CHAPTER 10.18

Gaseous Reduction in Aqueous Solutions

Jari Aromaa, Mari Lundström, and Olof Forsén

Gaseous reduction is one means of recovering a metal from aqueous solution. The method is also sometimes called *hydrothermal* or *solvothermal* reduction. A reducing gas such as hydrogen, sulfur dioxide, or carbon monoxide is used to reduce dissolved metal ions. The first application was used for nickel production. Leaching and recovery processes were developed by Chemical Construction Corporation and Sherritt Gordon Mines in the 1950s (Schaufelberger 1956; Mackiw et al. 1957).

Nickel and other metals are industrially produced by the reduction of ammoniacal solution by hydrogen under pressure at elevated temperatures in mechanically agitated autoclaves. The processes are commercially confidential and site specific. Gaseous reduction of metals from salt solutions is an alternative to electrowinning that uses electric energy for metal deposition. Gaseous reduction is also useful in production of specialty products such as metal powders.

The most important applications are reduction of nickel and cobalt by hydrogen (Crundwell et al. 2011). Sulfur dioxide has found limited use. Carbon monoxide has been studied in recovery of silver, copper, nickel, and cobalt, but no processes have been developed (Burkin 2001). Hydrogen is relatively inexpensive to produce on a large scale. The reaction products in an aqueous solution are either hydrogen ions or hydroxyl ions. Neither creates by-products that would cause operating or disposal problems. Sulfur dioxide is toxic and causes sulfuric acid formation in the solution and production contamination. Carbon monoxide has also shortcomings, as it is toxic, explosive, difficult to synthesize, and expensive, and it changes the acid–base balance. Sulfur dioxide and carbon monoxide can be used for precipitation of metal powders from alkaline and ammonia (NH_3) solutions (Naboychenko 2009).

THERMODYNAMICS OF REDUCTION

The gaseous reduction is based on the electrochemical potential difference between dissolved metal and the reducing gas. The standard electrode potentials (E°) show thermodynamic limits for gaseous reduction. The gaseous reduction is possible only when the equilibrium potential of the metal to be reduced is higher than that of the reducing gas that in turn becomes oxidized. Some relevant standard electrode potentials are shown in Table 1. By comparing these standard electrode potentials, it is seen that theoretically, only copper can be reduced by carbon monoxide or hydrogen; and copper, copper–ammonia complexes, ferric iron, lead, and tin by sulfur dioxide.

The operating conditions are never in the standard state described by the standard electrode potentials shown in Table 1. The equilibrium potential of the metal at any temperature and reacting species concentration is given by the Nernst equation (Equation 1). For a simple metal ion reduction reaction $Me^{z+} + ze^- = Me$, the equilibrium potential is given by the following equation:

$$E = E^\circ - RT/zF \cdot \ln(1/[Me^{z+}]) \qquad \textbf{(EQ 1)}$$

where E is the equilibrium potential (V), E° is standard electrode potential (V), R is general gas constant (8.3143 J mol^{-1} K^{-1}), T is absolute temperature (K), z is the number of electrons in the reaction, F is the Faraday constant (96,485 C mol^{-1}), and $[Me^{z+}]$ is the concentration of metal ions in the solution (mol dm^{-3}).

The equilibrium potential of the metal should be as high as possible to provide stronger driving force for the reaction. The equilibrium potential calculated by Equation 1 increases with increasing metal ion concentration. When calculating the equilibrium potential, it must be noted that the activity coefficient of metal in solution usually decreases with increasing concentration. The activity coefficient changes in the typical concentration, ranging from 0.1 to 1 M, are not large (Meddings and Mackiw 1964; Burkin 2001), but the decrease in activity coefficient loses some of the beneficial equilibrium potential increase. As the activity coefficients are less than 0.1 (Meddings and Mackiw 1964; Burkin 2001), the metal equilibrium potentials usually decrease slightly with increasing temperature.

The equilibrium potential of the reducing gas is also calculated from the Nernst equation. To maintain a high driving

Jari Aromaa, Senior Lecturer, Aalto University, Espoo, Finland
Mari Lundström, Professor, Aalto University, Espoo, Finland
Olof Forsén, Professor Emeritus, Aalto University, Espoo, Finland

Table 1 Standard electrode potentials of reactions of interest in metal gaseous reduction

Reaction	Standard Electrode Potential, E° (V)	Reaction Type
$Ag^+ + e^- \leftrightarrow Ag$	0.799	Metal ion reduction
$[Ag(NH_3)_2]^+ + e^- \leftrightarrow Ag + 2NH_3$	0.375	Metal complex reduction
$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.337	Metal ion reduction
$CO + H_2O \leftrightarrow CO_2 + 2H^+ + 2e^-$	0.104	Reducing gas oxidation
$H_2 \leftrightarrow 2H^+ + 2e^-$	0.000	Reducing gas oxidation
$Fe^{3+} + 3e^- \leftrightarrow Fe$	–0.037	Metal ion reduction
$[Cu(NH_3)_4]^{2+} + 2e^- \leftrightarrow Cu + 4NH_3$	–0.023	Metal complex reduction
$[Cu(NH_3)_2]^+ + e^- \leftrightarrow Cu + 2NH_3$	–0.124	Metal complex reduction
$Pb^{2+} + 2e^- \leftrightarrow Pb$	–0.126	Metal ion reduction
$Sn^{2+} + 2e^- \leftrightarrow Sn$	–0.136	Metal ion reduction
$SO_2 + 2H_2O \leftrightarrow SO_4^{2-} + 4H^+ + 2e^-$	–0.157	Reducing gas oxidation
$Ni^{2+} + 2e^- \leftrightarrow Ni$	–0.250	Metal ion reduction
$Co^{2+} + 2e^- \leftrightarrow Co$	–0.277	Metal ion reduction
$Cd^{2+} + 2e^- \leftrightarrow Cd$	–0.403	Metal ion reduction
$[Ni(NH_3)_6]^{2+} + 2e^- \leftrightarrow Ni + 6NH_3$	–0.497	Metal complex reduction

Source: Outotec 2015

force, the equilibrium potential of the gas oxidation reaction should be as low as possible. Some of the theoretical oxidation reactions of reducing gases are given by the following equations:

$$H_2 = 2H^+ + 2e^- \quad \textbf{(EQ 2)}$$

$$SO_2 + H_2O = SO_4^{2-} + 4H^+ + 2e^- \quad \textbf{(EQ 3)}$$

$$CO + H_2O = CO_2 + 2H^+ + 2e^- \quad \textbf{(EQ 4)}$$

The Nernst equation to calculate equilibrium potential for hydrogen reaction (Equation 2) is shown in the following equation:

$$E = E^\circ - (RT/2F)\cdot\ln\{p(H_2)/a(H^+)^2\} \quad \textbf{(EQ 5)}$$

where $p(H_2)$ is the partial pressure of H_2 in atmospheres and $a(H^+)$ is the activity of a hydrogen ion. The equilibrium potentials of sulfur dioxide oxidation (Equation 3) and carbon monoxide oxidation (Equation 4) are given in Equations 6 and 7, respectively.

$$E = E^\circ - (RT/2F)\cdot\ln\{p(SO_2)/(a(SO_4^{2-})\cdot a(H^+)^4)\} \quad \textbf{(EQ 6)}$$

$$E = E^\circ - (RT/2F)\cdot\ln\{p(CO)/(p(CO_2)\cdot a(H^+)^2)\} \quad \textbf{(EQ 7)}$$

The equilibrium potentials of the gas oxidation reactions (shown in Equations 2 through 4) decrease with increasing pH and increasing gas pressure. The equilibrium potential of the sulfur dioxide oxidation reaction (Equation 3) decreases with decreasing sulfate ion concentration and that of the carbon monoxide oxidation reaction (Equation 4) with decreasing carbon dioxide partial pressure.

