Recovery of Heavy Metals with Calcium Silicon Alloy. III. Stoichiometric Discussion on the Reduction of Copper(II) Ions

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For the reduction of Cu^{2+} ions with Ca-Si alloy in aqueous solutions, the following elementary reactions were postulated:

$$Ca^0+Cu^{2+}=Ca^{2+}+Cu^0, \quad (1)$$

$$Ca^0+2H_2O=Ca^{2+}+H_2+2OH^-, \quad (2)$$

$$Si^0+2Cu^{2+}+3H_2O=H_2SiO_3+2Cu^0+4H^+, \quad (3)$$

$$Si^0+3H_2O=H_2SiO_3+2H_2. \quad (4)$$

From these reactions, amounts of Si^{IV} species were estimated by using those of H_2 and increments of H^+ ions. Total equivalents of the reduction products showed good agreement with those of the oxidation products, indicating the validity of the elementary reactions. The remained problems of the stoichiometric disagreement and the phenomenon of pH decrease indicated in Part II could be solved by using these elementary reactions. At the beginning of the reaction, a small amount of Cu^+ ions formed. Decomposition of water occurred subsequently to the Cu^{2+} reduction. A contribution of Si^0 to the reaction became greater than that of Ca^0 at higher Cu^{2+} concentrations than *ca.* 10 matom dm^{-3}. Thus, it proved that Si^0 in the alloy exhibits a great reducing effect.

Various metal ions having high standard electrode potentials are reduced effectively with Ca-Si alloy.[1-3] In Part II,[3] discussions were made on the reduction of Cu^{2+} ions about the reaction rate and the effects of acids, salts, and other metal ions. The following phenomena have remained uninterpreted. At lower Cu^{2+} concentrations than 5 matom dm^{-3}, equivalents of Cu^{2+} ions reduced well accounted for total equivalents of Ca^{II} and Si^{IV} species dissolved in the solution, and the pH tended to increase as the reaction proceeded. On the other hand, at higher Cu^{2+} concentrations, the equivalents of Cu^{2+} ions reduced became considerably greater than the total equivalents of Ca^{II} and Si^{IV} species dissolved in the solution, and the pH decreased from 4 to 2 or lower. The objectives of the present study are to solve these problems and, at the same time, to elucidate the mechanism of the whole reaction inclusive of decomposition of water as a side reaction. To this end, potential elementary reactions were postulated basing on the observed phenomena, and stoichiometric discussions were made on the reaction products.

Experimental

One dm^3 of *ca.* 2.5—40-matom dm^{-3} Cu^{2+} solutions was prepared and the pH was adjusted to 4.0 with HCl or NaOH. The sample solution was placed in a 25 °C thermostat. Prior to a run, nitrogen was bubbled thoroughly to purge dissolved oxygen. To the solution was added 3.0 g of Ca-Si alloy powder, and nitrogen bubbling and magnetic stirring were continued. An aliquot of the solution was taken at intervals and filtered quickly under reduced pressure through a membrane filter 0.30 μm in pore size. Then, analyses were made on the filtrate. The increment of H^+ or OH^- ions was determined by titration with either *ca.* 0.01-mol dm^{-3} standard NaOH or HCl solution, respectively. Cu^+ ions were determined by colorimetry with Bathocuproinesulfonate (disodium 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonate).[4] Cu^{2+} and Ca^{2+} ions and dissolved silicate were determined in the same way as reported previously.[3] Separately, similar runs were made in a closed system to determine the volume of H_2 being collected in a graduated cylinder. The same materials were used as those in the previous report.

Results and Discussion

Postulation of Elementary Reactions. On adding Ca-Si alloy, Cu^{2+} ions are reduced effectively and recovered entirely from the solid phase as Cu^0. At the beginning of the reaction, a small amount of Cu^+ ions form. At the same time, decomposition of water occurs generating H_2. On the other hand, the alloy is oxidized to form Ca^{II}, Si^{IV} species, H^+, and OH^- ions in the solution.

It was indicated previously that, at high Cu^{2+} concentrations, equivalents of Cu^0 were greater than the total equivalents of Ca^{II} and Si^{IV} species dissolved in solution. The main causes of such disagreement are considered to be the neglect of effects of water decomposition and the possibility of existence of oxidation products (Ca^{II} and/or Si^{IV} species) also in the solid phase. For the former cause, H_2 and the increment of H^+ or OH^- ions were determined in the present study. As for the latter, their existence was not recognized in the X-ray diffraction pattern of the solid product. There is little possibility of formation of insoluble amorphous calcium silicate under the present experimental conditions of low pH (4—2 or lower). Consequently, Ca^{II} species exists entirely in the dissolved form, Ca^{2+} ions. The IR absorption spectrum of the solid products showed a broad and strong absorption band in the wave number range from *ca.* 900 to 1350 cm^{-1}. It is characteristic of amorphous silica, and was not found in the spectrum of the original alloy. It is, therefore, necessary to take into account the amount of silica present in the solid phase for the stoichiometric discussion. However, it was practically impossible to determine its amount at the time of interruption of the reaction by solid-liquid separation, since oxidation of unreacted alloy by water proceeded under the wet condition even after the separation.

