A comprehensive review on the hydro metallurgical process for the production of nickel and copper powders by hydrogen reduction

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Abstract

Production of nickel and copper powders from leach solutions and other aqueous streams by hydrogen reduction under pressure has been reviewed in the present paper. By optimising the optimum process condition, powders or composite materials of required specification could be produced from different types of acidic and alkaline solutions by coating nickel or copper powders on the secondary materials such as graphite, tungsten carbide and aluminium. The paper also highlights the kinetics of reduction and the use of various inorganic and organic additives to improve the quality of the powder on bench and commercial scale. Effect of various experimental factors such as pH of the solution, concentration of metals, particle size and nature of additives, operating condition of autoclave, etc. on the rate of reduction and quality of powder are also discussed.
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Keywords: C. High pressure; A. Metals; D. Surface properties

1. Introduction

With the depletion of high-grade reserves of ores/concentrates and increasing concern on environmental pollution, attention is now being focused on the processing of lean/complex ores, secondaries, wastes-sludge/residue, effluents, etc. to recover the metals therein before disposal. Such materials could be processed effectively by hydrometallurgical processes involving a suitable lixiviant, which can be employed on small/medium scale. Hydrometallurgical processing of ores/concentrates/wastes/secondaries, involves the use of different lixiviants viz. acidic, alkaline or ammoniacal solutions to dissolve the metals of interest depending on the composition of the material. Sometimes complexing agents are also added to improve the leachability of the metals. The metals or salts from such complex leach solutions could be recovered after solution purification. Various methods such as ionic precipitation, electrolytic reduction or gaseous reduction are practiced for the production of powder. To process the leach solution, hydrogen reduction is considered as one of the efficient methods to obtain metals in the form of the value added product as powder for Powder metallurgical application, composite materials which will be more attractive and cost effective than the metal/salt production. Possibility of precipitation of metals from aqueous solutions of their salts with

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hydrogen was for the first time established in the 1860s by N.N. Beketov, Professor of the Kharkov University, who at that time worked in Paris in J. Duma's Laboratory. Attempts to precipitate copper with hydrogen from sulphate solution (298 K, MPa) were made by T. Tammann and W. Nernst (1892), but they were not successful. The idea of N.N. Beketov was further developed by V.N. Ipatyev, a famous Russian scientist, author of many discoveries and inventions in the field of technical chemistry. Researchers from the Chemical Construction Corporation (USA) headed by F. Schaufelberger have developed process technology and equipment for precipitation by hydrogen (in the late 1940s), which permitted them in cooperation with the scientists at the University of British Columbia (Vancouver, Canada) headed by F. Forward and the Sherritt Gordon Company to build a unique plant in Fort Saskatchewan (Alberta, Canada) for pressure treatment of nickel concentrates via ammonia route with precipitation of nickel and cobalt with hydrogen. Further developments and extensive research has been conducted by many scientists in the USA, Canada, Germany, UK, China, Russia, India and other countries. A number of publications have appeared on the production of copper and nickel powders from different leach solutions, effluents, bleed electrolytes, etc. [3–6] by hydrogen reduction under pressure in autoclaves. The use of metal precipitation at high temperature and pressure in an autoclave was discussed in a monograph [7] by a team of authors headed by S.S. Naboichenko, a corresponding member of the Russian Academy of Sciences, has successfully tackled with the autoclave processes. The monograph considers physicochemical foundations of hydrometallurgical processes carried out at elevated temperatures and pressures and discusses their thermodynamics and kinetics. Examples of application of autoclave processes in manufacture of alumina, nickel, cobalt, zinc, copper, noble, and less common metals are described. A special section is devoted to engineering implementation of the autoclave technologies.

Information from various sources in the literature referring to the use of hydrogen reduction of nickel and copper from solutions with the purpose to produce metallic powders has been summarized in the article. The technology of copper and nickel precipitation with hydrogen in metallic form has been successfully applied in the industry since a long time. Due to the high intensity and possibility to produce various products (tens of varieties of powders and briquettes) such processes compete with the electrolytic refining processes. The process flow diagrams of the existing and planned plants comprising production of powders in autoclaves have been designed for treating intermediate nickel and copper–nickel sulphide products and oxide nickel ores. The authors have discussed issues relating to hydrometallurgical processing of low-grade raw materials, secondary materials, sludge, residues, different aqueous media and complexing agents such as ammonia, sodium hydroxide, sodium carbonate, sodium acetate, etc. by hydrogen reduction of copper and nickel in the form of commercial-grade metallic powders. This paper also highlights the kinetics and mechanism of powder production from different solutions in the presence of inorganic and organic additives have also been discussed.

1.1. Theoretical aspect of hydrogen reduction

Hydrogen gas is considered to be very attractive for the aqueous reduction of metal ions to produce powders as it is more efficient from the energy point of view, more ecofriendly and for the same energy consumption, hydrogen reduction has a potential of producing more metal powders compared to conventional electrolysis process [1]. This is because hydrogen is capable of three types of interaction with metals of different groups of the periodic table, namely (a) ionic bond (H^-; Ia, IIa), (b) metallic bond ($H^\pm$; IIIa, IVa, Va) and (c) interstitial solid solution (H^+; VIa, VIIa, VIII). Hydrogen is capable of self-trapping in metals and can attracts free electrons, causing a state of electrostatic shielding. The small size enables specific types of hydrogen interaction with the metals. At high temperatures, they use the thermal energy either to surpass the activation energy peaks (quantum diffusion) or to crawl through them via tunnels (tunnel diffusion). At low temperatures, H^+ particles migrate by alternation of travelling alone and in the company of the surrounding lattice distortions, another version of the tunnel mechanism [2].

