COBALT PRECIPITATION BY REDUCTION WITH SODIUM BOROHYDRIDE

by

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ABSTRACT

The reaction of cobalt reduction with borohydride is very complicated. Various authors obtained different reaction stoichiometries and have proposed a number of mechanisms. There are conflicting claims about the removal of cobalt from zinc electrolyte with sodium borohydride. The present research has focused on the stoichiometry of cobalt reduction with borohydride and on the removal of cobalt from zinc sulphate solution.

Cobalt reduction with borohydride releases hydrogen ions resulting in a decrease in the pH of the solution. The efficiency of cobalt reduction increased with increasing concentration of NaOH in the reducing solution. The NaOH in the reducing solution neutralized the hydrogen ions released during cobalt reduction. The best reduction efficiency without the precipitation of cobalt hydroxide is one mole of sodium borohydride to reduce one mole of cobalt (II). If the pH was controlled at 4, the maximum reduction efficiency was about 81 % for a ten-minute addition time and the addition of more sodium borohydride did not increase the reduction efficiency. The reduction efficiency increased with increasing pH from nil at pH 2 to 96% at pH 6 and decreased with increasing temperature.

X-ray diffraction patterns and TEM patterns of the recovered precipitates showed them to be amorphous. After a two-hour heat-treatment at 500 0 C, the X-ray diffraction pattern of the precipitate showed well-defined peaks due to Co₂B with the main peak attributable to cobalt. The single crystal TEM pattern obtained was consistent with that of Co₂B. The particle size was about 20-100 nm. The atom ratio of Co to B increased with increasing temperature.

The reduction of cobalt ions in the absence of interfering species was completed within several seconds. The time for the reduction of most of the cobalt ions decreased with increasing temperature from 24 seconds at 5 $^{\circ}$ C to less than 2 seconds at 35 $^{\circ}$ C.

Zinc ions had a dramatic inhibitory effect on cobalt reduction. Several tens of μ mol/L of zinc ions completely inhibit cobalt reduction with borohydride. The main cause of inhibition is that zinc ions compete with those of cobalt for borohydride ions and zinc borohydride forms and hydrolyzes rapidly. The resulting zinc ions react further with borohydride. Zinc ions catalyze the hydrolysis of borohydride. Zinc ions also have an inhibitory effect on nickel, cadmium and lead reduction.

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1. INTRODUCTION

Sodium borohydride discovered by Schlesinger is an efficient water sol5ble reducing agent [1-3]. It has the following features: (1) a low reducing equivalent weight of 4.75 g/mole e, (2) high reducing power (-1.24 V SHE at pH 14) and (3) redox reaction in different media (water and organic solvents, and acidic, neutral and alkaline conditions). It was first used in the paper and textile industries and the military [4]. The commercial importance of sodium borohydride reached its first peak in the fifties in U.S. military research programs [4, 5]. Recently borohydride reduction of metal ions is the basis of several commercial processes including: (1) the preparation of selective catalysts, magnetic materials [6-24], (2) the recovery of precious metals (silver, gold, platinum and palladium group metals) [6, 25-35], (3) the removal and recovery of heavy metals (mercury, lead, copper, nickel, cobalt and silver) from aqueous discharge streams [36-47], and (4) the electroless plating of nickel, cobalt, copper, silver and gold onto metallic or nonmetallic surfaces such as glass, ceramics and plastics [5, 6, 48-63]. Sodium borohydride has also widely used to reduce metal cations for analysis [5, 64-72]. Finally it may be potentially applicable to emerging hydrometallurgical applications.

Most of the world's zinc is now produced by the roast-leach-electrowinning process because it has the following advantages over the pyrometallurgical method: (1) a better zinc recovery and energy efficiency, (2) a high purity product, (3) efficient labour utilization [73]. The zinc electrowinning process is very sensitive to the presence of impurities in the electrolyte. Some impurities such as antimony, germanium, cobalt, nickel and copper can cause extensive redissolution of the electrodeposited zinc, leading to a decrease in the current efficiency of zinc electrodeposition with time and an impure zinc product [74-83]. Therefore zinc electrolyte purification is a key operation for the economical extraction of zinc by the hydrometallurgical process. Many methods have been proposed [84-113], but they are still not satisfactory because they are expensive, inefficient, and potentially toxic. Sodium borohydride reduction has been proposed as a way to overcome these disadvantages.

Cobalt reduction with sodium borohydride has been widely used to make magnetic materials and catalysts and to remove and recover cobalt from waste water. It is considered as a new available technology for treating waste water for cobalt removal [41, 42].

Cobalt reduction with sodium borohydride is very sensitive to reaction conditions including temperature, the method and rate of addition, pH and the presence of other ions such as zinc and copper. The stoichiometry and reaction mechanism of cobalt reduction with sodium borohydride is still unclear. There are various reports with differing results.

Polyakov *et al* [114, 115] reported that 1.1 moles of sodium borohydride can reduce 4 moles of cobalt ions to lower the concentration of cobalt ions in zinc sulphate electrolyte (120 g/l zinc ions) to 0.01 ppm in the presence of triethanolamine. However, Awadalla *et al* [47] reported that 2 moles of sodium borohydride can only reduce 1 mole of cobalt ions and that zinc ions have a strong negative effect on cobalt reduction. Cominco staff [116] have reported that borohydride cannot reduce cobalt from zinc sulphate solution.

Thus it is necessary that a careful study of cobalt reduction with sodium borohydride be conducted to see if this might be a feasible process. Consequently the present research was undertaken with the following objectives:

1. To understand the stoichiometry of the reduction of cobalt ions with sodium borohydride and optimize the cobalt reduction efficiency.

2. To study the feasibility of removing cobalt from zinc sulphate electrolyte with sodium borohydride.

It was hoped that the results of this study would help to increase the efficiency of cobalt reduction with sodium borohydride and cobalt removal and recovery from aqueous solutions.

The presentation of this work is divided into four major sections. Chapter 2 deals with a review of the literature, providing a summary of the current ideas about cobalt reduction or its removal from aqueous solution with sodium borohydride. Chapter 3 describes the experimental procedures used in this study and the experimental parameters tested, while Chapter 4 provides a review and discussion of the experimental results. Chapter 5 presents a summary of the work.

2

2. LITERATURE REVIEW

2.1 APPLICATIONS OF SODIUM BOROHYDRIDE

Sodium borohydride was discovered by Schlesinger in 1942 while looking for volatile uranium compounds [1]. Brown [2] pioneered the chemistry of this compound. The first application of sodium borohydride was its solvolysis in the presence of cobalt salts to produce hydrogen gas [3]. Today, it is used in numerous applications in the paper and textile industries, in stabilizers for organic materials and in catalysts. Sodium borohydride is a very efficient water soluble reducing reagent and has the following features:

1. Sodium borohydride has a low equivalent weight of 4.75 g/mol e⁻ and one mole of sodium borohydride can supply eight moles of electrons. Table 2-1 lists the theoretical weight ratio of reduced metals obtainable from ionic species per amount of sodium borohydride.

Metal ions	Weight ratio(g metal/g reductant)
Pb ²⁺	22
Ag^+	. 22
Hg ²⁺	21
Au ³⁺	14
Ir ⁴⁺	10
Pd ²⁺	11
• . Pt ⁴⁺	10
Cu ²⁺	7
Ni ²⁺	6
Co ²⁺	6
Cd ²⁺	12

Table 2-1 Theoretical weight ratio of reduced metals obtainable from ionic species per amount of sodium borohydride

2. Sodium borohydride has a high reducing power. Its redox potential is -1.24 V vs. SHE at pH 14 decreasing to -0.48 V at pH 0.

3. Sodium borohydride redox reaction can take place in different media such as water and organic solvents, and under acidic, neutral and alkaline conditions.

These properties distinguish it favourably from other reducing agents. Hence sodium borohydride has been widely used to reduce a variety of metal cations to metallic state. These technologies are the basis of several commercial processes and are also important to the analytical chemistry of many elements [4-72].

2.1.1 PREPARATION OF ULTRAFINE AMORPHOUS MATERIALS

Amorphous materials have usually been prepared by three techniques: liquid quenching, vapor deposition and solid-state reactions. However, a method of chemical reduction with borohydride to prepare ultrafine amorphous powders has recently attracted increasing attention because of the unique preparation process and the fine morphology of the resulting powder. Amorphous materials can used as ferrofluids, catalysts, and magnetic recording materials [6-24].

As catalysts, amorphous materials were found to be more active and to exhibit different catalytic properties as compared to the corresponding crystalline metals [5, 12].

Much attention has focused on nickel and cobalt reduction. The reduction reaction generally takes place as follows:

$$4BH_{4}^{-} + 2M^{2+} + 9H_{2}O = M_{2}B + 3H_{3}BO_{3} + 12.5H_{2}$$
(2-1)

where M is Ni or Co.

2.1.2 RECOVERY OF PRECIOUS METALS IN HYDROMETALLURGY

<u>GOLD</u>

Sodium borohydride can be used as an efficient agent for reducing gold and silver in acidic solutions of thiourea, thiocyanate, thiosulfate, chloride, and nitrate [25, 26]. The Au(I) ion is reduced to metallic gold in the form of very fine crystals. The reduction reaction from thiourea solution can be represented as follows:

$$8Au[CS(NH_2)_2]^+ + BH_4^- + 2H_2O = 8Au + 8CS(NH_2)_2 + BO_2^- + 8H^+$$
(2-2)

The recovery of gold from cyanide solutions can be carried out effectively if the cyanide is first oxidized to cyanate.

$$8Au(CNO)_{2} + 3NaBH_{4} + 24OH^{-} = 3NaBO_{2} + 24CNO^{-} + 18H_{2}O + 8Au$$
(2-3)

Also it is reported that gold was recovered directly from cyanide and thiourea leach solutions [27].

Carbonate is used as an eluant for gold in a carbon-in-pulp process and the direct and selective recovery of gold from carbonate solutions has been reported [28]. The barren solution is in a condition such that it can be recycled to the upstream process. Gold ions are present on the activated carbon as cyanide complexes and are expected to be in the carbonate eluate also as cyanide complexes. The reaction can be represented as follows:

$$2Au(CN)_{2}^{-} + BH_{4}^{-} + 2OH^{-} = 2Au + 4CN^{-} + BO_{2}^{-} + 3H_{2}$$
(2-4)

SILVER

Sodium borohydride is also used to recover silver from various sources such as spent photographic fixer solution, electronic scrap, mirrors etc. [5]. In the case of spent photographic fixer, for example, the reaction may be written as :

$$8Ag(S_2O_3)_2^{3-} + BH_4^{-} + 2H_2O = BO_2^{-} + 8H^{+} + 16S_2O_3^{2-} + 8Ag$$
(2-5)

Silver is recovered from a carbonate solution having a pH in the alkaline range by the addition of stabilized alkali metal borohydride [28].

PLATINUM GROUP METALS

Sodium borohydride can be used as an efficient agent to reduce platinum group metals from acidic solutions, such as leach or strip liquors at ambient temperature [5, 29-33]. Compared to the common reductants, the use of sodium borohydride leads to higher recovery, lower cost, and simpler operation. The reaction for $PtCl_6^{2-}$ is:

$$2PtCl_{6}^{2-} + BH_{4}^{-} + 2H_{2}O = 2Pt + BO_{2}^{-} + 8HCl + 4Cl^{-}$$
(2-6)

Sodium borohydride is also used to separate iridium [34] and to reduce rhodium in the process of solvation and purification of rhodium [35].

2.1.3 POLLUTION CONTROL APPLICATION

Several industries now employ sodium borohydride to reduce heavy metal cation impurities from their effluent streams to meet stringent environmental requirements [5, 36-47]. These include:

1. The use of sodium borohydride to remove and recover copper, lead, etc. from their electroless plating baths and etchants in printed circuit board manufacturers.

2. The use of sodium borohydride to remove silver and cadmium from plant effluents in photographic film manufacture to meet discharge limits.

3. The use sodium borohydride to remove soluble mercury from the effluents in mercury-cell chloralkali plants.

4. The use of sodium borohydride to remove and recover cobalt, copper and lead from other waste water sources.

2.1.4 ELECTROLESS PLATING

Sodium borohydride is a highly effective reducing agent for the electroless plating of nickel, cobalt, silver, gold and copper on metallic and nonmetallic surfaces [5, 6, 48-63]. Depending on the bath conditions, either a metal or a metal boride layer may be formed. Borohydride-reduced coatings provide superior hardness, wear resistance, lubricity and uniformity, solderability and brazability and lower labor costs. Nickel electroless plating has been most widely studied and used to prepare amorphous coatings with different properties such as Ni-B, Ni-P, Ni-P-B.

2.1.5 ANALYTICAL CHEMISTRY

Sodium borohydride has been widely used to reduce metal cations for analysis [5, 64-72]. The sodium borohydride reduction of nanogram quantities of arsenic, antimony, bismuth, tin, germanium, mercury, tellurium, selenium, and lead to produce votatile hydrides for detection by atomic absorption, gas chromatography and emission spectroscopy has been widely reported [5, 66-70]. Sodium borohydride is also used to reduce silver, copper and nickel in the spectrophotometric determination [64].

2.2 HYDROMETALLURGICAL EXTRACTION OF ZINC

2.2.1 INTRODUCTION

In 1880, Luckow [73] applied for the first patent for electrolytic zinc production. Since then, the process has advanced to the point where more than 80 % of the world's production of zinc is produced by the roast-leach-electrowinning process (RLE). The RLE process has been adopted in many plants because it offers a number of advantages including good zinc recovery and energy efficiency, a high purity product, efficient labour utilization and relatively minor environmental problems.

Basically, the RLE process consists of the following five major steps:

1. Concentrates containing zinc sulphide plus several other impurities are roasted in air at 800 - 975 ⁰C to form acid-soluble zinc oxide, other less soluble oxides, and sulfur dioxide gas.

2. Calcine containing zinc oxide and other oxides is leached in electrolyte containing sulphuric acid.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O \tag{2-7}$$

Zinc ferrite and certain other impurities such as silver, bismuth, lead, and barium form insoluble precipitates. Additional leaching steps are often used to dissolve more insoluble zinc ferrite (e.g. $ZnFe_2O_4$).

3. Dissolved iron and other impurities such as arsenic, antimony, germanium, indium, tin, mercury and lead are precipitated from solution as hydroxides when the pH is adjusted to 4.5-5.1 by returning acid and calcine addition.

$$2Fe^{3+} + 3ZnO + 3H_2O = 2Fe(OH)_3 + 3Zn^{2+}$$
(2-8)

Copper, nickel, cobalt, aluminum, arsenic and germanium are only partially coprecipitated [74] or absorbed with iron, while cadmium, magnesium and chloride remain in solution. Further treatment is needed before zinc can be efficiently electrowon from solution. 4. Dissolved impurities such as cadmium, copper, cobalt and nickel are removed from solution by zinc dust cementation. This step is divided into two stages. The first is the removal of copper, cadmium, nickel, arsenic, thallium and antimony at about 50 $^{\circ}$ C; the second is the removal of cobalt at above 70 $^{\circ}$ C in the presence of "activators", either antimony, antimony-copper or arsenic-copper, for successful cementation.

$$M^{2+} + Zn = M + Zn^{2+} \tag{2-9}$$

5. Zinc is recovered from the purified electrolyte by electrowinning onto aluminum cathode sheets. The zinc deposit is stripped off the cathodes, melted and cast into bars or ingots for shipment. The generated sulphuric acid is recycled to the leach step.

$$ZnSO_4 + H_2O = Zn + H_2SO_4 + 1/2O_2$$
(2-10)





2.2.2 IMPURITIES IN ZINC ELECTROLYTE

Electrolyte purification is a key operation for the economical extraction of zinc by the hydrometallurgical method. Impurities in the electrolyte can lead to:

1. A decrease in the current efficiency during electrowinning [75, 76].

2. Formation of dendrites on the deposited zinc, leading to short circuits and stripping difficulties.

3. A decrease in the quality and purity of the final zinc product.

Low levels of cobalt, copper, antimony, iron, cadmium, arsenic, germanium, tin, selenium, silver, bismuth, and barium in the electrolyte can affect the quality of the zinc product and the current efficiency [77, 78]. These impurities can codeposit with the zinc and become incorporated into the cathodic zinc, or can lower the hydrogen overpotential.

Ohoyama *et al* [79] ranked the effects of impurities by the amount of H_2 evolved on the zinc cathode. Cobalt was considered to be one of the more detrimental impurities in the zinc electrolyte. At cobalt concentrations larger than 0.5 mg/L, cobalt alone reduces the zinc electrowinning current efficiency. However, the presence of cobalt can also exacerbate the effects of other impurities on current efficiency [80]. The range of impurities in some zinc plant electrolytes is listed in Table 2-2.

Impurities	Cominco [81]	National Zinc[82]	VM Balen [83]	Kidd Creek [80]
Со	0.3	0.7	0.23	0.3
Cu	0.2	< 0.1	0.2	0.1
Cd	0.3	2.3	5	< 0.1
Fe	< 5.0	< 0.1	15	5
Sb	0.03	0.01	0.01	< 0.02
As	-	< 0.01	0.01	< 0.02
Ni	< 0.05	0.3	0.01	< 0.1

Table 2-2 Impurity levels in various zinc plant electrolytes (mg/L).

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2.2.3 METHODS OF COBALT REMOVAL FROM ZINC ELECTROLYTE

The seriousness of cobalt impurities was realized as early as 1917, when the Electrolytic Zinc Company of Australasia attempted to treat the Broken Hill N. S. W. ores, which were high in cobalt content. Since then a number of methods have been patented and or employed for the removal of cobalt from zinc sulfate electrolytes, depending on the operating conditions in the zinc electrowinning plants.

