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Recovery of Heavy Metals with Calcium Silicon. I. Its Stability in Water and Reducing Effect on Metal Ions

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The stability of calcium silicon in aqueous solutions was studied by determining dissolution rates of Ca and Si at a constant pH. Calcium silicon was found to be fairly stable in solutions of pH 3.0—8.0, at most less than 2.8%of Ca and 0.5% of Si being dissolved after 24 h. In a strong acid solution of pH 2.5 or less the dissolution rates of Ca and Si considerably increased. Ca dissolution reached a plateau and the whole amount of Ca did not dissolve even in a 3.0-mol dm^{-3} HCl solution, while Si dissolution continued to increase. Calcium silicon apparently reduces metal ions to the elemental state for metal ions having higher standard electrode potentials than Cd(II) ions except Ni(II) and Co(II) ions. For Ag(I) ions, nitrate ions interfere with the reduction, but chloride ions favor it. Reduction of Cr(VI) and Fe(III) ions terminated at the stage of Cr(III) and Fe(II). Pb(II), Cu(II), and Hg(II) ions were reduced to the metals, the acidity of the solution and the metal ion concentration not affecting the reduction. Calcium silicon is effective also for low-solubility compounds of these elements in suspension.

The amount of heavy metals discharged into water has increased with development of industrial activities, causing serious environmental pollution. On the other hand the heavy metals are valuable resources and it is important to develop techniques for their recovery. The method utilizing reducing agents is effective for recovering metals. Base metals such as iron, aluminum, or zinc in the form of powder or scrap have been used for recovering metals of higher standard electrode potentials, such as Cu and Hg.1—5) However, such processes are generally low in efficiency, requiring time and post-treatment of the reductant brought into solution.

McKaveney *et al.*6) proposed an alloy process in which silicon alloys including Ca, Al, Ba, Fe, or Mg are used as reductants to remove heavy metals from waste water and brine solution in the pH range of 2—12. Both batch and continuous flow operations can be applied, As, Cd, Cu, Cr, Fe, Hg, Pb, and Zn being removed successfully. By using Ca or Mg silicon alloy, no post-treatment of the exchanged metal ions is necessary. Case7) studied the silicon alloy process using magnesium ferrosilicon and calcium silicon granules. Both alloys afforded a high rate removal of Cu(II), Zn(II), Cr(III), and Cr(VI) ions, but a difference in percentage removal and pH variation was observed among the methods of contact between the alloy and metal-bearing solution (magnetic stirring, tumbling and continuous flow methods were examined). Calcium silicon was found to be very effective for removing Hg(II) ions, which were removed as insoluble Hg(I) compound and Hg(0); as much as *ca.* 40 matom (*ca.* 8 g) of Hg(II) ions were removed per unit mass of calcium silicon.8)

Calcium silicon has long been used in the steel manufacturing industry as a deoxidizing agent, and was rarely used in water until the time McKaveney *et al.* carried out their study. In this report discussions are given on the behavior of calcium silicon in aqueous solutions and its use for the recovery of various metal ions.

Experimental

Calcium Silicon. Calcium silicon (Shin-Etsu Chemical Industry Co., Ltd.) was pulverized with a crusher. Particulates passed through a 200-mesh sieve (0.074 mm) were used. The composition was 31.3% Ca, 60.4% Si, and 0.40% C.

Reagents. Chlorides were used for the runs of Mn(II), Zn(II), Cr(III), Cd(II), Co(II), Ni(II), Sn(II), Pb(II), Cu(II), Fe(III), and Hg(II) ions. $FeSO_4$, K_2CrO_4, and $AgNO_3$ were used. All of these were of reagent grade and used by dissolving in distilled water.

