Metal Powders by Hydrometallurgical Techniques

Fathi Habashi

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Metal Powders by Hydrometallurgical Route – A Review

THE AUTHOR

Fathi Habashi is Professor Emeritus of Extractive Metallurgy at Laval University in Quebec City. He holds a B.Sc. degree in Chemical Engineering from the University of Cairo, a Dr. techn. degree in Inorganic Chemical Technology from the University of Technology in Vienna, and Dr.Sc. h.c. from the Saint Petersburg Mining Institute in Russia (1991). He was a postdoctoral fellow at the Department of Chemistry, University of Vienna. Then he enjoyed the benefits of the Canadian Government Scholarship in Ottawa and lectured at Montana College of Mineral Science & Technology. After this, he worked at the Extractive Metallurgical Research Department of Anaconda Company in Tucson, Arizona before joining to Laval in 1970. In 1998 he was elected Fellow of the Canadian Institute of Mining, Metallurgy, and Petroleum. In 1999 he received its silver medal. He is an Honorary Professor at the Technical University of Oruro in Bolivia, Honorary Citizen of the city of Oruro, Governor at the Foundation de l’Université Laval, and Member of Le Cercle des Ambassadeurs in Quebec City. He is the author of a number of textbooks on extractive metallurgy and editor of “Handbook of Extractive Metallurgy” in 4 volumes.

1 Introduction

Metal powders can be obtained in two steps by crystallizing or precipitating a compound from aqueous solution and then reducing it by thermal methods, or in one step by directly reducing the metal ion from the aqueous phase. For example, nickel hydroxide can be precipitated from nickel sulfate solution by adjusting the pH and then thermally reducing the hydroxide to metal. In the other method, nickel powder can be produced directly from nickel sulfate solution by precipitation with hydrogen under pressure at 200°C in an autoclave. The precipitation of metal powders from aqueous solution is an oxidation-reduction process:

Oxidation: reduced species $\rightarrow$ oxidized species + ne

Reduction: $M^{n+} + ne \rightarrow M$

Overall reaction: $M^{n+} + \text{reduced species} \rightarrow M + \text{oxidized species}$

The process may be homogeneous (the reduced species is ionic or non-ionic) or heterogeneous (reduction takes place on a solid surface) [1].

2 Production of metal powders in a two step process

Metal powders can be obtained by reducing crystals obtained from aqueous solution or reducing a precipitate obtained after adding a suitable precipitating agent.

2.1 Crystallization

Copper sulfate pentahydrate can be crystalized from aqueous solutions, dehydrated, and then reduced by hydrogen or CO at 400°C to yield metallic copper powder [2–3]:

$$CuSO_4 \cdot H_2 \rightarrow Cu + SO_3 + H_2O \quad (1)$$

The reaction goes through the formation of $Cu_2SO_4$ as an intermediate product. This is the only case known for a sulfate to produce metal by reduction [4].

2.2 Oxides, hydroxides, or hydroxyl salts

Dust collected in pyrometallurgical plants can be treated to recover metal powders. For example, during roasting of molybdenite concentrates from porphyry copper deposits, dust collected in the dust recovery system contains appreciable mounts of rhenium oxide. The oxide is dissolved in water, the solution is purified, ammonium peroxide is precipitated, filtered, and then reduced to rhenium powder:

$$Re_2O_7 + H_2O \rightarrow 2HReO_4 \quad (2)$$

$$HReO_4 + NH_4OH \rightarrow NH_4ReO_4 + H_2O \quad (3)$$

$$NH_4ReO_4 + 7/2 H_2 \rightarrow Re + NH_3 + 4H_2O \quad (4)$$

Similarly, dust collected during the treatment of anodic slimes from copper and nickel electrowinning contains appreciable amounts of selenium dioxide. This is dissolved in water to form selenious acid from which red amorphous selenium is recovered after precipitation by bubbling sulfur dioxide:

$$SeO_2 + H_2O \rightarrow H_2SeO_3 \quad (5)$$

$$H_2SeO_3 + SO_2 \rightarrow Se + H_2SO_4 \quad (6)$$

Hydroxides or hydroxyl salts can be precipitated from solution and reduced to metals. Precipitation of a metal hydroxide from dilute solutions normally takes place within a narrow pH range:

$$M^{n+} + nOH^- \rightleftharpoons M(OH)_n \quad (7)$$

Under certain conditions of pH, temperature, and concentration of metal ion in solution, hydroxy or basic salts are obtained instead of hydroxides. For example, pale blue hydroxyl copper sulfate is precipitated and can easily be reduced by hydrogen at 200°C according to:

$$2Cu^{2+} + SO_4^{2-} + 2H_2O \rightarrow Cu(OH)_2 \cdot CuSO_4 + 2H^+ \quad (8)$$

$$Cu(OH)_2 \cdot CuSO_4 + 3H_2 \rightarrow 2Cu + SO_2 + 4H_2O \quad (9)$$

2.3 Polyacids and their salts

Anions like carbonate, nitrate, manganese, and perchlorate always exist in simple form; all other ions undergo a process of limited or extensive condensation to form polyions. For example, sulfate ion forms the disulfate, chromate forms dichromate, and uranate forms diuranate. These polyions are formed from the condensation of two anions with the loss of an oxide ion, for example:

$$2SO_4^{2-} - O^{2-} \rightarrow SO_3^{2-} \quad (10)$$

Examples of other anions capable of extensive condensation are molybdate and tungstate.