2.2.3.1 COBALT REMOVAL BY CHEMICAL OXIDATION

1. A strong oxidant, lead peroxide or calcium plumbate was used in the early 1920's to oxidize cobalt to its cobaltic state at 40-50 $^{\circ}$ C followed by precipitation or hydrolysis of Co₂(SO₄)₃ [84, 85]. Livingston and Field [86] reported that cobalt could be removed by agitating the electrolyte with lead peroxide or manganese dioxide, followed by precipitation of cobalt:

$$2C_0SO_4 + PbO_2 + H_2O = Co_2O_3 + H_2SO_4 + PbSO_4$$
(2-11)

$$2C_0SO_4 + MnO_2 + H_2O = Co_2O_3 + H_2SO_4 + MnSO_4$$
(2-12)

2. Sodium hypochlorite is used to oxidize cobalt to its cobaltic state [87]. Ammonia has to be added as a neutralizing agent and the temperature is about 70 0 C and The residence time necessary was about 2-3 hours. The reaction is:

$$NaOCl + 2Co^{2+} + 2H_2O = Co_2O_3 + NaCl + 4H^+$$
(2-13)

2.2.3.2 PRECIPITATION METHODS

1. Clevenger patented two methods in 1918 [88, 89]: a process of cobalt removal during iron purification with the addition of permanganates or manganates and a precipitation process for cobalt as the red cobalt-nitroso-beta-naphthol with nitroso-beta-naphthol or both beta-

naphthol and sodium nitrite, added together or separately. Alpha-nitroso-beta-naphthol (in the form of sodium naphthenate and sodium nitrite) has been used to precipitate cobalt from zinc sulfate solutions commercially. Zinc electrolytic plants in Australia make use of this technology [90]. The precipitated cobalt-nitrosonaphthate is recovered and oxidized at elevated temperatures to a cobalt oxide. Richard et al [91] reported that when alpha-nitroso-beta-naphthol dissolved in a minimal amount of ethanol is added to the zinc sulfate solution, 97-99 % of the cobalt is precipitated.

2. Cobalt can be removed from zinc sulfate solution with organic nitrogen-containing complexing agents in 100 - 120 % stoichiometric excess. Suitable agents are ethylenediamine, hydroxylamine or urea [92]. The reaction is carried out in the presence of barium oxide or sulphide, in an amount equal to 3 times that of the cobalt present. The compound is added after the complexing agent in the form of a powder [92].

3. The xanthate method in which cobalt is precipitated as cobalt xanthate was widely used in Russia [93]. Cobalt is precipitated in the form of cobalt xanthate.

2.2.3.3 SOLVENT EXTRACTION METHOD

Solvent extraction has been studied to remove cobalt from zinc sulfate solution containing 190 g/L Zn and 50 ppm cobalt and the following complexing reagents gave the best results: alpha-nitroso-beta-naphthol, beta-nitroso-alpha-napthol, 1, 2-cyclohexane dione dioxime (nioxime), di-2-pyridyl ketone oxime, and dimethyglyoxime [91]. These reagents in suitable solvents (kerosene plus isodecanol) lowered the cobalt and nickel levels to < 0.1 ppm. Stripping of the complexed reagents from the loaded organic phase was not possible except for nioxime. This method has not been applied commercially.

2.2.3.4 COBALT CEMENTATION WITH ZINC DUST

Because of the favourable redox characteristics of zinc metal, it is used to electrochemically precipitate less electropositive impurities from zinc electrolyte. Of all the impurities in zinc electrolyte, cobalt has been found to be one of the most troublesome to remove by cementation, despite favourable thermodynamics. The cobalt cementation equilibrium constant is 2×10^{16} , which suggests that cobalt should be completely removed from the solution with zinc dust and no back reaction would be expected [94, 95]. However, cobalt cementation is very slow and unless special measures are taken such as the addition of activators, e.g. arsenic or antimony trioxide, the Co²⁺/Zn reaction is practically useless for the removal of cobalt from the zinc sulfate electrolyte. As shown in Fig. 2-2, the cementation of cobalt with zinc dust is slow even in the absence of zinc ions and the addition of only 1 g/L zinc ions to the solution slows down the rate of cobalt cementation significantly. The pH of the zinc electrolyte is usually controlled in the range of 4-5. Too low a pH (<4) increases the rate of the competing hydrogen reduction reaction and too a high a pH (> 5) can result in the formation of hydroxide or basic zinc sulfate salts and thus passivation of the residue's surface.



Figure 2-2 Reaction data for the isothermal cementation of cobalt onto zinc in the presence of additional zinc ions [93]

The following are some of the technologies which have been applied to cobalt removal by zinc cementation.

1. Cobalt cementation with zinc dust at 75 ^oC in the presence of copper and arsenic was patented in Australia in 1919 [96]. The process is believed to take place via precipitation of

cobalt arsenide [94, 97-99]. In the copper-arsenic process, typical additions of copper and arsenic to the electrolyte are, respectively, 200 mg/L and 50-200 mg/L and the temperature is above 90 0 C [94, 97]. It has been proposed that a galvanic cell is formed between zinc dust and copper particles. Cobalt is deposited on the copper by the galvanic current. Its deposition is improved greatly when it co-deposits with arsenic [100].

2. In 1946, antimony compounds were found to be substitutes for As_2O_3 with the advantage of lower toxicity, but cobalt cementation with copper-antimony activation requires more zinc dust than when copper-arsenic is used and proceeds at a lower rate [98]. Typical additions are 30 mg/L copper as copper sulfate and 1.5 mg/L antimony as antimony tartrate with 4 g/L zinc dust at a temperature above 70 $^{\circ}C$ [100]. The addition of antimony only, improves the cementation of cobalt to some extent, whereas copper by itself has an almost negligible effect on the rate. The combination of the two elements gives the best results.

3. A method for purification with pretreated zinc dust was patented in 1972 [101]. Atomized zinc dust containing 0.002-5 wt % Sb and 0.05-10 wt % Pb was used at 60-80 $^{\circ}$ C. A similar method was patented in 1975 in Japan [102]. The zinc dust containing antimony and 0.01-5% graphite was reported to improve the removal of cobalt from zinc sulphate solution [103].

4. Addition of Sb (V) is more effective than the addition of Sb(III) in promoting the removal of cobalt ions from zinc sulphate solution by zinc cementation. The time of purification and the amount of zinc consumed are reduced [104, 105].

5. Finely divided antimony powder was used as a substitute for soluble antimony. The addition of only 0.002 mg/L antimony dust could remove all cobalt at 90 0 C when no copper was present [105, 106].

6. Indium [108], tin [109], thallium [110], and mercury [111] compounds were found to accelerate cobalt cementation with zinc dust.

2.2.3.5 COBALT CEMENTATION WITH MANGANESE DUST

In order to increase the efficiency of cobalt removal from zinc electrolyte, manganese powder has been tested for the cementation of cobalt [112, 113]. Considering the more

favourable redox characteristics of manganese, the rate of the Co (II)-Mn reaction should be very high, but the reaction rate is still slow and the antimony and copper compounds have to be added to the solution to accelerate the reaction and prevent the redissolution of reduced cobalt. The cobalt removal rate using manganese powder was improved by a factor of 3 compared to using similarly sized zinc powder. However, fifty times the stoichiometric requirement for manganese powder was needed, and there was a strong tendency for the cemented cobalt to redissolve. So manganese powder has not been used commercially for the purification of zinc electrolyte.

2.2.3.6 COBALT REMOVAL WITH SODIUM BOROHYDRIDE

The removal of cobalt from zinc electrolyte has been studied and practiced for about 80 years. Now most modern plants in the world employ the zinc cementation process with arsenic-copper or antimony processes to remove cobalt from the zinc electrolyte. However, these zinc dust purification processes are still not satisfactory. The main problem is that these processes have to use a very large excess of zinc dust, a high temperature and a long purification time (more than 2 hours). Thus they are an expensive component of the zinc hydrometallurgy process. In order to realize a more economic extraction of zinc by hydrometallurgical processes, zinc production plants have been looking for a better method to replace the present processes.

Sodium borohydride has been studied to remove cobalt from waste water and implemented as the best available technology for the treatment of such waste water. Polyakov [114, 115] reported the use of sodium borohydride to remove cobalt from zinc sulfate solution to 0.01 ppm. This purification process could have many advantages over the present process for example, the high reduction efficiency, the low purification temperature, the short reaction time, and the simplification of the purification process and equipment. However, Cominco Ltd.'s staff [116] reported that cobalt ions cannot be reduced from zinc sulfate solutions. In view of the conflicting reports it was deemed worthwhile to study carefully the possibility of cobalt removal with sodium borohydride from zinc sulfate solution.

2.3 CHEMISTRY OF BORON

2.3.1 PHYSICAL AND CHEMICAL PROPERTIES OF BORON

Boron is a unique and exciting element. It is the only non-metal in Group III of the periodic table and shows many similarities to its neighbor, carbon and its diagonal relative silicon. Thus, like carbon, and silicon, it shows a marked propensity to form covalent, molecular compounds, but it differs sharply from them in having one less valence electron than the number of valence orbitals, a situation referred to as "electron deficiency". This has a dominant effect on its chemistry. The chemistry of boron is discussed in a number of books [117-123].

Boron has two stable naturally occurring isotopes ¹⁰B and ¹¹B. The physical properties of elemental boron are greatly affected by its complex polymorphism and contamination by irremovable impurities. Boron is an extremely hard refractory solid of high melting point, low density, and very low electrical conductivity. Crystalline forms are dark red in transmitted light and powdered forms are black. The most stable (β -rhombohedral) modification has a melting point of 2180 °C, a boiling point of 3650 °C, and a density of 2.35 g cm⁻³ [119].

The chemical reactivity of boron itself obviously depends markedly on the purity, crystallinity, state of subdivision, and temperature. Crystalline boron is extremely inert chemically. It is unaffected by boiling HCl or HF, only slowly oxidized by hot, concentrated nitric acid when finely powdered, and either not attacked or only very slowly attacked by many other hot concentrated oxidizing agents. Finely divided amorphous boron can be pyrophoric in air, whereas massive crystalline boron oxidizes only slowly at 800 $^{\circ}$ C. Boron does not react directly with hydrogen or the inert gases, but reacts with all other non-metals (except germanium and tellurium) under suitable conditions. It also reacts readily and directly with all metals at elevated temperatures to form borides. Boron reacts with a number of oxides at elevated temperatures to form B₂O₃ or its derivatives. Boiling water reacts slowly with powdered boron of moderate purity, and the reaction can become violent at red heat. At 830 $^{\circ}$ C, a stream of water passed over boron at 10⁻³ to 10⁻⁶ atm produces H₃BO₃. A powdered mixture of boron and B₂O₃ is stable at 900 $^{\circ}$ C in vacuum.

2.3.2 BORON COMPOUNDS

Five types of boron compounds can be distinguished, each having its own chemical characteristics which can be rationalized in terms of the type of bonding involved with each resulting in highly distinctive structures and chemical reactions:

- 1. Metal borides ranging from M_5B to MB_{66} .
- 2. Boron hydrides and their adducts and derivatives including carboranes and polyhedral borane-metal complex.
- 3. Boron trihalides and their adducts and derivatives.
- 4. Oxo compounds including polyborate, borosilicates, peroxoborates.
- 5. Organoboron compounds and B-N compounds.

2.3.2.1 BORIDES

The borides comprise a group of over 200 binary compounds which show an amazing diversity of stoichiometries and structural types: M₅B, M₄B, M₃B, M₇B₃, M₂B, MB, MB₃, MB₆₆, etc. There are also numerous ternary and more complex phases. Metal-rich borides are extremely hard, chemically inert, involatile, refractory materials with melting points and electrical conductivities which often exceed those of the parent metals. Borides are normally prepared as powders. The ability to withstand attack by molten metals and salts has commended borides or boride-coated metals as high-temperature reactor vessels, vaporizing boats, etc..

There are about eight general methods to prepare borides:

- 1. Direct synthesis from the elements or boron and a metal hydride at about 1000 °C.
- 2. Reduction of metal oxides with boron.
- 3. Co-reduction with hydrogen of a volatile boron compound and of a volatile compound of the metal.
- 4. Reduction of BCl_3 or other halides with a metal.
- 5. Fused-salt electrolysis of a metal oxide with a source of boric oxide at 700 1000 ⁰C.
- 6. Co-reduction of oxides with carbon at temperatures up to 2000 ^oC.
- 7. Reduction of metal oxides (or $M + B_2O_3$) with boron carbide.

8. Co-reduction of a metal oxide and boric oxide by a metal such as Al and Mg.

Cobalt boride can be made by the direct combination of powdered Co and B at $1000 \, {}^{0}\text{C}$, and electrolytic deposition from fused salt media.

Cobalt has the following three main types of borides: Co_4B (orthorhombic), Co_3B (orthorhombic), Co_2B (tetragonal), CoB. Figure 2-3 is Co-B phase diagram. Cobalt boride is not attacked by HCl, or H₂SO₄ solutions but is soluble in hot nitric acid solutions.



Figure 2-3 Co-B phase diagram [124].

2.3.2.2 OXYGEN COMPOUNDS OF BORON

These are among the most important compounds of boron, comprising nearly all of the naturally occurring forms of the element.

1. Boron oxide. The principal oxide is boric oxide, B_2O_3 , which is formed when boron is heated in air or oxygen, but is generally prepared by dehydration of boric acid. Boric oxide dissolves in water with considerable evolution of heat to give a solution of boric acid, $B(OH)_3$.

2. Boric acids. The principal oxoacid of boron is orthoboric acid $B(OH)_3$. The other boric acids are metaboric acids, HBO₂, polyboric acid, $B_3O_3(OH)_4^-$ etc.. Boric acid is moderately soluble in water with a large negative heat of solution so that the solubility increases with temperature. It is a very weak and exclusively monobasic acid that is believed to act, not as a proton donor, but as a Lewis acid, accepting OH⁻[119]:

$$B(OH)_{4} + H_{2}O \Leftrightarrow B(OH)_{4}^{-} + H^{+}$$
 pk =9.25 (2-14)

At concentrations <0.025 M, essentially only the mononuclear species B(OH)₃ is present; but at higher concentrations the acidity increases, and pH measurement is consistent with the formation of polymeric species such as [118]:

$$3B(OH)_2 \Leftrightarrow B_2O_2(OH)_4^- + H^+ + 2H_2O$$
 pk = 6.84 (2-15)

When heated, boric acid loses water in stepwise fashion:

$$B(OH)_{3} \underset{H_{2}O}{\stackrel{Heat}{\Leftrightarrow}} HBO_{2} \underset{H_{2}O}{\stackrel{Heat}{\Leftrightarrow}} B_{2}O_{3}$$

$$(2-16)$$

2.3.2.3 BORON HYDRIDE (BORANE) AND TETRAHYDRIDES

Boranes are colourless, diamagnetic, molecular compounds of moderate to low thermal stability. The lower members are gases at room temperature but with increasing molecular weight they become volatile liquids or solids. The boranes are all endothermic and their free energy of formation is also positive; their thermodynamic instability results from the exceptionally strong interatomic bonds in both boron and H_2 rather than the inherent weakness of the B-H bond.

Boranes are extremely reactive and several are spontaneously flammable in air. They are extremely versatile chemical reagents but the very diversity of their reactions makes a general classification unduly cumbersome.

Diborane (B_2H_6) occupies a special place because all of the other boranes are prepared from it. It is also one of the most studied and synthetically useful reagents in the whole of chemistry. It is spontaneously flammable in air and has a higher heat of combustion per unit weight of fuel than any other substance except H_2 .

Borane, BH₃, appears to have a transitory existence during the thermal decomposition of diborane:

$$B_2H_6 \longleftrightarrow 2BH_3$$
 (2-17)

 BH_3 reacts rapidly with diborane to give B_3H_9 . The bridge bonds in B_2H_6 are readily cleaved, even by weak ligands, to give either symmetrical or unsymmetrical cleavage products. e.g.,

$$B_2H_6 + 2H^- \rightarrow 2BH_4^- \tag{2-18}$$

BH4⁻ itself can be unidentate, bidentate, or tridentate ligand as illustrated by its complexes.

2.3.2.4 METAL BOROHYDRIDE

Borohydride is also called tetrahydroborate. The elements known to form such compounds are shown in Figure 2-4 [123].

<u>Li</u>	Be
<u>Na</u>	<u>Mg</u> <u>Al</u>
<u>K</u>	<u>Ca</u> [Ga]
<u>Rb</u>	<u>Sr</u> [In] [Sn]
<u>Cs</u>	<u>Ba</u> <u>Ti</u> (I)
	<u>Ti</u> (IV) <u>Cr</u> [Mn] [Fe] [Co] Ni $[Cu]^*$ <u>Zn</u>
Y	$\underline{Zr}(IV)$ Nb $[Ag]^*$ [Cd]
	<u>Hf</u> (IV)
	La Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
	<u>Th</u> <u>U</u> <u>Np</u>

Figure 2-4 Elements forming metal tetrahydroborate compounds. Asterisks indicate compounds stabilized at room temperature by coordination with phosphine ligands.

The elements underlined form simple hydroborates, $M(BH_4)_n$, which are stable or decompose only slowly at ambient temperatures; those not underlined have only been isolated with other groups, in addition to the hydroborate group, attached to the metal, while those in brackets form compounds which have been reported to be unstable at room temperature but may be isolated at lower temperatures.

The stability of metal hydroborate compounds may be related qualitatively to the electronegativity of the central metal atom. Compounds involving those elements possessing an electronegativity higher than that of boron are unstable or do not exist e.g., $Si(BH_4)_4$ and $P(BH_4)_3$ and attempts to prepare them result in the corresponding hydride being formed, e.g. SiH_4 and PH_3 . In these compounds the element of higher electronegativity competes for the hydride ion of the hydroborate group, $BH_3 \cdot H^-$, more effectively than the borane group, BH_3 . In the transition metal series the stability of the compounds decreases across the series as the electronegativity increases. Thus, for example, while compounds of titanium, zirconium and hafnium are known, those of nickel, cobalt or copper only exist at ambient temperatures when ligands are also bonded to the metal atom, essentially reducing its electronegativity (e.g. $[Co(NH_3)_6]$ (BH_4)₂ $\cdot NH_3$).