During reduction, the metal concentration decreases from about 1 M solution to 0.1 M (Burkin 2001). This means that the thermodynamic activity of the metal deposition reaction will decrease. At the same time, the reducing gas pressure will decrease as it is consumed, and also the pH of the solution declines as hydrogen ions are produced. These changes will decrease the driving force. Figure 1 shows equilibrium potential values for nickel, copper, and hydrogen at T = 100°C. The metal equilibrium potentials have been calculated using Equation 1 and the activity coefficients from Meddings and Mackiw (1964) and Burkin (2001), and the hydrogen potentials using Equation 5.

The thermodynamic conditions necessary for metal reduction can also be estimated by using potential–pH or E–pH diagrams. These diagrams show the stability areas of selected compounds. Figure 2 shows a potential–pH diagram for copper and nickel. The reduction conditions must be selected so that the metal is the stable compound. In Figure 2, the lower dashed line is the hydrogen reaction equilibrium. As shown in Figures 1 and 2, the potential of hydrogen reaction must be lower than the reaction between solid and dissolved metal so that the metal reduction is thermodynamically possible. Reduction of copper is possible at the whole pH range shown, but reduction of nickel is possible only when pH is higher than approximately 5.5.

During the reduction process, the pH of the solution decreases because hydrogen ions are formed. The driving

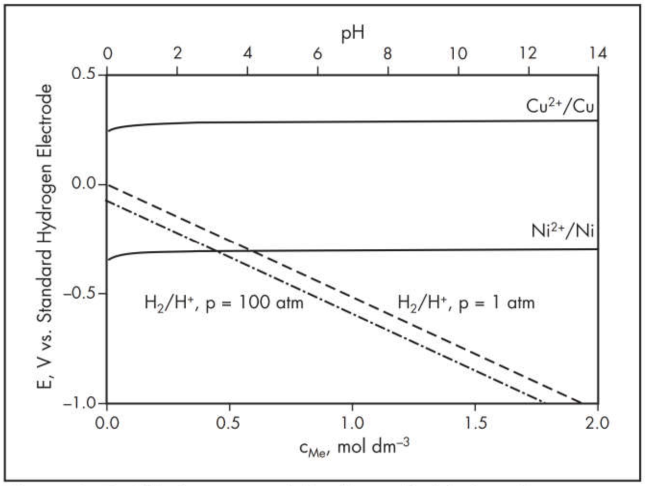


Figure 1 Equilibrium potential values of nickel and copper reduction and hydrogen oxidation

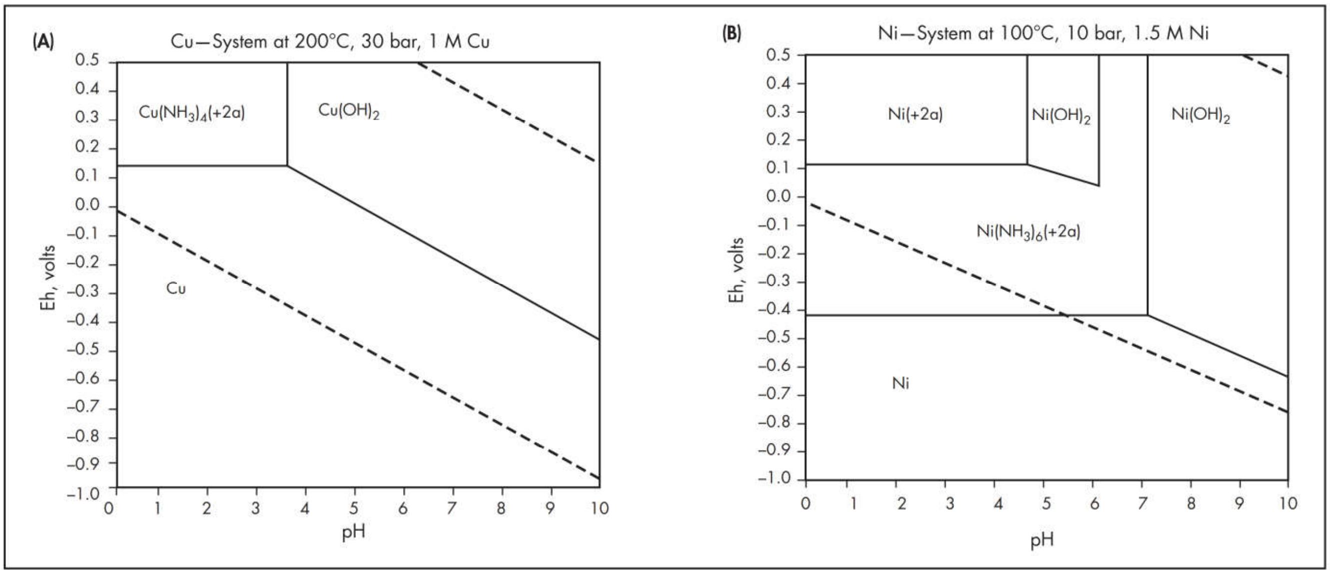


Figure 2 Potential–pH diagrams of copper (A) and nickel (B) related to hydrogen reduction

force of metal reduction decreases and finally metal deposition ceases. One approach to maintain the thermodynamic conditions is to neutralize the acid. This has been done by using anhydrous ammonia (Burkin 2001), but hydroxides and carbonates can also be used. The solubility of many metal salts first increases but then decreases with increasing temperature. Above a certain pH value, the hydrolysis of the metal becomes significant, causing formation of metal hydroxides that will not reduce to metals. To keep metals in solution, it is necessary to complex the cations. The equilibrium potential equations and information shown in Figure 1 must be modified to include the effect of the complexing ligands. In a complex system, the equilibrium (Equation 8) prevails, and its equilibrium constant β is given by Equation 9. In the following equations, n is the maximum coordination number of the metal ion with ligand L (Burkin 2001).

$$\mathrm{Me}^{z+} + n\mathrm{L} = \mathrm{MeL}_n{}^{z+} \qquad \textbf{(EQ 8)}$$

$$\beta = a(\mathrm{MeL}_n{}^{z+})/\{a(\mathrm{Me}^{z+})\cdot a(\mathrm{L})^n\} \qquad \textbf{(EQ 9)}$$

Using (Nernst) Equation 1 and equilibrium constants of the complexes, it is possible to calculate the equilibrium potential of the metal–metal complex as follows:

$$E = E - RT/zF\cdot\Sigma(\beta_i\cdot a_i) \qquad \textbf{(EQ 10)}$$

For many metals the most common method to complex metal cations and raise pH is to use ammonia to produce metal amines $[\mathrm{Me(NH_3)_x}]^{z+}$. As the ammonia concentration increases, the ratio of higher-to-lower complexes increases. The addition of ammonia will decrease the equilibrium potentials of metal–metal complexes and the hydrogen reaction but not in the same ratio. Thus, there will be a metal-to-ammonia ratio where the driving force of metal reduction has its maximum value. For nickel reduction, this will be in the ammonia-to-nickel ratio of 2.0–2.5 (Meddings and Mackiw 1964; Burkin 2001); for cobalt reduction, the relevant ratio is 2.5–3.0 (Burkin 2001); and for copper reduction, 2.2–2.5 (Naboychenko et al. 2009b).

