Recovery of Heavy Metals with Calcium Silicon Alloy. IV. Stoichiometric Discussion of the Reduction of Lead(II), Nickel(II), Iron(III), and Mercury(II) Ions

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(Received September 25, 1984)

The reduction of Pb^{2+} and Ni^{2+} ions to the metallic state with the Ca–Si alloy powder can be stoichiometrically interpreted by the following elementary reactions 1—4 including the decomposition of water, a side reaction:

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

$$(Ca^0 + 2Me^{z+} = Ca^{2+} + 2Me^{z-1}) \quad (1')$$

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

$$(Si^0 + 4Me^{z+} + 3H_2O = H_2SiO_3 + 4Me^{z-1} + 4H^+) \quad (2')$$

$$Ca^0 + 2H_2O = Ca^{2+} + H_2 + 2OH^- \quad (3)$$

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

The occurrence of a reaction other than the above ones was suggested for the reduction of Fe^{3+} to Fe^{2+} ion under strongly acidic conditions. The reduction of Pb^{2+} and Ni^{2+} ions proceeded very slowly. On viewing the equivalents oxidized, the contribution of Ca in the alloy to the overall reaction was greater than that of Si; Si scarcely participated at all in the reduction of Fe^{3+} ion. Based on the above elementary reactions, the reduction of Hg^{2+} ion was discussed stoichiometrically. Almost the same equivalents of Hg^0 and Hg^I species formed in a 20-matom dm^{-3} Hg^{2+} solution, with an initial pH of 4.0. The contribution of Si to the reaction was greater than that of Ca.

Cu^{2+}, Hg^{2+}, Fe^{3+}, Pb^{2+}, Cr^{6+}, Cd^{2+}, and Zn^{2+} ions can be effectively removed from aqueous solutions with some silicon alloy powders containing Ca or Mg.[1–4] It has been considered that the removal of these metal ions is mainly due to their reduction to the insoluble species in the lower oxidation states and to their hydrolysis by OH^- ion formed by the decomposition of water, a side reaction. However, the mechanisms of these reactions have not been well elucidated. Of these reactions, the reduction of Cu^{2+} ion with the Ca–Si alloy was, in Part III, investigated stoichiometrically under weakly acidic conditions in order to prevent the hydrolysis of metal ions.[5] It has proved that the overall reaction can be substantially represented by the following four elementary reactions:

$$Ca^0 + Cu^{2+} = Ca^{2+} + Cu^0 \quad (5)$$

$$Si^0 + 2Cu^{2+} + 3H_2O = H_2SiO_3 + 2Cu^0 + 4H^+ \quad (6)$$

$$Ca^0 + 2H_2O = Ca^{2+} + H_2 + 2OH^- \quad (7)$$

$$Si^0 + 3H_2O = H_2SiO_3 + 2H_2 \quad (8)$$

The reduction of metal ions had been thought to take place mainly by Ca in the alloy, which, in the elementary state, has an extremely low standard-electrode potential, $E^0 = -2.866$ V.[6] However, the above mechanism has shown that Si ($E^0 = -0.857$ V)[6] in the alloy, a practically nonreactive element in aqueous solutions, mainly because of the effect of passivation, also exhibits great reducing power. Especially in solutions with Cu^{2+} concentrations higher than *ca.* 10 matom dm^{-3}, the equivalents of Si oxidized were greater than those of Ca.