The stability of metal hydroborates has also been discussed in relation to their percentage ionic character, and those compounds with less ionic character than diborane are expected to be highly unstable [123]. The polarizability of the tetrahydroborate ion has been calculated to be 3.9 ± 0.1 Å, which is similar to that of the bromide ion (4.16 Å) [126]. The tetrahydroborates therefore vary in character from the ionic salt-like compounds of the alkali metals, which are only slowly hydrolyzed, to typically covalent volatile compounds such as those of aluminium, and zirconium, which show similar properties to diborane reacting explosively with air and being rapidly hydrolyzed.

Of all of the borohydrides, alkali metal borohydrides are most widely studied and used and their properties are better understood. The major reaction of alkali metal borohydrides can be divided into three types: metathetic reactions, protolysis reactions and substitution reactions.

The metathetic reactions are those in which the borohydride group is transferred from one element to another. A metal borohydride reacts with another metal compound (MX) in a suitable solvent precipitating the hydroborate derivative of M, or the metal hydroborate formed is more

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covalent and often volatile in nature, probably involving direct bonding between the metal and borohydride group in the form of hydrogen bridge bonds, e.g.,

$$NaBH_{4} + RbOH \rightarrow RbBH_{4} + NaOH \tag{2-19}$$

$$3NaBH_{4} + AlCl_{3} \rightarrow Al(BH_{4})_{3} + 3NaCl$$

$$(2-20)$$

$$2NaBH_{A} + ZnCl_{2} \rightarrow Zn(BH_{A})_{2} + 2NaCl$$

$$(2-21)$$

Sodium borohydride is the cheapest and most widely produced of all metal borohydrides. It is produced in three forms: powder, pellets and SWSTM (12 % solution of sodium borohydride in caustic soda). Some of physical and chemical properties are listed in Table 2-3.

Melting point (⁰ C)	505
Decomposition temperature (⁰ C)	315
Density (g/cm ³)	1.08
Enthalpy of formation, (kcal/mol ,298 K)	-43.8
Entropy (cal/mol., 298 K)	-30.19
Structure	Face centered cubic
Na-B distance, (Å)	3.08

Table 2-3 Some physical and chemical properties of sodium borohydride [122]

Zinc borohydride is a white, ether-soluble solid which quantitatively decomposes into the elements at > 85 0 C [125]. The preparation of zinc borohydride has been reported in ether or tetrahydrofuran by metathetic reactions involving zinc chloride with lithium, sodium or potassium hydroborate, and by the action of dioborane on zinc hydride. It reacts vigorously with water [123].

2.4 AQUEOUS CHEMISTRY OF SODIUM BOROHYDRIDE

2.4.1 AQUEOUS SOLUTION OF SODIUM BOROHYDRIDE

2.4.1.1 SOLUBILITY AND STABILITY

Sodium borohydride forms a dihydrate, NaBH₄• 2H₂O, which may be crystallized from cold aqueous solution. The stability regions of the two crystalline forms, NaBH₄ and NaBH₄•2H₂O, are shown in Figure 2-5. The curve below 36.4 $^{\circ}$ C shows the solubility of NaBH₄•2H₂O while that above 36.4 $^{\circ}$ C represents the solubility of NaBH₄.



Figure 2-5 The solubility of sodium borohydride in water at different temperatures [123].

The stability of sodium borohydride in water is dependent on the temperature and pH. The hydrolysis reaction is accelerated by increasing the temperature and lowering the pH. As the borohydride is basic, the higher the concentration, the more stable the solution. The pH of the solutions of sodium borohydride is shown in Table 2-4. The hydrolysis of sodium borohydride causes a rise in pH, and the rate of decomposition therefore decreases. For example, a 0.01 M solution of NaBH₄ has an intitial pH of 9.6 which changes during hydrolysis to 9.9. It is obvious that the addition of sodium hydroxide will stabilize aqueous sodium borohydride.

Concentration of NaBH ₄ (M)	pH
1.000	10.48±0.02
0.100	10.05±0.02
0.010	9.56±0.02

Table 2-4 pH of solutions of NaBH₄ at 24 ⁰C [5]

2.4.1.2 THERMODYNAMIC PROPERTIES OF BOROHYDRIDE

Sodium borohydride is an ionic salt-like compound which will dissociate into sodium ions and borohydride anions in water [125].

$$NaBH_4 \cdot 2H_2O \iff Na^+ + BH_4^- + 2H_2O$$
 $\Delta G^0 = -4070 \text{ cal}$ $K_{\text{equilibrium}} = 966 \text{ at } 25 \,^{0}\text{C}$ (2-22)

$$NaBH_4 \Leftrightarrow Na^+ + BH_4^ \Delta G^0 = -5660 \text{ cal} \quad K_{\text{equilibrium}} = 1.4 \times 10^4 \text{ at } 25 \,^{\circ}\text{C} \quad (2-23)$$

The equilibrium constant is 1.4×10^4 at 25 0 C, indicating that most of the sodium borohydride is dissociated.

In its physical behaviour, borohydride ion resembles the halide ions much as ammonium ion resembles the alkali cations. Its ionic radius of 2.03 Å lies between those of bromide and iodide ions. However, its polarizability of 3.94Å is slightly less than that of the bromide ions.

Figure 2-6 shows the E_h -pH diagram for the B-H₂O system at 25 ⁰C. The following species are considered: B, BH₄⁻, HBO₂, H₃BO₃, B(OH)₄⁻, and B₂O₃. The species BO₂⁻ is often referred to in the literature. However, spectroscopic studies have shown that BO₂⁻ is hydrolyzed to B(OH)₄⁻ [121] and so BO₂⁻ is not considered. Some polymeric species are not considered because under the practical reaction conditions, the concentration is much lower than 0.025 M. At pH < 9.24, the product of the oxidation of borohydride is H₃BO₃. Its redox reaction and potential are described by the following equations.
$$BH_4^- + 3H_2O = H_3BO_3 + 7H^+ + 8e \tag{2-24}$$

$$E_{\mu} = -0.481 - 0.0517 \, pH \tag{2-24A}$$

At pH > 9.24, the product of the oxidation of borohydride is $B(OH)_4^-$, but for simplicity, $B(OH)_4^-$ is often written as BO_2^- . The redox reaction and potential are expressed by the following equations,

$$BH_{4}^{-} + 8OH^{-} = B(OH)_{4}^{-} + 4H_{2}O + 8e$$
(2-25)

$$E_{h} = -0.413 - 0.0591pH \tag{2-25A}$$



Figure 2-6 E_h -pH diagram for the B-H₂O system at 25 ⁰C [127, 128]. The activity of species = 0.0001.

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2.4.1.3 HYDROLYSIS OF BOROHYDRIDE IONS

In spite of extensive studies on the hydrolysis of the borohydride ion, the details of the mechanism of the reaction and the intermediates involved, remain obscure. The ion is stable in alkaline solution since its salts are capable of recrystallization from such a medium. Hydrogen evolution becomes more rapid as the pH of the solution is decreased, and several early reports comment on the importance of pH on the hydrolysis reaction [123]. The hydrolysis is described by the following reaction:

$$BH_4^- + H^+ + 3H_2O = H_3BO_3 + 4H_2 \tag{2-26}$$

The borohydride ion undergoes acid catalyzed hydrolysis. Mesmer and Jolly [129] have studied the kinetics of the hydrolysis over the pH range 3.8-14 and have shown that the rate may be represented by the equation:

$$-d[BH_4^-]/dt = k_1[H^+][BH_4^-] + k_2[BH_4^-]$$
(2-27)

where $k_1 = 2.18 \times 10^{11}$ T exp(-4000/T) mole⁻ min⁻¹ and $k_2 = 1.72 \times 10^7$ T exp(-10380/T) min⁻¹. They measured the isotope effect in the hydrolysis reaction using heavy water and concluded that the most probable mechanism was one involving the initial formation of BH₅ in the rate-determining step, i.e.

$$BH_4^- + H^+ \xrightarrow{slow} BH_5 \longrightarrow BH_3 + H_2$$
 (2-28)

$$BH_3 + 3H_2O \xrightarrow{fast} H_3BO_3 + 3H_2$$
 (2-29)

Kreevoy [130] reported that borohydride undergoes acidic and non-acidic hydrolysis and proposed the following reaction mechanism:

$$H^{+} + BH_{4}^{-} \underset{k_{-H}}{\overset{k_{H}}{\Leftrightarrow}} H_{2}BH_{3}$$
(2-30)

$$H_2O + BH_4^{-} \underset{k_{-H_2O}}{\overset{k_{H_2O}}{\Leftrightarrow}} H_2BH_3 + OH^{-}$$
(2-31)

$$H_2BH_3 \xrightarrow{k_2} H_2 + BH_3 \tag{2-32}$$

$$BH_3 + 3H_2O \xrightarrow{\text{very fast}} 3H_2 + B(OH)_3 \tag{2-29A}$$

where $k_{\rm H} = 9.9 \times 10^5 \text{ M}^{-1} \text{sec}^{-1}$, $k_{-\rm H2O} = 2.2 \times 10^{-7} \text{ sec}^{-1}$ and $k_{-\rm H2O}/k_2 = 2.3$ at 25 $^{\circ}$ C.

Schlesinger first reported that some metal ions act as catalysts for the hydrolysis of borohydride ion [3]. Cobalt and nickel are particularly effective. The action of these compounds was attributed to the formation of the respective borides, Co₂B and Ni₂B, which served as the catalysts. The relative effect of various salts has been studied by Brown and Brown [131]. Their results are tabulated in Table 2-5.

Metals	Compounds	Compounds Time, min.	
Iron	FeCl ₂	eCl ₂ 38	
Cobalt	CoCl ₂	9	
Nickel	NiCl ₂	18	
Ruthenium	RuCl ₃	0.3	
Rhodium	RhCl ₃	0.3	
Palladium	PdCl ₂	180	
Osmium	OsO4	18.5	
Iridium	IrCl ₄	28	
Platinum	H ₂ PtCl ₆	1	

Table 2-5 Half-lives for hydrolysis of borohydride ion in the presence of transition ions [131]

Gomez-Lahoz [41] reported that borohydride undergoes cobalt-catalyzed and non-catalyzed hydrolysis. The following kinetic equation was proposed for the hydrolysis:

$$-\frac{d[BH_4^-]}{dt} = k_1[BH_4][H^+] + k_2[BH_4^-][H^+][Co_2B]$$
(2-33)

2.4.2 REDUCTION OF METAL IONS WITH BOROHYDRIDE

The metal reduction reaction with borohydride is sensitive to the reaction conditions. In neutral and acidic solutions (pH < 9.24), the reduction reaction of divalent metal ions is generally described by the following equation:

$$BH_{4}^{-} + 4M^{2+} + 3H_{2}O = H_{3}BO_{3} + 4M + 7H^{+}$$
(2-34)

In alkaline solutions (pH > 9.24), the reduction reaction is expressed by the equation:

$$BH_{4}^{-} + 4M^{2+} + 8OH^{-} = 4M + B(OH)_{4}^{-} + 4H_{2}O$$
(2-35)

What usually takes place is a combination of reduction and hydrolysis which depends on reaction conditions, concentration, mixing efficiency and the kinetics of the competing reactions. Therefore, the combined reaction at pH < 9.24 can be expressed as:

$$BH_4^{-} + 3H_2O + xM^{2+} = H_3BO_3 + xM + (4-x)H_2 + (2x-1)H^+$$
(2-36)

where x is less than 4.

For some noble metals such as silver and gold, the reduction products are pure metals and the reduction reaction can be expressed by the equations (2-34) and (2-36) [132-137].

The reaction with more electropositive metals such as Co, Fe, Ni, gives highly dispersed black products which contain metal and boron [7, 14, 15, 41, 42, 47, 135-138]. There is some adsorbed hydrogen on the products. They are usually called borides because their composition is similar to that of known borides. The reduction of cobalt with borohydride is generally expressed as:

$$4BH_{4}^{-} + 2Co^{2+} + 9H_{2}O = Co_{2}B + 3B(OH)_{3} + 12.5H_{2}$$
(2-37)

The formation of the borides correlates with the catalytic effects of Co, Ni and Fe. The other metals have little or no catalytic effect and the precipitates contain very little boron. The hydrolysis of borohydride is also catalyzed by Co, Ni, and Fe.

The stoichiometry of borohydride reduction depends on the experimental conditions, the electronegativity of the metal and catalysis on borohydride, pH, and the form of the metal salt in solution. Silver has a minimal catalytic effect on the hydrolysis of borohydride and the stoichiometry of silver (I) reduction with borohydride in different media (pH 3-10, and different water-soluble compounds) can be almost entirely expressed by equation (2-34). Silver metal is produced [134].

The reduction of arsenic, antimony, and bismuth compounds, such as trihalides or oxides of these elements, e.g. $(C_6H_5)_2AsCl_3$, $SbCl_4^-$, $K(SbO)(C_4H_4O_6)$, H_3SbO_3 , gives their hydrides, e.g. AsH_3 , As_2H_6 , SbH_3 , Sb_2H_6 , and BiH_3 , which partially react further with their compounds to produce elemental Sb, As [5, 123, 136, 139-141].

$$3BH_{4}^{-} + 4H_{3}SbO_{3} + 3H^{+} \rightarrow 4SbH_{3} + 3H_{3}BO_{3} + 3H_{2}O$$
 (2-38)

The reaction with zinc ions produces zinc borohydride which decomposes rapidly into hydride and borane. Zinc hydride is stable, but will hydrolyze. In acid solution, zinc enters the solution in the form of zinc ions and no precipitate is formed [136].

$$Zn^{2+} + 2BH_4^- \rightarrow Zn(BH_4)_2 \tag{2-39}$$

$$Zn(BH_4)_2 \rightarrow ZnH_2 + 2BH_3 \tag{2-40}$$

$$ZnH_2 + 2H^+ \rightarrow Zn^{2+} + 2H_2 \tag{2-41}$$

If the pH is higher than that required for the formation of zinc hydroxide, zinc is precipitated as zinc hydroxide.

Khain [132] reported that the reactions of borohydride ions with metal ions must be classified as reactions taking place via bridged active complexes, that is, by an inner-sphere mechanism. The first stage is the replacement of ligands by BH_4^- ion with a subsequent stage involving a spontaneous redox reaction or electron transfer of the intermediate complex. The role of the bridging ligand is played by the hydride ion, H⁻. The entire process can be represented as series of successive stages:

The formation of the intermediate compound,

$$M^{z+}(aq) + nBH_{4}^{-} \to M(BH_{4})_{n}^{(z-n)} + (aq)$$
(2-42)

The formation of a bridging bond,

$$M(BH_4)_n^{(z-n)} \to M^{z+} - (H^- - BH_3)_n \tag{2-43}$$

The transfer of a hydrogen atom and rupture of the bridging bond,

$$M^{z+} - (H^{-} - BH_3)_n \to MH_n^{z-n} + nBH_3$$
 (2-44)

The electron transfer and bond rupture,

$$MH_n^{z-n} \to M + (z-n)H^+ + (2n-z)/2H_2$$
 (2-45)

The catalytic decomposition of borane,

$$BH_3 \xrightarrow{M} B + 3/2H_2 \tag{2-46}$$

The hydrolysis of borane,

$$BH_2 + 3H_2O \rightarrow B(OH)_3 + 3H_2 \tag{2-47}$$

The increase in the alkalinity of the medium leads to an increase in the hydrolysis of the metal ions, and more stable hydroxocomplexes or inert polynuclear ions $M_q(OH)_p^{(qz-p)}$ are formed. In this case, initial $M(BH_4)_n^{z-n}$ formation is suppressed, and the reactions with BH_4^- become slower (M = Pt, Pd, Rh, Au) or practically stop (M = Pb, Sn, Cu).

2.4.3 AQUEOUS CHEMISTRY AND BOROHYDRIDE REDUCTION OF COBALT

2.4.3.1 AQUEOUS CHEMISTRY OF COBALT

The principal oxidation states of cobalt in aqueous solutions are +2 and +3. In the absence of ligands other than water, the solutions of cobalt (II) contain the pink, high-spin, hexa-aquo ion $[Co(H_2O)_6]^{2+}[142]$, which is the thermodynamically most stable state. Cobalt (III) is not thermodynamically stable in the absence of ligands. The redox reaction and potential for the Co(II)/Co couple are:

$$Co^{2+} + 2e = Co$$
 (2-48)

 $E_h = -0.277 - 0.0591 \log(a_{Co^{2+}})$ (2-48A)

Figure 2-7 shows the E_h -pH diagram for Co-H₂O system at $[Co^{2+}] = 0.5, 0.05, 0.005, 0.0005, 0.0005 M$ (assuming concentation = activity). From these diagrams, for $[Co^{2+}] = 0.5, 0.05, 0.005, 0.0005, and 0.00005 M$, the initial pH's for the precipitation of Co(OH)₂ are 6.6, 7.1, 7.6, 8.1, and 8.6 respectively. Therefore the cobalt reduction reaction should be carried out at a pH below that at which Co(OH)₂ will precipitate. Otherwise cobalt metal will not be produced. Furthermore, at pH's below 4.82, 5.32, 5.82, 6.32, 6.82 respectively for $[Co^{2+}] = 0.5, 0.05, 0.005$



Figure 2-7, E_h - pH diagram for the Co-H₂O system at Co activities of 0.5, 0.05, 0.005, 0.0005, and 0.00005 and 25 0 C [127, 128].