Reduction of both nickel and copper takes place under hydrogen pressure, which could be represented as

$$M^{2+} + H_2 \rightarrow M + 2H^+ \tag{1}$$

where M stands for copper, nickel. The above equation can be shown as two half cells

$$M \rightarrow M^{2+} + 2e \quad \Delta G_M \tag{2}$$

$$H_2 \rightarrow 2H^+ + 2e \quad \Delta G_{H_2} \tag{3}$$

The reduction is thermodynamically feasible when ΔG ($\Delta G_{H_2} - \Delta G_M$) is less than zero. Since ΔG is related to the reduction potential (E), E_{H_2} should be greater than E_M for reduction. The potential of both copper and nickel are
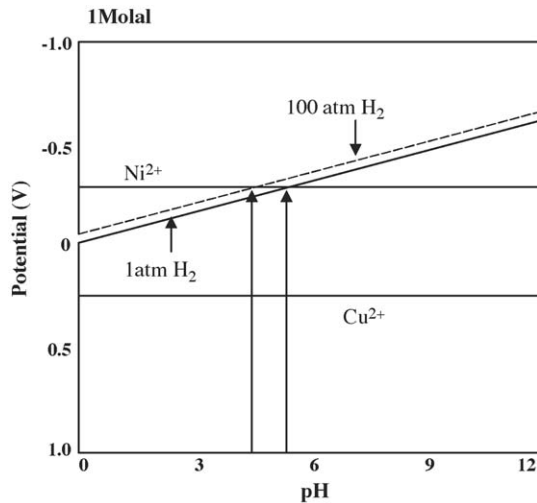
Fig. 1. Hydrogen and metal electrode potential.

presented in Fig. 1 against the concentrations of the respective metal species from 1.0 to 1×10^{-3} M. The oxidation potential (E_H) for the H_2/H^+ couple increases with the pH and partial pressure of hydrogen, but pH has more pronounced influence than the partial pressure of hydrogen on E_{H_2}. The diagram shows the possibility of reduction of Cu^{2+} even at 1 atm at all pH values. The reduction of nickel at atmospheric pressure is possible only above pH 5.2, which can be brought down marginally to 4.25 by applying a higher pressure of 10.1×10^3 ka (100 atm). Although the thermodynamic analysis indicates reduction of copper and nickel at atmospheric hydrogen pressure and low temperatures, a higher temperature of 413–473 K and pressure up to 5600 kPa are employed in actual practice to enhance the reaction kinetics. The process is carried out in suitable equipment under controlled conditions of temperature, pH and pressure in order to produce powder of the desired specification. The nucleation, grain growth and agglomeration of particles are controlled by adding inorganic and/or organic salts to produce the powder of the required size, morphology and structure, etc. These additives act as catalysts or complexing agents to enhance nucleation and formation of powders.

2. Discussion

2.1. Reduction of nickel from solution

Hydrogen reduction of nickel from different aqueous solutions have been extensively studied by several investigators [8–17]. Several review papers appeared highlighting various aspects of reduction processes. The fundamental and practical aspects of the Sherritt Gordon process for manufacture of nickel along with cobalt powders by reduction of aqueous solutions or slurries of metals have been reported [3,18–20]. Recently, Saarinen et al. [21] reviewed the precipitation of nickel from salt solutions by hydrogen reduction and described principal phenomena, use of inorganic and organic additives on the powder characteristics, etc. The use of the optical, X-ray microanalysis and X-ray phase analysis methods have been made to determine the structure of the powder and also to control the quality of the powder [10]. Practical issues associated with process design and scale-up of nickel powder production have been described by Willis and Von Essen [14]. A process was patented to produce sponge-like copper and nickel powders and their improvement by high temperature treatment [22]. According to the invention, the raw material used was metal ions in a liquid phase at a preliminary stage of the method the liquid phase containing metal ions is reduced with hydrogen at an increased pressure and raised temperature to produce porous, sponge like metal powder. The quality of this powder so obtained can be improved by further processing it at a high temperature.

The hydrogen reduction of nickel ions in most of the cases is carried out in presence of nucleating seed/catalyst materials, which is required only at the start of the reduction cycle. These are mainly inorganic and/or organic salts,

which provide the high surface area to initiate the formation of powder. These materials also eliminate the induction period to start the nucleation and improve the quality of the powder [23,24]. The inorganic materials are recycled nickel metal powder, ferrous sulphate (4.5 g/L), manganese salts, Fe(II)/Al(III) additive. About 0.1 g/L of these salts is a minimum amount of catalyst added during the process. This amount may be increased reasonably for its effective activity but excessive amount of it will be deleterious for the final metal powder produced as they may effect the purity of the powder [25–29]. Homogenous nucleation is also possible by adding salts of chromium, titanium and vanadium leading to a complete and quick reduction of a nonseeded solution at 323–373 K [26]. Once a salt is added in the solution, it precipitates and provides the nuclei on which the reaction initiates. Some precipitates may be catalytically active due to surface adsorption of hydrogen [25]. Ferrous sulphate in ammoniacal solution forms the ferrous hydroxide nuclei which catalyses the reduction and helps in the formation of very fine and active powder [26]. The hydroxide formation can be represented as:

$$FeSO_4 + 2NH_4OH \rightarrow Fe(OH)_2 + (NH_4)_2SO_4 \tag{4}$$

Ferrous hydroxide is not suitable for the production of extra high purity powder. Nickel metal as seed material is suitable in such cases, as it does not increase any foreign impurities in the product. Manganese salts also act as good catalysts like iron salts for reducing nickel [27]. Homogenous nucleation by Cr(II) from a nickel ammonium sulphate solution is possible at 343–373 K [28]. A small amount of chromium sulphate is used as catalyst, which nucleates Ni(II)–H_2 reaction. Similarly titanium and vanadium behaves like chromium allowing the reduction of a nonseeded solution to completion both quickly and easily at 323–373 K producing good seed powders. The seed materials are added only in the initial stage of the reduction. In the subsequent reduction cycle the same seed material is used so that the particles of the required size and density could be obtained. The density of the particles increases in the each recycle stage. The process is called densification cycle. The rate is found to decrease in the subsequent reduction stages, which may be due to agglomeration of very fine microscopic particles and therefore particle discharges are often performed to maintain an appropriate loading of solids in the autoclave.