KINETICS OF REDUCTION

The thermodynamic conditions can be estimated by using equilibrium potentials, taking into account the concentrations of reacting species, temperature, complex formation and changes in the metal concentration, reducing gas pressure and fugacity, and pH decrease. The reaction steps of metal reduction by reducing gases are nucleation, particle growth, and agglomeration. At first, very small stable particles of metal nucleate; this stage may need seeding. Clusters containing a few atoms are thermodynamically unstable and become stable after growing to particle size 1–5 nm (Naboychenko 2009). The nuclei grow by deposition of metal on particle surfaces. Particles can agglomerate and be permanently covered by overgrowing metal deposit. In general, the precipitation of metal by a reducing gas includes the following four stages (Burkin 2001; Naboychenko 2009):

1. Gas dissolution and saturation of the solution by the gas
2. Adsorption of the gas on the nuclei or seed surface and gas activation with the formation of an intermediate compound
3. Electrochemical metal ion reduction
4. Reduced metal remaining in solution and providing new adsorption site for reducing gas

The solubility of gas increases with increasing gas pressure and decreases with increasing concentration of dissolved species. The absorption of the reducing gas into solution takes place in two sequential steps: Dissolution of gas into the solution at the gas–liquid interface followed by diffusion of dissolved gas through the solution boundary layer accompanied by a chemical reaction. The gas adsorption rate increases with increasing stirring speed. The gas adsorption flux increases up to a certain stirring speed after which it remains constant. The main purpose of liquid stirring is to supply a constant flow of the gaseous reactant to metal surfaces.

The adsorption of gas and its activation result in active intermediate compounds. Molecular hydrogen is chemically inert and for metal reduction reactions, activation of the hydrogen molecule is necessary. Activation of the hydrogen results in intermediate metal hydrides. The activation can follow a homolytic activation path, producing two hydrogen atoms, or a heterolytic path, producing a proton H^+ and a hydride H^- (Osseo-Asare 2003; Naboychenko 2009). The homolytic path requires two metal cations, as shown in Equation 11; but the heterolytic path requires only a single metal cation, as shown in the next equations (Halpern 1959; Osseo-Asare 2003):

$$2Ag^+ + H_2 \rightarrow 2AgH^+ \qquad \textbf{(EQ 11)}$$

$$Ag^+ + H_2 \rightarrow AgH^\circ + H^+ \qquad \textbf{(EQ 12)}$$

$$Cu^{2+} + H_2 \rightarrow CuH^+ + H^+ \qquad \textbf{(EQ 13)}$$

Some of the metal hydride intermediates are unstable and they will react in reverse reactions to regenerate hydrogen gas or in reactions involving reduction of the metal ion or another aqueous species. For example, copper hydride (CuH^+) can react with cupric ions to produce cuprous ions after Equation 14, and the cuprous ions can then react to metallic copper and cupric ions in disproportionation reaction (Equation 15) (Von Hahn and Peters 1965). The reaction takes place at sufficiently high cuprous ion concentrations.

$$CuH^+ + Cu^{2+} \rightarrow 2Cu^+ + H^{+a} \qquad \textbf{(EQ 14)}$$

$$2Cu^+ \rightarrow Cu + Cu^{2+} \qquad \textbf{(EQ 15)}$$

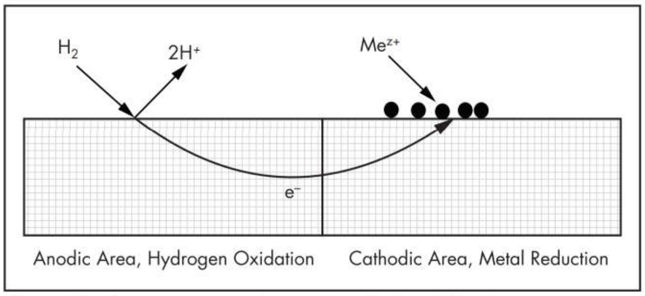


Figure 3 Spontaneous electrochemical cell for heterogeneous metal deposition

As the cupric ions can react directly with molecular hydrogen to produce metallic copper (Equations 13–15), the copper reduction process is homogeneous. Deposition of Ni^{2+} or Co^{2+} ions, however, requires the presence of a solid catalyst, and their reduction process is heterogeneous (Osseo-Asare 2003). Deposition by heterogeneous mechanism is electrochemical with separate anodic and cathodic reactions. The electrochemical reduction of metal ions in solution follows the principles of a corrosion cell (Figure 3). Oxidation of hydrogen gas releases electrons, which are used in the reduction of dissolved metal ions to solid metal. As the reactions in gaseous reduction of metals are electrochemical, the kinetic factors can be studied using Evans diagrams. The Evans diagram examples in Figure 4 show that to enhance the kinetics of the reactions, the electrochemical potential difference between the anodic gas oxidation and cathodic metal reduction should high, the exchange current densities of the reactions should be high, the polarization of the reactions should be low, and the concentration of the reacting species should be high to avoid mass transfer limitations.

Solutions for gaseous reduction are usually alkaline with complexing and buffering agents to maintain high metal concentration and to prevent increase in H^+ concentration that would decrease the driving force for reduction (Figure 1). The deposition processes proceed on solid material surfaces. To produce initial particles, catalysts are often used. The catalysts are chemical nucleating agents or metallic seed particles. Chemical nucleating agents act as homogeneous catalysts to nucleate metal particles, for example, ferrous sulfate in nickel reduction. Addition of nucleating agent results in formation

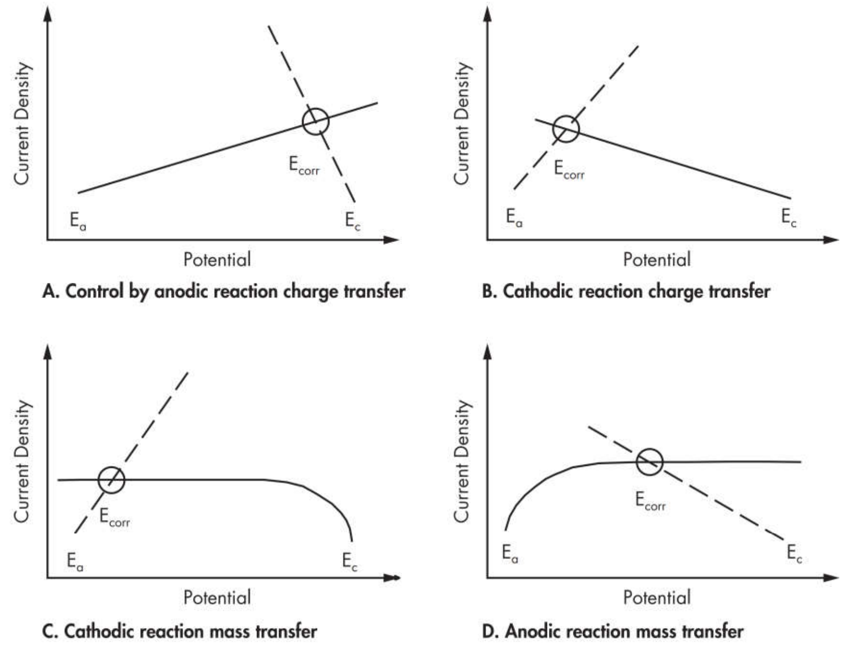


Figure 4 Evans diagrams showing the effect of polarization of anodic and cathodic reactions

of finely divided compounds on which metal nucleates. These particles act as seeds for further reduction.