Molybdate ion, $MoO_4^{2-}$, is stable above pH 7. When the pH is gradually decreased, insoluble polyions are formed:
MoO₄²⁻ → Mo₂O₇³⁻ → H₂MoO₄²⁻.
Molybdenite, MoS₂, the major source of molybdenum, is usually oxidized to MoO₃, and the oxide is dissolved in excess ammonium hydroxide to form molybdate ion:

\[
\text{MoO}_3 + 2\text{OH}^- \rightarrow \text{MoO}_4^{2-} + \text{H}_2\text{O} \quad (11)
\]

The resulting solution is subjected to a purification step which involves acidification to precipitate a series of hexaammonium molybdates. These precipitates may be considered to be composed of \( x\text{(NH}_3\text{)}_2\text{MoO}_4 y\text{H}_2\text{MoO}_4 \) (where \( x = 1.5, 2 \), and 2.5, when \( y = 4.5, 4, \) and 3.5, respectively).

This is a commercial product which can be thermally decomposed to pure oxide and then reduced to metal:

\[
\text{MoO}_3 + 3\text{H}_2 \rightarrow \text{Mo} + 3\text{H}_2\text{O} \quad (12)
\]

Tungstate ion, \( \text{WO}_4^{2-} \), is stable at pH>8. When the pH is gradually decreased by adding an acid, numerous polyions form:

\[
\text{WO}_4^{2-} \rightarrow \text{WO}_4^{2-} \rightarrow \text{WO}_4^{2-} \rightarrow \text{WO}_4^{2-} \rightarrow \text{WO}_4^{2-} \quad (13)
\]

Before the precipitation of the hydrated oxides, however, tungstic acid and hexatungstic acid are supposed to form first by polymerization and splitting of water:

\[
\text{H}_3\text{WO}_4 \rightarrow \text{H}_2\text{WO}_4 \rightarrow \text{H}_2\text{WO}_4 \rightarrow \text{H}_2\text{WO}_4 \quad (14)
\]

since stable crystals of sodium paratungstate, \( \text{Na}_8\text{W}_6\text{O}_{18}-28\text{H}_2\text{O} \), have been isolated as an industrial product. In practice, wolframite concentrates, FeWO₄, are leached with alkali to form the soluble tungstic acid which is filtered then acidified to form hydrated tungstic oxide:

\[
\text{WO}_4^{2-} + 2\text{H}^+ + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{WO}_4 + \text{H}_2\text{O} \rightarrow \text{WO}_4^{2-} + \text{H}_2\text{O} \quad (15)
\]

Scheelite concentrates, CaWO₄, are digested with acid to form \( \text{WO}_4^{2-}+\text{H}_2\text{O} \) which is filtered, washed, and purified by dissolution in alkali and then precipitation by acid. In both cases \( \text{WO}_4^{2-} \) is reduced by hydrogen to tungsten powder.

2.4 Chlorides

In Chile at the Mantos Blancos plant the mineral atacamite, \( \text{Cu}_2\text{Cl}_2(\text{OH})_2 \), occurs in abundance and as a result the leach solution contains chloride ion which is detrimental for subsequent operations. The problem was solved by precipitating \( \text{CuCl}_2 \), filtering, washing, and reducing it to metal. Since copper is present as \( \text{Cu}^{2+} \) ions in leach solutions, reduction to \( \text{Cu}^+ \) is necessary before precipitation. This is achieved by reduction with \( \text{Cu} \) in towers (Fig. 1):

\[
2\text{Cu}^+ + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu}^+ + 2\text{H}^+ + 2\text{e}^- + \text{SO}_4^{2-} \quad (16)
\]

\[
2\text{Cu}^+ + 2\text{Cl}^- \rightarrow \text{Cu}_2\text{Cl}_2(\text{solid}) \quad (17)
\]

Precipitation of cuprous chloride was also practiced at Duisburger Kupferhütte in Germany for copper recovery from pyrite cinder leach solution. Cuprous chloride when reacted with calcium hydroxide precipitated cuprous oxide which was reduced to metal:

\[
\text{CuCl}_2(\text{aq}) \rightarrow \text{Cu}^+ + \text{Cl}^- \quad (18)
\]

\[
\text{Cu}^+ + \text{OH}^- \rightarrow \text{Cu(OH)}_2 \quad (19)
\]

\[
2\text{Cu(OH)}_2 + \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (20)
\]

In both cases molten metal was produced by reduction with anthracite in a furnace. Evidently copper powder could also be obtained if reduction is conducted with a gaseous reducing agent.

2.5 Cyanides

In acidic or neutral medium, cuprous cyanide is practically the only cyanide insoluble in water. Consequently, a process was suggested by Treadwell Corporation in the USA for copper recovery from a leach solution by precipitation as cyanide. A pilot plant was constructed by Anaconda in Tucson, Arizona for this purpose (Fig. 2). Sulfur dioxide is added to the leach solution to reduce cupric to cuprous sulfate. Then HCN is passed through the solution to precipitate cuprous cyanide:

\[
\text{H}_2\text{CN} \rightleftharpoons \text{H}^+ + \text{CN}^- \quad (21)
\]

\[
\text{Cu}^+ + \text{CN}^- \rightarrow \text{Cu} \text{CN} \quad (22)
\]

Cuprous cyanide is a white, easily filterable precipitate that can be reduced with hydrogen at 400°C. HCN is regenerated for recycling:

\[
2\text{CuCN} + \text{H}_2 \rightarrow 2\text{Cu} + 2\text{HCN} \quad (23)
\]

2.6 Sulfides

Copper sulfides (Table 1) are of interest in hydrometallurgy because they can be readily precipitated from leach solutions in a pure form and can be treated in a variety of ways to yield pure metallic copper.

