Cl <sup>-</sup> ] = 6 M

coupled with an EDX (KEVEX Sigma). Analysis of powders was performed by X-ray diffraction (XRD) using CuKα radiation ( $\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$ ). Compounds were identified by using the software Difrac AT 3.2 with the JCPDF database.

The conditions of experiments carried out on iodide sorption with a copper/azurite mixture are described in Table 1. Experiments on mixtures of the two powders were carried out at  $20 \pm 3 \text{ °C}$  in stoppered polyethylene Nalgene 35-mL centrifuge tubes, filled with 30 mL of solution. When massive compounds were used, solutions contained in a reactor were deaerated by bubbling nitrogen throughout the experiment. Six samples were prepared always involving a mixture of copper/azurite and a solution of iodide. The first four experiments (CuAz-1, CuAz-1Cl, CuAz-2, CuAz-2Cl) were carried out on a mixture of powders; the difference between them came from initial iodide concentration (10<sup>-1</sup> M for CuAz-1 and CuAz-1Cl, 10<sup>-2</sup> M for CuAz-2 and CuAz-2Cl) and chloride presence in CuAz-1Cl and CuAz-2Cl. The last two experiments involved a massive solid (copper in (Cu)Az, azurite in Cu(Az)) with the other component of the mixture being a powder. The solution was always 10<sup>-2</sup> M KI.

## Results and Discussion

**Sorption of Iodide on Powders.** *Thermodynamic Calculations.* For reactions involving high concentrations and well-defined solid phases, thermodynamic calculations allow the selection of chemical systems that have the desired reactivity. Thus, from stability constants of copper iodide, malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>), azurite, and Cu<sup>+</sup> in water (24, 25), the chemical behavior of copper/azurite and copper/malachite toward iodide and chloride ions can be foreseen. Only azurite

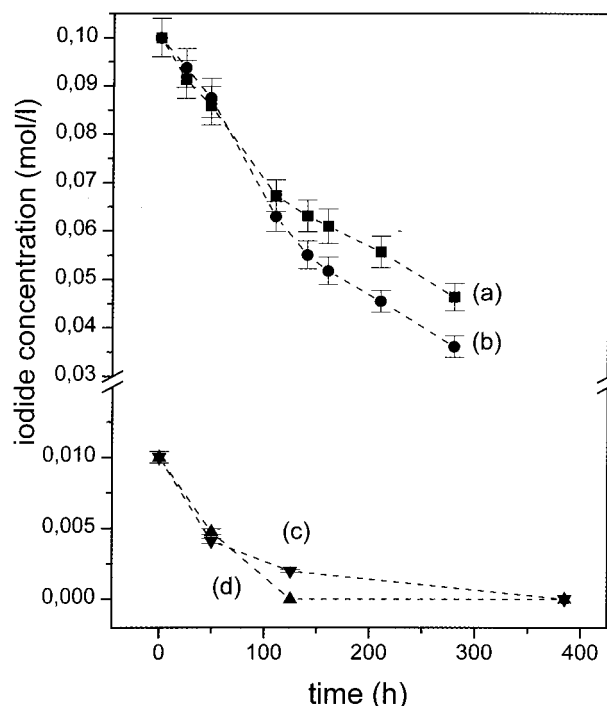


FIGURE 1. Concentration in solution of iodide in contact with copper/azurite mixture. Initial I<sup>-</sup> concentration was 10<sup>-1</sup> M for (a) and (b) and 10<sup>-2</sup> M for (c) and (d). Chloride (10<sup>-1</sup> M) was present in solution for (b) and (c).

and malachite were taken into account because these are the most common copper carbonate in the environment (26, 27).

Calculated equilibrium constants for reactions of halides (I<sup>-</sup> or Cl<sup>-</sup>) on a copper/carbonate copper system (azurite or malachite) in order to produce cuprous halogenides (CuI or CuCl) are presented in Table 2. It can be noticed that equilibrium constants for copper/azurite or copper/malachite mixtures are very similar, but there is a large gap between constants of equilibria involving iodide and chloride, leading to different behaviors of mixtures toward iodide and chloride. Identical calculations could be done with other Cu(II) compounds such as oxide or sulfate.