The reaction kinetics strongly vary depending on metal, complexing agent, base solution, and their respective concentrations. For some systems, such as copper in ammonia solution, the reaction rate does not depend on metal concentration. Rate laws for the hydrogen reduction of metal ions are typically of the form given in the following equation:

$$r = -d[Me]/dt = k \cdot [Me]^x \cdot P_{H2}^y \cdot S \cdot \exp(-E_a/RT) \qquad \textbf{(EQ 16)}$$

where r is reaction rate; t is time; k is an apparent rate constant; [Me] and P_{H2} represent dissolved metal concentration and hydrogen pressure, respectively; and x can range from 0 to 1 and y from 0.5 to 2. The factor S describes the catalyst surface area, and the effect of temperature is taken into account by the activation energy of the reaction, E_a (Osseo-Asare 2003). Depending on the presence of surface-active agents and inhibiting agents, the whole surface area of the catalyst does not necessarily support reduction.

The particle growth includes nucleation and metal reduction on the nucleus followed by metal deposition as shells on the growing particles. Growth involves diffusion of metals and reducing gas to the surface, adsorption, reduction reactions, particle deposition and incorporation in metal lattice, and desorption of reaction products. In the beginning of the deposition process, aggregation of small particles can be important to produce larger particles that can then grow to the desired size (Taty Costodes et al. 2006). When a critical particle size has been reached, aggregation ceases and particles grow by continuing deposition of shells. Particles can also break to smaller ones during the process because of particle collisions, surface attrition, and solution turbulence. In practice, the deposition process is finished when particles become too large to remain in suspension and the reactive area of the slurry becomes too small to maintain a meaningful reduction rate.

PROCESS DEVELOPMENT

The basic chemistries of gaseous reduction systems are well known. The product suitability for various applications depends on particle size distribution and particle morphology. For process development and optimization, several aspects can be studied, including solution composition, the effect of additives on nucleation, reduction, agglomeration and powder surface properties, the changes during densification steps, and particle size distribution and particle morphology.

Research and scale-up of deposition processes is often difficult because of complex particle forming including nucleation, growth, aggregation, and breakage processes. Also design of stirring and mixing to maintain gas distribution and slurry suspension is challenging when scaling from laboratory-scale to process equipment. Laboratory autoclaves usually measure less than 1 dm^3, pilot plant autoclaves are tens of cubic decimeters, and large-scale autoclaves in nickel production measure more than 22 m^3 (Crundwell et al. 2011).

For studying gaseous reduction, an autoclave is needed. The autoclave must be capable of operating at 150°–250°C and at pressures of several megapascals. Construction materials are stainless steel or titanium. Electric heating or steam coils are used for temperature control. Depending on the system, high-pressure gas lines for reducing gas and nitrogen might be needed. Change of gas flow between reducing gas and nitrogen must be simple and secure. As the reducing gases H_2, sulfur dioxide (SO_2), and carbon monoxide (CO) are potentially hazardous, the exit gas lines and treatment of exit gases must be designed according to relevant safety rules. The autoclave must have good stirring to dissolve gas and to maintain metal particles in suspension. Removable polytetrafluoroethylene reaction vessels can be used to prevent metal deposition on autoclave walls.

A typical test procedure starts with preparation and preheating of the solution, charging and sealing the autoclave, and heating the autoclave with stirring and possibly with nitrogen blanketing. On reaching the test temperature, flow of reduction gas is started. To maintain correct operating pressure and ensure the flow of reducing gas, the gas outlet valve must be partially open when operating with constant gas flow, or reducing gas is added when pressure in the autoclave decreases indicating consumption of the gas. Autoclave pressure monitoring cannot be used when CO is the reducing gas, as it produces carbon dioxide (CO_2) and no pressure change is noticed. A system for sampling of solution or slurry through a dip pipe from a pressurized autoclave to a sample vessel can be constructed to get samples for kinetic analysis. However, if the autoclave volume is small, then sampling can change the conditions inside. After the test, the autoclave is cooled and flushed with nitrogen before opening the vessel. The metal slurry is then collected, washed, and dried.

Tests for gaseous reduction include solution preparation, nucleation, reduction, and control of reduced metal powder properties. Solution preparation includes dissolving desired initial metal and complex forming compounds, adjusting the complex-to-metal molar ratio, pH adjustment and buffering, and addition of nucleation agents or metal seed and surface-active agents to control deposit morphology. In addition to the solution characteristics, reducing gas pressure, temperature, and stirring can affect reactions. All these system parameters can affect either nucleation or reduction of metal:

- Increasing metal concentration will increase the equilibrium potential of metal reduction reactions and thus the thermodynamic driving force; it will also increase the reduction rate.
- The complex-to-metal ratio will affect the thermodynamic driving force that will decrease with both very low and very high values. Too low a complex-to-metal ratio will cause too rapid a pH decrease and too high a ratio will decrease the concentration of active metal. Both will eventually stop the reduction process.
- An increase in acid concentration will decrease the driving force of the reduction reaction and reaction rate. As the oxidation reactions of gases produce hydrogen ions, buffering compounds are needed.
- Nucleation agent or metal seed is needed to control the nucleation stage. Nucleation and first densification steps will affect particle size and shape and plating of metal on vessel walls.
- Surface-active agents control deposition rate and aggregation and affect the shape of particles.
- Increasing the reducing gas pressure will provide more thermodynamic driving force, allow operation at lower pH, and enhance reduction kinetics.
- Increasing temperature will increase reaction rate and increase gas solubility under autoclave conditions.

- Intense stirring is needed to maintain good gas–liquid transfer and to keep the solids suspended for maximum reduction rate.

Studies on nucleation and first solids precipitation are essential. Too little precipitate does not provide enough surface for further nucleation, and the precipitate will deposit on autoclave internals. Too much precipitate, however, will result in too strong aggregation and decrease available surface area for subsequent densification steps (Saarinen et al. 1998). Reproducing the nucleation step without seeding is difficult. Therefore, tests to determine deposit growth rate, including aggregation and breakage, have to be done with controlled seeding.