Cobalt ions in aqueous solutions hydrolyze and form hydroxocomplexes [143-145]. As in the case of the hydrolysis equilibrium reactions for other metallic ions, the following reactions have been assumed to determine the equilibrium constants for the first ionization step of the hydrolysis of cobaltous ions:

$$Co(aq)^{2+} + H_2O \iff Co(OH)^+(aq) + H^+(aq)$$

$$(2-49)$$

The equilibrium constant $K_{a1} = 1.58 \times 10^{-10} [140]$. $Co(OH)^+ + H_2O \iff Co(OH)_2(aq) + H^+(aq)$ (2-50)

The equilibrium constant $K_{a2} = 1.26 \times 10^{-9}$ [143].

At higher concentrations, cobalt ions polymerize and form $Co_2(OH)_2^{2+}$ (pk = 9.44) and $Co_6(OH)_6^{6+}$ (pk_A = 42.55) [146].

For cobalt sulfate solution, there exist the following equilibrium reactions (147-149];

$$Co^{2+} + SO_4^{2-} \Leftrightarrow CoSO_4(aq)$$
 log K =2.69 at 25 °C [149] (2-51)

$$H^+ + SO_4^{2-} \iff HSO_4^{-}$$
 log K = 2.0 at 25 °C [148] (2-52)

2.4.3.2 BOROHYDRIDE REDUCTION OF COBALT ION

Borohydride reduction of cobalt ion has been used to prepare magnetic materials and catalysts, and remove cobalt from waste water and therefore the reaction has been studied. It is desirable to establish the mechanism of the reductions in order to determine the best conditions for the various applications. However relatively little systematic work has been done in this area. In the case of metal boride formation, such studies would be very difficult because of the extreme

rapidity with which the boride is generated. The following several reaction mechanisms have been proposed to explain the reaction product.

1. Mochalov first proposed a cobalt reduction mechanism according to his results [135].

The composition of the products obtained by the reaction of cobalt (II) with borohydride was expressed as Co_2B with some adsorbed hydrogen also present. However, the product behaved like a mixture of cobalt metal and elemental boron. Unlike the authentic boride, the products had non-stoichiometric compositions which varied with the experimental conditions. At 0 $^{\circ}C$, 25 $^{\circ}C$ and 75 $^{\circ}C$, the ratios of Co to B were 1.84, 2.05, and 2.48 respectively. Authentic Co_2B is kinetically inert and dissolves slowly in HCl solution (1:1) with the evolution of hydrogen. However, the product of the borohydride reduction of cobalt ions dissolved readily in HCl solution (1:1) and the amount of evolved hydrogen corresponded to the contents of free metal and boron. Even boiling water dissolved the product and the same stoichiometric hydrogen was obtained.

The precipitate was readily oxidized in air and was pyrophoric. If the product was exposed to water and air, it gradually changed into hydroxide and boric acid. The product was able to cement Pb, Cu, Ag, and Pd from solutions of their salts. It readily reduced MnO_3^- , NO_3^- , I, Ti⁴⁺, Fe³⁺ and was used in analytical chemistry.

When covered with water or other liquid, the precipitate was ground with mercury to produce an amalgam containing 8-10 % Co. The mercury was distilled and free cobalt metal precipitated.

X-ray investigations of the products produced under many conditions showed that they were amorphous and did not show any spectral features of authentic boride. However, when the product was boiled in water, the clear alpha and beta cobalt phases were apparent from the X-ray diffraction pattern.

Mochalov [131] concluded that the precipitate produced by the reduction of cobalt (II) with borohydride was a mixture of highly dispersed cobalt metals and boron. Except for the similarity in composition to real cobalt boride, the product had different properties and might be considered to be a pseudo-boride.

The proposed mechanism involves the initial formation of cobalt borohydride. Cobalt (II) strongly polarizes the borohydride, resulting in cobalt hydride and borane. The produced cobalt hydride is unstable and decomposes into cobalt metal and hydrogen. Catalysis by water may be involved. Borane (BH₃) can undergo two reactions: hydrolysis and decomposition into boron and hydrogen with the mixing metal cobalt to form the pseudo-boride due to the catalysis of highly dispersed metals. Dependent on the relative rates of above two competing reactions related to BH₃, the composition of the pseudo-boride should be variable and lie between Co_2B and Co. The reaction could be affected by temperature and solvents (water or ether).

At room temperature, the compositions of the pseudo-cobalt borides approach that of Co_2B . The reaction mechanism is expressed as:

$$2Co^{2+} + 4BH_4^- \rightarrow 2Co(BH_4)_2$$
 (2-53)

 $2Co(BH_4)_2 \rightarrow 2CoH_2 + 4BH_3 \tag{2-54}$

 $2CoH_2 \rightarrow 2Co + 2H_2 \tag{2-55}$

 $BH_3 \xrightarrow{catalyzed} B + 1.5H_2$ (2-56)

 $3BH_3 + 9H_2O \rightarrow 3B(OH)_3 + 9H_2$ (2-57)

$$2Co^{2+} + 4BH_4^- + 9H_2O = 2Co \cdot B + 3B(OH)_3 + 12.5H_2$$

2. Glavee *et al.* [14, 15] reported that the reduction of $CoCl_2(aq)$ with sodium borohydride yields ultrafine Co_2B as the primary product if the two reagents are rapidly mixed and the product is handled under argon. The procedure must be followed rigorously. Concentrations, BH_4 -M ion ratio, pH, method of mixing, and rate of mixing can determine the composition particle size and reactivity of the product. A broad main peak of Co_2B appeared on the X-ray diffraction pattern of the fresh precipitate suggesting amorphous Co_2B . After heat treatment at 500 ^{0}C under argon, the precipitate was identified as Co_2B by X-ray diffraction. The overall reaction can be expressed by equation (2-37). The following reaction mechanism was proposed:

$$Co(H_2O)_6^{2+} \Leftrightarrow [(H_2O)_5CoOH]^+ + H^+$$

$$(2-58)$$

$$[(H_2O)_5CoOH]^+ + H^+ + BH_4^- \rightarrow H_2 + [(H_2O)_5Co - OH - BH_3]^+$$
(2-59)

$$[(H_2O)_5Co - OH - BH_3]^+ + Co(H_2O)_6^{2+} \rightarrow H_2 + [(H_2O)_5Co - OH - BH_2 - OH - Co(H_2O)_5]^{3+}$$
(2-60)

$$3BH_{4}^{-} + [(H_{2}O)_{5}Co - OH - BH_{3} - OH - Co(H_{2}O)_{5}]^{3+} \rightarrow (H_{2}O)_{5}Co - OH - BH_{2} - OH - Co(H_{2}O)_{5} + 3BH_{3} + 1.5H_{2}$$
(2-61)

$$3BH_3 + 9H_2O \xrightarrow{rapid} 3B(OH)_3 + 9H_2$$
 (2-62)

$$[(H_2O)_5 - Co - OH - BH_2 - OH - Co(H_2O)_5] \rightarrow Co_2B + 12H_2O$$
(2-63)

$$2Co(H_2O)_6^{2+} + 4BH_4^- + 9H_2O \rightarrow Co_2B + 12.5H_2 + 3B(OH)_3$$

The equilibrium between $Co(H_2O)_6$ and $[Co(H_2O)_5OH]^{2+}$ is a well established example of the reason why aqueous solutions of transition metal ions are acidic. In the second step, H⁺ and BH₄⁻ may react with the $[(H_2O)_5CoOH]^+$ species. This hydrated cobalt-borane adduct would then react with another $[Co(H_2O)_6]^{2+}$ species. The resulting species ($[(H_2O)_5Co-OH-BH_2-OH Co(H_2O)_5]^{3+}$) is triply charged. Reduction could occur by reaction with 3 more equivalents of BH₄⁻ with concomitant formation of more H₂ (Equation 2-61). Finally, in the sixth step, the adduct could yield Co₂B which precipitates. The sum of all these steps yields the overall equation (2-37) with the experimentally observed stoichiometry based on Co²⁺ and BH₄⁻, and the formation of Co₂B. However, the 12.5 moles of H₂ predicted is a lightly lower than the values observed. Borohydride hydrolysis was invoked to explain this. In fact the hydrogen adsorbed on the precipitate affected the collection of hydrogen gas. The above reaction mechanism is really hard to realize because the intermediate products $[(H_2O)_5Co-OH-BH_2-OH-Co(H_2O)_5]^{3+}$ and $(H_2O)_5-Co-OH-BH_2-OH-Co(H_2O)_5$ are almost impossible to form and the reaction step 2-61 would require more than one step.

When the reduction was carried out in a nonaqueous medium (diglyme), the primary products were cobalt metal, H_2 and B_2H_6 [150]. In the presence of the catalytic cobalt particles, some of B_2H_6 was catalytically decomposed into boron and H_2 and the precipitate contained less boron than that formed in aqueous media. This suggests that water also plays an important role in the formation of Co_2B .

3. Gomez-Lahoz *et al* [41, 42] reported that the reduction of cobalt ions with borohydride released H^+ , the molar ratio of Co to B in the precipitate was 2, and borohydride underwent hydrolysis. Therefore the following reactions were proposed:

$$2Co^{2+} + BH_{4-} \rightarrow Co_{2}B_{+1}/2H_{2} + 3H^{+}$$
 (2-64)

$$3BH_4^- + 9H_2O + 3H^+ \rightarrow 3H_3BO_3 + 10H_2$$
 (2-65)

$$4BH_4^- + 2Co^{2+} + 9H_2O \rightarrow 3H_3BO_3 + Co_2B + 12.5H_2$$

The sodium hydroxide in stabilized borohydride solution was found to be the main factor in efficiency improvement, due to the inhibition of the hydrolysis of borohydride.

4. Dragieva *et al* [151, 152] reported that the amount of boron incorporated in the powders depended on the concentration of sodium borohydride in the reducing solution. It was impossible to establish the phase composition of the amorphous powders using electron and X-ray diffraction. The crystallization of powders was carried out at 650 K for one hour under

vacuum (10^{-6} Torr). The cobalt powders contained about 25 at. % B or had an approximate composition Co₃B. Therefore the following reaction was proposed for the reduction of metal ions:

$$2Me^{2+} + 2BH_4^- + 3H_2O \rightarrow 2Me \cdots BH_3 \langle \xrightarrow{Me_x B + 5/2H_2} Me_{+1_3BO_3 + 3H_2} \rangle$$
(2-66)

The addition of complex-forming agents usually decreases the amount of boron incorporated in the precipitate. The role of the counter ions of the initial cobalt salt was investigated and the boron contents of powder reduced from $CoSO_4$ (natural pH 6.7), $CoCl_2$ (natural pH 5.4) and $Co(NO_3)_2$ (natural pH 6.7) were 6.07, 5.57, 5.25 wt.% respectively. With increasing pH of the initial salt solutions, the boron content of the powders increased considerably. The content of hydrogen in the precipitate decreased with increasing initial pH (5.8-7.8) from 0.538 to 0.268 wt. %.

5. Saida et al [13] observed no distinct X-ray diffraction peak corresponding to a crystalline phase. A halo peak appeared in the vicinity of 45 degrees for all the samples prepared in the molar ratios (2-10) of KBH₄ to $\text{Co}^{2+}(\text{Ni}^{2+} \text{ and Fe}^{2+})$, indicating that a mostly single amorphous phase was formed for the Co-B or Ni-B alloys, and the structure of the two alloy systems was independent of the molar ratios of KBH₄ to Co^{2+} . The temperature did not have an appreciable influence on the amorphous structure which implied that there was no significant change in the reaction mechanism with temperature. Considering the charge and mass balance of the reaction and high B content of the precipitates, the following principal reactions were thought to be dominant:

$$4Co^{2+} + BH_4^- + 8OH^- \to 4Co + BO_2^- + 6H_2O$$
(2-67)

$$4Co^{2+} + 2BH_4^- + 6OH^- \to 2Co_2B + 6H_2O + H_2$$
(2-68)

The actual generation of hydrogen seems to support the appropriateness of the reaction (2-68). Reaction (2-67) indicates that the existence of BO_2^- in the residual aqueous solution is expected. The hydrogen adsorbed on the precipitate was not measured and so it is not reasonable to use the amount of evolved hydrogen gas to support the reaction mechanism.

6. Jianyi *et al* [12] studied the reductions of $CoCl_2$, NiCl₂ and FeSO₄ in aqueous solution with potassium borohydride solution (pH 12), and suggested three independent reactions:

$$BH_4^- + 2H_2O = BO_2^- + 4H_2 \tag{2-69}$$

$$BH_4^- + 2M^{2+} + 2H_2O = 2M + BO_2^- + 4H^+ + 2H_2$$
(2-70)

$$BH_4^- + H_2O = B + OH^- + 2.5H_2 \tag{2-71}$$

The relative extent of these reactions depends on the metal ions and the reaction conditions, and therefore there is no single reaction equation that can be used to express the overall reactions. Taking reaction (2-69) as a by-product reaction, the ratio of reaction (2-70) to reaction (2-71) is usually 1-1.5. The corresponding reduction reactions would be:

$$2BH_{4}^{-} + 2M^{2+} + 2H_{2}O = M_{2}B + HBO_{2} + 2H^{+} + 4.5H_{2}$$
(2-72)

$$5BH_{4}^{-} + 6M^{2+} + 6H_{2}O = 2M_{3}B + 3HBO_{2} + 7H^{+} + 11H_{2}$$
(2-73)

The overall reaction sequence can maintain the pH of the reaction mixtures at 3-4.5 by themselves because reactions (2-70) and (2-71) produce H^+ and OH^- ions, respectively which together form water. The reactions promote each other. The mole ratio of BH_4^- to metal ions for equivalent reactions was found to be 1.8 to 1.9.

Both the addition rate and concentration of BH_4^- solution affected the boron content in Fe-B and Ni-B but did not affect the boron content in Co-B. This effect is due to the different orders in BH_4^- of reactions (2-70) and (2-71) for the preparation of Fe-B and Ni-B.

Except for the thin layer of oxides of metals and boron on the surfaces (formed by passivation), the particles consisted of amorphous structures with average particle sizes from 40 to 60 nm.

7. Awadalla *et al* [47] studied the reaction of cobalt with sodium borohydride and found that the product of cobalt reduction was amorphous cobalt boride. The stoichiometry of cobalt reduction was expressed by Equation (2-37) and some ions such as Zn^{2+} and Cl^{-} had a negative effect on the reduction of cobalt which is described by the data listed in Table 2-6.

From Table 2-6, it can be seen that all impurities have negative effects on cobalt reduction. The complexing agents form complexes with cobalt and make cobalt difficult to be reduced and hence decrease the cobalt reduction efficiency. Ca^{2+} , Na^+ , Mg^{2+} , NH_4^+ and Zn^{2+} possibly form the corresponding borohydride and interfere with the combination of cobalt ions and borohydride ions. Zinc ions have a strong negative effect of cobalt reduction and 100 ppm zinc ions decreased the reduction efficiency from 97 % to 32 %. The zinc ions have a strong negativ% effect on the iron reduction, no effect on copper reduction [47] and a positive effect on gold (I) reduction [25]. The presence of 10 mg/l zinc ion in thiourea solution containing 10 mg/l Au decreased sodium borohydride consumption by 83 %. The possible cause is that zinc ions formed zinc borohydride which decomposes into zinc hydride and hydrogen. Zinc hydride hydrolyzes rapidly and so cobalt reduction efficiency is decreased, i.e., zinc ions competed with cobalt ions for borohydride ions.

The higher than the stoichiometric requirement of sodium borohydride was not beneficial because the excess of the reductant was consumed by hydrolysis. The reduction reaction was very fast and was completed in less than 3 minutes.

No.	Materials added	Amount added	Reduction Efficiency, %	
1	NaOH	0.0424 g/l	96	
2	CaO	0.05g/l	72	
3	Mg(OH) ₂	0.05 g/l	75	
4	NH4OH	0.15 g/l	91	
5	Na ₂ CO ₃	0.0848 g/l	82	
. 6	Cl ⁻	100 ppm	87	
		200 ppm	87	
		300ppm	86	
7	Zn ²⁺	100 ppm	32	
8	Sodium acetate	0.1391 g/l	70	
9	9 Sodium citrate 0.4990 g/l		0.0	
10	Sodium tartrate	0.1952 g/l	66.7	
11	EDTA	0.3158 g/l	0.0	
12	No impurities added	-	97	

Table 2-6 Effect of additives on the reduction of cobalt [47]. Initial Co concentration=100 PPM, Initial pH =6, the mol ratio of NaBH₄ to Co^{2+} was 2, pH was not controlled. Sodium borohydride was added as a solid powder.

* Nos. 1-5 were added to adjust pH 2.3 to pH 6.0

** For No. 7, 89% of zinc was precipitated in the form of zinc hydroxide and no zinc metal was precipitated.

*** For Nos. 7-11, the initial pH was not given (pH is the range of 5.0-7.5)

8. Polyakov *et al* [114, 115] reported that the stoichiometry of cobalt reduction can be expressed by Equation (2-34) and at a consumption of 110 % of the stoichiometric requirement, cobalt could be reduced from 20 ppm to 0.06 ppm [114] or 0.005 ppm [115] from zinc sulfate solution (120 g/L Zn) in the presence of trienthanolamine at pH 3. The reduction efficiency increased with increasing reaction time and decreased with increasing temperature and decreasing pH.

2.4.3.3 KINETICS OF COBALT REDUCTION WITH BOROHYDRIDE

There are few reports on the kinetics of cobalt reduction with borohydride because the reduction of cobalt ions from aqueous solution in the absence of some ligands is too fast to follow. In addition the reaction is very complicated. Thus far it appears that only Gomez-Lahoz [41] reported on the kinetics of cobalt reduction with borohydride. He found an autocatalytic effect on cobalt reduction and gave the following kinetic expression:

$$-\frac{d[Co^{2+}]}{dt} = k_1[BH_4][Co^{2+}] + k_2[BH_4^{-}][Co^{2+}][Co_2B]$$
(2-74)

By combining equations (2-33) and (2-74) and using a numerical method, Gomez-Lahoz obtained k_1 and k_2 . The reaction rate was also affected by pH. However, the pH changed greatly and so did the form of the cobalt ions (e.g. $Co(H_2O)^{2+}$, $[Co(H_2O)_5OH]^+$, $Co(OH)_2(aq)$.). The reaction rate was affected becoming lower with increasing pH.