2.6.1 Copper ammonium sulfides

Ammonium sulfide solution (natural pH about 8) extracts copper from oxidized copper ores. When SO₂ is bubbled through the solution at room temperature until pH 7 is reached, the cupric species are reduced to cuprous:

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+ \quad (24)
\]

\[
\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^- \quad (25)
\]

\[
[\text{Cu(NH}_3)_4]^{2-} + \text{e}^- \rightarrow [\text{Cu(NH}_3)_4]^{2+} \quad (26)
\]

The same behavior takes place when SO₂ is bubbled into a copper ammine solution

Table 1 • Copper sulfites of interest to hydrometallurgy

<table>
<thead>
<tr>
<th>Sulfite</th>
<th>Cu/ mass-%</th>
<th>S/ mass-%</th>
<th>NH₃/ mass-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₂·CuO</td>
<td>50</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>CuSO₃·Cu₂O</td>
<td>49</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>CuSO₄·Cu₂O</td>
<td>44</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Cu₂S·Cu₂O</td>
<td>33</td>
<td>50</td>
<td>17</td>
</tr>
</tbody>
</table>

(pH 10.5) until pH 7 is reached; the dark blue solution becomes colorless because of the oxidation-reduction reactions:

\[
\text{Cu}^+ + \text{OH}^- \rightarrow \text{Cu} \text{OH} \quad (27)
\]

\[
\text{Cu} \text{OH} \rightarrow \text{Cu(OH)}_2 \quad (28)
\]

\[
\text{Cu(OH)}_2 + \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (29)
\]

\[
\text{Cu}_2\text{O} + 2\text{Cu} \text{OH} \rightarrow 3\text{Cu} + \text{H}_2\text{O} \quad (30)
\]

\[
2\text{Cu}_2\text{O} + 2\text{Cu} \text{OH} \rightarrow 3\text{Cu} + \text{H}_2\text{O} \quad (31)
\]

\[
2\text{Cu}_2\text{O} + 2\text{Cu} \text{OH} \rightarrow 3\text{Cu} + \text{H}_2\text{O} \quad (32)
\]

\[
2\text{Cu}_2\text{O} + 2\text{Cu} \text{OH} \rightarrow 3\text{Cu} + \text{H}_2\text{O} \quad (33)
\]

\[
2\text{Cu}_2\text{O} + 2\text{Cu} \text{OH} \rightarrow 3\text{Cu} + \text{H}_2\text{O} \quad (34)
\]

\[
2\text{Cu}_2\text{O} + 2\text{Cu} \text{OH} \rightarrow 3\text{Cu} + \text{H}_2\text{O} \quad (35)
\]

\[
2\text{Cu}_2\text{O} + 2\text{Cu} \text{OH} \rightarrow 3\text{Cu} + \text{H}_2\text{O} \quad (36)
\]
When SO$_2$ is bubbled further until pH 3, two products can be obtained from these solutions [7]:

- By cooling, a double salt of cuprous ammonium sulfite having the composition Cu$_2$SO$_3$·(NH$_4$)$_2$SO$_3$ is formed. These crystals are cream colored shiny hexagonal platelets that are insoluble in water (Figure 4). When acidified, they precipitate metallic copper by disproportionation:

$$2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$$  \hspace{1cm} (28)

- When SO$_2$ is bubbled further until pH 3, a double salt having the composition Cu$_2$SO$_3$·(NH$_4$)$_2$SO$_3$·10H$_2$O is formed. These are water-soluble transparent needle crystals (Figure 3). When acidified, they precipitate metallic copper by disproportionation:

$$2\text{Cu}^{2+} + 4\text{NH}_4^+ + 4\text{H}_2\text{O} \rightarrow 2\text{Cu} + 4\text{NH}_3 + 2\text{SO}_2 + 2\text{H}_2\text{O}$$  \hspace{1cm} (29)

When slurried with water and heated at 150°C in an autoclave, precipitation of copper powder takes place:

$$\text{Cu}^+ + e^- \rightarrow \text{Cu}$$  \hspace{1cm} (30)

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2e^-$$  \hspace{1cm} (31)

$$\text{Cu}^+ + 4\text{NH}_4^+ + 4\text{H}_2\text{O} \rightarrow \text{Cu} + 4\text{NH}_3 + 2\text{SO}_2 + 2\text{H}_2\text{O}$$  \hspace{1cm} (32)

2.6.2 Chevreul’s salt

Named after its discoverer, the French chemist Michel Eugène Chevreul (1786–1889), the salt is a red crystalline solid having the composition Cu$_2$SO$_4$·CuSO$_3$·2H$_2$O (copper present in two valency states). It can be obtained in a variety of ways. For example:

- When copper oxide ore is dissolved in sulfuric acid, then the solution heated to:

$$\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$$  \hspace{1cm} (33)

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2e^-$$  \hspace{1cm} (34)

When NaHSO$_3$ is added to CuSO$_4$ leach solution at 60 °C:

$$3\text{Cu}^{2+} + 4\text{SO}_3^{2-} + 2\text{H}_2\text{O} \rightarrow 3\text{CuSO}_3\cdot\text{CuSO}_4\cdot2\text{H}_2\text{O} + \text{H}_2\text{SO}_4$$  \hspace{1cm} (35)

3.1 Ionic reducing agents

Table 2 shows examples of metal powder precipitation by reduction with ionic reducing agents. For example, gold and the platinum metals are separated on a commercial scale from the spent electrolyte during the electrolytic refining of gold. Figure 6 shows a scanning photomicrograph of gold powder precipitated from gold chloride solution by ferrous sulfate.