Reaction rate measurements are usually based on solution analyses. As the metal is precipitated, the solution concentration decreases with time. Pressure decrease has also been used to record progress of metal reduction with H_2. Analysis of particle formation rates can be made using particles collected after repeated tests (Ntuli and Lewis 2007) or using representative slurry samples (Ntuli and Lewis 2006). Reaction rate coefficients and reaction order can be calculated from the solution analysis $-d[Me]/dt$ data. The same data can be used to describe the factors that affect reaction kinetics, such as solution composition, reducing gas pressure, catalyst, and temperature as shown in Equation 16. The fraction of precipitated metal can be described by the following general equation:

$$X = 1 - \exp(-kt^n) \quad \textbf{(EQ 17)}$$

where X is conversion or the fraction of reduced metal at time t, and k and n are specific rate constants for nucleation and growth. Analysis of X versus t data can be undertaken using a double logarithmic plot (Equation 18) or surface reaction model akin to the shrinking core model shown in the next equation.

$$\ln(-\ln(1 - X)) = \ln(k) - n\cdot\ln(t) \quad \textbf{(EQ 18)}$$

$$1 - (1 - X)^{1/3} = k\cdot t \quad \textbf{(EQ 19)}$$

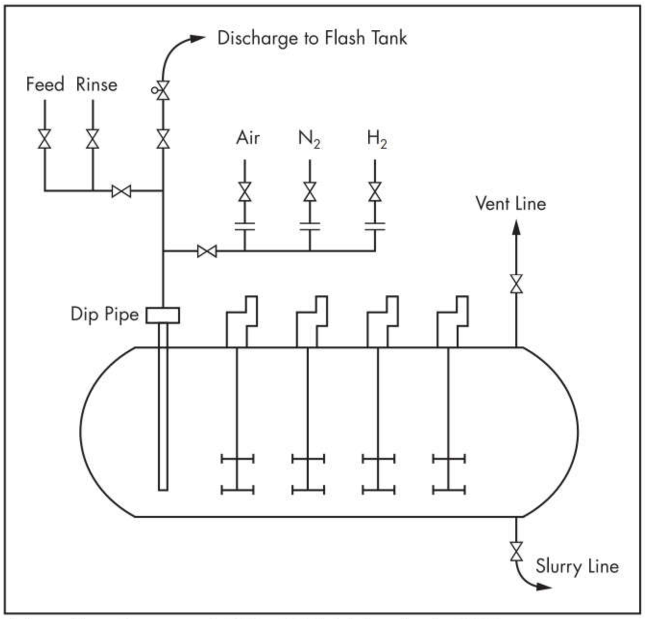
Plotting the $\ln(-\ln(1 - X))$ versus $\ln(t)$ or $1 - (1 - X)^{1/3}$ versus t gives constant values that can be used to estimate the effects of test parameters on reduction. The double logarithmic plot (Equation 18) can mask small changes in the reaction kinetics, and therefore it must be used cautiously.

The metal powder properties are determined by the relative rates and mechanisms of nucleation, growth, particle aggregation, and breakage. Open particles are more desirable than closed ones because they have larger surface area giving faster rates, they do not accumulate solution as impurity, and they are easier to turn to briquettes. The characterization of deposited metal includes determination of particle properties and bulk powder properties. The individual particle properties include size and shape. The bulk powder properties include chemical composition, particle size distribution, specific surface area, apparent density, and flow rate. Some of the factors that can influence the morphology of deposited particles include temperature, pH, reducing gas pressure, and the presence and concentration of impurities or contamination in solution or in reducing gas. The surface-active additives can change particle morphology by activation or passivation of the growing particle surface.

EQUIPMENT AND OPERATION

The gaseous reduction processes are typically batch autoclave processes. They operate at temperatures 120°–270°C, total pressure of 3–4 MPa, and reduction time of one cycle of 10–60 minutes. The metal concentration in feed solution is 40–100 g dm^{-3} and in the final solution, a few grams per cubic decimeter. For large-capacity hydrogen precipitation of metals, horizontal autoclaves with mechanical stirring and coils for heating or cooling are used. The autoclave body is usually made of steel and lined inside with a corrosion-resistant material, such as high-alloyed stainless steel, nickel alloy, or titanium. Schematics of an autoclave are shown in Figure 5. The autoclaves typically operate in batch mode and are constructed without baffles. Continuous production has been proposed since the 1960s; in the batch mode, the autoclave is under gas pressure and depositing metal less than half of the operating time. Continuous mode is more complicated than batch mode because of the risk of hydrogen leakage and the complexity of solution supply and especially of product discharge. The control of particle size and density is also more difficult (Naboychenko 2009). In reduction autoclaves, the prepared metal-bearing solution and wash solution are fed through a dip pipe. The dip pipe is also used for solution and gas removal under pressure to flash tanks. The process gases enter through a common header. Line blinds and valves are used to isolate the process gases not in use. Finished metal powder slurry is discharged through flash tanks or drained from the bottom at ambient pressure.

A schematic autoclave process is shown in Figure 6. The autoclave feed is prepared using metal-containing pregnant solution and compounds to control solution pH and complex formation, such as ammonia. The solution can be based on ammonia, sulfuric acid, hydrochloric acid, or organic media. An emerging trend is to use pulps containing metal hydroxides



Adapted from Benson and Colvin 1964; Naboychenko 2009; Crundwell et al. 2011

Figure 5 Autoclave

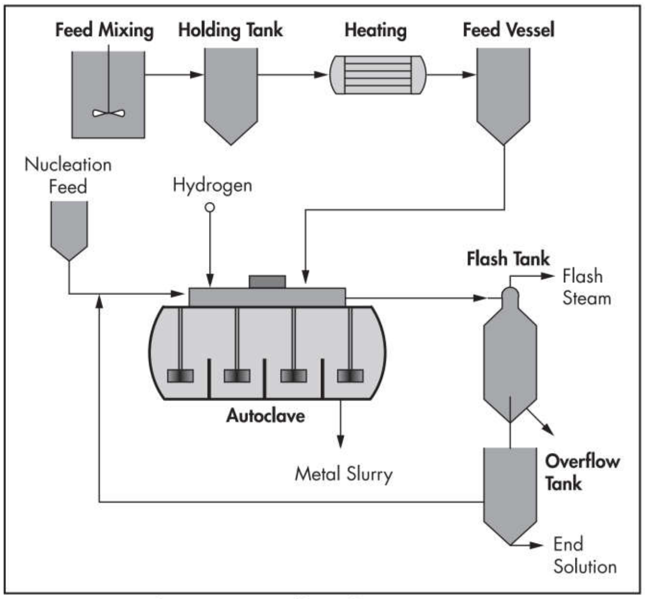


Figure 6 Autoclave process flow sheet

or oxides. Preparation of the feed solution requires control of metal concentration, impurities, and additives such as seeding and activating compounds. Deposition rate and metal recovery usually increase with increasing metal concentration in the feed as long as there is a sufficient amount of reducing gas available. Depending on the raw material composition and leaching method, the pregnant solutions contain various impurities. In preparation of autoclave feed, the suspended particles must be filtered away to prevent their action as seed. To prevent coprecipitation of impurity metals and product contamination, solution purification is required. Dissolved impurity metals are removed by chemical precipitation, ion exchange, or solvent extraction.