2.5 SUMMARY

Since sodium borohydride has unique redox features (a low reducing equivalent weight of 4.75 g/ mole e⁻, a high reducing power and utility in different media such as water and organic solvents, and acidic, neutral and alkaline conditions), it has advantages over other reducing agents. In addition since it is the cheapest of all the metal borohydrides, it has been widely used for various purposes. Now sodium borohydride reduction of metal ions is the basis of several commercial processes such as the preparation of selective catalysts and magnetic materials, the recovery of precious metals, the removal and recovery of heavy metals from waste water, and electroless plating.

With respect to cobalt, sodium borohydride is widely used to prepare cobalt-boron catalysts and magnetic materials and to remove cobalt from waste water. Cobalt removal with

sodium borohydride has been selected as the best available technology for the treatment of cobalt-bearing waste water.

The efficient removal of cobalt from zinc electrolyte continues to be a problem in the purification of the electrolyte and so zinc production plants have been looking for a better method to replace the present processes. If sodium borohydride could be used to remove cobalt from zinc sulphate solution, the purification process would have many advantages over the present technology, for example, high efficiency, the low reaction temperature, the short reaction time. Poyakov *et al* reported [114, 115] that sodium borohydride can reduce cobalt in zinc sulphate solution to 0.01 ppm in the presence of triethanolamine. However, Cominco's staff [116] has reported that cobalt can not be reduced from zinc sulphate solution with sodium borohydride. Awadalla [47] also found that zinc ions have a strong negative effect on cobalt reduction. Hence there are conflicting claims.

The reaction of cobalt reduction with borohydride is very sensitive to the reaction conditions such as pH, concentration, solution composition, the method of mixing reactants and the treatment of the precipitate. Therefore various authors have obtained different reaction stoichiometries and have proposed different reactions. Because of the extreme rapidity of the reaction and other complications, relatively little systematic work has been done in this area. Most authors reported that the stoichiometry of cobalt reduction with sodium borohydride is dependent on the reaction conditions and that there is no definite stoichiometry. Usually the reduction of one mole of cobalt needs about two moles of sodium borohydride and only Polyakov [114. 115] reported that 1.1 moles of sodium borohydride can reduce 4 moles of cobalt ions.

A more thorough study of cobalt reduction by borohydride is needed. Such a study could lead to a better understanding of the stoichiometry, and if possible, to increasing the reduction efficiency. Finally, the possibilities of using sodium borohydride for cobalt removal should be studied.

3. EXPERIMENTAL

3.1 EXPERIMENTAL OBJECTIVES AND METHODS

The main objective of this research was to investigate the stoichiometry of the reduction of cobalt ions with sodium borohydride and the effects of the addition of hydroxide, pH, temperature and the rate of sodium borohydride addition on the stoichiometry. Another key objective was to study the feasibility of removing cobalt from zinc sulphate electrolyte with sodium borohydride. Sodium borohydride solutions with different concentrations of sodium hydroxide were used as reducing agents in order to study the effect of the mol ratio of NaBH₄ to NaOH on cobalt reduction efficiency. A solution of sodium borohydride was added in order to maintain the addition at a uniform and continuous rate. To improve the reproducibility, a batch reactor was used. The pH was controlled manually by adding dilute sulphuric acid or sodium hydroxide solutions because the constituents of buffer solutions might affect the cobalt reduction with borohydride. Cobalt sulphate solution was used for all experiments because the ultimate intended application was cobalt removal from zinc sulphate solution with borohydride.

3.2 EQUIPMENT

A two-liter Pyrex glass reactor was immersed in a water bath where the temperature was controlled to within ± 0.2 ⁰C. The water in the bath was heated with heaters connected to an Omega CN 900A temperature controller, and cooled with cold water. A magnetic stirrer bar was used for agitation. An acrylic lid atop the reactor was used to minimize air in the reactor and evaporative loss. The solution was sparged with highly pure nitrogen to eliminate oxygen and agitated with a plastic-coated impeller connected to a stirrer motor (Caframo Model RZR1). The agitation (rotation) rate was checked with a phototachometer (Cole-Parmer 08210). A Corning pH probe and a Bach-Simpson Ltd. PHM82 standard pH meter were used to measure pH which was recorded by computer. The pH was controlled manually by adding 0.05 M sulphuric acid or sodium hydroxide. A Fisher platinum indicating electrode for redox titration and a saturated calomel reference electrode and Bach-Simpson Ltd. PHM82 Standard pH meter were also used to measure the solution redox potential which was recorded by a computer. The reducing solution

was pumped into the reactor (Cole-Parmer pump model 7519-20A equipped with a digital variable-speed console drive). Figure 3-1 is a schematic diagram of the experimental setup. The syringes and Cameo II 25 mm filters (DDN-02T25-50, 0.22 µ m pore size) were used to take the solution samples. The solutions were analyzed for cobalt by a colorimetric method using Nitroso-R-salt with a Bausch & Lomb Spectronic 20 spectrophotometer, and for nickel with a Perkin-Elmer 306 Atomic Absorption Spectrophotometer. The precipitates were obtained by filtering the reaction mixtures through a Millipore GS 0.22 µm membrane filter held on a Millipore Funnel/Support assembly. The precipitates were washed with deoxygenated water under a nitrogen atmosphere and then put under acetone. The precipitates were dried in a desiccator under vacuum at 0.001 mm Hg with a type JR-150 rotary vacuum pump produced by Japan Electron Optics, Tokyo Laboratory Co.. The precipitates were analyzed by the International Plasma Lab Ltd. for Co and B. The heat-treatment of the precipitate was carried out in a tube furnace at 10⁻⁶ Torr. The following equipment was used to obtain high vacuum: Balzers Type D U O 56 rotary pump as fore pump, Edwards high vacuum diffusion pump, and a Balzers KV 313 vacuummeter was used for measuring the vacuum. Fig. 3-2 is a schematic diagram of the precipitate heat-treatment experimental setup.

3.3 MATERIALS

(1) Fisher reagent grade sodium borohydride and sodium hydroxide were used to prepare the required sodium borohydride solutions.

(2) Fisher reagent grade zinc sulfate, cobalt sulfate, nickel sulfate, copper sulfate, lead chloride, cadmium sulfate, antimony tartrate, sodium arsenite, and deionized water were used to prepare the various solutions.

(3) Reagent grade triethanolamine and polyacrylamide were used as surface active agents. Polyacrylamide was used to prepare 1% polyacrylamide water solution.

(4) Reagent grade anhydrous zinc chloride, sodium borohydride and anhydrous tetrahydrofuran were used to prepare zinc borohydride.

(5) Highly pure nitrogen was used as an inert gas to remove dissolved oxygen.



Figure 3-1 Schematic diagram of the experimental setup



Figure 3-2 Schematic diagram of sample heat treatment apparatus

3.4 EXPERIMENTAL PROCEDURE

3.4.1 PROCEDURE FOR THE REDUCTION OF COBALT

(1) A one-liter solution was prepared according to the required compositions.

(2) The solution was added to the reactor.

(3) The solution was sparged with nitrogen gas for over 30 minutes to eliminate dissolved oxygen and heated until the temperature was within the required range.

(4)The surfactant solution was added to the reactor about 3 minutes before the sodium borohydride was added.

(5) $0.05 \text{ M H}_2\text{SO}_4$ or NaOH solution was used to adjust pH to the required value.

(6) The sodium borohydride solution was continuously and uniformly added to the reactor with a pump within the required time. If pH had to be controlled, sulphuric acid and sodium hydroxide solution were added manually to the reactor. For the kinetics of cobalt reduction, the sodium borohydride was added to the reactor with a syringe within one second.

(7) The solution samples were taken using syringes and syringe disk filters. The precipitates were taken by filtering the solution through a Millipore membrane filter under vacuum and were washed with deoxygenated water under a nitrogen atmosphere and then submerged under acetone.

3.4.2 HEAT TREATMENT OF THE PRECIPITATES

(1) The precipitates were dried in a vacuum desiccator in which the pressure was maintained at 0.001 mm Hg for one day.

(2) The dried precipitates were put into a boat which was pushed into the tube furnace. The furnace travelled along the quartz tube and the movable cooling system was positioned where the samples were so that the samples would not be heated.

(3) When the vacuum reached 10^{-6} Torr, the furnace was turned on.

(4) Due to the rise of the temperature in the tube, the gas was released and the pressure rose slightly. When the vacuum reached 10^{-6} Torr again at the required temperature, the heating part of the furnace was moved into position over the sample, and the sample was heated.

(5) After two hours, the furnace was moved so that the sample was no longer in the zone of the furnace. The movable cooling system was also put in place to cool the sample and so the sample temperature was lowered rapidly.

(6) Because the sample is readily pyrophoric, the furnace was cooled for two days and argon was passed through the tube holding the sample. Finally the cover was removed and the sample was withdrawn.

3.4.3 X-RAY DIFFRACTION OF THE PRECIPITATES

(1) The heat treated precipitates were ground to fine powder with a mortar and pestle.

(2) The samples were put onto a glass plate and dispersed uniformly with acetone.

(3) The sample was put into the diffraction chamber. The radiation wave length was 1.504 Å (CuK_{α}) .

3.4.4 SCANNING ELECTRON MICROSCOPIC ANALYSIS OF THE PRECIPITATES

(1) A fresh powder sample was directly put into acetone. Heat-treated samples were first ground with a mortar and pestle and then put in into acetone.

(2) The sample was placed onto a conductive plate and put into the chamber of the scanning electron microscope for analysis.

(3) The voltage of the electron beam was 20 kV.

3.4.5 TRANSMISSION ELECTRON MICROSCOPIC ANALYSIS OF THE PRECIPITATES

(1) Fresh powder samples were put directly into acetone. Heat-treated samples were first ground with a mortar and pestle and then put into acetone.

(2) The beaker holding acetone solution was put in a ultrasonic bath to separate particles.

(3) The sample was put onto a thin, electron transported, carbon support film.

(4) The film was put into the chamber of the TEM and examined at 200 kv.

4. RESULTS AND DISCUSSION

4.1 STOICHIOMETRY OF COBALT REDUCTION WITH SODIUM BOROHYDRIDE

The cobalt reduction with borohydride was carried out by adding the reducing solution continuously and at a uniform rate to the reactor. Therefore the amount of sodium borohydride added was proportional to the addition time. A 0.25 M NaBH₄ + 0.05 M NaOH solution was used to reduce cobalt. The cobalt reduction fraction, pH and potential of the reaction solution vs. time are shown in Figure 4-1. The total addition time was 10 minutes. Figure 4-2 shows similar data for a 5-minute addition time. The reaction is very fast and almost immediate and so the addition time can represent the reaction time.

From Figures 4-1 and 4-2, it can be seen that as the sodium borohydride was added to the mixture, the recorded pH values of the solution in the first several seconds were higher than the initial pH. This is simply due to the basic sodium borohydride solution increasing the concentration of OH⁻. The pH then went down because of the reaction of cobalt with borohydride which released hydrogen ions. After some time the pH stabilized. This could be accounted for by a balance between the release of hydrogen ions and borohydride hydrolysis which consumes hydrogen ions. After most of the cobalt was reduced, the pH went up rapidly because the main reaction became the hydrolysis of borohydride. The faster the addition rate, the greater the pH dropped (from 7 to 6.7 for a 10-minute addition time and from 7 to 6.2 for 5 minutes). The faster addition of sodium borohydride released more hydrogen ions per unit time. Several seconds after the beginning of the addition, the potential went down and then stabilized. As the pH went up, the potential went down reflecting the dependence of potential on the solution pH. The measured potential at pH 6.4 was about -0.63 V SCE. This potential is much higher than the redox potential of H₃BO₃/BH₄ (-1.05 V SCE at [BH₄] =[H₃BO₃]) and approximates the redox potential of H^+/H_2 (-0.624 V SCE). The concentration of borohydride is very low and so the measured solution potential is mainly dependent on the redox potential of H^+/H_2 couple. FigureS 4-3 and 4-4 are the same type of diagram for the cobalt reduction at $pH_{initial}=5.5$ and 8.0.

Considering that the reaction released hydrogen ions, reducing solutions with different sodium hydroxide concentrations (0, 0.05, 0.125 and 0.25 M) were used to reduce cobalt ions. For each case, different initial pH conditions were also applied (pH 5.5, 7.0, 8.0). From Figure 4-

50

1, and Figures 4-3 to 4-13, the pH of the solution increased with increasing concentration of sodium hydroxide in the reducing solution. Also with increasing concentration of sodium borohydride, the reduction efficiency increased greatly from 2.1-2.4 moles of sodium borohydride needed to reduce 1 mole of cobalt ion to 1.0 mole (see Table 4-1).

Initial pH	0.25 M NaBH ₄	0.25 M NaBH ₄ +	0.25 M NaBH ₄ +	0.25 M NaBH ₄ +
		0.05 M NaOH	0.125 M NaOH	0.25 M NaOH
5.5	2.4	1.95	1.6	1.1
7.0	2.2	1.85	1.5	1
8.0	2.1	1.8	1.5	~ 1

Table 4-1 Moles of sodium borohydride needed to reduce one mole of cobalt ions for different basic solutions and different initial pH values.

NaOH in the reducing solution neutralized the hydrogen ions released by the cobalt reduction reaction. This suppressed the borohydride hydrolysis and increased the reduction efficiency. The initial pH also has some effect on the cobalt reduction efficiency. A low initial pH leads to lower cobalt reduction efficiency probably because of the hydrolysis of more borohydride. However, in the pH range of 5.5-8, the initial pH has less effect on the cobalt reduction efficiency than the hydroxide concentration of the reducing solution. The higher the concentration of sodium hydroxide, the less the effect of initial pH. For 0.25 M NaBH₄ solution (no added NaOH), 2.4, 2.2, and 2.1 moles of sodium borohydride were needed to reduce 1 mole of cobalt ions respectively at initial pH's of 5.5, 7.0, 8.0 respectively. However, for 0.25 M NaOH+0.25 M NaBH₄ solution, the reduction efficiencies are almost the same. Apparently because the rate of cobalt reduction is much higher than that for the hydrolysis at pH's greater than 7, pH has a little effect on the reduction efficiency for the same composition of reducing solution. The NaOH in the reducing solution played the main role in increasing the reduction efficiency and decreasing borohydride hydrolysis. The hydrogen ions released by the cobalt reduction act to promote the hydrolysis. The hydrogen ions released were consumed by NaOH (neutralization) or NaBH₄ (hydrolysis). The more basic the reducing solution, the less the hydrolysis of NaBH₄. Gozm-Lahoz [41] reported that sodium hydroxide in the sodium borohydride solution can improve the reduction efficiency.

At an initial pH of 5.5 (see Figures 4-3, 4-5, 4-8 and 4-11), as sodium borohydride solution was added to the reaction solution, the pH first rose rapidly, which suggests that sodium borohydride hydrolysis was dominant, then stabilized and finally rose rapidly. At an initial pH of 7.0 (see Figure 4-1, 4-6, 4-9 and 4-12), the pH went up a little to start, then dropped, stabilized and finally rose rapidly for the reducing solutions with 0.0, 0.05, 0.125 M NaOH. But for the reducing solution with 0.25 M NaOH, pH first went up a little, stabilized, and then finally went up rapidly. At an initial pH of 8 (see Figures 4-4, Fig. 4-7, Fig. 4-10 and Fig.4-13), the pH first went up a little, decreased, then stabilized and finally went up rapidly. However the reducing solution with 0.25 M NaOH, the pH went down by less than 0.20, which might be caused by the buffering effect of the boric acid product. It is possible that the reaction of one borohydride and one cobalt ion produced one hydrogen ion. An attempt was made to use more basic reducing solutions (with 0.5 M and 0.75 M NaOH) to reduce cobalt ions, but it was found that the pH increased rapidly and some blue cobalt hydroxide was precipitated. Apparently if the reaction of cobalt reduction released 2 or more hydrogen ions and a reducing solution with a mole ratio of NaOH to NaBH₄ =2 was added to the reaction solution, the pH would not go up so fast and cobalt hydroxide would not precipitate.



Figure 4-1 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4-2 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4-3 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added NaBH₄.



Figure 4-4 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.

Time, min.

(b)

6

4

7.0

Ò

ż

-0.8

10

8



Figure 4-5 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4- 6 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4- 7 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4-8 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.




Figure 4-9 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4- 10 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4- 11 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4- 12 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.





Figure 4- 13 (a) Cobalt reduction fraction, (b) pH and potential vs. time, $[Co^{2+}]_{initial} = 30 \text{ mg/L}$. Note that time is directly proportional to the amount of added borohydride.

The industrial zinc electrolyte pH is usually controlled below 4.5. Therefore one attempt was tried to reduce cobalt ions with sodium borohydride at pH 4 in the absence of zinc ions in solution. From Figure 4-14, after the mol ratio of NaBH₄ to Co²⁺ exceeded 4, the reduction fraction was not increased. This means that all the borohydride after this point was consumed in the hydrolysis. The rate of Co (II) reduction became equal to the rate of redissolution and cobalt played the role of catalyzing the hydrolysis. The redox potentials $E(H^+/H_2) =- 0.244$ V SHE at pH 4 and $E(Co^{2+}/Co)=-0.277$ V SHE for $a_{Co(II)} = 1$ and -0.377 V SHE for $a_{Co(II)} = 0.0005$, indicate that the H⁺ should first be reduced and then cobalt ions. However, cobalt ions react with borohydride ions much faster than do hydrogen ions and this makes it possible for cobalt ions to be reduced by borohydride.

The stoichiometry of cobalt reduction is dependent on the reaction conditions, pH and basicity of the reducing solutions.



