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RADIATION-INDUCED PREPARATION OF METALS FROM THEIR AQUEOUS SALT SOLUTIONS

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16. Abstract

Eleven metals, copper, zinc, cadmium, thallium, tin, lead, antimony, nickel, cobalt, iron, and palladium, were prepared from their aqueous salt solution by irradiation with 2-MeV electrons. In the more successful attempts, the metal yields nG(M) (atoms per 100 eV multiplied by the valence change n) averaged about 2. The yields have been interpreted in terms of the radical scavenging mechanism and the chemistry of the metal system involved.

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SUMMARY

Aqueous salt solutions of 20 metals were irradiated with 2-MeV electrons. Three aqueous systems were studied: a metal salt solution containing methanol, a basic solution of a metal salt containing 2-propanol, and a basic metal salt solution containing sodium hypophosphite. The irradiation of these solutions caused precipitation of metal powders for 11 of the metals; included were copper, zinc, cadmium, thallium, tin, lead, antimony, nickel, cobalt, iron, and palladium. In the more successful attempts, the yield nG(M) (atoms per 100 eV multiplied by the valence change n) averaged about 2; however, the full range of nG(M) was from 20 to 0.001. Only nG(M) for nickel in ammoniacal hypophosphite was greater than 4.7. For the most part, higher values of nG(M) were obtained for the less electropositive metals.

The results have been interpreted in terms of the radical scavenging mechanism and the chemistry of the metal involved. Factors considered were the potential of the metal-metal ion couple, the stepwise reduction of the metal ion, and the reaction of both hydrogen atoms and hydroxyl radicals with metal ions.

The unusally high nG(M) of greater than 20 for nickel in the ammoniacal nickel-hypophosphite system suggests a different mechanism, one in which the nickel metal formed catalyzes further reaction.

INTRODUCTION

Numerous applications require the use of pure metal powders. Because of an increasing demand for powders of higher purity, new preparative techniques are being sought. Our previous work (refs. 1 and 2) suggests that the use of radiation chemistry for this purpose may be a promising new method. Because little is known about the

method, it is necessary to make a fundamental study and general survey of it before specific applications are attempted.

Previously we have demonstrated that powdered copper (Cu) (ref. 1) and nickel (Ni) (ref. 2) can be deposited from their aqueous salt solutions. The purpose of the present work was to ascertain which additional metals can be made from aqueous solution by this radiation chemical method. The results of this work on the high-energy electron irradiation of aqueous salt solution of 20 metals are presented. These metals are representative of groups in the periodic table. The yields of the metals prepared are given, in most cases, for three different aqueous systems. These results are interpreted on the bases of the chemistry of the metals and the mechanism of the radiation process.

The radical scavenging mechanism postulated in the previous reports (refs. 1 and 2) should also apply to the preparation of other metals from their salt solutions. The initial step is the decomposition of water (H_2O) by the radiation into hydrogen (H) atoms and hydroxyl (OH) radicals:

$$H_2O + \text{Energy} \rightarrow H^{\cdot} + OH^{\cdot}$$

An additive, usually a readily oxidizable organic compound, scavenges the OH radicals by reducing them:

$$\text{Additive} + OH^{\cdot} \rightarrow \text{Oxidized additive}$$

The remaining H atoms then reduce the metal ions to the free metal.

As shown in reference 1, a copper yield G(Cu) of about 2.2 atoms per 100 eV is obtained for most of the reducing organic additives investigated. These additives include primary alcohols (i.e., methanol), secondary alcohols (i.e., 2-propanol), polyhydroxyl alcohols (i.e., glycerine), and aldehydes (i.e., formaldehyde). A maximum copper yield G(Cu) of 2.7 atoms per 100 eV was proposed for the ideal radical scavenging mechanism involving high-energy electrons.

Under similar conditions using aqueous nickel sulfate (ref. 2) instead of copper sulfate, the nickel yield G(Ni) is about 0.07 atom per 100 eV. This comparatively low nickel yield is attributed to the tendency of the active metal nickel to reduce hydrogen ions; higher nickel yields are thus expected and indeed found in basic solution. In ammoniacal nickel sulfate solution, G(Ni) is about 0.85 with the secondary alcohol, 2-propanol, and is about 0.20 with primary alcohols. A surprisingly high nickel yield G(Ni) of about 11.5 is obtained in ammoniacal nickel solutions containing hypophosphite. This unexpectedly high yield is believed to be due to a mechanism other than a radical scavenging type.