Analysis. Concentration of metals in solution was determined with a Model 503 Atomic Absorption Spectrophotometer (The Perkin-Elmer Corporation). Mn, Zn, Fe, Cr, Cd, Ni, Sn, Pb, and Cu were determined by flame atomic absorption spectrophotometry, and Ca, Co, and Ag by flame emission spectrophotometry. Hg was determined by flameless atomic absorption spectrophotometry with a MV-253 Mercury Vapor Meter (Beckman-Toshiba, Ltd.). Cr(VI) and Fe(II) were determined by colorimetry9) with diphenylcalbazide and 1,10-phenanthroline, respectively. Silicate was determined by the Molybdenum Blue method.10) Solid products were analyzed for chemical species by means of X-ray diffraction with a Model 2100 Diffractometer (Rigaku Corporation) with Ni-filtered Cu $K\alpha$ radiation.

Stability of Calcium Silicon in Aqueous Solutions. Three grams of calcium silicon was added to 2.0 dm^3 of aqueous solution, which was placed in a 25 °C thermostat and agitated with a magnetic stirrer. The pH of the solution was maintained constant in the course of the run by using a Model HSM-10A pH Stat (Toa Electronics Ltd.) with 0.1-mol dm^{-3} HCl for a run of pH 8.0, 0.25-mol dm^{-3} HCl for runs of pH 6.0, 4.0, and 3.0, and with 1.0-mol dm^{-3} HCl for runs of pH 2.5 and 2.0. Calcium silicon was added to a 1.0-mol dm^{-3} HCl solution, the acidity not being controlled. At intervals an aliquot was taken and filtered through a glass fiber filter paper (Whatman GF/A), analysis being made on the filtrate for Ca and Si.

Recovering Metals with Calcium Silicon. In a 100-cm^3 glass-stoppered Erlenmeyer flask, 100 cm^3 of *ca.* 18- or 0.2-matom dm^{-3} metal ion solution was prepared, the acidity being adjusted to pH 1∼4, 0.1 mol dm^{-3}, and 1.0 mol dm^{-3} with HCl. With addition of 0.3 g of calcium silicon, the solution was shaken intermittently at room temperature. After 24 h it was filtered through a glass fiber filter paper, and the filtrate was analyzed for the metal, Ca, and Si. The residue was dried at *ca.* 60 °C under reduced pressure and its X-ray diffraction pattern was obtained.

Results and Discussion

Stability of Calcium Silicon in Aqueous Solutions. In reducing metal ions in an aqueous solution with a reductant, its stability in water is an important factor especially in acid solutions, since too strong a reductant decomposes water, evolving hydrogen gases in solutions of high acidity. Calcium silicon is composed of elemental calcium and silicon, both strong reducing agents; the former reacts with water violently while the latter is stable in water due to the irreversibility of the oxidation-reduction reaction and to passivation by a film of silica in acid solution.[11] The reactivity of elemental calcium and silicon with water has been studied but not that of calcium silicon.

When calcium silicon is added to water, the pH tends to increase with dissolution of Ca moiety ($Ca+2H_2O=Ca(OH)_2+H_2$), the dissolution rate decreasing when the solution turns alkaline. In order to find the relation between pH and the stability of calcium silicon, the dissolution rates of Ca and Si were determined in solutions of constant pH maintained with a pH stat. The concentrations of dissolved Ca and Si were found to be lower than their respective solubilities, and thus they exist in the soluble form. The results are given in Figs. 1 and 2. The amounts of Ca and Si dissolved in solution are given in terms of percentage to the respective initial amounts contained in the calcium silicon added.

The dissolution of Ca was very small at pH 3.0 or higher; only 1.2, 1.8, 1.9, and 2.8% of Ca dissolved after 24 h at pH 8.0, 6.0, 4.0, and 3.0, respectively. When pH was not maintained constant, the dissolution decreased to less than 1% in a solution of an initial pH of 3.9 (final pH 9.1). At pH below 2.5 the dissolution became significant but did not increase continuously with lapse of time, plateaus being observed according to the acidity. At pH 2.5 and 2.0, a steady state was reached after *ca.* 8 and 3 h with dissolution of 21.4 and 62.8% of Ca, respectively. In the 1.0-mol dm^{-3} HCl solution, the plateau was reached within 5 min with dissolution of 74.3% of Ca. In the 2.0- and 3.0-mol dm^{-3} HCl solutions, 83.7 and 84.1% of Ca dissolved, respectively. The Ca moiety would not entirely dissolve even in a strong acid solution, possibly due to the formation of silica film on the surface of calcium silicon which prevents the dissolution.