Different organic compounds such as anthraquinone (2 g/L) [30], ethylene maleic anhydride (5–10 mg/L) are used as additives during the reduction to improve the quality of the product. They form coatings on the solid particles present and affect interaction of gas-liquid-solid, resulting in achieving different properties of the produced powder [24,29]. Thus, these compounds control the particle size, shape, apparent density, surface area and topography [31]. Some of the additives viz. ammonium polyacrylate, gum Arabic, gelatin, dextrin, dextrose, and fatty acids, etc. avoid the agglomeration of the particles and deposition on the reactor wall. The surface texture of the powder has been controlled with the use of ethylene maleic anhydride (EMA) polymers. The addition of anthraquinone (up to 0.04 g/L) in ammoniacal nickel sulphate or carbonate solution not only helps in production of smooth regular-shaped particles, but also increases the rate of reduction. The size and distribution of typical as-reduced nickel powder from ammoniacal nickel carbonate solutions varies from 96% of −5 μm to 90% of +44 μm.

Hydrogen reduction has been employed to produce different composite materials such as nickel/titanium [32] and nickel/aluminium [33] by precipitation of nickel on the surface of titanium and aluminium powders. The quality of coating was found to depend on the cleanliness of the core surface and addition of surface catalytic activator.

During the reduction of nickel ions in the solution, the pH of the solution decreases. Since the reduction takes place at a pH above 5.2 it has to be maintained by the addition of different complexing agents or alkalies such as sodium hydroxide, sodium carbonate, sodium acetate or ammonia to obtain the powder of desired purity.

2.1.1. Nickel/cobalt ammine sulphate solution

Ammoniacal solution forms soluble ammine complexes with nickel [$\{Ni(NH_3)_x\}^{2+}$, where $x = 2$–6] and raises the pH of the solution to the desired level which helps in maintaining the pH of the solution during hydrogen reduction. It also raises the electrode potential with increase in ammonia concentration (Fig. 2) [5]. The maximum potential difference [$E_{H_2} - E_{Ni}$] is obtained at the NH_3/Ni ratio of 2–2.5, and this condition is maintained in commercial plants. The main reason for an NH_3/Ni ratio of 2 is to help maintain the pH of the solution. As each nickel ion is reduced to nickel metal the two molecules of ammonia are freed up to neutralize the hydrogen ions produced. Different investigators studied the reduction of nickel ions in ammoniacal systems to produce powder [24,26,34–38]. The seed
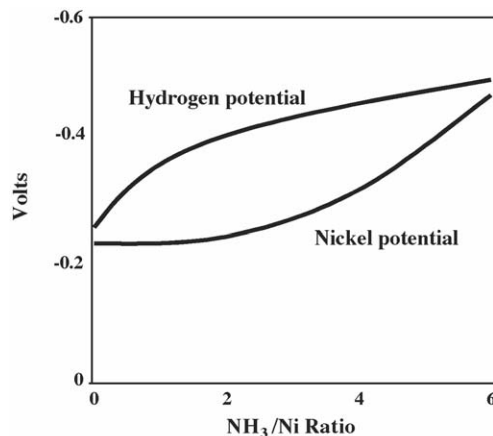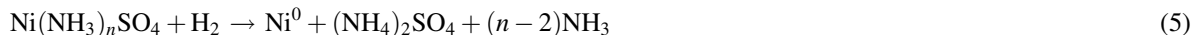
Fig. 2. Hydrogen and nickel potential in a Ni^{2+}–NH_3 system.

materials viz. ferrous sulphate/nickel power, etc. is added in the solution [33]. The nickel deposits on the nucleating sites according to the reaction [39]

$$Ni(NH_3)_nSO_4 + H_2 \rightarrow Ni^0 + (NH_4)_2SO_4 + (n-2)NH_3 \tag{5}$$

The particles become denser and larger by recycling the same seed materials for a number of times [40]. The reduction rate and morphology of particles depend on temperature, pressure, pH and additive, etc. The process is in commercial application since 1954 for the production of nickel powder by Corefco Refinery (Previously known as Sherritt Gordon Mines) in Fort Saskatchewan, Alberta [26,41–44]. In this plant the efficient separation of cobalt from nickel (and other impurities) is a fundamental objective in the refining of cobalt [45]. Based on recent experience at the Fort Saskatchewan refinery, the identification of a novel process for the selective precipitation of cobalt from an aqueous ammonia leach was discovered. The addition of calcium sulphate, $CaSO_4 \cdot 2H_2O$ (gypsum), to an aqueous solution containing cobalt(III) hexamine sulphate, $[Co(NH_3)_6]_2(SO_4)_3$, will result in the precipitation of a sparingly soluble double salt having the stoichiometry, $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2CaSO_4 \cdot xH_2O$ where $x = 4$ or 6. Leach residues, which may contain a significant quantity of cobalt associated with the cobalt calcium double salt, can be washed with process solutions that contain ammonium carbonate to recover the contained cobalt. The simplicity of this elemental separation and its high selectivity for cobalt, as well as its demonstrated usefulness in improving cobalt recoveries, are the basis for the potential applications of this process. The purified nickel ammine sulphate, $Ni(NH_3)_2SO_4$, solution [80–95 g/L Ni, 9–15 g/L Co, 170–190 g/L $(NH_4)_2SO_4$ and 125–135 g/L NH_3 per mole of nickel plus cobalt] obtained from the leaching of sulphide concentrate was subjected to hydrogen pressure at 3500 kPa, 453 K and for 30 min in the presence of ferrous sulphate additive. In the absence of nuclei of ferrous hydroxide, nickel has been found to deposit on the walls of the autoclave and the agitators, which are difficult to remove from their surface. After completion of the reduction, the nickel powder is washed, dried, compacted into briquettes and then sintered in a hydrogen atmosphere to form consolidated metal. The company also developed a process to produce extra-high purity powder from the purified nickel sulphate solution where the contamination of ferrous hydroxide catalyst was avoided using ammonium carbonate which forms a fine suspension of solid basic nickel carbonate acting as a nucleating sites (Fig. 3). The ammonium carbonate in an amount of 5 g/L was effective for reduction. The quality of powder improved with the reduction of sulphur content from 0.02 to 0.005%. The powder was also produced on commercial scale from the purified leach solution of low-grade lateritic ore by Freeport Nickel Company [47–50]. In this plant, the powder was produced at 463 K, 4623 kPa hydrogen pressure by adjusting the pH to 0.9–1.8 with ammonia. The metal recovery of 95% was obtained.