Then potential elementary reactions were postulated on the basis of the observed phenomena, and are shown in Fig. 1. The elementary reactions are composed of reduction of Cu^{2+} ions and decomposition of water

$$Ca^0 + Cu^{2+} = Ca^{2+} + Cu^0 \qquad (1)$$

a a a

$$Ca^0 + 2H_2O = Ca^{2+} + H_2 + 2OH^- \qquad (2)$$

b b b 2b

$$Si^0 + 2Cu^{2+} + 3H_2O = H_2SiO_3 + 2Cu^0 + 4H^+ \qquad (3)$$

c c 2c 4c

$$Si^0 + 3H_2O = H_2SiO_3 + 2H_2 \qquad (4)$$

d d 2d

Fig. 1. Elementary reactions and stoichiometric relations for the reduction of Cu^{2+} ions with Ca–Si alloy in aqueous solution.

by Ca^0, reactions 1 and 2 respectively, and of Cu^{2+} reduction and water decomposition by Si^0, reactions 3 and 4 respectively. In reaction 3, Si^0 is oxidized to form silicic acid, when decomposition of water occurs inevitably to form H^+ ions. This can interpret the unsolved phenomenon of decrease in pH accompanying the reduction of Cu^{2+} ions. Silicic acid may exist in other forms, which can be ignored in the stoichiometric discussion. Reduction of one atom of Si^0 always results in formation of four H^+ ions. Part of silicic acid forming in reactions 3 and 4 exists in the form of amorphous silica in the solid phase. In addition, there exist consecutive reactions $Cu^{2+}+e=Cu^+$ and $Cu^++e=Cu^0$ in the initial stage of the reaction. For the sake of simplification, these elementary reactions were discussed stoichiometrically at the time when the reduction of Cu^{2+} ions to Cu^0 had been complete.

In these elementary reactions, Ca^{2+} and H_2 can be determined directly. The increment of either H^+ or OH^- ions can be determined by neutralization titration. The amount of Cu^0 can be estimated from residual Cu^{2+} concentration. Then the total amount of Si^{IV} species forming in both liquid and solid phases at the time of the interruption of the reaction was estimated by using amounts of other determinable components dissolved in the solution as follows: Let a and b be numbers of atoms of Ca^0 oxidized in reactions 1 and 2, respectively. And let c and d be those of Si^0 in reactions 3 and 4, respectively. Then, we get

$$a + b = Ca^{2+},$$
$$a + 2c = Cu^0,$$
$$b + 2d = H_2,$$
$$4c - 2b = \Delta H^+ \text{ (or } -\Delta OH^-).$$

Solving these equations for Si^{IV}, we get

$$Si^{IV} = c + d = 1/2H_2 + 1/4\Delta H^+ \text{ (or } -1/4\Delta OH^-).$$

Unfortunately, a, b, c, and d cannot be determined individually by this method. But it became possible to discuss the whole reaction only with the reaction products in the solution and H_2.

Stoichiometric Discussion. The validity of these deductions was examined by comparing the total equivalents of the reduction and oxidation products of *ca.* 2.5—40-matom dm^{-3} Cu^{2+} solutions. Values at the time when the Cu^{2+} reduction was almost complete (*ca.* 3—8 min after the alloy addition) were used in order to minimize the effects of water decomposition and to exclude those of Cu^+ formation. Equivalents of Ca^{2+} and Si^{IV} as the oxidation products and the total of both values are plotted against total equivalents of Cu^0 and H_2 as the reduction products in Fig. 2. In addition, equivalents of H_2 are plotted to show the degree of water decomposition. The results show that the total of the found Ca^{2+} and the calculated Si^{IV} values are approximately on a straight line with a slope of 1.0 passing the origin 0. This indicates the validity of postulated elementary reactions 1—4, and consequently that of estimation of the amount of Si^{IV}. Thus, the remained problems of stoichiometric disagreement and pH decrease phenomenon are solved. The stoichiometric agreement at low Cu^{2+} concentrations in the previous study may be due to entire dissolution of Si^{IV} species and little water decomposition. It has been considered that Cu^{2+} ions are reduced mainly by Ca^0. But, as a matter of fact, the contribution of Si^0 to the reduction was greater than that of Ca^0 at high Cu^{2+} concentrations. It was very small at 2.5 matom dm^{-3} but increased linearly with the amounts of reduction. On the other hand, the contribution of Ca^0 became small relatively at high reduction values, where Ca^0 in the alloy was mostly consumed. Thus, it proved that Si^0, practically an inactive element due to passivation by silica film on the surface, exhibits its original strong reducing power in Ca-Si alloy when the fresh surface appears after dissolution of Ca^0. Proportion of H_2 in the reduction values became smaller at higher values, indicating that the alloy was used more effectively for the reduction of Cu^{2+} ions.