Percentages of dissolved Si were fairly low in comparison to those of Ca. The stability of calcium silicon in an aqueous solution is mainly affected by that of Ca moiety. Dissolution of Si was insignificant at pH 3.0 or higher, less than 0.5% of Si being dissolved. This was also the case even in the alkaline solution of pH 8.0. In strong acid solutions of pH 2.5 or less, the dissolution of Si as well as of Ca increased significantly, spontaneously combustible silicon hydride, SiH_4, being produced in a 1.0-mol dm^{-3} HCl solution at the first stage of the reaction. On the other hand, elemental silicon dissolves in a hot alkaline solution but not in an acid solution.[11] Significant increase in Ca dissolution in a solution of low pH might promote Si dissolution, *i.e.*, degradation of alloy particulates caused by dissolution of Ca moiety may favor Si dissolution. Since the amount of Si dissolved is much lower than the solubility of silicate, the dissolution of Si increases continuously without reaching a plateau.

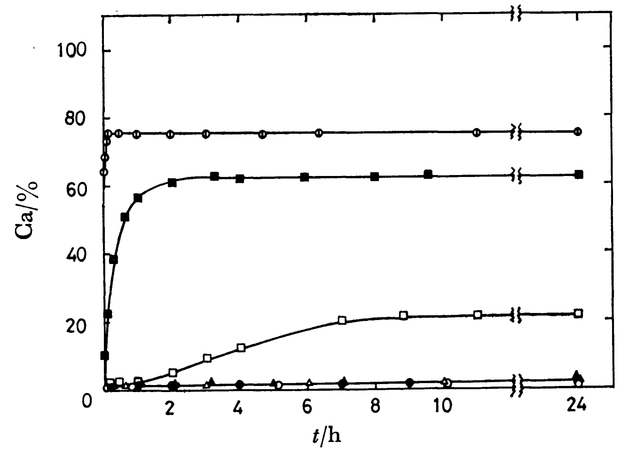

Fig. 1. Dissolution rates of calcium at various acidities. Acidity; ○: pH 8.0, ●: pH 6.0, △: pH 4.0, ▲: pH 3.0, □: pH 2.5, ■: pH 2.0, ⦶: 1.0 mol dm^{-3} HCl.

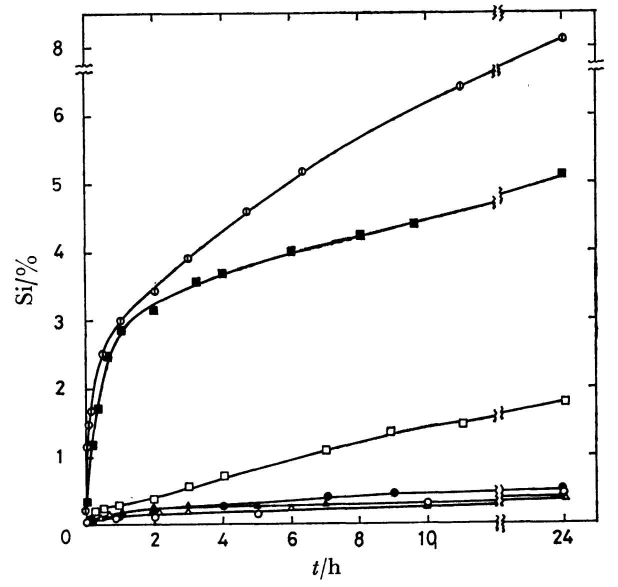

Fig. 2. Dissolution rates of silicon at various acidites. Acidity; ○: pH 8.0, ●: pH 6.0, △: pH 4.0, ▲: pH 3.0, □: pH 2.5, ■: pH 2.0, ⦶: 1.0 mol dm^{-3} HCl.