A process has been developed to produce nickel powders from the purified leach solution of cobalt–nickel–copper sulphide concentrate by National Lead Company [50,51]. Nickel was precipitated by hydrogen reduction at 491 K and 4268 kPa from the ammine sulphate solution containing 1.8 M ammonia for each mole of nickel, after copper precipitation and solution purification. Thus nickel powder containing 0.10% Co, 0.02% Cu, 0.003% Fe, 0.013% S and 0.047% C was produced. Further, Elmarghani [52], Elmarghani and Sliepcevich [53] produced nickel powder with a
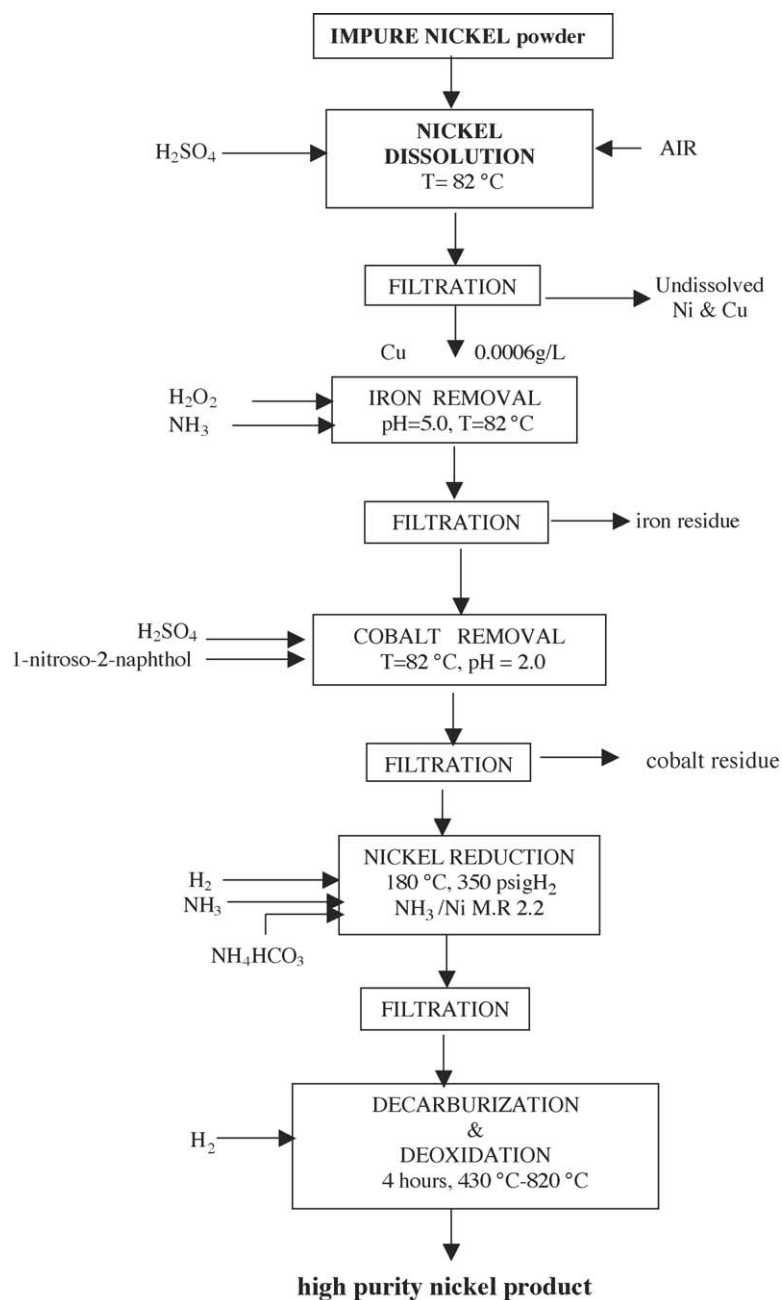
Fig. 3. Flow sheet for preparation of high purity nickel powder [46].

yield of 90% at 472 K and 3850 kPa pressure in a single pass in 5 min by sparging hydrogen gas from the bottom of continuous flow reactor from ammoniacal nickel sulphate solution containing ferrous sulphate.