The objectives of the present study are to elucidate the reaction mechanism of the reduction of metal ions other than Cu^{2+} ion with the Ca–Si alloy powder and to investigate the behavior of the reaction products, which has been obscure in the previous studies. By applying the method used for the reduction of Cu^{2+} ion, stoichiometric discussions will be made of all the reaction products of the reduction of Pb^{2+}, Ni^{2+}, Fe^{3+}, and Hg^{2+} ions, which differ in standard electrode potential and in the variation of the pH and the oxidation state. In Part I, the reducing effects of the alloy on various metal ions were examined by determining the dissolved components after a 24-h reaction period under the reaction conditions of *ca.* 0.2- to 18-matom dm^{-3} metal-ion concentrations and acidities of pH *ca.* 4 to 1-mol dm^{-3} HCl.[3] Subsequent studies by the author have revealed the following facts: The reducing effects on Ni^{2+} and Co^{2+} ions become appreciable only at neutral conditions, oxidation products of Si exist in the solid phase as well as in the solution, and the reaction rates greatly vary with the metal ions, resulting in different degrees of the side reaction. Therefore, in the present study, reactions were carried out under conditions agreeing with the respective metal ions. Concentration changes of the reaction products with the passage of time were determined in order to discuss their behavior and the relation between the metal-ion reduction and the side reaction.

Experimental

Metal-ion Solutions. Sample solutions were prepared by dissolving lead(II), nickel(II), iron(III), and mercury(II) chlorides of a reagent grade in distilled water.

Experimental Procedure. The procedure used was that reported in Part III.[5)]

Results and Discussion

Outline of the Overall Reaction. In weakly acidic aqueous solutions, Cu^{2+}, Pb^{2+}, and Ni^{2+} ions are reduced by the Ca–Si alloy to form Cu^0, Pb^0, and Ni^0, respectively, in the solid phase. In the reduction of Hg^{2+} ion, insoluble Hg^0 and Hg^I species form simultaneously. A decrease in the pH is observed in these metal-ion solutions at high concentrations. Fe^{3+} ion is reduced to Fe^{2+} ion, and no solid product of iron, except hydroxide, forms. At that time, the pH tends to increase independently of the Fe^{3+} concentration.

The alloy, on the other hand, is oxidized concurrently with the metal-ion reduction to form Ca^{II} and Si^{IV} species. In addition to these reactions, there occurs a decomposition of water by the alloy as a side reaction. As has been reported previously, the alloy is practically stable and scarcely causes decomposition of water in metal-ion-free aqueous solutions above pH *ca.* 3.[3)] It can, therefore, be said that the reaction with metal ions increases the active surface of the alloy, consequently causing such an appreciable side reaction.

Method of Stoichiometric Discussion. From the phenomena accompanying the reduction of metal ions by the alloy, the overall reaction is considered to be composed of the following elementary reactions, similarly to the case of the Cu^{2+} reduction:

$$Ca^0 + Me^{2+} = Ca^{2+} + Me^0 \tag{1}$$

$$(Ca^0 + 2Me^{z+} = Ca^{2+} + 2Me^{z-1}) \tag{1'}$$

$$Si^0 + 2Me^{2+} + 3H_2O = H_2SiO_3 + 2Me^0 + 4H^+ \tag{2}$$

$$(Si^0 + 4Me^{z+} + 3H_2O = H_2SiO_3 + 4Me^{z-1} + 4H^+) \tag{2'}$$

$$Ca^0 + 2H_2O = Ca^{2+} + H_2 + 2OH^- \tag{3}$$

$$Si^0 + 3H_2O = H_2SiO_3 + 2H_2 \tag{4}$$

Reactions 1 and 2 are for a reduction of divalent metal ions to the metallic state, such as those of Pb^{2+} and Ni^{2+} ions. Reactions 1′ and 2′ are for a one-electron reduction, such as those of Fe^{3+} and Hg^{2+} ions. Whether or not the above reactions are valid can be decided by ascertaining the equality between the total equivalents of the reduction and the oxidation products. The total-reduction equivalent is expressed by the sum of the equivalents of metal ions reduced and hydrogen produced. Both of them can be determined except in the reaction of Hg^{2+} ion, where Hg^0 and Hg^I species form in the solid phase and where, consequently, their separate determination is difficult. On the other hand, the total-oxidation equivalent is expressed by the sum of the equivalents of Ca^{II} and Si^{IV} species. Ca^{II} species is considered to be present in acidic solutions entirely in the form of Ca^{2+} ion, consequently it can readily be determined. However, the determination of Si^{IV} species is very difficult, since they exist not only in the dissolved form, but also in amorphous silica in the solid phase, together with the unreacted alloy. If the above elementary reactions are valid, the amounts of Si^{IV} species must be equal to either $(H_2+\Delta H^+)$ in equivalent when the pH decreases in the course of the reaction or to $(H_2-\Delta OH^-)$ when the pH increases. Therefore, the validity of the above reactions was evaluated by using the values of Si^{IV} calculated in such a way, while those of the other products were determined directly. For this purpose, stoichiometric discussions were made of the reactions of Pb^{2+}, Ni^{2+}, and Fe^{3+} ions, where only a single species of the metal product forms, and where, consequently, the equivalents of the metal ion reduced can readily be determined.