Since calculated constants are characterizing equilibria with different stoichiometric coefficients, the results of these equilibria are difficult to represent. Then, it is useful to apply them for a medium where only halide concentrations are free in a solution representative of groundwaters, i.e., pH 8, [HCO<sub>3</sub><sup>-</sup>] = 10<sup>-3</sup> M, [Cl<sup>-</sup>] = 10<sup>-1</sup> M (28). From the results shown in Table 3, it can be seen that both the Cu/Cu(II) carbonate mixtures make iodide concentrations decreasing below 10<sup>-5</sup> M. Calculated chloride concentrations in equilibrium with both mixtures are above natural concentrations; therefore, these systems do not react with chloride ions. Thus,

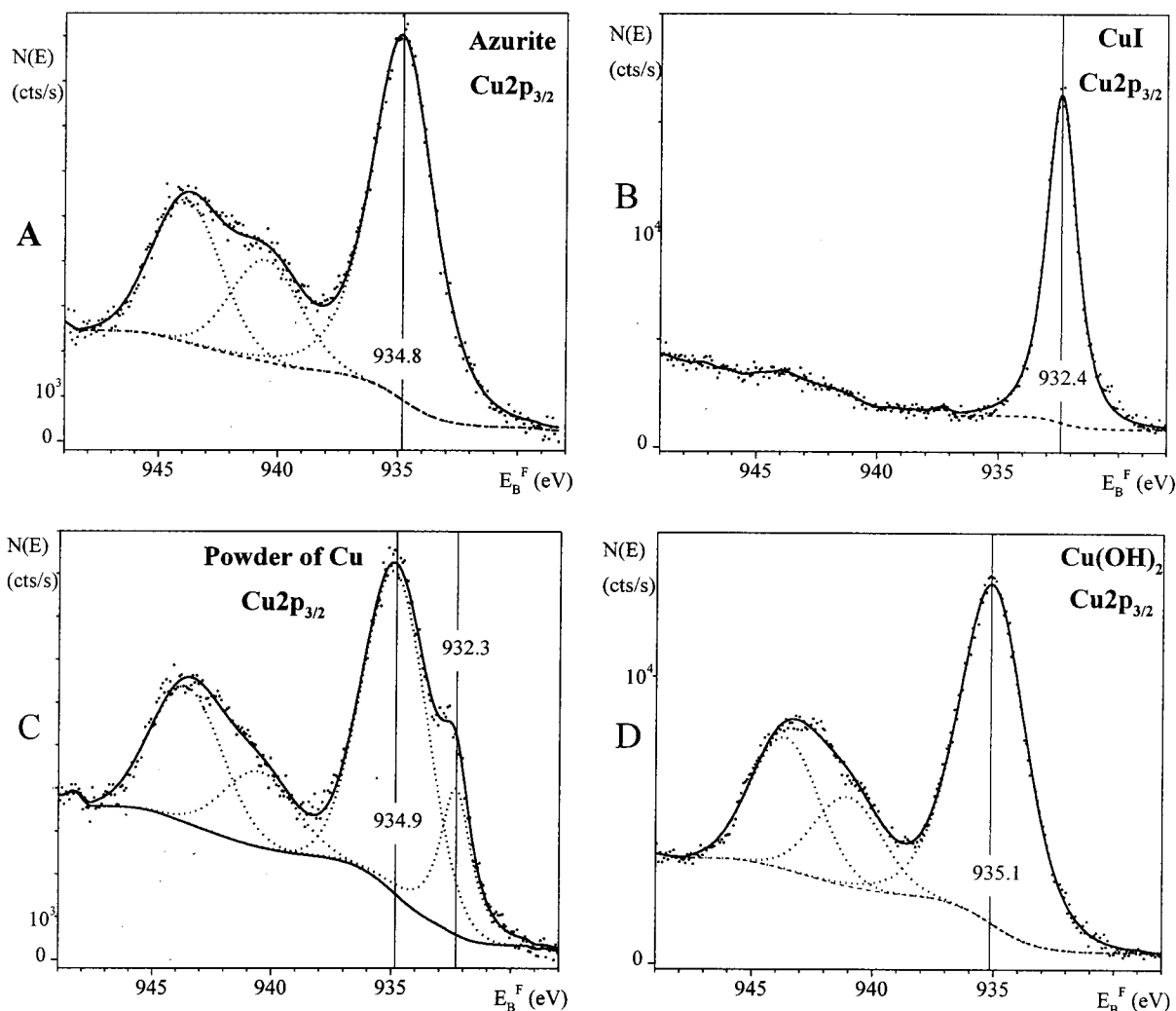


FIGURE 2. XPS spectra of reference samples ( $\text{Cu}2p_{3/2}$  line). The surface of the copper particles (panel D) was oxidized as evidenced by a satellite structure (940–946 eV) and by the binding energy of ca. 935 eV for the  $\text{Cu}2p_{3/2}$  line, indicative of  $\text{Cu(II)}$  compounds.

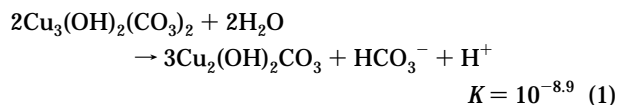
TABLE 4. ESCA Binding Energies ( $\pm 0.2$  eV) of Some Relevant Copper Compounds

species	$\text{Cu}2p_{3/2}$ (eV)	ref
Cu	932.2–933.1	29
	932.6	this work
$\text{Cu}_2\text{O}$	932.0–932.7	29
	932.8	this work
CuI	932.3	30
	932.4	this work
$\text{Cu(OH)}_2$	934.4–935.1	29
	935.1	this work
azurite	934.8	this work

these mixtures selectively uptake iodide ions, even if a high chloride concentration is present.

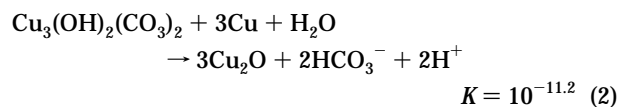