3.1.1 Sulfite ion

Sulfite ion may be used as an aqueous solution of sulfur dioxide:

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + 2\text{H}^+ + \text{SO}_4^{2-}$$  \hspace{1cm} (36)

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2e^-$$  \hspace{1cm} (37)

3.1.2 Precipitation of copper

On passing SO$_2$ into a solution of copper sulfate at room temperature, copper sulfite will precipitate. However, if precipitation is carried out at 150°C and 350 kPa, metallic copper is precipitated according to:

$$\text{Cu}^{2+} + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{Cu} + 2\text{H}^+ + \text{SO}_4^{2-}$$
The drawback to this process is the low yield of copper due to the intermediate formation of cuprous ion which disproportionate precipitating only half of the copper (Fig. 7):

\[ \text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \]

\[ 2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+} \]

This process can be improved by using an ammoniacal solution of ammonium sulfite instead of SO\(_2\):

\[ \text{Cu}^{2+} + \text{SO}_3^{2-} + 2\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Cu} + 2\text{NH}_4^+ + \text{SO}_4^{2-} \]

This results in complete precipitation of copper but it has the inconvenience of producing ammonium sulfate by-product.

3.1.3 Precipitation of selenium

Sulfite ion in the form of sulfur dioxide is also used to precipitate elemental selenium from selenous acid:

\[ \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2e^- \]

\[ \text{SeO}_3^{2-} + 6\text{H}^+ + 4e^- \rightarrow \text{Se} + 3\text{H}_2\text{O} \]

Overall reaction:

\[ \text{SeO}_3^{2-} + 2\text{H}^+ + 2\text{SO}_3^{2-} \rightarrow \text{Se} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \]

or

\[ \text{H}_2\text{SeO}_3 + 2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{Se} + 2\text{SO}_4 + 2\text{H}_2\text{O} \]

Selenious acid is obtained by water scrubbing of SeO\(_3\) fumes evolved during the treatment of anodic slimes of copper and nickel electrorefining.

3.2 Non-ionic reducing agents

Table 3 shows non-ionic reducing agents used in hydrometallurgy.

3.2.1 Hydrogen

Hydrogen at high temperature and pressure leads to the precipitation of nickel, cobalt, and copper powders on industrial scale. The investigation of these reactions was started in Russia at the beginning of the 20th century by Vladimir N. Ipatieff (1867–1952) and was further explored in the 1940s by Felix A. Schaufelberger (1911–2009) to overcome a precipitation problem of ammoniacal copper formate solution in pipes used for carbon monoxide scrubbing in the ammonia synthesis industry in the U.S. This experience in the chemical industry was put into practice in the metallurgical industry when Frank A. Forward (1902–1972) and Vladimir N. Mackiw (1923–2001) were developing pressure leaching technology for nickel-copper sulfide ore in Canada [8].

Reduction is usually carried out in horizontal stainless steel autoclaves equipped with agitators, baffles, heating or cooling coils, and the necessary connections for feed and gas inlets and outlets (Fig. 8). The product of this technique is a high-purity powder that can be used in that form or be hot pressed and rolled into strips. Canadian nickels, for example, were produced by this technique from 1960 to 2001 (Fig. 9).

Table 2 • Precipitation by ionic reduction

<table>
<thead>
<tr>
<th>Reducing Ion</th>
<th>Reaction</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfite</td>
<td>SO(_3)(^2-) + H(_2)O → SO(_4)(^2-) + 2H(^+) + 2e(^-)</td>
<td>Cu(^{2+}) + 2e(^-) → Cu</td>
</tr>
<tr>
<td>Dithionite</td>
<td>S(_2)O(_3)(^2-) → 2SO(_3)(^2-) + 2e(^-)</td>
<td>Cu(^{2+}) + 2e(^-) → Cu</td>
</tr>
<tr>
<td>Hypophosphite</td>
<td>H(_2)PO(_4)(^-) + H(_2)O → H(_2)PO(_4)(^-) + 2H(^+) + 2e(^-)</td>
<td>Ni(^{2+}) + 2e(^-) → Ni</td>
</tr>
<tr>
<td>Ferrous</td>
<td>Fe(^{3+}) → Fe(^{2+}) + e(^-)</td>
<td>Ag(^+) + 3e(^-) → Ag</td>
</tr>
<tr>
<td>Formate</td>
<td>HCOO(^-) + CO(_2) + H(^+) + 2e(^-)</td>
<td>Pt(^{II}) + 4e(^-) → Pt</td>
</tr>
<tr>
<td>Oxalate</td>
<td>C(_2)O(_4)(^2-) → 2CO(_3)(^2-) + 2e(^-)</td>
<td>Pd(^{II}) + 2e(^-) → Pd</td>
</tr>
</tbody>
</table>

Hypophosphite can be used instead of SO\(_2\) because both oxygen and hydrogen gases are released in this process. The precipitation of copper leads to the precipitation of nickel, cobalt, and manganese. The precipitation of nickel and cobalt is usually carried out in horizontal stainless steel autoclaves equipped with agitators, baffles, heating or cooling coils, and the necessary connections for feed and gas inlets and outlets. The product of this technique is a high-purity powder that can be used in that form or be hot pressed and rolled into strips. Canadian nickels, for example, were produced by this technique from 1960 to 2001 (Fig. 9).
For the reaction:

$$M^{n+} + H_2 \rightarrow M + 2H^+$$  \hspace{1cm} (50)

the equilibrium constant is given by:

$$K = \frac{[H^+]^2}{[M^{n+}]} \cdot p_{H_2}$$  \hspace{1cm} (51)