Reduction of Pb^{2+} Ion. The equality of the total equivalents between the oxidation products $(Ca^{2+}+Si^{IV})$ and the reduction products (Pb^0+H_2) was examined with 10.0-, 20.0-, and 30.0-matom dm^{-3} Pb^{2+} solutions, all with an initial pH of 4.0. The standard electrode potential for the reduction of Pb^{2+} ion to Pb^0 is not very high: $E^0 = -0.126$ V.[6)] The reaction proceeded slowly, and only 61, 52, and 44% of the Pb^{2+} ions were reduced in 60 min in the 10.0-, 20.0-, and 30.0-matom dm^{-3} solutions, respectively. All the Pb^{2+} ions was not reduced even in 3 h. However, separate experiments showed that all the Pb^{2+} ions was reduced at Pb^{2+} concentrations lower than *ca.* 1 matom dm^{-3} in 1 h. The pH decreased to *ca.* 3.6, 3.0, and 2.7 after 60 min in the 10.0-, 20.0-, and 30.0-matom dm^{-3} solutions, respectively, because of the formation of H^+ ion in the reduction of Pb^{2+} ion by Si. Equivalents of the reaction products in a 60-min reaction period for each sample solution are collectively illustrated in Fig. 1.

The total-oxidation equivalents $(Ca^{2+}+Si^{IV})$ showed good agreement with the total-reduction equivalents (Pb^0+H_2) through the 60-min reaction period in each solution. This fact indicates that the above elementary reactions 1—4, just as in the reduction of Cu^{2+} ion, are also valid for the reduction of Pb^{2+} ions. Consequently, the estimation of the equivalents of Si^{IV} oxidized is also appropriate.

In each solution, the equivalents of Ca oxidized showed a small increase in the vicinity of 60 min. On the other hand, that of Si showed a tendency to increase. This seemed related to the relative amounts of Ca and Si remaining unreacted. The equivalents of Ca oxidized were greater than those of Si, indicating the greater contribution of Ca to the reaction. It was more significant at higher Pb^{2+} concentrations. The proportion of the equivalents of H_2 to the total-reduction values became smaller at higher Pb^{2+} concentrations. Thus, the alloy acted more effectively on the reduction of Pb^{2+} ion.

Reduction of Ni^{2+} Ion. The results regarding a 5.0-matom dm^{-3} Ni^{2+} solution are shown in Fig. 2. The initial pH was adjusted at *ca.* 6 since, at pH's lower than *ca.* 5, Ni^0 forming in the reaction readily dissolves and does not deposit in the solid phase. The reaction rate was very small since the reaction was carried out at pH's around neutrality and since, in addition, the standard electrode potential for the reduction of Ni^{2+} to Ni^0 is very low: $E^0 = -0.250$ V.[6] About 17% of the Ni^{2+} ions were reduced in *ca.* 1 h; thereafter, the reaction became inappreciable. The pH rose to 7.2 after 5 min, but thereafter tended to decrease slowly, indicating the reduction of Ni^{2+} ion by Si. A satisfactory equivalence was established between the total equivalents of the reduction products and those of the oxidation products. Therefore, the redution of Ni^{2+} ion with a low standard-electrode potential can also be interpreted by the same elementary reactions as those for Cu^{2+} and Pb^{2+} ions. The reaction under neutral conditions (pH 6—7) is one of the causes of the slight extent of water decomposition. The equivalents of Ca oxidized were about twice those of Si, indicating that Ca contributes more greatly to the overall reaction, such as in the case of the Pb^{2+}-ion reduction.