As the results obtained with azurite or malachite as  $\text{Cu(II)}$  compounds are very close, the experiments described here have been carried out only with azurite. Nevertheless, stability of this mixture must be studied. Indeed, two phenomena could lead to a modification of the reagents.

First, azurite can lose carbonate groups and be transformed in malachite, according to



If a constant pH of 8 is fixed, the calculation of equilibrium concentration of  $\text{HCO}_3^-$  would give  $10^{-0.9}$  M. Therefore, for a natural concentration of  $10^{-3}$  M  $\text{HCO}_3^-$ , reaction 1 should take place, up to the total transformation of azurite. This thermodynamical result shows that the system whose characteristics toward  $\text{I}^-$  ions are described here should evolve toward a copper–malachite mixture. This latter system leads to iodide uptake too, as shown by results of Table 2. Thus, the results of this study can be extrapolated to the copper/malachite system.

Another reaction that can modify the initial system is the amphoterization of the reagents in  $\text{Cu}_2\text{O}$ , according to



For a constant pH of 8, the calculated equilibrium  $\text{HCO}_3^-$  concentration would be  $10^{2.4}$  M. So, this reaction should take place up to the total disappearance of the reagents but is not really observed in natural waters (16, 26), nor in the experiments described afterward. It is worth noting that whatever the origin of the  $\text{Cu(0)}/\text{Cu(II)}$  system, natural or artificial, its long-range stability is not absolutely necessary. Since such a system has a large anthropogenic occurrence, it can be concluded that its kinetic stability is important. Moreover, the product of reaction 2 is  $\text{Cu}_2\text{O}$ , a compound that can uptake iodide too (13–15), as specified below.