Figure 4-14 The reduction fraction vs. time and the mol ratio of NaBH4 to Co^{2+} . The reducing solution: 0.25 M NaBH₄ + 0.25 M NaOH. pH was manually controlled by adding dilute sulphuric acid solution.

4.2 THE EFFECT OF pH ON COBALT REDUCTION EFFICIENCY WITH BOROHYDRIDE

pH has a great effect on cobalt reduction efficiency below pH 5. From Figure 4-15, the cobalt reduction efficiency is seen to increase with increasing pH. At pH 2, cobalt reduction efficiency is almost zero and at pH 6, the reduction efficiency is 96 %. At a lower pH, from equation (2-27), the borohydride hydrolysis (reaction (2-26)) becomes faster and in accordance with the Eh-pH diagram for the cobalt-water system (Figure 2-6), cobalt is oxidized by H^+ and redissoves.

$$Co + 2H^+ \to Co^{2+} + H_2 \tag{4-1}$$

Therefore the reduction efficiency is low under these conditions.



Figure 4-15 Effect of pH on cobalt reduction efficiency. The reducing solution was 0.25 M NaBH₄ + 0.25 M NaOH. pH was manually controlled by adding dilute sulphuric acid solution at pH 2 ± 0.05, 3 ± 0.07, 4 ± 0.1, 5 ± 0.15, and 6 ± 0.22. $[Co^{2+}]_{initial} = 30$ mg/L, Mol ratio of NaBH₄ to $Co^{2+} = 2$.

4.3 THE EFFECT OF ADDITION RATE ON COBALT REDUCTION EFFICIENCY

At lower pH the cobalt metal product is readily redissolved, and so slow addition leads to the redissolution of more cobalt and a low reduction efficiency. Figure 4-16 shows the effect of the addition rate of sodium borohydride solution on the cobalt reduction efficiency. Fast addition of sodium borohydride increases the rate of the hydrolysis of sodium borohydride, However, the reaction with cobalt (II) is much faster than that of hydrogen ions and most of the sodium borohydride is used to reduce cobalt ions. Overall, therefore the shorter addition time increases the reduction efficiency.



Figure 4-16 The effect of addition rate of borohydride on cobalt reduction efficiency at $35\ ^{0}$ C, the reducing solution: 0.25 M NaBH₄ + 0.25 M NaOH, 500 rpm, the pH was manually controlled by adding dilute sulphuric acid solution.

4.4 THE EFFECT OF TEMPERATURE ON COBALT REDUCTION EFFICIENCY

Increasing temperature has a negative effect on cobalt reduction. The effect of temperature is shown in Figure 4-17. From 25 to 45 ^oC, the extent of cobalt reduction changes little with increasing temperature. Above 45 ^oC, the cobalt reduction efficiency decreases greatly with increasing temperature. At higher temperatures, the hydrolysis of borohydride and the redissolution become more active and the reduction efficiency becomes poorer. It can be seen that the shorter addition time increases the cobalt reduction efficiency because it decreases the amount of the redissoved cobalt.



Figure 4-17 The effect of temperature on cobalt reduction efficiency. The reducing solution was 0.25 M + 0.25 M NaOH, mol ratio of NaBH₄ to $\text{Co}^{2+} = 2$, and $[\text{Co}^{2+}]_{\text{initial}} = 30 \text{ mg/L}$.

4.5 THE REDISSOLUTION OF REDUCED COBALT

At pH 4 the redox potential of Co (II)/Co is below the redox potential of H^+/H_2 (see Fig. 2-6), so the reduced cobalt will be reoxidized by H^+ ions. As shown in Figure 4-18, the cobalt concentration decreased to 5 mg/L about 20 minutes after sodium borohydride was added to the solution. Further addition of sodium borohydride hardly decreased the cobalt solution concentration. At this point the cobalt reduction rate was equal to the rate of redissolution and sodium borohydride was consumed by hydrolysis. After the addition of sodium borohydride ceased, the cobalt concentration increased with time, due to the cobalt redissolution. Because the cobalt particles were small, the reduced cobalt was quickly redissolved, almost completely within 30 minutes.

After the addition of sodium borohydride, the solution potential dropped to about-0.49 V (SCE) and stabilized. This potential is a little lower than the potential of H^+/H_2 (-0.48 V (SCE) at pH 4, higher than the standard potential of Co (II)/Co (-0.517 V (SCE)) and much higher than the potential of H₃BO₃/BH₄ at pH 4 (-0.927 V (SCE) assuming [H₃BO₃]=[BH₄⁻]). Since the solution potential was measured with a platinum electrode which catalyzed borohydride hydrolysis [123], H₂, BH₄⁻ and probably the reduced cobalt particles adsorbed on the electrode and the measured potential is the mixed potential of H⁺/H₂, H₃BO₃/BH₄⁻ and Co²⁺/Co. The concentration of BH₄⁻ was very low and so the measured potential was determined mainly by the H⁺/H₂ redox couple. It was found that the measured potential did not reproduce well and was also determined by the electrode treatment method and electrode materials.



Figure 4-18 The redissolution of reduced cobalt. The reducing solution was 0.25 M NaBH₄ + 0.25 M NaOH. After the addition of sodium borohydride ceased, the pH was controlled at 4 ± 0.05 by adding dilute sulphuric acid.

4.6 IDENTIFICATION OF THE PRECIPITATE

4.6.1 MORPHOLOGY AND PROPERTIES OF PRECIPITATES

Figures. 4-19 and 4-20 are scanning electron micrographs revealing the shape and morphology of the fresh precipitates. The very small particles coalesced together and formed larger granules with sizes in the range of 10 to 20μ m. After the precipitates were treated ultrasonically in acetone, the small particles became separated to some extent. The particles were then immediately collected on a thin evaporated carbon film for transmission electron microscopy. The particle sizes of the resultant materials were in the range of 20-100 nm.

After heat treatment at 500 0 C and 10⁻⁶ torr for two hours, the particles became larger (about 200-500 nm). During the heat-treatment, the precipitates recrystallized and small particles combined to form larger particles as shown in Fig. 4-22.

The precipitates exhibited magnetic properties both in the as-precipitated and heat-treated conditions.

Cobalt boride is generally chemically inert and does not dissolve in sulphuric acid, but only in hot concentrated nitric acid. These precipitates showed high chemical reactivity and dissolved readily in dilute sulphuric acid. Even after the heat-treatment, the precipitate still dissolved in 0.1 M sulphuric acid solution. This chemical reactivity may be caused by the very small size which produces a large area-volume ratio and hence a high surface free energy-volume ratio.

A sample of precipitate was immersed in boiling water. After 80 minutes, the atom ratio of Co to B in the residues was 2.5. During this treatment, some boron was dissolved. The probable reaction may be written as:

$$Co_2B + 3H_2O \rightarrow 2Co + H_3BO_3 + 1.5H_2$$
 (4-1)



Figure 4-19 Surface morphology of the precipitate prepared under the conditions: pH 5.5-7.5, 35 ° C, 500 rpm stirring rate, mol ratio of borohydride to cobalt ion = 2, 10- minute addition time and initial [Co (II)] = 30 mg/L, 200 x.



Figure 4-20 Surface morphology of the precipitate prepared under the conditions: pH 5.5-7.5 and 35 °C, 500 rpm stirring rate, mol ratio of borohydride to cobalt ion = 2, 10- minute addition time, initial [Co (II)] = 30 mg/L, 4,000 x.



Figiure 4-21 Transmission electron micrograph of the fresh precipitate prepared under the conditions: pH 5.5 -7.5, 500 rpm stirring rate, mol ratio of sodium borohydride to cobalt ion = 2, 10- minute addition time, initial[Co (II)] = 30 mg/L, 50,000 x.



Figiure 4-22 Transmission electron micrograph of the heat-treated precipitate prepared under the conditions: pH 5.5 -7.5, 500 rpm stirring rate, mol ratio of sodium borohydride to cobalt ion = 2, 10- minute addition time, initial [Co (II)]= 30 mg/L, 100,000 x.

4.6.2 IDENTIFICATION BY X-RAY DIFFRACTION

The X-ray diffraction pattern of the fresh precipitate (see Figure 4-23) showed a broad peak at 45 $\pm 2^{0}$. The strongest peak in Co₂B appears at 45.7 ⁰ (d₂₁₁ = 1.983 Å) and the strongest peak in Co appears at 44.3 ⁰. (d₁₁₁ = 2.0467 Å). There was no peak corresponding to B around 21.8 ⁰. The precipitate was probably Co₂B , Co or a mixture of Co₂B and Co. The chemical analysis of the fresh precipitate showed that the atom ratio of Co to B was 2.1 close to Co₂B. The broad peak in the X-ray diffraction pattern indicates that the crystalline phase had very low periodicity, typical of very fine crystallite size and approaching an amorphous material. After the precipitate was heat-treated for 2 hours at 500 ⁰C in a high vacuum of 10⁻⁶ Torr, the X-ray diffraction pattern of the precipitate showed well defined peaks due to Co₂B and also the main peak of Co. Furthermore, the preparation of cobalt boride from cobalt and boron powders requires a temperature of over 1000 ⁰C and 500 ⁰C is not enough to make cobalt boride. Therefore the precipitate likely consisted of amorphous Co₂B and Co. Under the heat treatment, the diffusion allowed the periodicity to increase giving a longer crystalline region (grain) of Co₂B and excess cobalt and particles became larger.

After fresh precipitates were placed in boiling water for 80 minutes, some boron was dissolved and the atom ratio of Co to B was 2.5, and the broad amorphous peak in the X-ray diffraction pattern (Figure 4-25) became larger. After a two-hour heat-treatment at 500 0 C, a stronger main peak of cobalt appeared (Figure. 4-26), which is consistent with the composition of the precipitate.

After heat treatment at 250 0 C for two hours, the precipitate still showed a broad X-ray diffraction peak, consistent with its being amorphous (Figure 4-27).



Figure 4-23 X-ray diffraction pattern of the precipitate prepared under the conditions: pH 5.5-7.5 and 35^{0} C, 500 rpm stirring rate, mol ratio of NaBH₄ to Co²⁺ = 2,and 10-minute addition time.



Figure 4-24 X-ray diffraction pattern of the precipitate prepared under the conditions: pH 5.5-7.5 and 35 °C, 500 rpm stirring rate, mol ratio of NaBH₄ to Co²⁺=2, 10-minute addition time and 500 °C heat-treatment for 2 hours.



Figure 4-25 X-ray diffraction pattern of the precipitate prepared under conditions: pH 5.5-7.5, 35 0 C, 500 rpm stirring rate, mol ratio of NaBH₄ to Co²⁺ = 2, 10-minute addition time, and heating boiling water for 80 minutes.



Figure 4-26 X-ray diffraction pattern of the precipitate prepared under the conditions: pH 5.5 -7.5, 35 $^{\circ}$ C, 500 rpm stirring rate, mol ratio of NaBH₄ to Co²⁺ = 2, 10-minute addition time, boiling water for 80 min., and 500 $^{\circ}$ C heat-treatment for 2 hours.

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Figure 4-27 X-ray diffraction pattern of the precipitate prepared under the conditions: pH 5.5-7.5, 35 °C, 500 rpm stirring rate, mol ratio of NaBH₄ to Co²⁺ = 2, 10-minute addition time, and 250 °C heat treatment for 2 hours.

4.6.3 TEM IDENTIFICATION OF THE PRECIPITATE

The transmission electron microscopy pattern of a cluster of fresh precipitates is shown in Fig. 4-28. It does not exhibit a sufficiently well-defined ring pattern that allows crystal identification. However, the X-ray energy spectrum showed a strong cobalt peak (k- α). After the precipitate was heat-treated for two hours at 500 ^oC, a single crystal transmission electron diffraction pattern was obtained from individual particles (see Fig. 4-29). An evaporated gold film (polycrystalline) was used to obtain an electron diffraction ring pattern from which the camera constant was calculated and this constant was used to index the unknown single crystal

electron diffraction pattern of the precipitate. The gold ring electron diffraction pattern is shown in Fig. 4-30, and the details of the calculation are listed in table 4-2.

$h^2 + k^2 + l^2$	h	k	1	d(h,k,l) Å	radius of rings for Au	camera constant
					pattern $(r_{h,k,l})$ (mm)	$r_{h,k,l} \times d_{(h,k,l)} (mm \text{ Å})$
3	1	1	1	2.355	12.75	30.026
4	2	0	0	2.039	- 14.6	29.769
8	2	2	0	1.442	20.7	29.849
11	3	1	1	1.230	24.5	30.135
12	2	2	2	1.1774	25.5	30.024
Average						29.96

Table 4-2 Calculation of the camera constant (Au calibration) for TEM

The camera constant is given by the product $r \times d$, where r is the ring diameter and d is the interplanar spacing of the diffraction ring. The average value of the constant is 29.96 mm Å. The d-spacings of the reflection on the unknown pattern obtained from the camera constant and the distance (r) of the diffraction spot from the center are listed in Table 4-3 and compared with the known d-spacings for Co₂B, and the indices (h, k, l) were obtained. According to the indices, the angles of the planes were calculated using electron diffraction pattern software [153]. A protractor was used to measure the angles between the rel-vectors of the diffraction pattern The values of the angles are listed in Table 4-4. It can be concluded that the single crystal electron diffraction pattern is consistent with that of Co₂B and that the precipitate was cobalt boride. The zone [u, v, w] of Figure 4-29 is identified as [110].

u: v: w = $(k_1l_2 - k_2l_1)$: $(l_1h_2 - l_2h_1)$: $(h_1k_2 - h_2k_1)=(0\times 2 - 1\times 2)$: $(2\times 1-2\times 0)$: $(0\times 1-1\times 0)=1$: (-1):0. So the plane (h, k, l) belongs to the zone [110] and hu + kv + lw = 0

$$h_1u + k_1v + l_1w = 0 \times 1 + 0 \times (-1) + 2 \times 0 = 0$$

 $h_2u + k_2v + l_2w = 1 \times 1 + 1 \times (-1) + 2 \times 0 = 0$

 $h_3u + k_3v + l_3w = 2 \times 1 + 2 \times (-1) + 2 \times 0 = 0$

 $h_4u + k_4v + l_4w = 3 \times 1 + 3 \times (-1) + 3 \times 0 = 0$

 $h_5u + k_5v + l_5w = 1 \times 1 + 1 \times (-1) + 0 \times 0 = 0$

radius (mm)	the calculated d-spacing	the theoretical d-spacing	the indices
	(Å)	(Å)	(h, k,l)
$r_1 = 14.2$	d ₁ =29.96/14.2=2.110	2.113	(002)
$r_2 = 16.5$	d ₂ =29.96/16.5=1.816	1.815	(112)
$r_3 = 22.1$	d ₃ =29.96/22.1=1.356	1.357	(222)
$r_4 = 29$	d ₄ =29.56/29.0=1.033	1.032	(332)
$r_5 = 8.3$	d ₅ =29.96/8.3=3.625	3.55	(110)

Table 4-3 The calculation of the d-spacings of the precipitate

Table 4-4 Calculated theoretical angles and measured angles

Calculated angle (using software)	Measured angle
$\alpha_{(002)/(112)} = 30.753^0$	310
$\alpha_{(002)/(222)} = 49.959^0$	50 ⁰
$\alpha_{(002)/(332)} = 60.742^0$	61 ⁰
$\alpha_{(002)/(110)} = 90^{0}$	90 ⁰
$\alpha_{(112)/(222)} = 19.206^0$	20 ⁰
$\alpha_{(112)/(332)} = 29.989^0$	300
$\alpha_{(112)/(110)} = 59.247^0$	60^{0}
$\alpha_{(222)/(332)} = 10.783^0$	10^{0}
$\alpha_{(222)/(110)} = 40.041^0$	40^{0}
$\alpha_{(332)/(110)} = 29.258^0$	30 ⁰



Figure 4-28, Transmission electron micrograph of the fresh precipitate prepared under the conditions: pH 5.5 -7.5, 500 rpm, the molar ratio of sodium to cobalt ion =2, the addition time=10 minutes, [Co]=30 mg/l, 200 kv.



Figure 4-29 Transmission electron micrograph of the precipitate prepared under the conditions: pH 5.5 -7.5, 500 rpm, mol ratio of sodium borohydride to cobalt ion = 2, 10-minute addition time, [Co (II)] = 30 mg/L and 500 °C heat-treatment for 2 hours, 200 kv.



Figure 4-30 Transmission electron pattern of gold film, 200 kv

4.6.4 THE EFFECT OF TEMPERATURE ON THE COMPOSITION OF THE PRECIPITATE

The reaction temperature has some effect on the composition of the precipitate. From Fig. 4-31, the atom ratio of Co to B increases with increasing temperature. At higher temperatures, the hydrolysis of borohydride (or borane) becomes more active and dominates over the cobalt-catalyzed formation of elemental boron. After the precipitate was boiled in water for 80 minutes, the atom ratio of cobalt to boron of the precipitate increased from 2.05 to 2.55, which means that some boron was oxidized by water and went into solution. At higher pH, the differences between the redox potential of Co^{2+}/Co and $\text{H}_2\text{O}/\text{H}_2$ or $\text{H}_3\text{BO}_3/\text{BH}_4^-$ become more positive and so cobalt is easier to reduce. This also favors a higher atom ratio of Co to B. At pH 4 some cobalt redissolved with the result that the atom ratio of Co to B in the precipitate became lower.



Figure 4-31 The effect of temperature on the composition of the precipitate produced with 500 rpm stirring rate, with a reducing solution of 0.25 M NaBH₄ + 0.25 M NaOH, initial [Co] = 30 mg/L. The pH was controlled by adding dilute sulphuric acid solution.

From Fig. 4-32, the addition rate (time) has little effect of the composition of the precipitate.



Figure 4-32 Th% effect of the addition rate on the composition of precipitate produced with 500 rpm stirring rate, with a reducing solution of 0.25 M NaBH₄ + 0.25 M NaOH, initial [Co] = 30 mg/L. The pH was controlled by adding dilute sulphuric acid solution.