Reduction of Fe^{3+} Ion. Fe^{3+} ion can readily be hydrolyzed and so become little subject to reduction by the alloy. The initial pH of the sample solution was adjusted at 2.0 to prevent the hydrolysis. It proved improper to use Fe^{3+} solutions of concentrations lower than *ca.* 10 matom dm^{-3} under such strongly acidic conditions, since the decomposition of water was dominant over the metal-ion reduction. Then a stoichiometric discussion was made of a 20-matom dm^{-3} Fe^{3+} solution where the reduction of Fe^{3+} ion was predominant. The results are shown

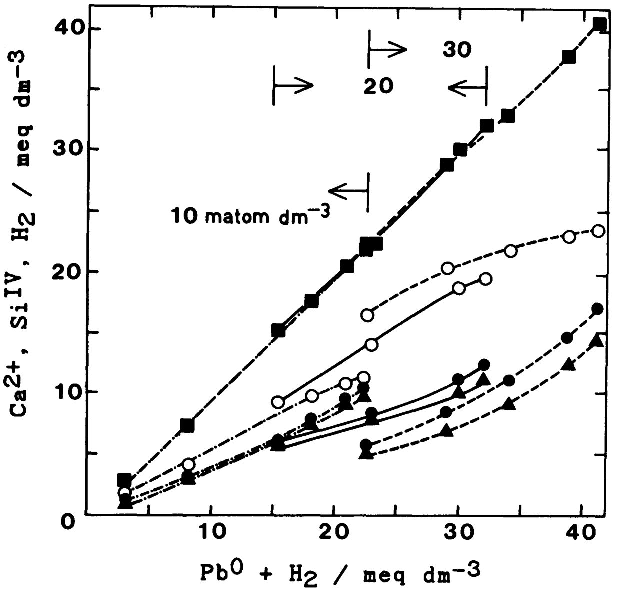

Fig. 1. Relation between equivalents of reduction products (Pb^0 and H_2) and oxidation products (Ca^{2+} and Si^{IV}).
○: Ca^{2+}, ●: Si^{IV}, ■: $Ca^{2+}+Si^{IV}$, ▲: H_2.

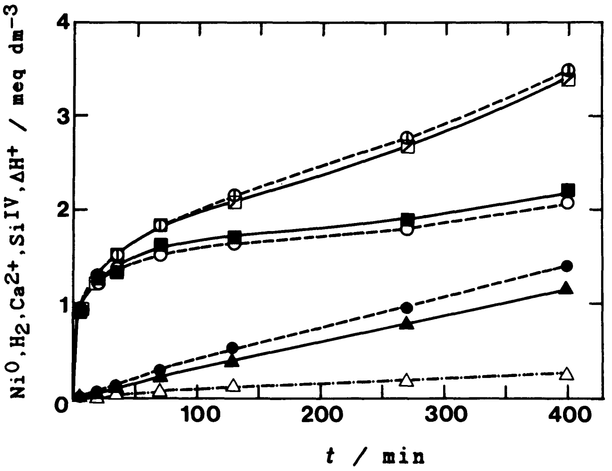

Fig. 2. Behavior of the reaction products in the reduction of 5.0-matom dm^{-3} Ni^{2+} solution and the relation between equivalents of reduction products and oxidation products.
■: Ni^0, ▲: H_2, ○: Ca^{2+}, ●: Si^{IV}, △: ΔH^+, ⧄: Ni^0+H_2, ⦶: $Ca^{2+}+Si^{IV}$.