EXPERIMENTAL DETAILS

The metals selected are representative of the groups in the periodic table. However, group I (A) (alkali metals), group III (B), and the rare earth metals were not investigated because of the high improbability that these metals can be isolated from water solution. Furthermore, the nonmetal elements, group VI (A) (chalcogens) and groud VII (A) (halogens) were not investigated because their preparation was deemed outside the scope of this report. The following metals were the ones studied:

Group II (A) - magnesium (Mg)
Group III (A) - boron (B), aluminum (Al), and thallium (Tl)
Group IV (A) - silicon (Si), tin (Sn), and lead (Pb)
Group V (A) - antimony (Sb)
Ferrous metals of group VIII - iron (Fe), cobalt (Co), and nickel (Ni)
Platinum metals of group VIII - palladium (Pd)
Group I (B) - copper (Cu)
Group II (B) - zinc (Zn) and cadmium (Cd)
Group IV (B) - titanium (Ti)
Group V (B) - vanadium (V)
Group VI (B) - chromium (Cr) and molybdenum (Mo)
Group VII (B) - manganese (Mn)

Materials

The starting chemicals were either reagent, certified A.C.S., or CP grade and were used without further purification. Most of the metal salts were commercially available; the others were synthesized at Lewis by means of accepted methods.

Solutions

The aqueous systems used fell into the following three categories: (1) a metal salt solution (netural to acid) containing methanol, (2) a basic solution of a metal salt containing 2-propanol, and (3) a basic solution of a metal salt containing sodium hypophosphite.

More specifically, aqueous system 1 was 0.1 molar in the metal salt and 1.0 molar in methanol (CH_3OH). The solutions were usually neutral; a few were slightly acid. Methanol was selected as the additive because it produced high copper yields (ref. 1) in a similar type system. For the most part, the sulfate and/or acetate was chosen because of its high water solubility and inertness toward radiation. Because of the insolubility

of lead sulfate in water, lead perchlorate ($Pb(ClO_4)_2$) was used as well as the acetate. Some of the metals salts used hydrolyze in water to form the insoluble basic salt. The acid corresponding to the anion was added to prevent this hydrolysis; thus, sulfuric acid was added to tin (II) sulfate ($SnSO_4$) solution, and hydrochloric acid was added to the antimony (III) chloride ($SbCl_3$) and to the palladium (II) chloride ($PdCl_2$) solutions. The amount added was just sufficient to form a clear solution. Thus, while most solutions were nearly neutral, some were actually acidic. From practical considerations of stability in aqueous media and availability, the compounds used for B, Si, Ti, Sb, Mo, and Pd were, respectively, boric acid (H_3BO_3), hexafluorosilicic acid (H_2SiF_6), sodium hexafluorosilicate (Na_2SiF_6), titanium (III) chloride ($TiCl_3$), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$), antimony (III) chloride ($SbCl_3$), molybdic acid (H_2MoO_4), and palladium (II) chloride ($PdCl_2$).

Aqueous system 2 was 0.1 molar in the metal salt and 1.0 molar in 2-propanol ($CH_3CHOHCH_3$). These solutions were made basic, generally, by making them 1 molar in ammonia (NH_3). The precipitation of cobalt hydroxide in ammoniacal solution was avoided by the presence of ammonium sulfate ($(NH_4)_2SO_4$), which decreases the hydroxide ion concentration sufficiently to maintain solution. For manganese sulfate ($MnSO_4$) and iron (II) sulfate ($FeSO_4$), complexing with citric acid prevented the formation of a precipitate on addition of ammonia. However, with some metal salts, ammoniacal solutions could not be readily made. Such was the case for Al, Si, Sn, Pb, V, and Mo. The basic solutions of salts of these metals were more conveniently made by the addition of sodium hydroxide (NaOH) to a warm solution or suspension of the metal salt until complete solubility was obtained. The formation of the sodium salt of the oxygenated metal anion resulted. The secondary alcohol, 2-propanol, was used in these basic solutions because it was the only organic additive that resulted in relatively high nickel yields (ref. 2) in ammoniacal systems. In the $SbCl_3$ - NaOH solution, however, methanol was used in place of 2-propanol because of the limited solubility of the latter in the solution involved.