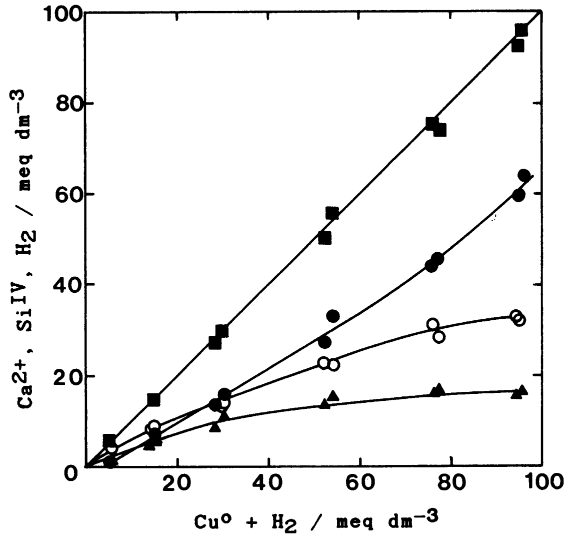

Fig. 2. Relation between equivalents of reduction products (Cu^0 and H_2) and oxidation products (Ca^{2+} and Si^{IV}).
○: Ca^{2+}, ●: Si^{IV}, ■: $Ca^{2+}+Si^{IV}$, ▲: H_2.

Behavior of Reaction Products. In order to know the whole aspect of the reaction, behavior of all the products was studied with the 10.0-matom dm^{-3} Cu^{2+} solution. Concentrations of the products in meq dm^{-3} are plotted in Fig. 3 against the time after addition of the alloy. At the beginning of the reaction (after *ca.* 1.5 min), pH decreased from 4.0 to 2.2 because of formation of H^+ ions in the reduction of Cu^{2+} ions

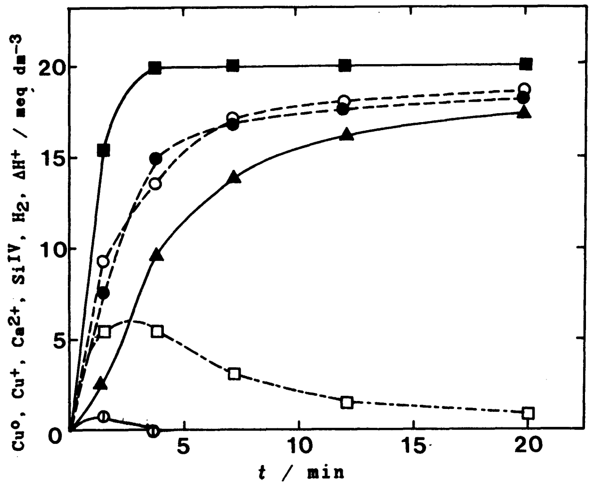

Fig. 3. Behavior of the reaction products in the reduction of 10.0-matom dm^{-3} $\mathrm{Cu^{2+}}$ solution.
■: $\mathrm{Cu^0}$, ⦶: $\mathrm{Cu^+}$, ○: $\mathrm{Ca^{2+}}$, ●: $\mathrm{Si^{IV}}$, ▲: $\mathrm{H_2}$, □: $\mathrm{\Delta H^+}$.

by $\mathrm{Si^0}$. Then, *ca.* 0.8 and 2.3 matom dm^{-3} of $\mathrm{Cu^+}$ and $\mathrm{Cu^{2+}}$ ions, respectively, were found in the solution. The remainder of copper species was recovered from the solid phase as $\mathrm{Cu^0}$. According to Charlot,[5] the reduction process of $\mathrm{Cu^{2+}}$ to $\mathrm{Cu^0}$, potentially including formation of $\mathrm{Cu^+}$ species, is subject to pH value and the concentration of $\mathrm{Cl^-}$ ion. Therefore, the details of the reduction process of $\mathrm{Cu^{2+}}$ through $\mathrm{Cu^+}$ are unknown with the present data. After *ca.* 4 min, the $\mathrm{Cu^{2+}}$ reduction was almost complete when $\mathrm{Cu^+}$ and $\mathrm{Cu^{2+}}$ ions were undetectable in the solution. The reduced $\mathrm{Cu^{2+}}$ was entirely recovered from the solid phase.

Decomposition of water proceeded almost simultaneously with the $\mathrm{Cu^{2+}}$ reduction, and became slow in rate after completion of the $\mathrm{Cu^{2+}}$ reduction. A considerable amount of alloy was consumed in the decomposition of water. Calculated values of $\mathrm{Si^{IV}}$ species were much greater than those found in the solution. $\mathrm{Ca^0}$ and $\mathrm{Si^0}$ exhibited almost similar contribution to the entire reaction. After *ca.* 4 min, the increment of $\mathrm{H^+}$ ions decreased because of completion of $\mathrm{Cu^{2+}}$ reduction by $\mathrm{Si^0}$ and because of formation of $\mathrm{OH^-}$ ions in the decomposition of water by $\mathrm{Ca^0}$.

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