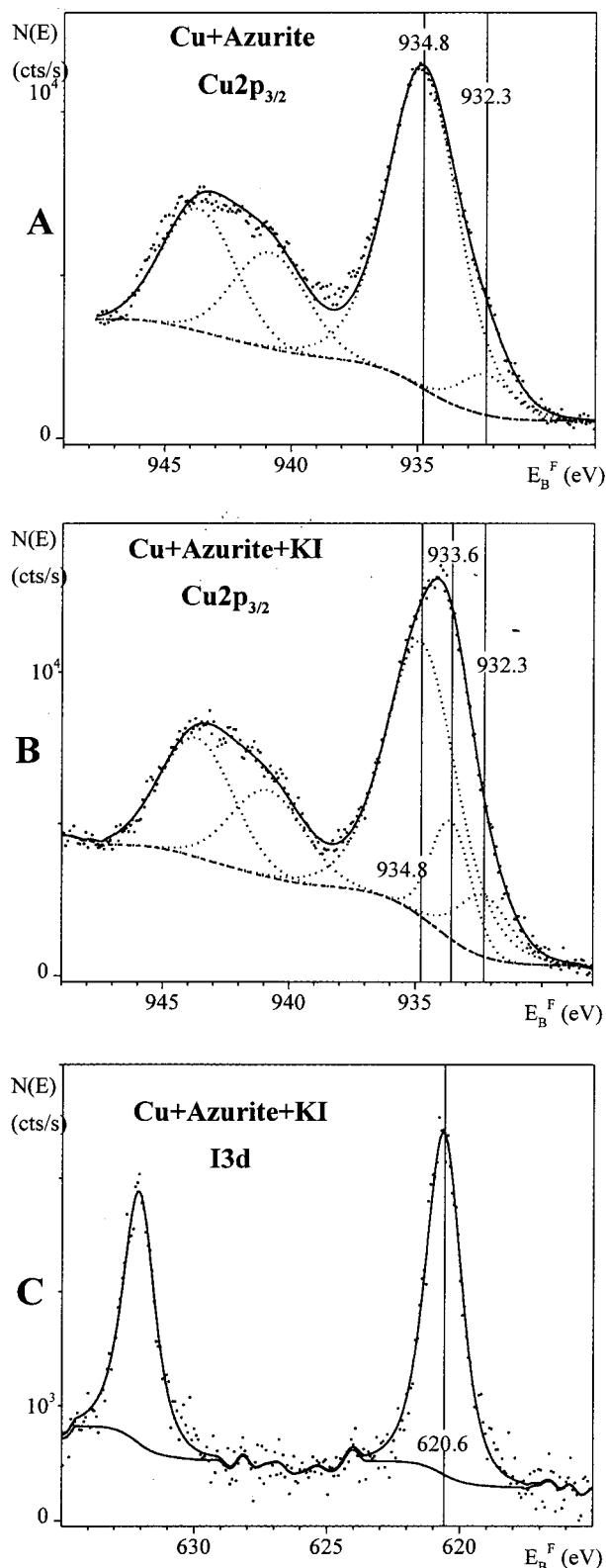


FIGURE 3. XPS spectra ( $\text{Cu}2p_{3/2}$  and  $\text{I}3d$  lines) of (panel A) blank copper/azurite mixture, (panels B and C) after 12 days in contact with iodide (experiment CuAz-1).

**Experimental Data.** Since the calculations showed that a mixture of copper/azurite is efficient and selective enough for iodide uptake, experiments could be carried out in order to verify these results and to obtain more information about the kinetics and mechanisms. We began with experiments on mixture of powders whose compositions are described in Table 1. The evolution of iodide concentration as a function

of reaction time is shown in Figure 1. For the highest initial iodide concentration, a decrease of 50% is reached after 8 days. This value was obtained more rapidly when iodide concentration was initially lower. The presence of chloride ions hardly affected iodide uptake, and we have checked that chloride concentration stayed at its initial value throughout the experiments. The pH, initially equal to  $7.0 \pm 0.5$ , was measured at the end of the experiments. It reached ca. 10 for those where  $[\text{I}^-]_0 = 10^{-1} \text{ M}$  and was between 8 and 9 for the other ones. Moreover, an XRD analysis was performed with samples where  $[\text{I}^-]_0 = 10^{-1} \text{ M}$ . From these data, the whole pattern was described by  $\text{CuI}$ , copper, and azurite. Malachite and cuprite were barely present, which indicates that reactions 1 and 2, although thermodynamically possible, do not occur in these mixtures. A slow kinetics could be the reason of this experimental observation.