4.7 POSSIBLE REACTIONS DURING COBALT REDUCTION WITH BH₄⁻

X-ray diffraction patterns show that the precipitate was a mixture of cobalt boride and cobalt. The atom ratio of cobalt to boron increases from 2.05 to 3.2 with increasing temperature from 25 to 75 $^{\circ}$ C, but is quite insensitive to the addition rate. From the pH vs. time results obtained by using sodium borohydride solution with different concentrations of sodium hydroxide, the reduction of cobalt with borohydride may release one hydrogen ion. One mole of borohydride can reduce at most one mole of cobalt ions without the precipitation of cobalt hydroxide. Therefore, according to the inner-sphere mechanism proposed by Khain [132] and similar to Equation 2-42 to 2-47, the main reactions might be the following reactions:

The formation of intermediate compound,

$$Co^{2+}(aq) + BH_4^{-} \rightarrow [CoBH_4]^{+} + (aq)$$

$$\tag{4-2}$$

The formation of a bridging bond,

$$[CoBH_4]^+ \to Co^{2+} - (H^- - BH_3) \tag{4-3}$$

The transfer of a hydrogen atom and rupture of the bridging bond,

$$Co^{2+} - (H^- - BH_3) \to CoH^+ + BH_3$$
 (4-4)

The electron transfer and bond rupture,

$$CoH^+ \rightarrow Co + H^+$$
 (4-5)

Summing up the above reactions, we get,

$$Co^{2+}(aq) + BH_4^- \to Co + H^+ + BH_3 + (aq)$$
 (4-6)

The catalytic decomposition of some borane by cobalt,

$$BH_3 \xrightarrow{C_0} B + 3/2H_2 \tag{4-7}$$

Most of the produced cobalt condensed together with boron to form amorphous Co₂B.

$$2Co + B \to Co_2 B \tag{4-8}$$

The hydrolysis of the other borane,

$$BH_3 + 3H_2O \rightarrow H_3BO_3 + 3H_2 \tag{4-9}$$

The hydrolysis of borohydride,

$$BH_4^{-} + 3H_2O + H^+ \to H_3BO_3 + 4H_2 \tag{4-10}$$

The atom ratio of cobalt to boron depends principally on reactions (4-7) and (4-9). At a high temperature, the hydrolysis of borane (BH₃) would become more active and less boron is formed. Therefore the atom ratio of cobalt to boron is high. The overall reaction can be written as:

$$2Co^{2+} + 2BH_4^{-} + 3(1+0.5x)H_2O \rightarrow (1-0.5x)Co_2B + xCo + 2H^{+} + (1+0.5x)H_3BO_3 + (4.5+0.75x)H_2$$
(4-11)

where x is the range of 0-2. If the ratio of reaction (4-7) to reaction (4-9) is 1, that is, x = 0, the overall reaction may be written as:

$$2Co^{2+} + 2BH_4^{-} + 3H_2O \to Co_2B + 2H^+ + H_3BO_3 + 4.5H_2$$
(4-12)

If the hydrogen ions are not neutralized, combining reactions (4-10) and (4-12), we can get the following overall reaction:

$$2Co^{2+} + 4BH_4^{-} + 9H_2O \rightarrow 2Co_2B + 3H_3BO_3 + 12.5H_2$$
(4-13)

If the hydrogen ions are neutralized by sodium hydroxide, reaction (4-10) can be suppressed. The rate of hydrolysis is much slower than that of reaction (4-6) at lower temperatures (below 35 0 C) and high pH (above 7). If sodium borohydride is added slowly to the cobalt solution and the hydrogen ions are neutralized by sodium hydroxide in the reducing solution, reaction (4-10) can be suppressed to the maximum extent and sodium borohydride reduction efficiency for cobalt ions can be optimized. The reaction can then be written as:

$$2Co^{2+} + (4-y)BH_4^{-} + yOH^{-} + [3(3+0.5x) - 4y]H_2O \rightarrow (1-0.5x)Co_2B + xCo + (3+0.5x - y)H_3BO_3 + (12.5+0.75x - 4y)H_2$$
(4-13)

where y is in the range of 0-2. If y is 2, we can get the following reaction.

$$2Co^{2+} + 2BH_4^- + 2OH^- + (1+1.5x)H_2O \rightarrow (1-0.5x)Co_2B + xCo + (1+0.5x)H_3BO_3 + (4.5+0.75x)H_2$$
(4-14)

If y = 0, i.e. $[OH^-]/[BH_4^-]$ is 0 in sodium borohydride solution, 2 moles of borohydride are needed for reducing 1 mole of cobalt ions; if y = 0.4, i.e. $[OH^-]/[BH_4^-] = 0.2$, 1.8 moles of borohydride for 1 mole of cobalt ions, if y = 1, i.e. $[OH^-/[BH_4^-] = 0.5, 1.5$ moles of borohydride for 1 mole of cobalt ions, and if y = 2, i.e. $[OH^-]/[BH_4^-] = 1$, 1 mole of borohydride is needed for 1 mole of cobalt ions. These results are well consistent with the data at pH 7, and 8, listed in Table 4-1. At lower pH e.g. 5, because of the hydrolysis of borohydride, the amount of borohydride needed for the reduction of cobalt ions is higher than the above calculated values.

4.8 KINETIC STUDIES OF COBALT REDUCTION WITH BOROHYDRIDE4.8.1 FEATURES OF KINETICS ON COBALT REDUCTION

The reduction of cobalt ions with borohydride is almost instantaneous. In fact as soon as sodium borohydride solution was added to the solution at normal temperature (from 25 - 35 ⁰C), a black precipitate appeared, the amount of which did not increase with time. This means that the reduction was almost immediate and was completed within a few seconds. When the temperature was lowered to 5 ^oC, it was observed that after 5 seconds the black precipitate appeared and then the solution became black immediately. Because the reaction was too fast to follow, it was difficult to measure the cobalt concentration in the solution as a function of time. From pH vs. time data, we can see how the reaction progressed. Figure 4-33 shows the measured pH and potential vs. time at 15 ^oC. The reaction can be divided into three stages. In the first stage, alkaline sodium borohydride solution was added to the reactor and raised the pH of the solution and only a small proportion of cobalt ions was reduced. The pH should have gone up faster and to higher values. but it did not. The two causes of this result are that the reduction of cobalt released hydrogen ions, and cobalt sulphate had some buffering effect.

The buffering effect of cobalt sulphate was the main cause. Figure 4-34 shows the pH of various solutions to which different additions were made over time. When 0.25 M NaBH₄ + 0.05 M NaOH or 0.05 M NaOH was added to pure water, the pH went up very quickly and after 4 seconds, the measured pH exceeded 9. The pH for 0.05 M NaOH went up a little faster and reached a little higher value than that for 0.25 M +0.05 M NaOH. Sodium ions may affect pH measurement because the measured pH of 0.05 M , 0.125 M and 0.25 M NaOH were 12.44, 12.91, 13.14 respectively which were a little higher than the pH of 0.25 NaBH₄ + 0.05 M NaOH, and 0.25 M NaBH₄ + 0.25 M NaOH solutions, 12.37, 12.88, 13.13 respectively at 23 $^{\circ}$ C. Another cause may be the buffering effect of the produced boric acid.

The pH vs. time plots for 0.05 M NaOH and 0.25 M NaBH₄ + 0.05 M NaOH added to 30 mg/L Co^{2+} solutions are almost the same within the first two seconds, which means that cobalt sulphate acts as a buffer and keeps the pH from rising rapidly. After about two seconds, the pH for 0.05 M NaOH continued to increased and the pH for 0.25 M NaBH₄ + 0.05 M NaOH

decreased because the cobalt reduction released hydrogen ions. However, after 10 seconds the pH was higher than for the former because of sodium borohydride hydrolysis and the consumption of cobalt ions. The final pH's for 30 mg/L Co^{2+} and 0.25 M NaBH₄ + 0.05 M NaOH are much lower than that for pure water and 0.25 M NaBH₄ + 0.05 M NaOH although cobalt ions were reduced. This is because the boric acid produced buffered the solution.

In the second stage, cobalt(II) was reduced, and the reduction was autocatalyzed by reduced cobalt metal. The hydrolysis of borohydride was also catalyzed by reduced cobalt. After this stage, the measured concentration of cobalt ions was less than 1 mg/L.

By the third stage, most of the cobalt ions were reduced and the main reaction became the hydrolysis of BH_4^- which caused the pH to rise rapidly.



Figure 4-33 pH and potential of the solution vs. time. The reducing solution was 0.25 M NaBH₄ + 0.05 M NaOH, the mol ratio of NaBH₄ to Co^{2+} was 2, $[Co^{2+}]_{initial} = 30$ mg/L.



Figure 4-34 pH vs. time for solutions with different compositions and addition of different additives 15 ^oC, and 2500 rpm stirring rate.

4.8.2 EFFECT OF TEMPERATURE ON REACTION RATE

The pH vs. time data at different temperatures are shown in Figure 4-35. With increasing temperature the reaction rate increased greatly. The reduction of most of the cobalt needs 24 seconds at 5 °C, 5 seconds at 15 °C, and about two seconds at 25 °C and less than two seconds at 35 °C. Above 15 °C the reaction rate was dependent on mass transfer and the pH measurement was affected by the time required for the pH probe to reach equilibrium and by the time required to add the reducing solution. The pH meter response time was about 1 second and so the real peak in pH was not detected.



Figure 4-35 pH vs. time at different temperature, the reducing solution (4 ml) contained 0.205 M NaBH₄ + 0.05 M NaOH and the solution was added within 1 second, $pH_{initial} = 5.5$ and $[Co^{2+}]_{initial} = 30$ mg/l.

4.8.3 EFFECT OF pH ON REACTION RATE

At higher pH, cobaltous hydrocomplexes such as $Co(OH)^+$ and $Co(OH)_2$ (aq) form and the concentration of free Co (aq)²⁺ decreases. This slows the reaction rate of cobalt reduction with borohydride. The time needed for the reduction of most of the cobalt is 5 seconds for an initial pH of 5.5 (see Figure. 4-33), 8 seconds for an initial pH of 6 (Figure. 4-36), 9 seconds for an initial pH of 7 (see Figure. 4-37), 14 seconds for an initial pH of 7.5 (see Figure. 4-38) and 27 seconds for an initial pH of 7.8 (see Figure. 4-39) respectively at 15 °C. At 35 °C the time required is less than 2 seconds for an initial pH of 5.5 (see Figure. 4-35), 2 seconds for an initial pH of 7.0 (see Figure. 4-40), 3 seconds for an initial pH of 7.8 (see Figure. 4-41). At lower temperatures, pH has a large effect on the rate and at higher temperatures, it has less effect on.



Figure 4-36 pH vs. time at initial pH 6.0, 4 ml of reducing solution and $[Co^{2+}]_{initial} = 30 \text{ mg/L}.$



Figure 4-37 pH vs. time at initial pH 7.0, 4ml of reducing solution and $[Co^{2+}]_{initial} = 30 \text{ mg/L}.$



Figure 4-38 pH vs. time at initial pH 7.5, 4ml of reducing solution and $[Co^{2+}]_{initial} = 30 \text{ mg/L}.$



Figure 4-39 pH vs. time at initial pH 7.8, 15 0 C, 4 mL of reducing solution and $[Co^{2+}]_{initial} = 30 \text{ mg/L}.$



Figure 4-40 pH vs. time at initial pH 7.0, 35 $^{\circ}$ C, 4 mL of reducing solution and $[Co^{2+}]_{initial} = 30 \text{ mg/L}.$



Figure 4-41 pH vs. time at initial pH 7.8, 35 0 C, 4 mL of reducing solution and $[Co^{2+}]_{initial} = 30 \text{ mg/L}.$

4.8.4 AUTOCATALYTIC EFFECT OF COBALT ON COBALT REDUCTION

The reduced cobalt has an autocatalytic effect on cobalt ion reduction. An initial 0.66 ml of sodium borohydride solution was added to a solution containing 35 mg/L Co^{2+} it was found that cobalt reduction released hydrogen ions and caused a drop in pH. At the 25th second, 4 ml of sodium borohydride solution was added to the solution containing 30 mg/l Co^{2+} . From the pH vs. time (Fig. 4-42), only 2 seconds were needed to reduce most of cobalt ions. In another experiment 5 mg/L of cobalt ions was first reduced by adding 0.6 mL of sodium borohydride solution was added to 6. Then 4 mL of sodium borohydride solution was added to the solution containing 30 mg/l cobalt ions. From the pH vs. time graph (see Fig. 4-43), it can be seen that the time for the reduction of most of the cobalt ions was 4 seconds compared with the 8
seconds for the solution without pre-reduced cobalt present. Apparently, the reduced cobalt has a catalytic effect on cobalt reduction.



Figure 4-42 pH vs. time data for the autocatalytic effect on cobalt reduction



Figure 4-43 pH vs. time data demonstrating the autocatalytic effect on cobalt reduction.

4.9 COBALT PRECIPITATION FROM ZINC SULPHATE SOLUTION

4.9.1 INHIBITORY EFFECT OF ZINC IONS ON COBALT AND NICKEL REDUCTION

The strong negative effect of zinc ions on cobalt reduction is surprising. The results are shown in Figure 4-44. When the zinc sulfate concentration exceeds several 10 μ mol/L zinc, cobalt ions cannot be reduced by borohydride. The inhibitory effect is dependent on the addition rate (time) of sodium borohydride solution. The concentration of zinc sulphate at which no cobalt reduction occurs is 30 μ mol/L for 10-minute addition time, 40 μ mol/L for 5 minutes, 70 μ mol/L for 2 minutes and 120 μ mol/L for 1 minute. Zinc sulphate also has a strong negative effect on nickel reduction. From Figure 4-44, the concentration of zinc sulphate for no cobalt reduction is 150 μ mol/L for 10-minute addition time, 200 μ mol/L for 5 minutes, 250 μ mol/L for 2 minutes and 300 μ mol/L for 1 minute. It was also found that zinc sulphate has a strong effect on cadmium



Figure 4-44 The inhibitory effect of zinc ions on cobalt reduction with the mol ratio of NaBH₄ to $Co^{2+} = 2$ and 0.25 M NaBH₄ + 0.25 M NaOH reducing solution, pH was controlled by adding dilute sulphuric acid solution.

and lead reduction. At $[ZnSO_4] > =0.05$ or $[ZnCl_2] > 0.2$ M, lead (30 mg/L initially) was not reduced and no precipitate formed at pH 4. However copper ions were reduced at $[ZnSO_4] > 2$ M. This means that zinc sulphate has a strong negative effect on reduction of electropositive metals and less effect on reduction electronegative metals.

In order to verify that zinc ions suppress cobalt reduction, zinc chloride, magnesium sulphate and sodium sulphate were added to the reaction mixture. Zinc chloride has the same inhibitory effect on cobalt reduction, but magnesium sulphate and sodium sulphate have less effect on cobalt reduction. From Figures 4-46 to 4-49, it can be seen that only when their concentrations exceed 0.1 M was cobalt reduction inhibited. Under these conditions, the cations Mg^{2+} or Na⁺ may combine with borohydride ions to form associated sodium borohydride salts.



Figure 4-45 The inhibition effect of zinc ions on nickel reduction with the mol ratio of NaBH₄ to $Ni^{2+} = 2$ and 0.25 M NaBH₄ + 0.25 M NaOH reducing solution, pH was controlled by adding dilute sulphuric acid solution.

and so decrease the concentration of free borohydride ions. The SO_4^{2-} may be complexed by Co^{2+} to form $CoSO_4$ (aq) and thereby decrease the reactivity and potential of cobalt.

Figure 4-49 shows the pH vs. time data for 30 mg/L Co^{2+} ($\approx 0.0005 \text{ M}$) + 0.0001 M Zn^{2+} after the addition of sodium borohydride solution. Compared to the pH vs. time plot for Co^{2+} alone, the pH for the $\text{Co}^{2+} + \text{Zn}^{2+}$ system rose more slowly due to the buffering effect of both zinc sulphate and cobalt sulphate, but it did not exhibit the characteristic initial rise and fall observed when Co^{2+} is reduced. The reaction was suppressed by zinc ions. Much less cobalt powder was precipitated compared to Co^{2+} in the absence of zinc ions and some cobalt was deposited on the glass reactor wall. From the above results, it is clear that zinc ions have a negative effect on cobalt reduction with borohydride.



Figure 4-46 Effect of the additives (ZnSO₄, ZnCl₂, MgSO₄, Na₂SO₄) on cobalt reduction. The reducing solution was 0.25 M NaBH₄ + 0.25 M NaOH, the pH was manually controlled by adding dilute sulphuric acid solution.



Figure 4-47 Effect of the additives (ZnSO₄, ZnCl₂, MgSO₄, Na₂SO₄) on cobalt reduction. The reducing solution was 0.25 M NaBH₄ + 0.25 M NaOH, the pH was manually controlled by adding dilute sulphuric acid solution.



Figure 4-48 Effect of the additives (ZnSO₄, ZnCl₂, MgSO₄, Na₂SO₄) on cobalt reduction. The reducing solution was 0.25 M NaBH₄ + 0.25 M NaOH, the pH was manually controlled by adding dilute sulphuric acid solution.



Figure 4-49 Effect of the additives (ZnSO₄, ZnCl₂, MgSO₄, Na₂SO₄) on cobalt reduction. The reducing solution was 0.25 M NaBH₄ + 0.25 M NaOH, the pH was manually controlled by adding dilute sulphuric acid solution.



Figure 4-50 pH vs. time data for 30 mg/L Co^{2+} and 30 mg/L Co^{2+} + 0.0001 M Zn^{2+} after the addition of 0.25 M NaBH₄ + 0.05 M solution.