Therefore:

$$\log[M^{n+}] = -2pH - (\log K + \log p_{H_2})$$  \hspace{1cm} (52)

This means that when precipitation is carried out at constant hydrogen pressure and constant temperature, then at equilibrium there is a linear relation between $\log[M^{n+}]$ and the pH of the solution, and the slope of this straight line equals –2. This was confirmed as shown in Figures 10 and 11. It is clear from the above equation that more metal will be deposited if the hydrogen ions are removed as soon as they are formed. This is conveniently done by operating in ammoniacal medium:

$$[M(NH_3)]^{n+} \rightarrow nNH_3 + M^{n+}$$  \hspace{1cm} (53)

$$M^{n+} + H_2 \rightarrow M + 2H^+$$  \hspace{1cm} (54)

$$H^+ + NH_3 \rightarrow NH_3$$  \hspace{1cm} (55)

It can be seen that increasing the ammonia concentration has two opposing effects:

- Precipitation is favored due to the neutralization of the liberated acid.
- Precipitation is hindered because of a decrease in the reducible metal ions $M^{n+}$ due to the complexing action.

Therefore, there must be an optimum $[NH_3]/[M^{n+}]$ ratio at which these opposing effects are balanced. In the precipitation of nickel, the optimum molar ratio was found to equal two, which agrees with the overall reaction:

$$Ni^{2+} + 2NH_3 + H_2 \rightarrow Ni + 2NH_3$$  \hspace{1cm} (56)

The amount of ammonia in solution also influences the rate of precipitation. In the case of cobalt, the rate of precipitation achieves a maximum when $[NH_3]/[Co^{2+}] = 2$, as shown in Fig. 12. In the case of copper, however, the metal can be precipitated from acidic medium (Fig. 13).

Another way of removing the hydrogen ions as soon as they are formed during reduction is by reducing hydroxide slurries:

$$M(OH)_2 + H_2 \rightarrow M + H_2O$$  \hspace{1cm} (57)

$$M^{n+} + H_2 \rightarrow M + 2H^+$$  \hspace{1cm} (58)

$$OH^+ + H^+ \rightarrow H_2O$$  \hspace{1cm} (59)

Overall reaction:

$$M(OH)_2 + H_2 \rightarrow M + H_2O$$  \hspace{1cm} (60)

### 3.2.2 Nucleation

In some cases, the presence of a solid surface for precipitation is essential; such a solid is termed a “catalyst.” Strictly speaking, the process is heterogeneous (contact catalysis) but is different from the heterogeneous process described later.

If no catalyst is provided, the internal surface of the autoclave itself acts as a catalyst and deposition of metals takes place on the walls or on stirrers. In the commercial precipitation of nickel from the ammonium sulfate system, nucleation is induced by adding a small amount of ferrous sulfate which, after heating to the reaction temperature, hydrolyzes to ferrous hydroxide thus furnishing the catalytic surface required. Nickel deposited in the first step acts as a catalyst for the next. After each reduction, the nickel particles are allowed to settle to the bottom of the autoclave, while the spent solution is drawn off and replaced with...
fresh pregnant solution. In this way, the nickel particles grow to the desired size, at which point the suspension is discharged and the nickel powder then separated.

3.2.3 Role of additives
The presence of certain organic or inorganic substances in the aqueous phase greatly affects the physical nature of the metal that is precipitated. It is possible to precipitate metal powder with a given physical property by simply adding a certain amount of additive. However, when organic additives are used, the carbon content in the powder produced is increased and a special heat treatment is necessary to lower it to under 0.01%. Additives may be used for the following purposes:

- **Anti-agglomeration**: Agglomeration of the precipitated metal particles may take place, especially at high temperature. This is undesirable because the agglomerated particles entrap solution causing an impure product. Reagents are therefore added to control the particle size. These are the same as those commonly used to promote uniform growth of cathodes in the electrowinning of metals, e.g., ammonium polyacrylate, arabic gum, gelatin, dextrin, dextrose, and fatty acids such as oleic and stearic. These additives are adsorbed on the individual particles, thus preventing their agglomeration.

- **Smooth surface formation**: When anthraquinone or its derivatives are added during reduction, the nickel particles produced are smooth and regular because of uniform deposition. In the absence of anthraquinone, they are coarse and irregular (Fig. 14). Anthraquinone has no effect on the precipitation of cobalt. The addition of this additive to ammoniacal nickel sulfate or carbonate solutions also accelerates the precipitation, and this effect increases with increasing anthraquinone concentration up to a certain value, beyond which it has no further effect.

- **Crystalline product**: Figure 15 shows hexagonal platelets of metallic cobalt precipitated in the presence of a suitable additive.

3.2.4 Precipitation of copper powder from non-aqueous medium
Copper ions are extracted by organic solvents by forming a coordination bond. When this loaded organic phase is treated by hydrogen at high temperature and pressure in an autoclave, the metal precipitates in powder form and the organic phase is regenerated. The process may be described as “precipitation by substitution” since no ionic species are taking part in the reaction as compared to precipitation by hydrogen from an aqueous phase. The substitution reaction can be represented as follows:

\[
\begin{align*}
H_{2(g)} & \rightarrow H_{2(\text{org})} \\
R\text{M}_{\text{org}} + H_{2(\text{org})} & \rightarrow 2RH_{\text{org}} + M_{(s)}
\end{align*}
\]

where RH is the organic solvent and M is a divalent metal. For the precipitation of copper powder from hydroxy-quinoline-kerosene phase containing copper the reaction is:

\[
\begin{align*}
2\text{Cu}^{2+} + 4\text{NH}_3 & \rightarrow \text{Cu}_{2}^{2+} + 4\text{NH}_4^{+} \quad (64) \\
\text{Cu}^{2+} + \text{CO} + \text{H}_2\text{O} & \rightarrow \text{Cu} + \text{CO}_2 + 2\text{H}^+ \quad (65)
\end{align*}
\]