Most of the metals reduced by gases from solution require seeding, such as deposition of nickel and cobalt. Copper is an exception and no seeding is necessary as the reaction is self-nucleating through the copper disproportionation reaction. For copper, the metal surface has no significant effect. The deposition of nickel and cobalt are heterogeneous reactions, and they are affected by the catalytic properties of the metal surface. Seeding by additives or solid particles provides active sites for reducing gas, and the induction period is eliminated. Seeding does not only accelerate the nucleation, but helps to control particle size. Surfactants prevent metal deposition on the autoclave surfaces, and they affect deposited powder shape, texture, and dispersion. The surfactants are organic substances such as polyacrylic acid, polyacrylates, thioacetamide, and anthraquinone and its derivatives. Some of the surfactants are strong reducing compounds, promoting nucleation and deposition (Naboychenko 2009).

The feed is heated and pumped into the autoclave. Additives or small seed particles to promote nucleation, possible surface-active additives, and reducing gas are fed to start the nuclei deposition process. After the nuclei forming step, the depleted solution is discharged, leaving the reduced metal slurry in the autoclave. The reduced metal of the first batch has small particle size and high surface area, and it is used as seed for the reduction in the actual deposition batches. The fresh process solution is fed into the autoclave, and metal is reduced by gas growing as a shell on the nuclei. When solution becomes depleted and reduction has ended, the mixers are stopped, the metal powder is allowed to settle to the bottom of the autoclave, and the spent solution is removed from on top of the settled particles. With repeated batch reductions, the metal particle size increases and particles become more compact. This results in a powder with higher apparent density, and thus each batch reduction is termed *densification.* The particle size increase often follows a logarithmic law. To maintain the densification process, it is necessary to increase gas pressure, temperature, and time as the number of cycles increases (Saarinen et al. 1998).

The rate of gaseous precipitation of metals in the autoclave is determined by hydrodynamics, pressure of reducing gas, temperature, and solution composition as shown in rate law Equation 16. Saturation of the liquid by the reducing gas and uniform composition of the slurry are achieved by sufficient stirring. Stirring intensity is limited by increasing energy consumption, stirrer seal design, and solution foaming. When the gas pressure is increased, the concentration of dissolved gas in the solution increases proportionally. This increases the reduction rate. Maximum pressure is limited by design of the autoclave and gas lines and plant safety. The use of higher temperature increases reaction rates, but it leads to higher energy consumption, more expensive construction because of higher pressure, and sometimes higher risk of corrosion. Also, the composition of the solution may change with temperature because of hydrolysis, decreasing solubility of the dissolved species, and sintering of metal particles. For example, some sulfates are known to crystallize at high temperatures and dissolve back when the temperature is lowered.

When the size of the metal particles in the autoclave becomes too large to maintain a suspension and to serve as an effective catalyst, the gas is flashed from the autoclave, and both the powder and depleted solution are discharged. In the flash tank, the temperature of the gas decreases rapidly. For an efficient flash system, several stages with different pressure decrease can be built as a flash train. The slurry with deposited metal powder is taken to further processing, and evaporated gas goes to a gas scrubbing system. After this, a new cycle is prepared. Any metal deposited to the internal surfaces of the autoclave is dissolved away between batches. Control of seeding for nucleation is essential to minimize plating on autoclave internals and downtime between deposition batches. In nickel production, the leaching time can be 6–7 hours (Crundwell et al. 2011). To maintain continuous operation, parallel autoclave lines are needed to stagger the operating stages. This way, continuous feed from solution preparation can match the deposition and cleaning stages of autoclaves (Benson and Colvin 1964; Saarinen et al. 1998). Typically, the number of parallel autoclaves is six to seven in nickel production and two to three in cobalt production.

APPLICATIONS

Gaseous reduction is a special production method. The most important hydrometallurgical applications are production of nickel and cobalt using ammoniacal solutions. Gaseous reduction is also used in the production of special metal powder products, and it has been suggested as a method to remove excess metals in purification of hydrometallurgical process solutions.

Nickel Production

Nickel powders are used as an alloying element, in powder metallurgy, for catalysts, in rechargeable batteries, as conductive fillers for electrical applications, and in thermal spray coatings. Nickel powders are produced by carbonyl process, gaseous reduction, atomization, solid phase reduction, reduction with organic compounds, and electrolysis. Some of these methods can also produce nickel-clad powders for special applications. The nickel deposition is mainly accomplished using nickel ammoniacal sulfate solutions, but basic nickel carbonate, nickel ammonium acetate, and reduction of nickel oxide and nickel hydroxide have been proposed as alternatives. Nickel powder produced by hydrogen reduction is less pure than electrowon nickel, but suitable for most applications. Hydrogen reduction requires less plant space, energy, and labor force than electrowinning. The operating costs depend on the cost of chemicals, mainly on the source and production of hydrogen (Crundwell et al. 2011).

Nickel cannot nucleate homogeneously from a solution, and therefore solid particles are needed on which nickel can deposit. A catalyst is used to start the nucleation and precipitation in the first reduction batch. Known nickel-reduction catalysts include ferrous sulfate, ferrous sulfate modified with aluminum sulfate, platinum chloride, palladium chloride, and silver sulfate (Saarinen et al. 1998). As the reduction proceeds, the particles become denser and larger. The rate of reduction and the yield are functions of temperature, hydrogen pressure, seed addition, mass transfer, amount of alkali used, and the identity of the catalyst and its concentration. The pH of the solution determines the reduction rate and the morphology of the particles to a great degree (Saarinen et al. 1998). The overall reaction is shown in the following equation. Free ammonia is necessary to neutralize the hydrogen ions arising during reduction.

$$\mathrm{Ni(NH_3)_nSO_4 + H_2 \rightarrow Ni^O + (NH_4)_2SO_4 + (n-2)NH_3} \qquad \textbf{(EQ 20)}$$

The principal products of nickel reduction are powder with a particle size of 0.1–0.2 mm and ammonium sulfate, $(NH_4)_2SO_4$, which can be purified and sold as fertilizer. The nickel powder is washed and dried, and most of the nickel is briquetted with a polyacrylic acid binder and sintered. Deposited nickel is removed from autoclave internals by leaching with ammonia–ammonium sulfate solution and compressed air (Crundwell et al. 2011).

Nickel hydrogen reduction was originally developed to recover metal from air–ammonia leaching of sulfide concentrates. Nowadays, the plants process sulfide mattes and intermediate sulfide precipitates. Industrially, hydrogen reduction of nickel is practiced at BHP Billiton in Kwinana, Australia; Minara Resources in Murrin Murrin, Australia; Sherritt in Fort Saskatchewan, Canada; Ambatovy Joint Venture in Toamasina, Madagascar; Norilsk Nickel in Harjavalta, Finland; and Impala Platinum in Springs, South Africa (Crundwell et al. 2011). All these plants use the process developed by Sherritt Gordon during the 1950s and use nickel–ammonium sulfate solutions. The world nickel production by hydrogen reduction is about 240,000 t/yr (metric tons per year) (Crundwell et al. 2011). Of these plants, the BHP Billiton, Sherritt, Norilsk Nickel, and Impala Platinum use sulfide ore mattes and precipitates as raw material, whereas Minara Resources, Ambatovy, and partly Sherritt use lateritic ores that are converted to sulfides and re-leached before metals reduction. Leaching of sulfides is done either with air and ammonia or oxygen and sulfuric acid. The acid liquors are ammoniated for metals recovery.