Aqueous system 3 was the same as system 2 except that the alcohol was replaced by a 0.5 molar concentration of sodium hypophosphite (NaH_2PO_2). The strongly reducing hypophosphite ion was of interest as an additive because its use resulted in unusally high yields of nickel (ref. 2).

Procedure

The reaction vessel (fig. 1) and the general procedure are described in an earlier report (ref. 1). To summarize, the metal salt solution was agitated during irradiation by passing helium through a glass frit at the base of the reaction vessel. The contents of the reaction vessel were kept at about 20° C during irradiation by immersing the

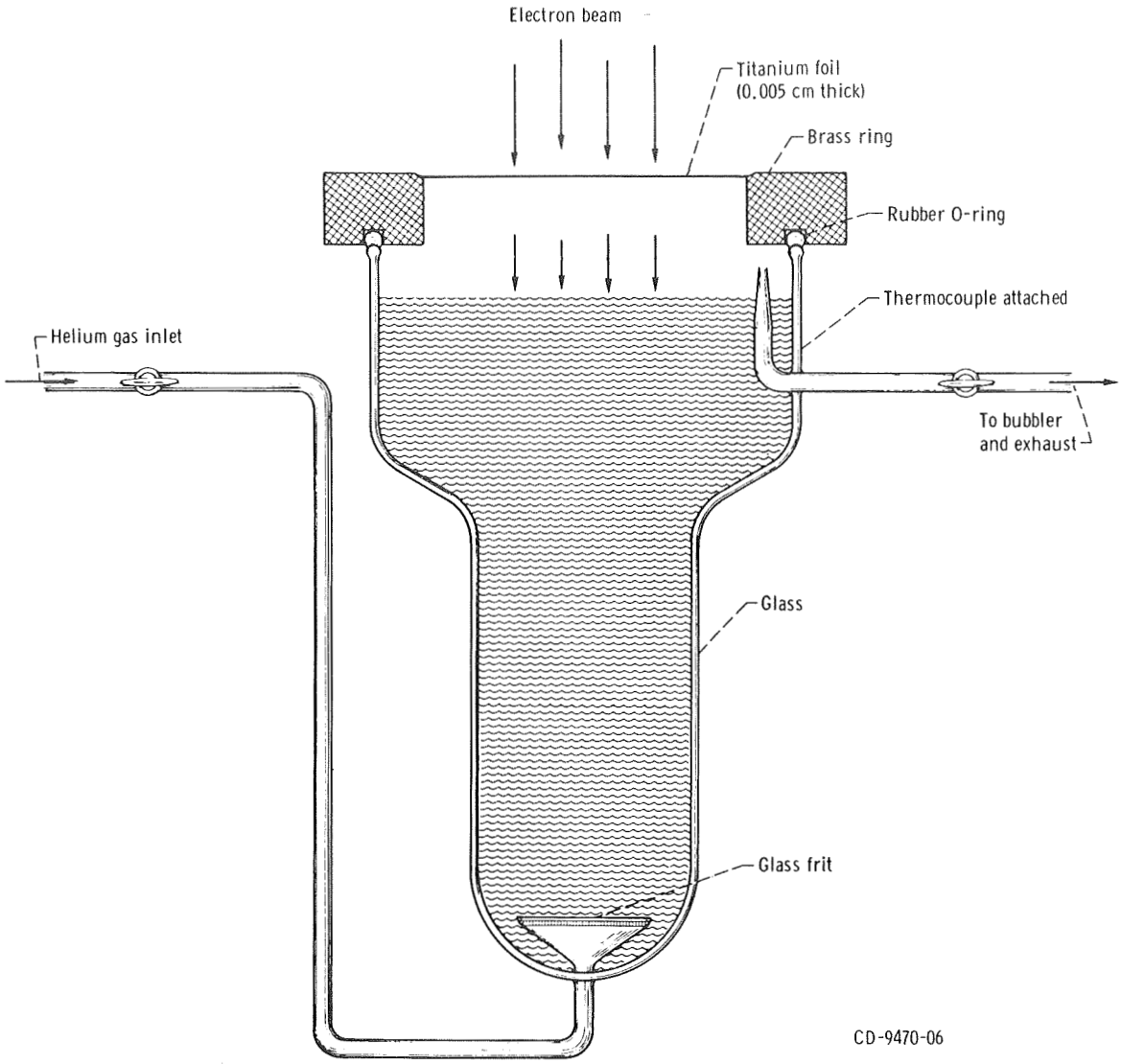

Figure 1. - Irradiation vessel.

vessel in a water bath. The electron beam was furnished by a Dynamitron accelerator (ref. 3) capable of supplying accelerating potentials between 0.3 to 3.0 million volts with a voltage stability greater than 99.9 percent. The Dynamitron has a controllable electron beam current capability between 1 microampere and 10 milliamperes.

An arbitrary choice of 2-MeV electrons for all irradiations proved to be convenient for ease of using the accelerator. Because of practical considerations such as heat generation, irradiation time, and quantity of metal produced, a beam current of 20 microamperes for a dose of 0.12 coulomb (read on a beam current integrator) was selected. In anticipation of high metal yields with basic hypophosphite solution (ref. 2),

a lower beam current of 5 microamperes and a lower total dose of 0.03 coulomb were used.

After irradiation, the insoluble metal powder (when present) was removed by centrifuging and washed thoroughly with water. The wet powder was then suspended in acetone, filtered on a fritted glass filter, and dried at room temperature overnight. The filter containing the metal was further dried at about 70° for 2 hours and weighed. The relatively low drying temperature