Precipitation takes place at 150°C with CO partial pressure of 5,000 kPa. The solution is then boiled to precipitate zinc as basic carbonate. Precipitation of metals by CO is much slower than by hydrogen. This may be due to the fact that CO first reacts with water to form hydrogen:

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO}_2
\end{align*}
\]

3.2.5 Carbon monoxide
Carbon monoxide has been used for precipitating silver from AgNO₃ solution and copper from [Cu(NH₃)₄]²⁺ solution obtained by leaching brass scrap in ammoniacal ammonium carbonate:

\[
\begin{align*}
[\text{Cu(NH}_3)_4]^{2+} & \rightarrow \text{Cu}^{2+} + 4\text{NH}_3 \\
\text{Cu}^{2+} + \text{CO} + \text{H}_2\text{O} & \rightarrow \text{Cu} + \text{CO}_2 + 2\text{H}^+ \\
\text{Cu}^{2+} + \text{CO} + \text{H}_2\text{O} & \rightarrow \text{Cu} + \text{CO}_2 + 2\text{H}^+
\end{align*}
\]

Because of its high cost, its use in metallurgy is limited.

3.2.6 Hydrazine
Hydrazine, H₂N–NH₂, is an ammonia-like colorless gas produced industrially by the oxidation of methyl alcohol which in turn is produced from coal or petroleum gases. It is mainly used for the manufacture of synthetic resins and as a reducing agent. It is effective in acid and in alkaline medium. In acid medium, formic acid is created:

\[
\begin{align*}
\text{HCHO} + \text{H}_2\text{O} & \rightarrow \text{HCOOH} + 2\text{H}^+ + 2\text{e}^- \\
\text{HCHO} + 3\text{OH}^- & \rightarrow \text{HCOO}^- + 2\text{H}_2\text{O} + 2\text{e}^-
\end{align*}
\]

Formaldehyde sodium sulfoxylate, known in industry as Rongalit C, is a crystalline solid having all the reducing properties of formaldehyde but the convenience of being easily handled. It is prepared by reacting formaldehyde with sodium sulfoxylate in alkaline medium:
Formaldehyde sodium sulfoxylate, known as OSONa, is a powerful reducing agent prepared industrially by the oxidation of formaldehyde but the convenience of being highly soluble and having all the reducing properties of formaldehyde. It is used for the manufacture of synthetic resins of which methyl alcohol which in turn is produced from natural gas produced industrially by the oxidation of carbon monoxide. Carbon monoxide has been used for precipitating metals as it reacts with the metal ion in solution. Reactions take place through transfer of electrons at the surface of the solid.

### 3.2.6 Hydrazine

Hydrazine, H₂N–NH₂, is a powerful reducing agent prepared industrially by the oxidation of ammonia by hypochlorite via the intermediate formation of chloramine:

\[
\begin{align*}
\text{NH}_3 + \text{OCl}^- &\rightarrow \text{NH}_2\text{Cl} + \text{OH}^- \\
\text{NH}_2\text{Cl} + \text{OH}^- &\rightarrow \text{H}_2\text{N}–\text{NH}_2 + \text{Cl}^- + \text{OH}^- \\
\text{H}_2\text{N}–\text{NH}_2 &\rightarrow \text{N}_2 + 4\text{H}^+ + 4\text{e}^-
\end{align*}
\]

Aqueous solutions of hydrazine are capable of reducing many metal ions to a lower valency state or to metals:

\[
\begin{align*}
\text{H}_2\text{N}–\text{NH}_2 + \text{M}^{n+} &\rightarrow \text{N}_2 + \text{M}^{(n-2)+} + 2\text{H}^+ + 2\text{e}^- \\
\text{H}_2\text{N}–\text{NH}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Because of its high cost, its use in metallurgy is limited.

### 3.3 Electrochemical reduction

Precipitation of metal powders by electrochemical methods is a heterogeneous process in which the reducing agent is activated chemically or thermally. Reactions take place through transfer of electrons at the surface of the solid.
3.3.1 Precipitation by activated charcoal
Activated charcoal has been used for many years to precipitate gold from solutions obtained by leaching gold ores with chlorine water:

\[
\text{AuCl}_3 + 3\text{Cl}^- \rightarrow \text{Au}^{3+} + 3\text{Cl}_2
\]

Overall reaction:

\[
\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-
\]

Gold precipitated on the surface of charcoal can be recovered by burning the charcoal.

3.3.2 Precipitation by metals
Precipitation of a metal from an aqueous solution of its salts by another metal is known as “cementation”. The precipitated metal powder usually adheres loosely to the surface of the precipitating metal. The process can be predicted in terms of electrode potentials. The metal with the more positive (oxidation) potential will pass into solution and displace a metal with a less positive potential provided the solutions are dilute and the metal ion is un-complexed. The process is electrochemical in nature as shown in Fig. 16.