The Sherritt Fort Saskatchewan plant uses purified solution from precipitate leaching containing 70–75 g dm^{-3} Ni, 35–40 g dm^{-3} NH_3, and 320–340 g dm^{-3} $(NH_4)_2SO_4$. The pregnant leach liquor is purified by separating cobalt by precipitation as cobalt hexamine salt, removing copper by deposition as sulfide, and converting all sulfur compounds to sulfates by oxidation and hydrolysis in autoclave (Naboychenko et al. 2009c). The operating temperature is 185°C and pressure 3.0–3.5 MPa. The NH_3/Ni ratio is approximately 1.9. The seed is 10-mm nickel particles. To produce particles of 0.1–0.2-mm size, 60–80 densification steps are needed, and a single densification step lasts up to an hour. The Fort Saskatchewan plant operates seven 7–22-m^3 autoclaves to produce 32,000 t/yr of nickel (Crundwell et al. 2011).

Minara Resources' Murrin Murrin plant uses laterite ores as raw material. The Ni-Co ore is first leached in autoclaves. From the pregnant solution, a mixed nickel and cobalt sulfide is precipitated by hydrogen sulfide gas. The mixed sulfide is then leached in an autoclave with oxygen to produce a sulfate solution. Impurities, such as Zn, Fe, and Cu, are removed, and cobalt and nickel are separated using solvent extraction. The nickel is precipitated in six parallel autoclaves. The nickel powder particle size is 250–300 mm at maximum. The powder is dried before forming briquettes that are sintered in a furnace. The product is more than 99.9% Ni with some Co, Fe, and Si as impurities. The Murrin Murrin plant produces 40,000 t/yr of nickel.

The Impala Platinum Springs plant uses purified solution from leaching of nickel matte containing 55–65 g dm^{-3} Ni and 330–350 g dm^{-3} $(NH_4)_2SO_4$. The operating temperature is 180°C and pressure 2.8 MPa. The NH_3/Ni ratio is 1.8–1.95. The time for one densification step is 10 minutes. The Springs plant produces 13,000 t/yr of nickel (Crundwell et al. 2011).

Cobalt Production

Cobalt is usually present in nickel and copper ores and is recovered during production of those metals. The world production of cobalt was 86,000 t in 2013 as metal, oxides, hydroxides, and other compounds. About half of the cobalt is produced as solid metal or powders (Fisher 2011). Cobalt and cobalt-alloy powders are used in rechargeable batteries, in the powder metallurgy industry in production of permanent magnets, and as high-temperature superalloys and wear-resistant alloys. Cobalt powder is used also in tool and die steels and as a binder in cemented carbides. Other applications of cobalt include catalysts, drying agents, and magnetic recording media. Cobalt metal can be produced by gaseous reduction, solid phase reduction, atomization, carbonyl process, and electrolysis. The gas reduction process is well known, but electrowinning is normally preferred because of lower capital and operating costs, higher metal recovery, and easier and less stringent operability and maintenance (Fisher 2011). Gaseous reduction is usually practiced along the Sherritt nickel production process. Cobalt metal is produced by Sherritt in Fort Saskatchewan, Minara Resources in Murrin Murrin, Impala Platinum in Springs, and Ambatovy Joint Ventures in Toamasina. Cobalt is produced from solution coming from cobalt–nickel separation in nickel production. The cobalt must be removed before gaseous reduction of nickel to ensure nickel purity. The cobalt was previously deposited as complex cobalt hexamine sulfate and redissolved, but currently, solvent extraction is used for cobalt–nickel separation. The cobalt-containing stream is then processed in its own gaseous reduction process.

The cobalt reduction mechanism is heterolytic and seed is needed. Cobalt seed is made by precipitation from cobaltous diamine solution using sodium sulfide particles and sodium cyanide and catalyst (Crundwell et al. 2011; Naboychenko et al. 2009a). The cobalt reduction reaction is shown in the following equation:

$$[Co(NH_3)_2]SO_4 + H_2 = Co + (NH_4)_2SO_4 \qquad \textbf{(EQ 21)}$$

Cobalt reduction is slightly faster than nickel reduction, and the resulting cobalt particles are slightly larger and more irregular because of particle agglomeration. Cobalt plated on the autoclave is dissolved by cobaltic hexamine solution (Crundwell et al. 2011).

The Sherritt plant in Fort Saskatchewan uses purified cobalt-rich solution from nickel production. The production is 4,000 t/yr (Crundwell et al. 2011). The feed liquor contains 75–80 g dm^{-3} Co, 550 g dm^{-3} $(NH_4)_2SO_4$, and 50 g dm^{-3} NH_3. The plant operates two 7-m^3 stainless-steel autoclaves. The operating pressure is 3.5 MPa and temperature 175°C. The seed is 0.01 mm, and 60–80 densifications, each taking approximately 45 minutes, are used to produce 0.2-mm particles (Crundwell et al. 2011).

Copper Production

Copper powders are used in powder metallurgy, when high electrical and thermal conductivities, ductility, and corrosion resistance are needed for the parts. Copper powders are also used in paints, coatings, inks, metal-polymer composites, and brazing pastes. Copper powder is produced mainly by reduction of copper oxide, atomization of molten metal, chemical precipitation, and electrolytic deposition. Copper powders can be precipitated from ammoniacal, sulfurous, and organic media by reduction with hydrogen, carbon monoxide, and sulfur dioxide, as respectively shown by the following three equations (Naboychenko et al. 2009b):

$$Cu(NH_3)_2^{2+} + H_2 \rightarrow Cu + 2NH_4^+ \qquad \textbf{(EQ 22)}$$

$$Cu(NH_3)_2^{2+} + CO + H_2O \rightarrow Cu + CO_2 + 2NH_4^+ \qquad \textbf{(EQ 23)}$$

$$Cu(NH_3)_2^{2+} + SO_2 + 2H_2O \rightarrow Cu + SO_4^{2-} + 2NH_4^+ + 2H^+ \qquad \textbf{(EQ 24)}$$

Hydrogen reduction in an autoclave from the leach liquors of ores and concentrates was reported in 1957 and reduction of copper from the bleed stream of copper electrorefining and various leach solutions since 1983 (Agrawal et al. 2006). Contrary to nickel and cobalt production, there is no copper metal production using hydrogen reduction. Hydrogen reduction is used for production of copper powders, and it has been tested for purification of copper electrolysis bleed solutions (Agrawal et al. 2006) and complex solutions containing several metals (Park et al. 2015). The copper production process is similar to the hydrometallurgical methods of nickel and cobalt production. The main differences are that reduction of copper does not need seeding as copper precipitation proceeds by the disproportionation reaction of Cu^+ ions (Equation 15) and the number of densification cycles is small. The reduction of copper with hydrogen can be achieved under pressure from both acidic and ammoniacal solutions (Agrawal et al. 2006).