was used to prevent undue oxidation of the metal powder. Except for iron, the product was identified by X-ray diffraction. This identification was done as quickly as possible because the metal powders tend to oxidize on long exposure to the atmosphere. The iron was nonidentifiable by X-ray diffraction because of the trace amount formed and the fine particle size. However, the powder was found to be ferromagnetic.

RESULTS AND DISCUSSION

Eleven metals, Cu, Zn, Cd, Tl, Sn, Pb, Sb, Fe, Co, Ni, and Pd were prepared. The experimental results for these successful metal preparations are presented in table I. Column 1 gives the metal salt used. The yields of metal for the three aqueous systems are shown in the last three columns. These yields are expressed in a slightly different manner from those given in previous reports. Previously, the yields were expressed in the commonly used term of G(M) (atoms of metal (M) formed per 100 eV energy). In this report the yields are expressed in terms of nG(M), where n in the valence change that occurs when the metal ion is reduced to the metal. This new expression facilitates the comparison of the efficiency of the method for reactions involving different valence changes and is directly associated with the hydrogen atom yield $G(H\cdot)$. If all the hydrogen atoms produced take part in reducing the metal salt to free metal, then $G(H\cdot) = nG(M)$. Values of nG(M) shown in the table range from greater than 20 for Ni in ammoniacal solution containing hypophosphite to about 0.001 for Fe. All runs were made in duplicate, and the results are the average of two runs. We estimate the error in the nG(M) to be about 10 percent.

Given in table II are the aqueous systems for the nine metals, Mg, B, Al, Si, Ti, V, Cr, Mo, and Mn, which did not deposit from solution upon irradiation. This is not surprising for Mg, B, Al, Si, Ti, and Mn because of their high reduction potential.