A metal may also be recovered from an aqueous suspension of one of its insoluble salts by this method, e.g., silver from silver chloride:

\[
2\text{AgCl} + \text{Fe}^{2+} \rightarrow 2\text{Ag} + \text{FeCl}_2
\]

Although AgCl is insoluble in water, a certain amount of Ag⁺ ions do exist in solution and their continuous removal by metallic iron shifts the equilibrium:

\[
\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-
\]

to the right resulting in the ultimate disappearance of AgCl. Similarly, copper may be recovered from cuprous chloride suspensions by metallic iron:

\[
\text{Cu}_2\text{Cl}_2 + \text{Fe} \rightarrow 2\text{Cu} + \text{FeCl}_2
\]

In some cases, the metal to be precipitated exists in solution as a complex ion, e.g., gold or silver in cyanide solution exist as the complex cyanide ion [Au(CN)_3]⁻ and [Ag(CN)_2]⁻ respectively. Precipitation by metallic zinc takes place as a result of displacing the equilibrium of the complex ion according to:

\[
\text{Zn}^{2+} + 4\text{CN}^- \rightarrow [\text{Zn(CN)}_4]^{2-}
\]

Overall reaction:

\[
2[\text{Au(CN)}_3]^- + \text{Zn} \rightarrow 2\text{Au} + [\text{Zn(CN)}_4]^{2-}
\]

3.3.3 Factors affecting the physical properties of precipitated metals
For the cementation of copper by iron, a finer powder is obtained at high Cu²⁺ ion concentration, as shown in Table 4. Further, at a constant Cu²⁺ ion concentration, a finer powder is obtained at high H₂SO₄ concentration, as shown in Table 5. The form of the metal precipitated depends on the precipitating metal as shown in Fig. 17.

### Table 4 • Effect of Cu²⁺ concentration on the particle size of copper precipitated by iron [15]

<table>
<thead>
<tr>
<th>Screen analysis / %</th>
<th>3.7</th>
<th>15.0</th>
<th>27.0</th>
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<tr>
<td>100 mesh</td>
<td>7.7</td>
<td>4.1</td>
<td>1.6</td>
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<tr>
<td>100-150</td>
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<td>9.2</td>
<td>6.0</td>
</tr>
<tr>
<td>150-200</td>
<td>15.7</td>
<td>11.3</td>
<td>11.3</td>
</tr>
<tr>
<td>200-270</td>
<td>14.0</td>
<td>10.8</td>
<td>12.2</td>
</tr>
<tr>
<td>270-325</td>
<td>5.4</td>
<td>5.1</td>
<td>6.5</td>
</tr>
<tr>
<td>325</td>
<td>45.6</td>
<td>59.5</td>
<td>62.4</td>
</tr>
</tbody>
</table>

### Table 5 • Effect of H₂SO₄ on the particle size of copper precipitated by iron [15]

<table>
<thead>
<tr>
<th>Screen analysis / %</th>
<th>8.9</th>
<th>16.4</th>
<th>29.9</th>
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<tbody>
<tr>
<td>100 mesh</td>
<td>3.5</td>
<td>4.6</td>
<td>3.3</td>
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<td>100-150</td>
<td>8.6</td>
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<td>11.4</td>
</tr>
<tr>
<td>270-325</td>
<td>6.5</td>
<td>5.8</td>
<td>6.4</td>
</tr>
<tr>
<td>325</td>
<td>54.6</td>
<td>56.5</td>
<td>64.1</td>
</tr>
</tbody>
</table>
3.3.4 Purity and disposal of products

The precipitated metal usually contains appreciable amounts of the precipitating metal and therefore must be treated further to remove it. This is usually done by acid leaching. For example, excess zinc precipitated with gold or cadmium during cementation is removed by leaching with H₂SO₄. Cementation of copper from dilute leach solutions was conducted on a large scale as a cheap and rapid method of metal recovery. Drying cement copper is not an easy operation because of its tendency to form oxide. In a few cases, cement copper is purified and marketed as a powder. Purification methods yielding powder:

- Dissolution in H₂SO₄ in presence of oxygen whereby Fe²⁺ is converted to Fe³⁺ which can be precipitated and filtered off.
- The pure copper sulfate solution is then treated by hydrogen under pressure and high temperature to yield pure copper powder.
- Digestion with CuSO₄ solution, thus displacing the iron content by copper.

3.3.5 Methods and equipment

Small scale cementation reactions are batch processes conducted in agitated tanks, e.g., for precipitating cadmium from zinc sulfate solution and gold and silver from cyanide solutions and zinc dust. In case of gold and silver, the solution must first be de-aerated as mentioned earlier. Precipitation in rotating drums is a continuous process using pear-shaped vessels (Fig. 18) charged from time to time with pieces of the precipitating metal. Due to the rotation, the precipitated metal flows out with the exit solution and is collected by filtration. Large-scale cementation reactions are conducted principally for the recovery of copper from dilute solutions using scrap iron. This is conducted in launders or in inverted cone reactors.

Launders (Fig. 19) are narrow tanks about 170 m long, 1.3–3 m wide, and 0.3–1.3 m deep, inclined at a slope of about 2%. The launders are continuously charged with the iron scrap. The injection of the solution over the area of the tank above the stainless steel screen and accumulates on the bottom side discharge at the opposite side. The annular space between the inner cone and the tank is covered by a stainless steel screen mounted as a continuation of the cone that is anchored to the cone and tank. The cone supports a series of pressure nozzles arranged in a configuration that creates a vortex when the copper-bearing solution is pumped into the cone. The inner cone and the area of the tank above the stainless steel screens are filled with shredded de-tinned iron scrap. The injection of the solution through the mass of iron has the effect of not only rapidly precipitating copper, but also removing the metallic copper from the iron surface. The copper settles down through the stainless steel screen and accumulates on the sloped false bottom of the tank. Copper can then be discharged either intermittently or continuously. This technology has been abandoned and replaced by solvent extraction followed by electrolytizing.