Noble Metal Production

The noble metals include silver, gold, and platinum group metals (PGMs). Production methods of noble metal powders include chemical precipitation, thermal decomposition of metal salts, electrolysis, hydrogen reduction, and melt atomization (Naboychenko et al. 2009d). For noble metal reduction, hydrogen and carbon monoxide can be used. The reduction of noble metals is less critical on solution conditions than the reduction of base metals such as nickel, cobalt, and copper.

In gaseous reduction, the dissolved metals are typically chloride complexes. The general reaction of PGM reduction is as follows:

$$H_yMeCl_x + y/2H_2 \rightarrow Me + xCl^- + 2yH^+ \qquad \textbf{(EQ 25)}$$

As the PGMs are noble metals, their reduction can be accomplished using relatively low temperatures and hydrogen gas pressures. The metal ion concentration is typically grams per liter, but it can be as low as a few tens of milligrams per liter (Naboychenko et al. 2009d). To maintain complex stability, the chloride content is high, for example, 1 M hydrochloric acid (HCl). Use of an autoclave is not always necessary and reduction can happen at atmospheric pressure. Selective precipitation can be carried out by controlling temperature and hydrochloric acid concentration.

SUMMARY

Metal production by gaseous reduction started in the 1950s when Chemical Construction Corporation and Sherritt Gordon Mines developed a method to produce nickel. Much of the theoretical background was developed in the 1950s and 1960s. Gaseous metal reduction from aqueous solutions is mainly used in the production of nickel and cobalt, and approximately 30% of nickel metal is produced by reduction with hydrogen. The main method for nickel and cobalt production is electrowinning. Another application is production of metal powders for various applications. In this field, gaseous reduction is just one of many alternative methods. The reduction techniques are site specific. The general principles are the same, but details in solution preparation, practice of reduction stage operation, use of additives, and so forth, vary.

REFERENCES

Agrawal, A., Kumari, S., Bagchi, D., Kumar, V., and Pandey, P.D. 2006. Hydrogen reduction of copper bleed solution from an Indian copper smelter for producing high purity copper powders. *Hydrometallurgy* 84(3-4):218.

Benson, B., and Colvin, N. 1964. Plant practice in the production of nickel by hydrogen reduction. In *Unit Processes in Hydrometallurgy*. Edited by M.E. Wadsworth and F.T. Davis. New York: Gordon and Breach.

Burkin, A.R. 2001. *Chemical Hydrometallurgy*. London: Imperial College Press.

Crundwell, F.K., Moats, M.S., Ramachandran, V., Robinson, T.G., and Davenport, W.G. 2011. *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals*. Amsterdam: Elsevier.

Fisher, K.G. 2011. Cobalt processing developments. In *6th Southern African Base Metals Conference*. Johannesburg: Southern African Institute of Mining and Metallurgy.

Halpern, J. 1959. Homogeneous catalytic activation of molecular hydrogen by metal ions and complexes. *J. Phys. Chem.* 63(3):398.

Mackiw, V.N., Lin, W.C., and Kunda, W. 1957. Reduction of nickel by hydrogen from ammoniacal nickel sulfate solutions. *J. Met.* 9(6):786.

Meddings, B., and Mackiw, V.N. 1964. The gaseous reduction of metals from aqueous solutions. In *Unit Processes in Hydrometallurgy*. Edited by M.E. Wadsworth and F.T. Davis. New York: Gordon and Breach.

Naboychenko, S.S. 2009. Reduction methods of powder production. In *Handbook of Non-Ferrous Metal Powders—Technologies and Applications.* Edited by O.D. Neikov, S.S. Naboychenko, I.V. Murashova, V.G. Gopienko, I.V. Frishberg, and D.V Lotsko. Amsterdam: Elsevier.

Naboychenko, S.S., Murashova, I.B., Neikov, O.D. 2009a. Production of cobalt and cobalt-alloy powders. In *Handbook of Non-Ferrous Metal Powders—Technologies and Applications.* Edited by O.D. Neikov, S.S. Naboychenko, I.V. Murashova, V.G. Gopienko, I.V. Frishberg, and D.V. Lotsko. Amsterdam: Elsevier.

Naboychenko, S.S., Murashova, I.B., Neikov, O.D. 2009b. Production of copper and copper-alloy powders. In *Handbook of Non-Ferrous Metal Powders—Technologies and Applications.* Edited by O.D. Neikov, S.S. Naboychenko, I.V. Murashova, V.G. Gopienko, I.V. Frishberg, and D.V. Lotsko. Amsterdam: Elsevier.

Naboychenko, S.S., Murashova, I.B., Neikov, O.D. 2009c. Production of nickel and nickel-alloy powders. In *Handbook of Non-Ferrous Metal Powders—Technologies and Applications.* Edited by O.D. Neikov, S.S. Naboychenko, I.V. Murashova, V.G. Gopienko, I.V. Frishberg, and D.V. Lotsko. Amsterdam: Elsevier.

Naboychenko, S.S., Murashova, I.B., Neikov, O.D. 2009d. Production of noble metal powders. In *Handbook of Non-Ferrous Metal Powders—Technologies and Applications.* Edited by O.D. Neikov, S.S. Naboychenko, I.V. Murashova, V.G. Gopienko, I.V. Frishberg, and D.V. Lotsko. Amsterdam: Elsevier.

Ntuli, F., and Lewis, A.E. 2006. The effect of a morphology modifier on the precipitation behavior of nickel powder. *Chem. Eng. Sci.* 61(17):5827.

Ntuli, F., and Lewis, A.E. 2007. The influence of iron on the precipitation behaviour of nickel powder. *Chem. Eng. Sci.* 62(14):3756.

Osseo-Asare, K. 2003. Hydrogen reduction of metal ions: An electrochemical model. In *Hydrometallurgy 2003*, Vol. 2. Edited by C.A. Young, A.M. Alfantazi, C.G. Anderson, D.B. Dreisinger, B. Harris, and A. James. Warrendale, PA: The Minerals, Metals & Materials Society.

Outotec. 2015. HSC Chemistry software database. www.outotec.com/products/digital-solutions/hsc-chemistry/. Accessed July 2018.

Park, K.H., Mishra, D., Nama, C.W., Sahub, K.K., and Agrawal, A. 2015. Selective reduction of Cu from aqueous solutions through hydrothermal route for production of Cu powders. *Hydrometallurgy* 157(1):280.

Saarinen, T., Lindfors, L.-E., and Fugleberg, S. 1998. A review of the precipitation of nickel from salt solutions by hydrogen reduction. *Hydrometallurgy* 47(2-3):309.

Schaufelberger, F.A. 1956. Precipitation of metal from salt solution by reduction with hydrogen. *J. Met.* 8(5):695.

Taty Costodes, V.C., Mausse, C.F., Molala, K., and Lewis, A.E. 2006. A simple approach for determining particle size enlargement mechanisms in nickel reduction. *Int. J. Miner. Process.* 78(2):93.

Von Hahn, E.A., and Peters, E. 1965. The role of copper(I) in the kinetics of hydrogen reduction of aqueous cupric sulfate solutions. *J. Phys. Chem.* 69(2):547.