2.1.2. Kinetics of nickel reduction with hydrogen

Different investigators have studied the kinetics of the reduction of nickel ions with hydrogen under pressure [39,53]. The reduction of nickel has been found to depend on the diffusion of nickel and hydrogen to the surface of the growing metal particles and chemical reactions at the surface [34]. The rate was directly proportional to the nth power of the partial pressure of hydrogen, where n depends on agitation and varies in the range of 0.5–1.0 [39]. The

chemically controlled reduction rate was reported in presence of chromous ions from nickel ammonium sulphate solution. The rate was proportional to the amount of nickel powder and the square root of hydrogen partial pressure, and was not influenced by the concentration of nickel ions in solution up to the point at which most of the nickel is reduced. Both activation of hydrogen molecules and phase transformation of nickel are believed to proceed on the surface of the added nickel powder. The reaction can be considered to proceed in five steps. In the presence of alumina powder as seed material [35], the rate of reduction of nickel was first-order with respect to nickel ion concentration and independent of molecular hydrogen concentration in the solution and hydrogen pressure in ammoniacal ammonium sulphate solution. The improvement in nickel powder was made by using the catalyst such as metal hydrides, metal borohydrides and metal borides (0.45–1.90 wt.% of the metal) from the sulphate solution containing ammonia [54]. Further, it was reported that the stirring rate [55] had significant effect on the reduction of metal from nickel solution containing 0.5 M Ni at 473 K. The rate was found to be first order with respect to nickel ion concentration for Reynolds no. (Re) >18,000 and the order became fractional and finally, zero as Re decreased to zero progressively. The apparent activation energy decreased from 74.0 to 16.7 kJ/mol indicating a chemically controlled reaction changing to the diffusion control phenomena with decrease in the stirring intensity.

2.1.3. Basic nickel carbonate solution

Basic nickel carbonate (BNC) suspension which itself acts as nucleating agent, is prepared by dissolving metallic nickel, higher nickel oxide or nickel carbonate in the ammoniacal solution and then precipitated by evaporating ammonia with steam. The BNC is reduced to produce nickel powder under hydrogen pressure in autoclave [11,59–61] according to the reaction:

$$2NiCO_3 \cdot 3Ni(OH)_2 + 5H_2 \rightarrow 5Ni + 2CO_2 + 8H_2O \tag{6}$$

It is employed as nucleating agent in production of extra-high purity powder from the nickel ammine sulphate solution [45]. A process has been developed by Sherritt for the production of nickel powder from BNC suspension [58,59]. The powder was produced from the BNC suspension under the varying operating condition (408–423 K and 2525–3030 kPa) with particles of fairly regular spherical shape (0.3–1.0 μm) [60]. The ultra-fine nickel powders of spheroidal (diameter 0.1–2.0 μm) shape were also obtained from water slurry of BNC at 448 K [11].

Different additives viz. ammonium carbonate, Tamol 731 and anthraquinone were used during the hydrogen reduction to produce the nickel powder from the purified nickel solution of Korean smelter by-product. The spheroidal shape powder of 99.9% purity was obtained by nucleating with anthraquinone. With the use of additive-alkali/lithium carbonate and anthraquinone, nickel powder of the size 0.2–1.0 μm was obtained by hydrogen reduction at 2525 kPa and 448 K [14]. The structural and physical properties of the powder obtained from water suspensions of nickel basic salts were studied by Durkovic et al. [8]. Further, the kinetics of reduction from ammoniacal carbonate solution [58] were found to be proportional to the initial surface area of seed and hydrogen pressure in the temperature range 408–453 K, similar to the one for ammoniacal sulphate solution [26] in presence of nickel powder seed.

Hydrogen reduction process has been used to coat the different materials from the nickel ammine sulphate solutions [56,57]. Materials such as graphite, SiO_2, Ti, W, V, Fe, Mo, etc. were coated with nickel at 393–443 K in presence of anthraquinone as surface activator [56]. The fine nickel coated tungsten powder of the average particle size of 5 μm was produced at 403–413 K and 4000 kPa pressure, which was confirmed by X-ray and scanning microscopic analysis. No impurities such as residual chemical agents and oxides were detected by X-ray and chemical analysis.

2.1.4. Basic nickel sulphate solution

Basic nickel sulphate (BNS) suspension is obtained by neutralising nickel sulphate solution with sodium hydroxide. The composition of the complex BNS [$NiSO_4 \cdot Ni(OH)_2$] precipitate obtained by neutralization mainly depends on the pH, time, temperature and the concentration of nickel in the solution [38,61]. The reaction may be represented as:

$$(x + y)NiSO_4 + 2yNaOH \rightarrow yNi(OH)_2 \cdot xNiSO_4 + yNa_2SO_4 \tag{7}$$

where x and y are the number of moles of corresponding species involved in the chemical reaction.

The suspension acts as a catalyst and nucleating agent for the nickel reduction with hydrogen according to the reactions [62,63]

$$Ni(OH)_2 + H_2 \rightarrow Ni^0 + 2H_2O \tag{8}$$

$$NiSO_4 + H_2 \rightarrow Ni^0 + H_2SO_4 \tag{9}$$

$$Ni(OH)_2 + 2H^+ \rightarrow Ni^{2+} + 2H_2O \tag{10}$$

Several studies have been reported for the production of nickel powder from BNS suspension [62–68]. In the reduction of basic nickel sulphate, the slurry is first dissolved under hydrothermal conditions i.e. in the aqueous condition at the temperature above the boiling point and below the critical temperature of water, and then metal ions are reduced to metal powder [65]. The reduction proceeds in three distinct stages:

• Dissolution of hydrogen.
• Reduction in solution.
• Deposition of metal.