4.9.2 EFFECT OF OTHER ADDITIVES ON COBALT REDUCTION

1. Triethanolamine and polyacrylamide(0-200 mg/L) were added to the solution (0-120 g/L Zn^{2+} , 30 mg/l Co^{2+}) at temperatures (15-75 ^{0}C). Polyakov *et al* [114, 115] reported that the cobalt concentration was lowered to 0.06 mg/L in the presence of these two additives. But the additives had no effect on the reduction of cobalt and on the protection of cobalt from redissolution.

2. Zinc dust was added to the solution to help reduce cobalt ions, but there was not any positive effect on the reduction of cobalt in the zinc sulphate solution.

3. Antimony tartrate, sodium arsenite, and copper sulphate are used to activate the reduction of cobalt with zinc dust in zinc electrolytes in industry. Therefore these reagents were added to test the solutions to help reduce the cobalt ion. Unfortunately these additives did not show any positive effect on cobalt reduction. When sodium borohydride was added to the solution containing arsenite and antimony tartrate as well as zinc and cobalt ions, almost no precipitate appeared. The possible cause is that antimony tartrate and arsenite reacted with borohydride to produce stibine, SbH₃, and arsine, AsH₃. It was found that copper was first reduced and cobalt remained in solution.

$$AsO_2^- + BH_4^- + H_2O \rightarrow AsH_3 + H_3BO_3 \tag{4-14}$$

$$SbO^{+} + BH_{4}^{-} + 2H_{2}O \rightarrow SbH_{3} + H_{3}BO_{3} + 2H_{2}$$
 (4-15)

4. Hydrazine sulphate which is a strong reducing agent and is sometimes used as a corrosion inhibitor, was added to the zinc sulphate solutions. However, it not show any positive effect on the reduction of cobalt with borohydride.

5. The precipitate prepared by cobalt reduction with sodium borohydride from cobalt sulphate solution was added to the zinc and cobalt sulphate solutions to promote the nucleation of cobalt. However, the cobalt reduction with borohydride was still not improved. This means that the negative effect of zinc ions on the cobalt reduction is not the nucleation inhibition by zinc ions.

4.9.3 POSSIBLE INHIBITORY MECHANISM OF ZINC IONS

Zinc ions might have some catalytic effect on the hydrolysis of sodium borohydride. When sodium borohydride was added to the solution, the local solution became cloudy and gas evolution occurred possibly due to hydrogen gas formation. The potential of the solution increased with increasing concentration of zinc ions. After sodium borohydride was added to the solution, zinc ions competed with cobalt ions for borohydride ions to form zinc borohydride. The rate of the formation of zinc borohydride is probably much faster than that of the cobalt reduction. According to the literature [135], the following reactions may occur:

$$Zn^{2+} + 2BH_4^- \rightarrow Zn(BH_4)_2 \tag{4-17}$$

$$Zn(BH_4)_2 \to ZnH_2 + 2BH_3 \tag{4-18}$$

$$ZnH_2 + 2H^+ \rightarrow Zn^{2+} + 2H_2 \tag{4-19}$$

$$BH_3 + 3H_2O \rightarrow H_3BO_3 + 3H_2 \tag{4-20}$$

According to this scheme, the zinc borohydride decomposes into zinc hydride and borane both of which hydrolyze rapidly. The hydrolysis of zinc hydride produces zinc ions which further react with borohydride ions and thus catalyze the hydrolysis of borohydride. With increasing pH the hydrolysis of zinc ions increases and the rate of the formation of zinc borohydride decreases and even reaches zero. At a high pH the zinc hydride is relatively more stable and so the catalytic effect on the hydrolysis of borohydride is low. As the sodium borohydride solution (0.25 M NaBH₄ + 0.25 M NaOH) was gradually added to the solution containing 30 mg/L Co²⁺and 10 mg/L Zn²⁺, the pH increased and when it exceeded 7, the black precipitate began to appear.

From Figures 4-43 and 4-44, the inhibitory effect of zinc ions decreased with increasing addition rate of sodium borohydride. For example, the concentration of zinc ions required to completely sto0 cobalt reduction was 3×10^{-5} M for a 10-minute addition time, 4×10^{-5} M for

5 minutes, 7×10^{-5} M for 2 minutes and 1.2×10^{-4} M for 1 minute. Apparently if a sufficient excess of borohydride is present in solution, some cobalt reduction can occur.

5. CONCLUSIONS

The stoichiometry of cobalt reduction with sodium borohydride is dependent on reaction conditions such as temperature, pH, and composition of the reducing solution.

Cobalt reduction with sodium borohydride causes the pH of the solution to drop indicating the release of hydrogen ions. The extent of the pH drop depends on the relative rates of cobalt reduction and the hydrolysis of sodium borohydride. The progress of the reaction can be divided into three stages. When sodium borohydride is added to the solution, the pH first decreases, which indicates that the reduction of cobalt is the dominant reaction rather than the hydrolysis of sodium borohydride. Next the pH reaches some value and stabilizes briefly. At this stage there is a balance between the cobalt reduction and the hydrolysis of sodium borohydride and the rate of the production of hydrogen ions is equal to the rate of its consumption. Finally the pH increases rapidly, meaning that most of the cobalt is reduced and the main reaction becomes the hydrolysis of borohydride. Because the reaction of cobalt reduction releases hydrogen ions, which catalyze the hydrolysis of sodium borohydride, sodium hydroxide was added to the solution of sodium borohydride to neutralize the hydrogen ions produced by the cobalt reduction. It was found that with increasing content of sodium hydroxide in the sodium borohydride solution, the cobalt reduction efficiency increased. The reduction of 1 mole of cobalt ions required 2.4 moles of sodium borohydride for the sodium borohydride solution without sodium hydroxide, 1.8-1.95 moles for the solution with 0.05 M sodium borohydride solution, 1.5-1.60 moles for the solution with 0.125 M sodium hydrooxide and 1.0-1.1 moles for the solution with 0.25 M sodium hydroxide. When more basic sodium borohydride solutions (0.50 and 0.75 M sodium hydroxide) were tried it was found that the reduction efficiency increased, but some cobalt was precipitated in the form of cobalt hydroxide. So the best reduction efficiency without the precipitation of cobalt hydroxide is about one mole of sodium borohydride to reduce one mole of cobalt ions.

If the reaction solution pH is controlled at 4, the maximum reduction efficiency is about 81 % for a10-minute addition time and further addition of sodium borohydride added did not increase the extent of reduction. This means that the rate of redissolution of cobalt metal was equal to the rate of the reduction.

The reduction efficiency of cobalt increases with increasing pH. At pH 2 almost no cobalt was reduced. At pH 6, 96 % of cobalt was reduced if two moles of sodium borohydride were used to reduce one mole of cobalt ions. If the pH was controlled at a low value, the reduction efficiency increased with increasing rate of cobalt addition. For example, at pH 4, 2 moles of sodium borohydride can reduce 0.614. mole of cobalt for a 10-minute addition time, 0.633 mole for 5 minutes, 0.743 for 2 minutes and 0.771 for 1 minute. The shorter addition time can reduce the amount of cobalt redissloved but increases the hydrolysis of sodium borohydride. Overall it has a positive effect.

The reduction efficiency decreased with increasing temperature above 35 $^{\circ}$ C. For example, at pH 4 the reduction efficiency decreased from 61.4% at 35 $^{\circ}$ C to 7 % at 75 $^{\circ}$ C for a 10-minute addition time.

X-ray diffraction was used to identify the precipitates, but only a broad peak was obtained near the main peak for Co_2B . After the precipitate was heat-treated for two hours, the X-ray diffraction pattern showed the peaks of Co_2B and a weaker main peak of cobalt, suggesting that the precipitate consisted of Co_2B and Co. Transmission electron microscopy was also used, but failed to identify the fresh precipitate. After two hours of heat-treatment at 500 $^{\circ}C$, the single crystal transmission pattern obtained was consistent with that for Co_2B .

The atom ratio of cobalt to boron in the precipitate increased with increasing temperature which is consistent with the tendency of borohydride hydrolysis to increase with increasing temperature.

The reduction of cobalt ions is completed within several minutes. The reaction process can be divided into three stages. During the first stage as sodium borohydride solution is added to the solution, the pH rises quickly and little cobalt is reduced. Because of the buffering effect of cobalt sulphate the pH did not go very high. In the second stage, cobalt is reduced and the reaction is autocatalyzed by the reduced cobalt. The pH decreases and the main reaction is cobalt reduction. In the third stage after the reduction of most of the cobalt, the hydrolysis of borohydride, which also catalyzed by the reduced cobalt, becomes the main reaction and the pH rises rapidly. The initial pH of the solution has some effect on the reaction rate of cobalt reduction. A high pH decreased the rate of cobalt reduction. The reaction time of cobalt reduction decreased with increasing temperature from 24 seconds at 5 0 C to less than 2 seconds at 35 0 C. Cobalt reduction was strongly catalyzed by reduced cobalt.

Attempts were made to use sodium borohydride to remove cobalt from zinc sulphate solution, but it was found that zinc ions had a dramatic inhibitory effect on cobalt reduction. Several tens of μ mol/l of zinc ions lead to no cobalt reduction. The main cause of inhibition is likely that zinc ions compete for borohydride ions with the cobalt ions. Zinc borohydride forms and hydrolyzes rapidly producing zinc ions which react again with borohydride. Zinc ions may catalyze the hydrolysis of borohydride. Zinc ions also had an inhibitory effect on nickel and lead reduction.

6. RECOMMENDATIONS

Cobalt reduction with borohydride is very complicated with its stoichiometry depending on the reaction conditions and the procedures. This research has shown that the reaction stoichiometry and the precipitate composition are mainly dependent on pH and temperature. So far different reaction mechanisms have been proposed in the literature to account for the results such as the effects of pH, the solution composition, the rate of the addition of borohydride, the amount of the hydrogen gas evolved and the mol ratio of borohydride to cobalt ion. A reasonable reaction mechanism has not been developed to explain the results because the reaction is too fast and intermediate products are difficult to detect.

Further studies should focus on the mechanism of cobalt reduction with borohydride by investigating the intermediate products at lower temperatures, e.g. 0 ^oC where the reaction rates are slower. Measuring the amount of hydrogen evolved and hydrogen adsorbed on the cobalt particles might be used to explain the present results and control the compositions and properties of the precipitate.

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APPENDIX 1 Joint Committee Powder Diffraction (JCPDS) Card of a Randomly Oriented Cobalt (Cubic)

5-806	JCPDS-ICDI) Copyright (c) 1991	Quality: *				
Co					d A	Int. ++-	h k 1
Cobalt					2.0467 1.7723 1.2532 1.0688	100 40 25 30	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
Rad: CoKal Cutoff: Ref: Natl. Bur.	Lambda: 1. Int: Diffr Stand. (U.	.78897 Filt. ractometer I/Icc S.) Monogr. 25, 25	er: Fe d-s or: 10 (1965)		1.0233	12	222
Sys: Cubic a: 3.5447 A: Ref: Ibid.	b: B:	S.G.: Fm3m (225) c: C:	A: Z: 4	С: mp:			
Dx: 8.789 D	a:	SS/FOM: F5=224(.0	04,5)		4 1 5 7		
ea: Ref:	nv8:	еу:	Sign: 2V:		- 1 1 1 1		
Color: Dark gra Pattern at 25 C cobalt oxalate 1.0Z each of Ni Ed., p. 272. C 58.93. Volume[y . CAS no.: in H2 for 1 and Sb; ar u type. Tu CD]: 44.54.	7440-48-4. Sample 10 minutes at 300 C. nd 0.01 to 0.1% each ingsten used as inte	was prepared at NBS Spectroscopic analy of Al and Fe. Merck rnal standard. PSC:	by heating sis: 0.1 to Index, 8th cF4. Hvt:			

Strong lines: 2.05/X 1.77/4 1.07/3 1.25/3 1.02/1 0.00/1 0.00/1 0.00/1

129

APPENDIX 2 Joint Committee Powder Diffraction (JCPDS) Card of a Randomly Oriented Co₂B (tetragonal)

			uua:				
o B					d A	Int. ++-	h k 1
z Cobalt Boride					: 3.55 2.51 2.113 1.983	6 18 30 100	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Rad: Cu Lambda: 1.54056 Filter: Ni d-sp: Cutoff: Int: Diffractometer I/Icor: Ref: Havinga, Philips Research Lab., Eindhoven, Netherlands, Private Communication, (1973)					1.815 1.775 1.616 1.588	7 3 13 15	1 1 2 2 2 0 2 0 2 3 1 0
ys: Tetragonal : 5.015	b:	S.G.: I4/mcm (1) c: 4.22	40) 0 A:	C: .8415	1.357		2 2 2 3 1 2
Ref: Havinga et al., J. Less-Common Met., 27 169 (1972) Dx: 8.053 Dm: SS/FDM: F22=17(.045.29)					1.254 1.192 1.183	2 20 7	$\begin{array}{ccccccc} 4 & 0 & 0 \\ 2 & 1 & 3 \\ 3 & 3 & 0 \\ 4 & 1 & 1 \end{array}$
 a: ef:	nv8:	ey:	Sign:	`2V:	1.079	3	
12Cu type. PS	C: t112.	To replace 3-878.	Mvt: 128.68. V	'olume[CD]: 106.13.	1.032 0.9727 0.9202 0.9095	11 3 12 9	3 3 2 2 0 4 4 1 3 5 2 1
					0.9068 0.8915	1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
					1 7 7 8 8		

ι

Strong lines: 1.98/X 2.11/3 1.19/2 2.51/2 1.17/2 1.59/2 1.62/1 0.92/1

APPENDIX 3 Joint Committee Powder Diffraction (JCPDS) Card of a Randomly Oriented B (rhombohedral)

12-377	JCPDS-ICDD Copyri	pht (c) 1991	Qualit	y:					
: ; ; 8						d A	 Int. ++	h k 1	
Boron						4.25 4.07 3.544 2.545	45 100 20 70	$\begin{array}{cccc} 0 & 0 & 3 \\ 1 & 0 & 1 \\ 0 & 1 & 2 \\ 1 & 0 & 4 \\ 1 & 1 & 0 \end{array}$	
Rad: CuKa lambda: 1.5418 Filter: Ni d-sp: Cutoff: Int: Diffractometer I/Icor: Ref: Decker, Kasper, Acta Crystallogr., 12 503 (1959)						2.180 2.132 2.113 2.113 2.029	4	0 1 5 1 1 3 0 2 1	
Sys: Rhombohed a: 4.908 A: Ref: Ibid.	ral (Hex) S.G.: b: B: Dm: 2 460 SS/FON	R-3∉ (166) c: 12.567 C:	A: Z: 36	C: 2.56 mp:	05	1.666 1.634 1.603 1.482	4 8 8 8 8	1 0 7 2 0 5 2 1 1 0 1 8	5 5 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
ea: Ref:	n#B: 6	y:	Sign: 2 ⁴	V:	·	1.424 1.403 1.376 1.359		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 5 6 6 7 1
CAS no.: 7440-4 Boron. Low ter cell: a=4.908, Plus 16 reflec	42-8. Single-crysta mperature form. hkl c=12.567. Rhombohe tions to 0.778. Nwt	l data taken. indices based dral cell: a=5. : 10.81. Volum	Referred to on triply pr 057, alpha=50 me[CD]: 262.10	as alpha-rhom imitive hexag 8.06. PSC: h 6.	bo. Jonal R12.	1.346 1.268 1.230 1.199 1.178 1.161 1.125	15 12 2 4b (2 4b (2 (2) (2)	3 0 3 2 0 8 2 2 0 2 1 7 2 2 3 3 1 2 1 2 8	
d A ; Int.	 h k 1		Int.:	 h k l	I d A	: Int.:	 b k	1 ;	
1.105 2 1.081 <2	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.996 0.987 0.944 0.932 0.922	4 (2 2 15 (2	3 0 9 1 3 7 3 1 8 3 2 4 2 2 9	0.913 0.909 0.906 0.880	<pre></pre>	4 0 2 3 4 1 0 2	7 5 3 13	

Strong lines: 4.07/X 2.55/7 2.11/6 4.25/5 3.54/2 1.44/2 1.35/2 0.93/2

APPENDIX 4 Procedure for Colorimetric Cobalt Analysis

The colorimetric cobalt analysis is based on the complexation of cobalt with Nitroso-R-salt $(C_{10}H_4(OH)(SO_3Na)_2NO)$. Cobalt and Nitroso-R salt form a soluble coloured cobalt complex, whose intensity was measured colorimetrically with a Bausch and Lomb Spectronic 20. spectrophotometer. By comparing the measured intensity with those of known standards, the cobalt concentration was determined.

COLORIMETRIC METHOD:

- 1. Pipet 2 ml of sample into a clean, dry 125-ml flask.
- 2. Add 20 ml of distilled water.
- 3. Add 5 ml of Nitroso-R-salt solution.
- 4. Boil 1.5 minutes.
- 5. Add 1ml potassium bromate solution to oxidize and destroy uncomplexed nitroso-R salt.
- 6. Boil 1 minute.
- 7. Add 1 ml of concentrated nitric acid to destroy other organic complexes other cobalt.
- 8. Cool solution.
- 9. Transfer solution to test tube.
- 10. Measure intensity of the colour with colorimeter at 520 nm wavelength.
- 11. Compare intensity with intensity of standards.

PREPARATION OF STANDARDS:

Standards and Nitroso-R-salt solution were made up every day, because the colour of cobalt Nitroso-R-salt complex deteriorates with time.

Nitroso-R-salt: 0.5%.

Dissolve 0.5 g salt in 100 ml distilled water.
Potassium Bromate solution: 3 wt.% Dissolve 3.0 g salt in 100 ml distilled water.

Blank

Distilled water.

Standards

5, 15, 30 ppm cobalt as cobalt sulphate in zinc sulphate solution. The standards were prepared in the same manner as the sample. The relationship between the intensity of the standards and the cobalt concentration was linear and consistent.