Thus, all of these experimental data are consistent with reactions in Table 2. A mixture of azurite/copper can make the iodide concentration decrease to  $10^{-4} \text{ M}$ , without the competing effect of chloride species.

The iodide final concentration reached in the presence of a copper/azurite mixture is low enough for a treatment of radioactive liquid wastes whose iodine concentrations can be about  $10^{-2} \text{ M}$  (20). Indeed, copper, whose the surface is naturally oxidized in  $\text{Cu}_2\text{O}$  (13), uptakes 95% of iodide at an initial concentration of  $10^{-4} \text{ M}$  by exchange of iodide ions with hydroxyl groups present at the surface of  $\text{Cu}_2\text{O}$  (13), whereas an initial concentration of  $10^{-3} \text{ M}$  leads to the uptake of only 30%. This shows that the amount of iodide uptake is due to the presence of  $\text{Cu(II)}$  donor (i.e., azurite) since the copper alone cannot sorb such a quantity.

Iodide-bearing radioactive liquid wastes have widely variable pH, according to their origins (18, 20). The performance of the copper/azurite system, which is well suited with the final iodide concentration in solution, depends obviously on the pH. In very acidic solutions, important dissolution of azurite is expected, leading to a strong release of  $\text{Cu}^{2+}$  species. For iodide and cupric ions concentration high enough, iodide ions could readily react with  $\text{Cu}^{2+}$ , giving  $\text{CuI}$  and elemental iodine (26). This latter would be then reduced by metallic copper. However, in oxidant acidic medium, metallic copper is dissolved, and this reaction of reduction does not take place. For higher pH values, the iodide equilibrium concentration is defined by the reaction constant presented in Table 2 (first line). This concentration depends linearly on proton concentration, decreasing when pH increases.

Once iodide is trapped as  $\text{CuI}$ , this uptake is irreversible if the solution contains a iodide concentration greater than equilibrium concentration, or else precipitated cuprous iodide will redissolve until the solubility product is reached. However, since the solubility of this compound is very weak, this method is believed to be compatible with the waste immobilization options.

**XPS and SEM Studies.** Surface analysis by XPS and scanning electron microscopy have been used to further investigate the interactions between iodine and a mixture of copper and azurite.

The  $\text{Cu}2p_{3/2}$  line of reference samples are presented in Figure 2. Spectra for azurite,  $\text{CuI}$ , and the powders of  $\text{Cu}$  and  $\text{Cu(OH)}_2$  are respectively presented in Figure 2A–D. Some values of the binding energies are also compared to values previously published (29, 30) in Table 4. It is well established that the chemical shifts between  $\text{Cu(0)}$  and  $\text{Cu(I)}$  compounds are very low, making them difficult to distinguish without using the Auger line shape. Then, it appears that the binding energy of the  $\text{Cu}2p_{3/2}$  line of  $\text{CuI}$  (Figure 2B) and of  $\text{Cu(0)}$  (Figure 2C) are quoted at the same value, i.e.,  $932.3 \pm 0.2 \text{ eV}$ . However, the  $\text{Cu}2p_{3/2}$  shape of  $\text{Cu(II)}$  compounds is characterized by the presence of strong satellites around 940–