TABLE I. - YIELD OF METAL FROM IRRADIATION OF AQUEOUS

METAL SALT SOLUTIONS WITH 2-MeV ELECTRONS

Metal salt (0.1 M)	System 1 (neutral to acid; 1 M in methanol; current, 20 μA; dose, 0.12 C)	System 2 (basic; 1 M in ammonia unless specified 1 M in 2-propanol; current, 20 μA; dose, 0.12 C)	System 3 (basic; 1 M in ammonia unless specified 0.5 M in NaH_2PO_2; current, 5 μA; dose, 0.03 C)
	Metal yield, nG(M), (valence change)(atoms/100 eV)		
Copper (II) sulfate	4.4		
Zinc sulfate	.040	0.008	0.006
Zinc acetate	.28		
Cadmium sulfate	.90	.60	.70
Cadmium acetate	1.8		
Thallium (II) acetate	.13	.79	4.4
Tin (II) chloride	[a].20	[b].20	[b]1.0
Lead (III) perchlorate	2.3		
Lead (II) acetate	3.2	[b]3.0	[b]3.0
Antimony (III) chloride	[a].26	[b, c]2.7	[b]5.1
Nickel (II) sulfate	.15	1.7	[d]20.0 [d, e]20.0
Cobalt (II) sulfate	.044	[e].60	[e].048
Cobalt (II) acetate	.060		
Iron (II) sulfate	0	[f].001	[f].001
Palladium (II) chloride	[a]4.7		

[a]Corresponding acid added to just affect solution of metal salt.
[b]No ammonia added, NaOH added to just affect solution of metal salt.
[c]Methanol used instead of 2-propanol.
[d]Product contained about 2.5 percent Ni_2P.
[e]Also 0.1 M in $(NH_4)_2SO_4$.
[f]Also 0.25 M in citric acid.

TABLE II. - COMPOUNDS FROM WHICH METALS WERE NOT PRECIPITATED FROM AQUEOUS SYSTEMS BY IRRADIATION WITH 2-MeV ELECTRONS

[Current, 20 μA; dose, 0.12 C.]

Metal salt (0.1 M)	Additives
Magnesium acetate	1.0 M in methanol
Ortho boric acid	1.0 M in methanol
Ortho boric acid	1.0 M in NH_3, 1.0 M in 2-propanol
Ortho boric acid	1.0 M in NH_3, 0.5 M in NaH_2PO_2
Aluminum sulfate	1.0 M in methanol
Aluminum sulfate	1.0 M in 2-propanol, enough NaOH to just affect solution
Hexafluorosilicic acid	1.0 M in methanol
Sodium hexafluorosilicate	1.0 M in 2-propanol
Sodium hexafluorosilicate	0.5 M in NaH_2PO_2
Titanium (III) chloride	1.0 M in methanol
Ammonium hexafluorotitanate	1.0 M in 2-propanol
Ammonium hexafluorotitanate	0.5 M in NaH_2PO_2
Chromium (III) acetate	1.0 M in methanol
Vanadyl sulfate	1.0 M in methanol
Vanadyl sulfate	1.0 M in 2-propanol, enough NaOH to just affect solution
Vanadyl sulfate	0.5 M in NaH_2PO_2, enough NaOH to just affect solution
Molybdic acid	1.0 M in 2-propanol, enough NaOH to just affect solution
Molybdic acid	0.5 M in NaH_2PO_2, enough NaOH to just affect solution
Manganese (II) acetate	1.0 M in methanol
Manganese (II) sulfate	1.0 M in 2-propanol, 1.0 M in NH_3, 0.25 M in citric acid
Manganese (II) sulfate	0.5 M in NaH_2PO_2, 1.0 M in NH_3, 0.25 M in citric acid

Form of Metal Deposits

In general, the radiation process under the conditions specified in table I produced finely divided reactive but nonpyrophoric metal powders which settle to the bottom of the reaction vessel. The soft metals, Cd, Sn, and especially Pb, formed sponge-like conglomerates, probably because of the coalescing of small crystallites produced initially in the reaction zone.

In addition to the conglomerates, an aqueous suspension of colloidal lead formed on irradiating lead acetate solution containing methanol. In these runs the reaction vessel was coated with a lead mirror. In contrast, no colloid formation was observed with the perchlorate salt. Lead acetate solution is a weak electrolyte and thus is able to furnish the proper ion concentration to maintain a stable colloid. On the other hand, lead perchlorate, a strong electrolyte, gives solutions of high ion concentration which neutralize the charge on the initially formed colloidal particles, thereby coagulating them.

Comparison of nG(M) Values

From the proposed maximum, G(Cu) of 2.7 for the ideal scavenging mechanism reported earlier (ref. 1), the maximum value of nG(M) is 5.4 for the preparation of any metal from aqueous solution using high energy electrons. Except for the special case of the divalent nickel-hypophosphite system (ref. 2) discussed later, all values of nG(M) in table I are less than this 5.4 value.