The explosive reactivity of elemental Ca with water is thus reduced considerably by making an alloy containing silicon. The Si moiety is very stable against water. Calcium silicon is sufficiently stable as a solid reducing agent in aqueous solutions of pH higher than 3.0.

Recovering Metals with Calcium Silicon. The reduction-oxidation reaction of a metal in an aqueous solution can be discussed in terms of the standard electrode potential. For practical use in acid solutions, the standard electrode potential of a reductant should be higher than *ca.* −0.7 V to avoid decomposition of water, and somewhat lower than that of a metal

TABLE 1. RECOVERY OF METAL IONS WITH CALCIUM SILICON

Metal ion	ε° [a] V	Initial concn matom dm^{-3}	Removal %	Acidity[b] Initial	Final	Dissolution Ca matom dm^{-3}	Si
Mn(II)	−1.180	18.0	0	pH 3.5	pH 7.8	0.3	0.10
		18.3	1	0.1	pH 1.8	16.0	3.56
		18.3	1	1.0	—	16.8	3.06
Zn(II)	−0.763	18.0	4(−1)	pH 3.5	pH 6.1	0.5	0.09
		18.4	−1	0.1	pH 1.7	16.0	3.64
		18.4	3	1.0	—	16.8	3.17
Fe(II)	−0.4402	18.0	−2	pH 2.8	pH 4.0	0.1	0.08
		18.0	−3	0.1	pH 1.8	3.1	2.35
		18.0	−2	1.0	—	3.2	2.35
Cr(III)	−0.408[c]	18.0	20	pH 2.9	pH 3.3	7.8	1.69
		18.0	7	0.1	pH 1.7	13.3	3.44
		18.0	8	1.0	—	14.5	2.91
		0.2	50(10)	pH 3.1	pH 4.8	0.5	0.14
Cd(II)	−0.4029	18.0	6(0)	pH 3.1	pH 6.6	0.5	0.09
		18.0	32	0.1	pH 1.7	16.8	3.92
		18.0	5	1.0	—	17.0	2.96
		0.2	10(0)	pH 3.1	pH 6.4	0.4	0.15
		0.2	2	0.1	pH 1.7	17.2	4.71
Co(II)	−0.277	17.9	0	pH 3.6	pH 5.7	0.4	0.09
		17.9	1	0.1	pH 1.7	15.1	4.09
		17.9	1	1.0	—	16.4	3.35
Ni(II)	−0.250	18.0	7(0)	pH 3.5	pH 7.4	0.6	0.30
		18.1	3	0.1	pH 1.8	16.8	3.27
		18.1	3	1.0	—	17.2	2.96
Sn(II)	−0.136	16.8	69	0.1	pH 1.6	11.9	2.80
Pb(II)	−0.126	18.0	82(81)	pH 3.5	pH 4.8	15.2	2.98
		18.0	83	0.1	pH 1.7	16.5	3.47
		18.0	79	1.0	—	16.8	3.39
		0.2	100(5)	pH 3.5	pH 8.5	0.4	0.17
		0.2	40	0.1	pH 1.5	18.1	2.97
Cu(II)	0.337	18.1	98	pH 3.4	pH 2.5	16.3	3.77
		18.1	99	0.1	pH 1.6	16.9	4.69
		18.1	93	1.0	—	16.8	3.78
		0.2	96(96)	pH 3.5	pH 6.2	0.5	0.07
Fe(III)	0.771[d]	18.0	8(3)	pH 2.0	pH 4.1	12.6	1.48
		18.1	7	0.1	pH 1.7	16.8	2.47
		18.1	5	1.0	—	16.6	2.15
Ag(I)	0.799	18.5	12	pH 3.9	pH 3.2	0.6	0.03
		18.5	100	0.1	pH 1.7	13.2	3.64
		18.5	100	1.0	—	15.3	3.03
		0.2	61	0.1	pH 1.7	14.3	4.59
Hg(II)	0.920[e]	18.0	99	pH 3.9	pH 2.3	11.1	2.53
	0.788[f]	18.0	99	0.1	pH 1.7	15.8	5.14
		18.0	99	1.0	—	16.8	2.66
Cr(VI)		18.0	8	pH 3.2	pH 5.4	0.1	0.48
		18.0	50	0.1	pH 2.7	16.1	4.73
		18.0	2	1.0	—	15.9	2.36
		0.2	0	pH 3.5	pH 10.1	0.5	0.54
		0.2	0	0.1	pH 1.4	18.7	2.84