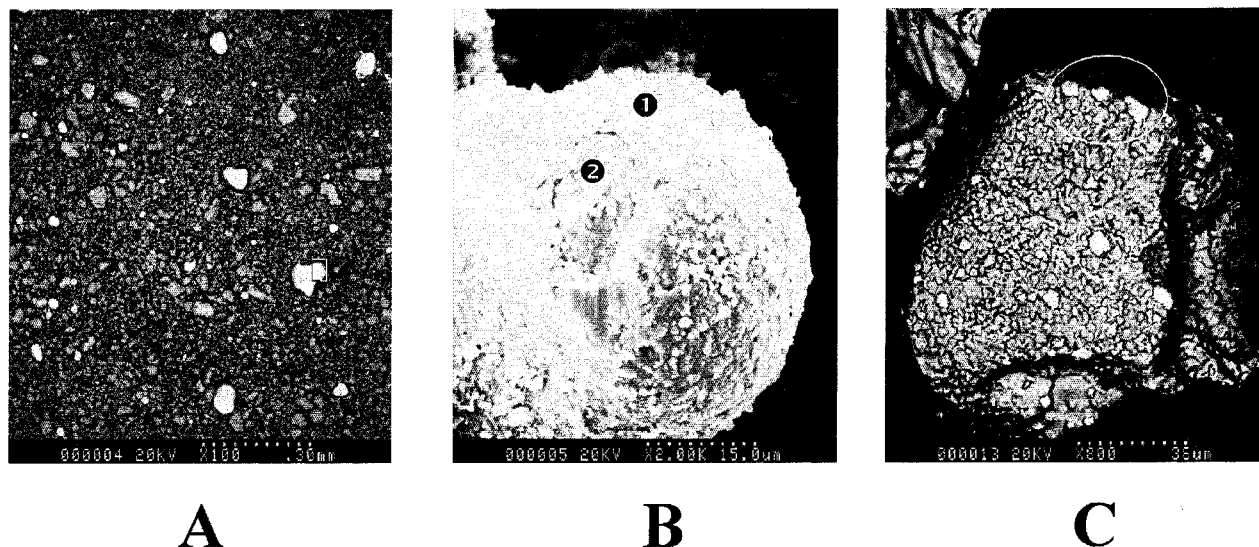


FIGURE 4. (Panels A and B) Back-diffusion scanning electron micrographs of mixture of copper/azurite powders after reaction with iodide (experiment CuAz-1). Heavy elements (like iodine) appear to be brighter. Panel B shows the framed particle in panel A in greater detail. EDX of area (1) and (2) gave following results in atomic percentage. (1) O, 29%; Cu, 50%; I, 21%; and (2) O, 33%; Cu, 63%; I, 4%. (Panel C) Micrographs of copper particle in Cu(Az) (see description of experiments in Table 1). CuI particles are indicated by circles.

945 eV and a chemical shift of about 2.5 eV. These satellites, whose origin has been extensively discussed in the literature (31–33), can be clearly observed in Figure 2, panels A, C, and D. On the surface of azurite, the C1s line presents two components at 289.2 and 284.6 eV assigned respectively to the carbonate functional groups and to the surface contamination. This last peak has been used for the correction of the charge effect. The I3d<sub>5/2</sub> line is pointed out at a binding energy of 619.4 eV consistent with the literature (30). Finally, the surface analysis of the powder of copper used in this study deserves further comments as it appears that the spectra of the Cu2p<sub>3/2</sub> line is dominated by Cu(II) features (presence of satellites and binding energy of the main peak at around 935 eV). This sample is at least partly covered by an overlayer of probably an oxyhydroxide of copper. The value of the binding energy of the Cu2p<sub>3/2</sub> main peak matches quite well with those reported on Cu(OH)<sub>2</sub> (Figure 2D).