The general trend in the values of nG(M) depends on the reduction potential of the metal being produced. Highest yields, nG(M) above 4.0, were found for those metals such as copper and palladium which are below hydrogen in the electromotive series. Intermediate values, nG(M) between 1.0 and 3.0, were found for the more active metals; for example, lead and nickel. Yields, nG(M) for iron and zinc, having the highest reduction potential of the metals prepared were below 0.3.

Conditions Affecting nG(M)

Atomic hydrogen produced by the radiation is thermodynamically capable of reducing most of the common metal salts to the free metal. Nevertheless, for the most part, reducing reactions in aqueous systems are limited to those below the hydrogen discharge potential. This limitation arises from the tendency of a strongly reducing metal of fine partical size to reduce water with the discharge of hydrogen gas. The comparatively lower yield of the more active metals is attributed to this tendency. The

fact that the strongly reducing metal, zinc, can actually be isolated from aqueous solution is probably a consequence of its high hydrogen overvoltage, which inhibits its oxidation by hydrogen ions.

The reduction potential of metals with respect to the hydrogen discharge potential is a function of pH. The yields of metals such as thallium, nickel, and cobalt are in accord with this dependence. Greater yields of these metals are obtained from solutions of high pH (basic) than from acid or even neutral solutions (table I). In basic solution these metal couple potentials fall below that of the hydrogen couple. As expected from dependence of yields on pH of simple metal salt solutions, acetates afford higher metal yields than salts of strong acids such as sulfates. The acetate ion decreases the hydrogen ion activity by forming the weakly ionized acetic acid and thereby hindering oxidation of the free metal by hydrogen ions generated during metal formation. Yields from cadmium and zinc acetate solutions are significantly higher than those for the same metals in ammoniacal (basic) solution. The explanation, at least for zinc, may involve its amphoteric property. However, cadmium is not considered to be amphoteric. The lower yield in ammoniacal solution for both zinc and cadmium could be related to an inhibition effect of ammonia in the reaction mechanism for their deposition. Such an inhibition effect of ammonia on nickel deposition is described in an earlier report (ref. 2).

A unit stepwise valence change has been shown to occur in the deposition of copper from solutions containing divalent copper ion (ref. 1). This was anticipated because greater than a unit stepwise valence change would entail a multibodied collision involving more than one hydrogen atom with the metal ion; this is statistically unlikely. Therefore, one can logically assume that the mechanism for the reduction of all metal ions involves a two-body collision between the metal ion and one hydrogen atom resulting in a unit stepwise decrease in oxidation state of the metal ion. Antimony is the only metal produced from a salt with an oxidation state above +2. As a consequence of this stepwise process, the formation of metals from their high oxidation state salts would be difficult because of the additional reactions which must take place. Therefore, it may not be possible to prepare metals from metal salts when the oxidation state of the metal is above +3 (i. e., vanadyl sulfate and molybdic acid).

Another condition resulting in poor metal yields arises when a metal ion present in the solution is an active reducing agent. In such a case, the metal ion can be oxidized by OH radicals to a higher oxidation state. The species in the higher oxidation state can then be reduced by hydrogen atoms to its original oxidation state, which results in a steady-state condition between the two states. Using the divalent-iron - trivalent-iron system as an example, the mechanism may be illustrated as follows:

$$Fe^{+2} + OH^{\cdot} \rightarrow Fe^{+3} + OH^{-}$$

$$Fe^{+3} + H\cdot \rightarrow Fe^{+2} + H^{+}$$

$$H^{+} + OH^{-} \rightarrow H_2O$$

The overall result is the consumption of H atoms in an unproductive series of reactions, which thereby decreases the number of H atoms available for metal production. The same situation exists for the Cr^{+2}-Cr^{+3} system, which could account for our failure to precipitate chromium metal.