### 3.4 Electrolytic reduction

Metal powders are obtained by electrolytic reduction under certain conditions. Metal deposits are always crystalline, but they vary from large-grained coarse adherent deposits to fine-grained loosely adhering powder [17]. While the rate of metal deposition, according to Faraday’s laws, depends only on the current applied and not on factors such as temperature, concentration, etc., the character of metal deposit is a direct function of these other factors. As a result of the...
discharge process at the cathode, the concentration of the metal ion is decreased at the interface. This loss is compensated by diffusion of a fresh supply of metal ions from the body of the solution. The rate of diffusion is given by:

\[
\text{Rate of diffusion} = \frac{DA}{\delta} (C - C_i) \quad (85)
\]

The rate of discharge of the ions by the current is given by:

\[
\text{Rate of discharge} = \frac{I}{nF} \quad (86)
\]

At the steady state, the two rates are equal, i.e.,

\[
\frac{I}{nF} = \frac{DA}{\delta} (C - C_i) \quad (87)
\]

or:

\[
I = \frac{nFAD}{\delta} (C - C_i) \quad (88)
\]

With increasing current density, \(I/A\), the value \(C - C_i\) should increase, since the metal ions at the interface, \(C_i\), will be rapidly depleted. At constant current density, when the electrolyte is stirred, thus decreasing the thickness of the boundary layer, \(\delta\), the difference \(C - C_i\) should decrease, i.e., \(C_i\) increases. The form of the deposit depends on many factors since two processes are taking place during electro-deposition:

- nucleation
- crystal growth

When the rate of nucleation is much larger than the rate of crystal growth, the product will be fine powder. On the other hand, when the rate of crystal growth is much larger than the rate of nucleation, the product will be coarse-grained. When \(C_i\), the concentration of metal ion at the interface, tends to zero, i.e., when the process becomes diffusion-controlled, the rate of nucleation becomes much greater than the rate of crystal growth, thus favouring the deposition of powders. In other words, powder formation occurs when the diffusion process is diffusion-controlled and coarse-grain deposits occur when the process is chemically-controlled. The following factors influence the value of \(C_i\) and therefore determine the nature of metal deposited:

- **Current density:** At low current density, the discharge of ions is slow, i.e., the process is chemically-controlled. The rate of crystal growth is much greater than the rate of nucleation. Therefore the product will be a coarse deposit. At high current density, the opposite is true. Figure 22 shows the effect of current density on particle size distribution. It can be seen that at 10.5 amp/dm\(^2\) the most common particle size of electrodeposited copper powder is 0.1 mm while at 18 amp/dm\(^2\) it is only 0.05 mm.

- **Concentration of electrolyte:** At low electrolyte concentration, the rate of diffusion is slow and usually governs the whole process, i.e., the process becomes diffusion-controlled and powder formation is favoured. The opposite is true at high electrolyte concentration. Table 6 shows that the more dilute the electrolyte, the more finely-grained are the electrodeposited particles of the metal.

- **Temperature:** Increasing the temperature increases the rate of diffusion and the rate of crystal growth. Both factors favour the formation of coarse deposits. Therefore, increasing temperature results in the formation of coarser deposits.

- **Stirring of bath:** The higher the speed of stirring, the coarser the deposited particles (Table 7), because under these conditions, the thickness of the boundary layer is decreased, resulting in an increased rate of diffusion. The process becomes chemically-controlled.

- **The presence of an indifferent electrolyte:** An indifferent electrolyte does not react at the cathode but decreases the transference number of the deposited cation. A decrease in the transference number will decrease the diffusion process to such an extent that it becomes almost zero.

- **Potential of electrolyte:** The presence of an indifferent electrolyte is not sufficient to suppress the diffusion process and the electrodeposition occurs in the form of powder. An indifferent electrolyte does not react at the cathode but decreases the transference number of the deposited cation. A decrease in the transference number will decrease the diffusion process to such an extent that it becomes almost zero.
it becomes rate-controlling, thus favouring powder formation.

- Presence of colloidal substances in the electrolyte: Small additions of gelatine, agar, glue, gums, peptones, sugars, etc., result in the formation of a smooth fine-grained deposit. If, however, the concentration of the colloids exceeds about 0.05 g/L, a loose deposit is obtained. The reason is that colloids are adsorbed on the nuclei of metal crystals, thus preventing their growth, and the ions are compelled to start new nuclei.

The previous discussion is somewhat simplified because side reactions are usually superimposed. For example, when conditions are favourable for powder deposition and the process has progressed for some time, the effective surface area of the cathode increases, resulting in decreased current density. Consequently, the conditions may be shifted toward coarse-grain deposition. Also, the nature of the electrolyte may affect the type of deposit. For example, lead deposited from nitrate solution is soft, but it is smooth from silicofluoride solution. Silver deposited from nitrate solution is coarse, while from cyanide solution it is smooth. Thus the complexing state of metal ion in solution plays an important role. In the case of silver with cyanide, the free Ag⁺ ions are extremely small due to the equilibrium:

\[ \text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag(CN)}]_2^- \]  

No powder is formed, but an extremely smooth and bright deposit is obtained instead.

If hydrogen is released during deposition, the solution at the immediate vicinity of the interface will be depleted of H⁺ ions thus becoming alkaline and causing precipitation of colloidal hydroxides. This may inhibit crystal growth, favouring powder formation. On the other hand, the stirring action due to hydrogen bubble movements may favour the production of large grain size deposits. While powders are formed at low electrolyte concentrations and low temperature, sponge formation is favoured at low electrolyte concentration and high temperature.

### 4 Summary

Table 8 gives a summary of metal powder production by hydrometallurgical methods.

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