It was also pointed out that reduction could not proceed from an insoluble hydroxide in alkaline solution [12], but in the presence of PdCl$_2$, as an activator, the reduction was obtained [67]. The nickel powder of spheroidal shape and 350 nm size was produced from nickel hydroxide at 498 K in the presence of anthraquinone as an activator [66]. The particle size of nickel powder was found to increase with increasing temperature and decreasing pH. The surface reaction was the rate controlling step during the reduction following the expression, $1 - (1 - x)^{1/3} = kt$, where x is a reduction ratio i.e. the fraction and t is reaction time. The rate-determining step was different at low (423–433 K) and high temperature (448–473 K) ranges having activation energies 377.2 and 65.9 kJ/mol respectively. A zero order reduction rate was reported in the temperature range of 443–523 K [62]. Saarinen et al. [63] pointed out the importance of neutralizing procedure of nickel sulphate solution with sodium hydroxide on the reduction of suspension in the temperature range 403–433 K. The time for reduction was found to decrease drastically to the extent of 50% when precipitate-II [nickel sulphate solution addition in sodium hydroxide solution] suspension was used instead of precipitate-I [sodium hydroxide addition in nickel sulphate solution]. This was due to the formation of a stable compound in precipitate-I, which is not soluble, even at pH 2.0 and 298 K. The sulphur content in the powder increased from 1.5 to 5.0% during the reduction process [63]. The precipitate disappeared on completion of the hydrogen reduction.

2.1.5. Nickel reduction from acetate solution

Sodium acetate buffer solution is employed to maintain the acidity and prevent hydrolysis of nickel cations at elevated temperatures, and control the powder properties. The reaction may be represented as [69]:

$$Ni(H_2O)_6{}^{2+} + H_2 \rightarrow Ni + 2H^+ + 6H_2O \tag{11}$$

Such acetate buffered solution has been extensively used to produce nickel powder in the presence of tungsten carbide, aluminium, bismuth, graphite, etc. as catalysts [68–72]. The nickel or composite powders with required properties viz. particle size, shape and morphology have been produced from such solutions. The composite powders containing 80–85% Ni, 20–25% graphite and 10–20% Ni, 80–90% tungsten carbide [18,73,74] were produced at 443 K; hydrogen partial pressure 3000 kPa; and mixing rate 600 min^{-1} from the solution containing 30 g/L Ni, 82 g/L CH$_3$COONa, and 80 g of tungsten carbide or 8 g graphite powder. The coating on aluminium, tungsten carbide and graphite was also made under the hydrogen pressure of 2020–4040 kPa and 423–453 K from 20 to 40 g/L Ni [70].

Rate of nickel reduction were investigated under different operating conditions in presence of additives from acetate solution and was found to be proportional to the surface area of the nickel catalyst and the square root of the partial pressure of hydrogen above 4.3 pH [68,69]. In presence of graphite, aluminium and tungsten carbide catalysts [67,70,75], the kinetics of nickel reduction was first order with regard to nickel concentration from the acid buffered solution. The rate was proportional to the square root of the partial pressure of hydrogen and independent of the mixing rate in the range of 400–700 min^{-1}. Activation energies were 77.6 and 80.1 kJ/mol for graphite and tungsten carbide catalyst respectively, which indicated the kinetics to be dependent on chemical control rather than diffusion control.

First-order kinetics with regard to nickel concentration in the presence of aluminium catalyst was reported by Wodka and Charewicz [71]. The rate was proportional to the partial pressure (1000–3000 kPa) of hydrogen to the 0.6 power in the temperature range (423–463 K) and at the pH of 4.0–4.8 of the reduced solution. The activation energy of reduction was 85.4 kJ/mol. Both the rate of reduction and the quality of the nickel coating on aluminium were strongly dependent upon the initial pH of the reduced solution. The compact, uniform and continuous nickel coating was produced at 443 K, pH 5.0 and P_{H_2} 3000 kPa.

As bismuth can be easily reduced by hydrogen in acetate solutions [76], its effect on the reduction of Ni(II) was studied by varying Bi(III) concentration in the range 0.1–2.0 g/L at pH 4.4. The molar ratio of acetate to nickel 2:1, at optimum temperature and hydrogen pressure was already established earlier [67] in presence of graphite and tungsten carbide powders. The studies showed that Bi(III) had a substantial effect on the reduction of Ni(II). The rate increased with increase in the concentration of Bi up to 0.5 g/L and then remained constant. The induction period of reduction became longer with increasing bismuth concentration and reduction even stopped when the concentration of bismuth exceeded 2 g/L [71]. Further, kinetics and mechanism of reduction with graphite were found to be governed by the adsorption of bismuth species on the surface of the powdered catalyst [72]. A three-stage mechanism for the reduction of Ni(II) was established involving adsorption of Bi(III) on the graphite surface, reduction of Bi(III) to metallic bismuth, and reduction of nickel(II) to metallic nickel on bismuth-coated graphite grains. A high quality composite powder with a compact and uniform nickel coating was obtained with the use of bismuth additive.

2.2. Reduction of copper from solution

The reduction of copper with hydrogen can be achieved under pressure in the absence of nucleating agent from the acidic and ammoniacal solutions [4,18,22,50,51,77–80]. The reactions can be presented from acidic and ammoniacal solutions as

$$Cu^{2+} + H_2 \rightarrow Cu + 2H^+ \tag{12}$$

$$Cu^{2+} + 2NH_3 + H_2 \rightarrow Cu + 2NH_4^+ \tag{13}$$

In the reduction of copper from acidic solution, the thermodynamic force for the copper reduction decreases with increase in the acidity of the solution as is evident from the pH-potential diagram (Fig. 1) [5]. The reduction of cupric salt and the kinetics may depend on the several stages of the reduction [81–86]. The cuprous ions initially formed may be accelerating the reduction reaction, which may be represented as [83–85]