Anomalous Behavior of Nickel Salt in Hypophosphite Solution

In one system, the ammoniacal nickel sulfate - hypophosphite solution, the nickel yield far exceeded the predicted maximum nG(M) of 5.4 for the radical scavenging mechanism. This indicates that a more productive mechanism must be operative. Because of the strong reduction potential of the hypophosphite ion, we postulated previously (ref. 2) that the electron beam simply supplied the activation energy to promote the thermodynamically feasible reduction of divalent nickel ion by hypophosphite. It is surprising to find that yields of other metals in hypophosphite systems listed in table I fall within the range appropriate to the radical scavenging mechanism. Thus, we assume that in all cases except nickel, the hypophosphite merely functions as a radical scavenger for hydroxyl radicals and is similar in this respect to the organic additives.

Because of the chemical similarity of nickel and cobalt by virtue of their being adjacent elements in the ferrous metals group of the periodic table, the relatively poor yield of cobalt in ammoniacal hypophosphite solution was unexpected. Thus we conclude that the mechanism pertaining to the fomation of nickel from the ammoniacal hypophosphite system is unique. It possibly involves an autocatalytic process; the catalyst would be the newly formed nickel.

Economic Feasibility

This investigation was intended only as a preliminary survey of the use of electron radiation in the field of preparative chemistry. As such only gram quantities were made in each preparation. Furthermore, no attempt has been made as yet to maximize yields, to design the most efficient apparatus or to make use of the maximum beam power of the accelerator. However, considering our results and the state of the art of particle accelerators, we believe it would be economically feasible to produce relatively

large quantities of high purity metal powders by this preparative technique.

If our accelerator is used at 2 MeV to its full electron beam current capability (10 mA), the amount of copper powder produced would be more than 1 kilogram per hour and the amount of nickel powder would be more than 370 grams per hour (ammoniacal nickel solution containing 2-propanol). Because no attempt was made to optimize various parameters for the maximum yields of other metals, any projection from the data for economic feasibility for their production may not be conclusive.

The accelerator used in this investigation was designed for a wide range of research programs. Thus its instrumentation and controls are rather sophisticated, and the result is a relatively low beam power efficiency and an instrument costly to operate. Use of a less sophisticated accelerator would result in a higher yield per hour and a lower cost per gram. Moreover, economy of operation may be further enhanced through utilization of lower energy electrons than reported in this work. Preliminary results show that the energy yield of copper G(Cu) is practically independent of electron energy between 0.5 and 2.5 MeV. The lower energy of the electrons can be compensated for with relative ease by increasing the beam flux.

CONCLUDING REMARKS

Figure 2 shows the periodic table of elements. The crosshatched areas indicate the metals that we believe are possible to prepare from aqueous solution by electron irradiation. Those whose symbols are underlined were actually prepared during this investigation. Our prediction that the metals in the crosshatched area are preparable is based on the criteria discussed in the previous section. Those metals not actually prepared are silver, gold, mercury, indium, arsenic, bismuth, ruthenium, rhodium, osmium, iridium, and platinum.

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	0
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Figure 2. - Periodic table of elements. Underlining indicates metals which were those actually prepared. Crosshatched areas indicate metals which should be preparable from aqueous solutions as well as ones actually prepared.

The use of nonaqueous solvents such as organic liquids may permit preparation of the more active metals outside the crosshatched area in figure 2. In some nonaqueous systems, the highly reactive solvated electron might be the reducing species; thus, one may conceivably deposit strongly electropositive metals such as magnesium and aluminum.

SUMMARY OF RESULTS

Eleven metals were successfully prepared from their aqueous solutions by irradiation with 2-MeV electrons. The metal deposits were in most cases finely divided powders. The energy yield in terms of nG(M) (atoms per 100 eV multiplied by the valence change n) is highest for metals below hydrogen in the electromotive series. The yields of some active metals are higher in basic than in acid solution because in basic solution the potential required to deposit the metal is less than that for the discharge of hydrogen. The chemistry of the metal salts, particularly those properties involving the oxidation states of the metal also have a significant bearing on the metal yield. The maximum predicted value of nG(M) for the scavenging mechanism is 5.4 atoms per 100 eV for any metal deposited from aqueous solution.

A notable anomaly is the divalent nickel-hypophosphite system in which the unusually high nickel yield is attributed to a mechanism other than the scavenging one.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 24, 1970,
129-03.

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