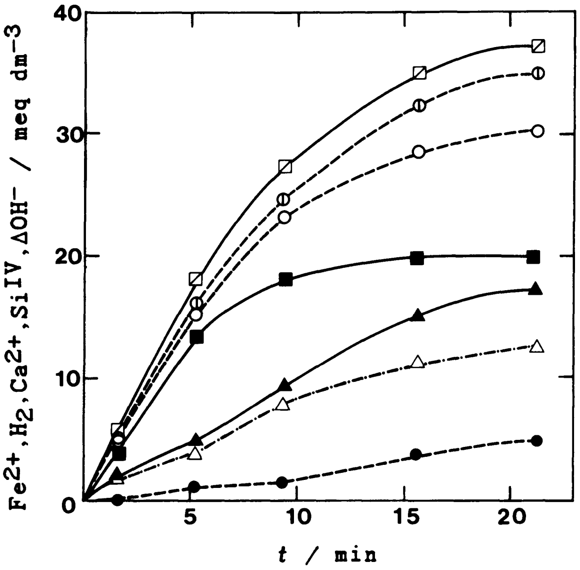

Fig. 3. Behavior of the reaction products in the reduction of 20.0-matom dm^{-3} Fe^{3+} solution and the relation between equivalents of reduction products and oxidation products.
■: Fe^{2+}, ▲: H_2, ○: Ca^{2+}, ●: Si^{IV}, △: ΔOH^-, ⧄: $Fe^{2+}+H_2$, ⦶: $Ca^{2+}+Si^{IV}$.

in Fig. 3. The standard electrode potential for the reduction of Fe^{3+} ion to Fe^{2+} ion is very high: $E^0=0.771$ V.[6] Fe^{3+} ion was entirely reduced in 15 min. Equivalence was not established between the total-oxidation equivalents and the total-reduction equivalents, the former being *ca.* 0.8—0.9 times the latter. Such a disagreement in equivalent has also been observed in the reduction of Cu^{2+} ion at an initial pH of 2.0, though the runs at an initial pH of 4.0 show complete agreement. This disagreement can principally be attributed to the existence of elementary reactions other than 1′, 2′, 3, and 4, for example, the formation of insoluble Ca^{II} species in the solid phase under such strongly acidic conditions.

The equivalents of Ca oxidized were much greater than those of Si. No decrease in pH at all was observed in the Fe^{3+} reduction, but a pH decrease was noticed in the Cu^{2+} run, even at an initial pH of 2.0. These facts indicate that Fe^{3+} ion is reduced mainly by Ca and that Si is consumed in the decomposition of water. It is a remarkable feature of the Fe^{3+} reduction that Si scarcely participates in the reduction reaction of a high standard-electrode potential. The cause of this has not yet been ascertained.

Reduction of Hg^{2+} Ion. Hg^{2+} ion is reduced by the alloy to form Hg^0 and Hg^I species (Hg_2Cl_2 in the present case, where chloride ion solely exists as an anion) simultaneously in the solid phase. Because of the difficulty of the separate determination of the two solid mercury species, different in the oxidation state, no detailed stoichiometric discussions have been made.[7] The above results in the present study indicate that the elementary reactions 1—4, 1′, and 2′ can also be applied as the reaction mechanism to the reduction of Hg^{2+} ion in weakly acidic solutions.

Based on these elementary reactions, the following two equations hold in equivalent: $Hg^0+Hg^I+H_2=Ca^{2+}+Si^{IV}$ and $Si^{IV}=H_2+\Delta H^+$. The amounts of Hg^0 and Hg^I can be estimated as follows:

Let x and y be the numbers of Hg^0 and Hg^I atoms formed, respectively, and let a and b be those of the removed Hg^{2+} and the total equivalent of the reduced Hg^{2+}, respectively. Then we obtain:

$$a = x + y \quad \text{and}$$
$$b = 2x + y.$$

By solving these equations, we get:

$$x = b - a \quad \text{and}$$
$$y = 2a - b.$$

In this way, the behavior of the reaction products in a 20-matom dm^{-3} Hg^{2+} solution with an initial pH of 4.0 was discussed. The results are shown in Fig. 4. Almost all the Hg^{2+} ions were removed in *ca.* 5 min. At that time, nearly equal equivalents of Hg^0 and Hg_2Cl_2 were formed in the solid phase, indicating that only one-third the initial amounts of Hg^{2+} ions were reduced to Hg^0, since the equivalent of Hg^0 is twice that of Hg^I. The standard electrode potentials for the reduction of Hg^{2+} to Hg^I and that of Hg^I to Hg^0 are 0.920 and 0.788 V, respectively.[6] These values are much higher than that of Cu^{2+} ion ($E^0=0.337$ V), which proceeds very efficiently to form the metallic species. In this system, the presence of Cl^- ion resulted in the formation of very stable Hg_2Cl_2, which made the reduction of Hg^{2+} ion incomplete. From *ca.* 5 min, Hg_2Cl_2 tended to decrease, while, in turn, Hg^0 increased. The rate of the reduction was small because of the very low solubility of Hg_2Cl_2. The covering of the alloy particles by the reaction products was not significant, just as in the other metal-ion runs.

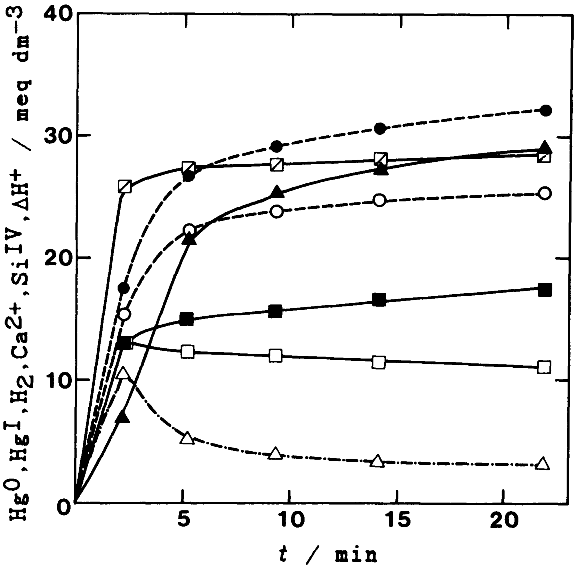

Fig. 4. Behavior of the reaction products in the reduction of 20.0-matom dm^{-3} Hg^{2+} solution.
⧄: Hg^0+Hg^I, ■: Hg^0, □: Hg^I, ▲: H_2, ○: Ca^{2+}, ●: Si^{IV}, △: ΔH^+.

The equivalents of Si oxidized were greater than those of Ca, indicating the greater contribution of Si to the overall reaction, such as in the case of the Cu^{2+} reduction. At the initial stage of the reaction, the pH decreased to *ca.* 2 because of the formation of H^+ ion in the reduction of Hg^{2+} ion by Si. In Hg^{2+} solutions of 5 matom dm^{-3} or lower, the equivalents of Si oxidized were smaller than those of Ca. The decomposition of water occurred subsequently to the Hg^{2+} reduction and exceeded the latter after *ca.* 20 min. After the greater part of the Hg^{2+} ions had been removed, the values of ΔH^+ decreased because of the formation of OH^- ion in the decomposition of water by Ca.

Regarding the contribution of Ca and Si in the alloy to the reaction, the following conclusions can generally be reached. The reduction of metal ions with low standard-electrode potentials, such as those of Ni^{2+} and Pb^{2+} ions, proceeds mainly by Ca. Ca in the alloy seems to have a still lower electrode potential than Si. In the reduction of high electrode potentials, such as those of Cu^{2+} and Hg^{2+} ions, the reduction of metal ions by Si becomes significant, as does that by Ca. The oxidation rates of Ca and Si increase as the electrode potential of the reduction of a metal ion and the metal-ion concentration increase. At the beginning of the reaction, the oxidation rate of Ca seems greater than that of Si because of its higher electrode potential. However, the oxidation rate of Ca tends to decrease greatly when the reaction has proceeded to some extent and, consequently, the amount of unreacted Ca has become relatively small. On the other hand, the oxidation rate of Si does not decrease so much because of its large equivalent, twice that of Ca, and its large content in the alloy.

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