$$Cu^{2+} + H_2 \rightarrow CuH^+ + H^+ \tag{14}$$

$$CuH^+ + Cu^{2+} \rightarrow 2Cu^+ + H^+ \tag{15}$$

$$Cu^+ + H_2 \rightarrow CuH + H^+ \tag{16}$$

$$CuH + Cu^+ \rightarrow 2Cu + H^+ \tag{17}$$

2.2.1. Copper powder from leach solutions

Production of copper powder from the leach solutions [87,88] is practiced on commercial scale as shown in Fig. 4. The purified ammonia-ammonium carbonate leach solution (140–160 g/L Cu) of copper scrap and cemented copper was reduced at 477 K and 6401 kPa pressure to produce copper powder in horizontal stirred autoclaves in the absence of any nucleation catalyst by Universal Minerals and Metals, Inc. [89–91]. Arizona Chemcopper Corporation [88,92,93] also produced copper powder by hydrogen reduction at 408 K under 3022 kPa in titanium lined horizontal stirred autoclaves from the leach solution. The solution was obtained from leaching cemented copper in acidic ammonium sulphate solution at 355 K with air at atmospheric pressure.

2.2.2. High acid copper solution

Reduction of copper can take place even from high acidic solution unlike nickel reduction which required alkaline solution [94–96]. The copper bleed electrolyte generated in the processing of sea nodules also contains copper and
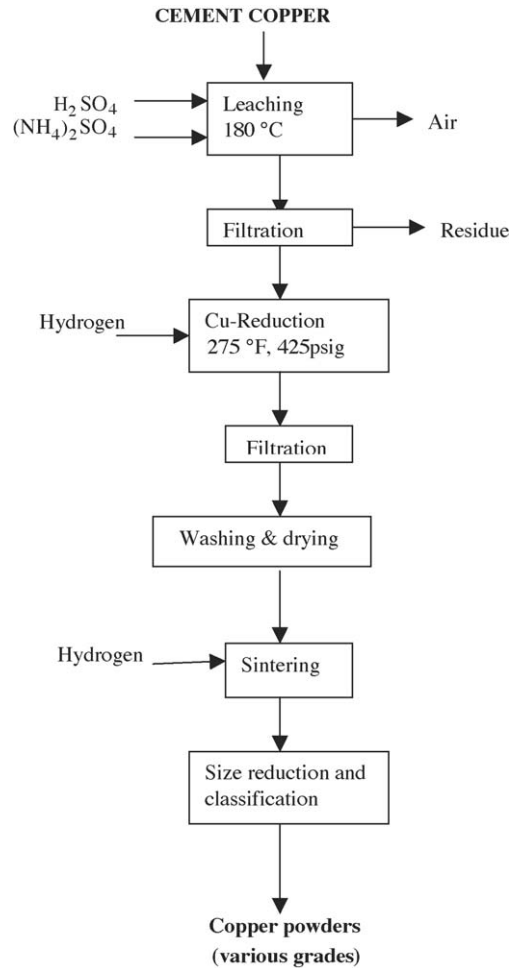
CEMENT COPPER

Fig. 4. Arizona chemcopper company powder production from cement copper [87].

nickel. A process for the selective reduction of copper and nickel from the mixed solution under hydrogen pressure was patented by Pandey et al. [97]. The spent electrolyte and mother liquor containing high acid were treated to recover copper and removal of arsenic [96]. The copper was selectively reduced in the first stage <443 K and 2000 kPa pressure to produce copper powder from the spent electrolyte of the copper plant containing 40 g/L Cu, 10 g/L As, 150 g/L H_2SO_4. Arsenic, antimony and bismuth present in the liquor have been found to catalyse reduction of copper. Subsequently, in the second stage a solid arsenic product (Cu_3As) was produced at 473 K temperature and 2500 kPa pressure. The electrolyte after powder production was considered suitable for reuse. The kinetics of reduction of Cu(II) were found to be proportional to the square root of the partial pressure of hydrogen. The low value of activation energy 30.1 kJ/mol suggested diffusion as controlling factor of reduction. The reduction of As(V) to As(III) was found to be slow as reported earlier. Recently, the pressure reduction of copper sulphate electrolyte containing high acid and arsenic was also reported by Wodka et al. [96].

Berezowsky patented a process for the production of copper by gaseous reduction [95]. This invention relates to the recovery of copper from aqueous systems in which it is present as a salt by reacting the system with a reducing gas at elevated temperature and pressure. More particularly, it is concerned with improvements in such processes whereby the physical and chemical characteristics of the copper powder produced by direct hydrogen reduction from acid sulphate solutions is controlled through use of an organic addition agent selected from the group consisting of polymeric polyamines having amino groups linked by alkyl groups having 2–4 carbon atoms. In the commercial scale production of copper and other metal powders by the prior art gas reduction procedures, the process is carried out on a batch basis. In this procedure, a fixed volume of metal bearing solution is charged into a pressure vessel such as an
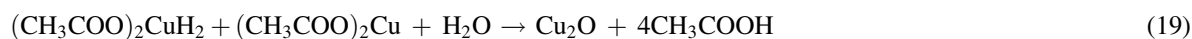
autoclave, the vessel is sealed and the solution heated and reacted with hydrogen. After completion of the reduction reaction, the metal depleted solution is discharged and the whole procedure is repeated again. The powder product may be discharged after each reduction However, serious problems are encountered with copper reduction, in carrying out the direct hydrogen reduction of metals from solution on a continuous basis such as agglomeration of particles and/or plastering or plating of metal on the interior walls of the reaction vessel and/or on the agitator and other internal fittings. This problem have been overcome to some extent, particularly insofar as nickel and cobalt reductions are concerned, by the use of small amounts of certain additives in the reduction feed solution such as ethylene maleic anhydride polymer, acrylic and polyacrylic acids, polymers/copolymers/derivatives/salts of acrylic and polyacrylic acids, lignin and derivatives of lignin, higher fatty acids and salts.