a) Standard electrode potential for an electrode reaction $M^{z+}+ze=M$ (unless otherwise noted); the value being quoted from "Kagaku Binran Kiso-hen II," Maruzen, Tokyo (1977), pp. 1203—1206. b) Adjusted with HCl, and the values are in mol dm^{-3} unless ohterwise noted. c) For the reaction $Cr^{3+}+e=Cr^{2+}$. d) For the reaction $Fe^{3+}+e=Fe^{2+}$. e) For the reaction $2Hg^{2+}+2e=Hg_2^{2+}$. f) For the reaction $Hg_2^{2+}+2e=2Hg$.

to be reduced for accomplishing the reduction-oxidation reaction. Since the standard electrode potential of calcium silicon is unknown, we estimated its strength as a reductant by reactions with various metal ions whose potentials are known. We employed finer particulates of calcium silicon and higher concentrations of metal ions than those used in the previous studies in order to analyze the solid products by means of X-ray diffraction. Since metal-ion reducing reactions proceed efficiently in acid solutions, reactions were carried out in solutions of various acidities in order to suppress hydrolysis of metal ions and examine the effects of acidity.

The results of metal ion recovery are given in Table 1. When occurrence of hydrolysis of metal ions was expected from the final pH, an aliquot of the sample solution was filtered after being maintained at near the initial pH for 5 min to dissolve the hydroxide. The metal ion removal thus attained is indicated in parentheses. Discussions are given on 0.2-matom dm^{-3} solutions of metal ions which proved to be reduced by calcium silicon.

Practically no reducing effects were observed for Mn(II), Zn(II), and Fe(II) ions which show very low standard electrode potentials. In the study of McKaveney *et al.*,[6] more than 99% removal was attained for Zn(II) ions in the column contact operation by using a parent solution of 0.15 Zn matom dm^{-3} and pH 5.6. More than 98% removal was attained at final pH of 9.95—7.95 in the batch operations by using a parent solution of 0.66 Zn matom dm^{-3} and pH 2.05.[7] At final pH of 5.05, the extent of removal significantly decreased down to 9%. Thus, it can be concluded that Zn(II) ions do not undergo reduction with calcium silicon but are removed only by hydrolysis which becomes significant from above pH *ca.* 6.5. The dissolution of Ca was much lower for Fe(II) ions than that for other cases, which seems to be due to presence of sulfate ions.

For Cr(III) ions, 20% removal was achieved in the run of initial pH of 2.9. The amounts of Ca and Si dissolved were much higher than those obtained in the above-mentioned metal-free solution of nearly the same pH (*ca.* 0.3 and 0.1 matom dm^{-3} for Ca and Si, respectively). This indicates the reduction of Cr(III) ions, the reaction $Cr^{3+}+e=Cr^{2+}$ being most likely to occur according to its standard electrode potential. However, no Cr(II) was detected since it is extremely unstable in aqueous solution and readily oxidized to Cr(III). Formation of Cr(0) is very unlikely to occur, since the standard electrode potentials for the reactions $Cr^{3+}+3e=Cr$ and $Cr^{2+}+2e=Cr$ are -0.774 and -0.913 V,[12] respectively. Although no pattern of chromium compounds was obtained by means of X-ray diffraction, the chromium removed was entirely recovered from the solid phase as Cr(III) ions by alkali digestion of the product. The removal of Cr(III) ions seems to be due to the formation of chromium(III) hydroxide.