The copper/azurite mixture after its reaction with KI 10<sup>-1</sup> M was analyzed by XPS. The Cu2p<sub>3/2</sub> spectrum of this powder, before and after its reaction with iodide, is shown in Figure 3A,B. The I3d lines (Figure 3C) are also shown. The Cu2p<sub>3/2</sub> spectra are dominated by Cu(II) compounds as attested by the presence of the satellites and by the binding energy of the main peak pointed at around 935 eV. However, the asymmetrical shape of the lines suggests the presence of Cu(0) or Cu(I) compounds. A crude deconvolution of these peaks shows in fact an increase of the component at 932.3 eV (Cu(0)) after reaction with iodide, and a peak at 933.6 eV appears. Furthermore, the presence of iodine as attested by the I3d<sub>5/2</sub> signal at 620.6 eV could be an evidence of the formation of CuI on the surface. The values of I3d<sub>5/2</sub> are 1.2 eV higher than the ones observed on the CuI reference sample. This shift could certainly be attributed to a differential charge effect that is very difficult to handle on heterogeneous samples such as a mixture of powders. It certainly means that the CuI formed is associated with Cu(0) patches. The peak at 933.6 eV, which is only present after reaction with iodide, correspond to the Cu2p<sub>3/2</sub> binding energy of CuI (932.4 eV) corrected with the differential charge effect.

Back-diffusion scanning electron micrograph of this sample (see Figure 4A) shows some particles of ca. 50 μm that appear to be brighter (light). This color is indicative of the presence of heavy elements and is certainly related to iodine. As XPS analysis showed that iodide was precipitated

in CuI, these particles are attributed to CuI. They seemed to contain the whole solid-phase iodide, since smaller particles were not been found, even if magnification was increased. If looking at greater detail (Figure 4B), it appears that these particles are not homogeneous. The EDX analysis reveals that a coating of CuI covers (oxidized or carbonated) copper particles. These data prove that cuprous iodide growth results from a surface precipitation process.

To better understand the mechanism of iodide uptake, it was useful to separate the two solid phases, i.e., copper and azurite. An experiment involving a massive solid (copper plate or azurite crystal) and a powder (azurite or copper, respectively) was carried out (see Table 1 for details). The knowledge of the function of each phase allows us to optimize this system for an industrial application and to predict where iodide will be accumulated in environmental problems.

After stirring of Cu(Az) experiment components (copper powder and azurite crystal in 70 mL of 10<sup>-2</sup> M KI) during 1 day, both phases were analyzed by XPS. Ratios of the I3d peak area/Cu2p peak area, related to iodide quantity per surface unit, were 0.03 on both experiments. If the huge difference of areas of the solids (ca. 4 × 10<sup>-5</sup> m<sup>2</sup> for azurite, 0.36 m<sup>2</sup> for copper) is considered, we are left with the conclusion that the precipitated iodide amount was larger on copper than on azurite.

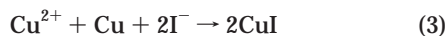
SEM micrographs for copper phase are shown in Figure 4C. On copper particles, CuI deposits (size around 5 μm) were present, as can be seen on the particle given in Figure 4C. On the azurite crystal, there are CuI particles too, but with a smaller size (less than 1 μm). They could be CuI particles trapped in defects of azurite crystal.

XPS analysis of the copper plate, after stirring of (Cu)Az experiment components (copper plate and azurite powder in 70 mL of 10<sup>-2</sup> M KI) during 7 days (duration for iodide concentration decrease equal to CuAz experiment), reveals a I/Cu ratio of 0.10. The I3d peak on azurite powder was not detected, leading to a I/Cu ratio of 0. A SEM micrograph of this plate shows that a porous overlayer was present. It consisted of square particles corresponding to CuI (cubic symmetry (34)) and trapezoidal particles assigned to azurite (monoclinic symmetry (35)). An EDX analysis of both these particles confirmed this attribution. This can be explained by the fact that azurite flakes were trapped in the CuI layer during its growth.

Both these experiments show a preferential CuI precipitation on copper. This leads us to consider the following steps in the reaction mechanism:

(a)  $\text{Cu}^{2+}$  release by azurite ( $[\text{Cu}^{2+}] = 9 \times 10^{-7} \text{ M}$  at pH 8 according to solubility product)

(b)  $\text{Cu}^{2+}$  reduction at copper surface promoted by its precipitation in the presence of iodide according to



This second step is the limiting one, so the kinetics of the global reaction is linked to the copper surface area. This is consistent with the difference in duration between experiments Cu(Az) and (Cu)Az to reach the same iodide concentration decrease (respectively, 1 and 7 days).

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