2.2.3. Leach liquor from alloy scraps

Copper powder has also been obtained by hydrogen reduction of the leach solutions obtained from the different sources [96–98]. The solution generated from leaching copper alloy scrap [Cu-25%, Zn-18%] in industrial waste acid [70% H_2SO_4 and 7% HNO_3] was subjected to reduction at 2020 kPa and 453 K. A low reduction of copper was observed due to the presence of high acid >170 g/L H_2SO_4. The addition of bismuth as catalyst improved the reduction to more than 96% [98]. Recently, the sulphuric acid leach solution of German silver scrap containing 48 g/L Cu, 350 g/L H_2SO_4 and 0.1 g/L Bi was reduced totally [99]. The polyethylediammine [0.1 g/L] was added to avoid copper cohesion and sticking to reactor wall. Won and Kang [100] compared the reduction of copper with actual and synthetic solutions of the ammoniacal etchant containing 14 wt.% Cu, 0.1 wt.% Ni and 0.001 wt.% Pb. A low recovery of 60% was obtained with actual solution as compared to 90% from the synthetic solution at 2000 kPa and 500 rpm in 30 min.

2.2.4. Reduction from copper acetate solution

Copper was also produced by the hydrogen reduction of cupric acetate solution [101]. Solutions containing cupric acetate (0.015–0.5 M), acetic acid and ammonium. acetate at a pH of 4.0 was reduced with hydrogen in a stirred reaction vessel between 383 and 423 K. It was observed the high acetate concentration (6 M) copper powder was produced and at low acetate concentration either cuprous oxide is formed or no solid product forms at the reaction temperature, but as the solution cools cuprous oxide is seen. During the reduction process, after the admission of hydrogen to the reaction vessel, the rate of reduction of cupric species accelerated steadily and was proportional to the concentration of molecular hydrogen in the solution whereas in the second stage of the reaction, at a constant hydrogen pressure the reduction rate was proportional to the concentration of cupric species in the solution. The mechanism for this reduction was proposed by Dakers and Halpern [82] as given below

$$(CH_3COO)_2Cu + H_2 \rightarrow (CH_3COO)_2CuH_2 \tag{18}$$

$$(CH_3COO)_2CuH_2 + (CH_3COO)_2Cu + H_2O \rightarrow Cu_2O + 4CH_3COOH \tag{19}$$

The kinetic studies showed that neither there was any initiation period before the start of reduction nor any acceleration of the reaction, hence the reaction was autocatalytic.

2.2.5. Reduction of copper from organic medium

Fine copper powder for the use in electronics industries with properties like particle size less than 5 μm, narrow size distribution, spheroidal shape and very low oxygen content can be prepared from organic medium by high-pressure hydrogen reduction [102]. Burkin [103] was the first one to produce pure copper powder from an organic solvent by hydrogen reduction. He found that it was possible to precipitate copper powder from 20 to 30% by volume solution of Versatic 911 in Shellsol T at 403–473 K and hydrogen pressure up to 3450 kPa. The autocatalytic precipitation kinetics of this system were studied recently by Distin [104]. Demopoulos and Distin [105] reported the hydrogen precipitation of copper from Kelex 100-decanol-kerosene system

$$CuL_2 \,(org) + H_2 \rightarrow Cu\,(s) + 2HL\,(org) \tag{20}$$

Navarro-Hernandez and Distin [106] reported the precipitation of copper from LIX 65N–decanol–kerosene solvents by H_2 reduction in the temperature range of 373–543 K at H_2 pressure of 690–4280 kPa. Thus heavily agglomerated

nonuniform particles were produced which on recycling coarsened the apparent particle size and accelerated the reaction kinetics indicating the heterogeneous nucleation growth mechanism.

Sarraf-Mamoory et al. [107] prepared copper powder having the required properties for thick film applications. The method involves the precipitation of Cu powder by hydrogen reduction under pressure from Kelex 100–decanol–Versatic 10–kerosene media. Under the optimised parameters such as temperature (453–573 K), hydrogen pressure (1030–3790 kPa) time, use of additives, solvent composition, etc. Powders with the following excellent properties were produced: d_{50} = 1μm; 80% spread-1.3 + 0.7 μm; specific surface area = 1 ± 0.2 m^2/g, spheroidal shape; and 0.056 wt.% oxygen content. The kinetics [108] of very fine copper powder (1–2 μm) produced by this method shows that Avrami-Erafeer model for nucleation growth processes is the best fit. The model parameters were correlated with reasonable success to the morphology of the Cu powder. The chemically controlled particle formation process was found to exhibit 30–58 kJ/mol activation energy depending on the temperature range and a complex dependency (from first order to fractional/zero order) on hydrogen pressure. A steric stabilization model has been advanced to interpret the cooperative action of Decanol and Versatic 10 in stabilizing the very fine Cu powder dispersion.

3. Conclusion

In the hydrometallurgical processing of ores/concentrates/secondaries, the metals from the leach solution, streams or effluents could be efficiently recovered in the form of powders by hydrogen reduction under pressure. The process is used on commercial scale to produce powders of the required specifications from different types of acidic and alkaline solutions. The presence of different additives, both inorganic and organic, helps in the production of nickel powders in order to initiate the reduction of nickel and improve the quality of the powder. The rate of reduction and quality of powder depend on several factors such as pH of the solution, concentration of metals, particle size and nature of additives, operating condition of autoclave, etc. By maintaining the conditions precisely it is possible to produce nickel and copper powders of the required specification. The copper powder could be produced even in the absence of additive from the high acidic solution. The composite materials are also produced by coating the nickel or copper powders on the secondary materials such as graphite, tungsten carbide, aluminium, etc. The hydrogen reduction process has a great potential to treat even the different waste effluents generated in the industries to produce the value added products like powders or composite materials.

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