For Cd(II) ions, removal higher than for the above-mentioned metal ions was achieved in the 18.0-matom dm^{-3}, 0.1-mol dm^{-3} HCl solution, formation of Cd(0) being recognized by X-ray diffraction of the solid product obtained. The removal deteriorated in the solutions of both lower and higher acidities as well as of lower cadmium concentration. Optimum conditions of acidity and cadmium concentration should be established in order to attain high efficiency of the reduction.

Although Co and Ni show higher standard electrode potentials than Cd does, the ions were not removed in acid solution. The cause of the ineffectiveness of calcium silicon on these ions is unknown. Thus, the reduction of metal ions with calcium silicon can not always be interpreted only in terms of standard electrode potential.

The high removal of Sn(II) ions in the 0.1-mol dm^{-3} HCl solution and the presence of Sn(0) confirmed by means of X-ray diffraction indicate that Sn(II) ions were removed by reduction to the metal.

For 18.0 Pb matom dm^{-3} solution, removal was attained regardless of the acidity and formation of Pb(0) was recognized in every case. In the run of initial pH of 3.5, removal of Pb(II) ions would not decrease significantly even by adjusting the final pH. This indicates that the removal of Pb(II) ions is due to the reduction of the ions to the metal. In the run of 0.2 matom dm^{-3}, initial pH of 3.5, the increase in pH interfered with the reduction of Pb(II) ions. The 40% removal for the run of 0.2 matom dm^{-3}, 0.1 mol dm^{-3} HCl, shows that the reduction of Pb(II) ions would not proceed so efficiently at such low concentration.

Considerably high removal was attained for Cu(II) ions in every solution irrespective of the acidity and Cu(II) concentration, indicating that Cu(II) ions can be reduced efficiently. The solid product was found to consist of Cu(0) and a trace amount of Cu_2O. The reaction was complete in 30 min after addition of calcium silicon.

Removal of Fe(III) ions was very low. However, the colorimetric determination of Fe(II) ions in the solution showed that Fe(III) ions are almost entirely reduced to Fe(II) ions. Reduction to Fe(0) is unlikely to occur according to the standard electrode potential.

Since no effect was observed with $AgNO_3$ solutions whose acidity was adjusted with HNO_3, the effect of calcium silicon on Ag(I) ions was examined with a suspension of AgCl precipitate prepared by addition of HCl to a $AgNO_3$ solution followed by addition of calcium silicon after 10 min. Thus the solid phase might contain AgCl precipitate, and the removal values given in Table 1 do not necessarily indicate that the removal was due to reduction of Ag(I) ions. Determination of Ag and AgCl in the solid product was made by means of X-ray diffraction. The areas of the diffraction peaks corresponding to $d=2.359$ and 2.774 Å for Ag and AgCl, respectively, were obtained by the integral mode, and their ratio was compared with a calibration curve similarly prepared by using mixtures of standard Ag and AgCl of various compositions. The silver compositions of the solid products were *ca.* 100, 100, and 43% for the runs at initial pH 3.9, 0.1-mol dm^{-3}, and 1.0-mol dm^{-3} HCl, respectively. The low Ag content for the 1.0-mol dm^{-3} HCl run can be attributed to flocculation of AgCl precipitate which interfered with the contact with calcium silicon. Chloride ions favored the reduction of Ag(I) ions while nitrate ions disturbed it. When calcium silicon was added 1 h after the formation of AgCl, the silver compositions of the solid phase were *ca.* 100 and 55% Ag for the runs at initial pH 3.3 and 0.1 mol dm^{-3}, respectively, a trace amount of Ag being contained in the solid phase of the 1.0-mol dm^{-3} run. Aging of AgCl precipitate adversely affected the reduction reaction.

Reduction of Hg(II) ions proceeded efficiently in all solutions, the recovered solid products consisting of Hg(0) and Hg_2Cl_2.[8)]

For Cr(VI) ions, 50% removal was attained in the 18.0-matom dm^{-3}, 0.1-mol dm^{-3} HCl solution. Of the chromium ions remaining in the solution, Cr(III) ions accounted for 72.5% and Cr(VI) ions the remainder, indicating that the reduciton of Cr(VI) to Cr(III) occurred. According to Pourbaix,[12)] both Cr(VI) and Cr(III) ions would not hydrolyze at the pH we employed. We carried out analysis of the solid phase obtained in order to find the cause for the removal of Cr(VI) ions. The solid product dried at 60 °C under reduced pressure was poorly soluble in HCl solution and completely soluble in NaOH solution, which showed a chromium composition of 89.7% Cr(III) and the remainder Cr(VI). Cr(VI) ions were reduced to Cr(III) ions which partly remained in the solution and partly precipitated into the solid phase. The solid product was further analyzed by X-ray diffraction to identify the chromium compounds. Although the product dried at 60 °C gave no evidence for the existence of any chromium compound on its X-ray diffraction pattern, the one heated at *ca.* 700 °C for 6 h gave patterns corresponding to chromium(III) oxide, Cr_2O_3 (ASTM File No. 6-0504), and calcium chromate, $CaCrO_4$ (ASTM File No. 8-458). We might attribute the formation of Cr_2O_3 and $CaCrO_4$ to the dehydration of their hydrous forms which were amorphous to X-rays but determined by the alkali digestion. Therefore, the reduction reaction $Cr_2O_7^{2-} + 8H^+ + 6e = Cr_2O_3(\text{hydrated}) + 4H_2O(\varepsilon^\circ = 1.242 - 0.0788\text{pH}^{12)})$ is most likely to occur, supporting the increase in pH from *ca.* 1 to 2.7. The reduction of Cr(VI) ions did not proceed efficiently at both higher and lower acidities than pH *ca.* 1, where bulk of the Cr(VI) ions remained not reduced to Cr(III). No reduction of Cr(VI) ions took place in dilute solutions.

Since calcium silicon exhibited reducing action on the suspension of AgCl precipitate, we examined the effectiveness on low-solubility compounds of Cd(II), Ag(I), Cu(I), Cu(II), Hg(II), and Pb(II). The effectiveness was judged on the X-ray diffraction pattern of the solid product obtained. Great reducing effect was observed on Cu_2Cl_2, in which formation of Cu(0) and a trace amount of Cu_2O was recognized. Partial reducing effect was observed on Ag_2O, Ag_2SO_4, $Cu(OH)_2$, CuS, PbO, HgO, and $HgSO_4$, in which metallic species were recognized as well as the starting material. It seems that the reduction of these low-solubility compounds is due to that of the metal ions dissolving in trace amount into the metal, which consequently causes dissociation of the molecular species.

Appreciable reducing effect to the metal is recognized on metal ions that show standard electrode potentials equal to or higher than that of Cd, except Ni(II) and Co(II) ions. The reduction reaction of Cr(VI) and Fe(III) ions terminates at the stage of formation of Cr(III) and Fe(II) ions, neither Cr(0) nor Fe(0) being produced. Dissolution of calcium silicon in aqueous solution increases pH, favoring the removal of metal ions through hydrolysis. The acidity of a solution would not affect the reducing effect for Pb(II), Cu(II), and Hg(II) ions that show high standard electrode potentials. Calcium silicon is effective also for low-solubility compounds of these metals.

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