

THE CONTROL OF MANGANESE IN ACIDIC LEACH LIQUORS, WITH SPECIAL EMPHASIS TO LATERITE LEACH LIQUORS

C.J. FERRON — SGS

TABLE OF CONTENTS

1. ABSTRACT	1
2. INTRODUCTION	1
3. REVIEW OF OPTIONS TO CONTROL MANGANESE IN ACIDIC LIQUORS	2
3.1. Selective Sulphide Precipitation	2
3.2. Selective Alkaline Precipitation	3
3.3. Electro Oxidation of Manganese	5
3.4. Solvent Extraction Separation of Manganese From Cu, Zn, Ni and Co	5
4. CASE STUDIES	6
4.1. The Copper-Manganese Separation	6
4.2. The Zinc-Manganese Separation	7
4.3. The Cobalt-Manganese Separation	9
5. MANGANESE CONTROL IN LATERITE LEACH LIQUORS	13
5.1. Commercial Operations	13
5.2. Upcoming Projects	14
5.3. New Processes Tested to Treat Laterite Liquors	16
6. CONCLUSIONS	18
7. REFERENCES	19
8. APPENDICES	22

1. ABSTRACT

Manganese is commonly found in acidic leach liquors of copper, zinc, cobalt and nickel, and its control is one of the challenges facing the metallurgist who has to minimise operating costs and maintain product quality.

Techniques at the disposal of the metallurgist to effect the control of manganese are numerous but the most practised are alkali precipitation, sulphide precipitation, electrolytic oxidation and solvent extraction. Practical examples are presented of Cu-Mn, Zn-Mn and Co-Mn separations from various acidic leach liquors; the focus is placed on the use of SO_2/O_2 mixtures as selective oxidant to oxidise/precipitate manganese from zinc and cobalt leach solutions.

The same technique, with some modifications, can be applied to laterite leach liquors, and this leads to the possibility of improving the purification process presently practised or proposed for several laterite projects.

2. INTRODUCTION

Manganese is frequently found in nature associated with copper, zinc, nickel and cobalt. During the processing of these metallic ores, the separation of manganese from the other metals is normally not efficient, and, therefore, manganese eventually ends up together with the other metals in leach solutions from which pure metals or compounds have to be produced. The presence of manganese within the base metals acidic leach liquors, if not controlled properly, can lead to additional operating costs

or even to contamination of the final product.

This paper aims at reviewing the current status of the manganese control strategies in acidic liquors of copper, zinc, cobalt and nickel, as they are commercially practiced, or discusses processes which have been proposed to improve current manganese control practices. In particular, a new process, developed by Lakefield Research, and based on the selective oxidation/precipitation of manganese using SO_2/O_2 , has been proposed and tested

numerous times on acidic liquors containing zinc and cobalt. Special emphasis is placed on the treatment of laterite leach liquors where manganese is frequently found in quantities exceeding cobalt, and here also selective oxidation/precipitation of Mn using SO_2/O_2 is shown to be successful.



REVIEW OF OPTIONS TO CONTROL MANGANESE IN ACIDIC LIQUORS

The separation of manganese from base metals of Cu, Ni, Co, Zn is not easy, and procedures that can be envisaged vary considerably, depending on the relative amounts of metals to separate, and the metal to separate the manganese from.

From the start, one could think of removing the manganese and leaving the metal in solution, or leaving the manganese in solution and removing the metal. Normally, one should try to remove the element present in lesser amounts, but that cannot be always done. In addition, the selection of a process will also depend on what is the intended fate of the manganese separated (discard, recycle, sell) and the metal from which it is separated from.

In the next few pages, we will review some of the techniques that can be considered for separating metals from solutions, with special attention being paid to manganese, copper, zinc, cobalt and nickel.

The next chapter will deal in more details with processes used for the separations of Cu- Mn, Zn-Mn and Co-Mn.

3.1. SELECTIVE SULPHIDE PRECIPITATION

The principles underlying sulphide precipitation are well known (1,2).

The main reactions can be written as:



Examination of the equations show that the sulphide precipitation reaction is thermodynamically favoured at decreasing acidity (higher pH) and higher H₂S partial pressure.

Obviously, besides these thermodynamic considerations, one has also to consider kinetic factors. Table 1 presents a list of the solubility products of the most common metal sulphides (at 25°C), from published data (3,4).

Table 1: Solubility Products of Selected Sulphides

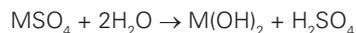
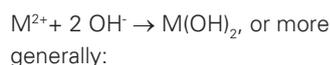
METAL SULPHIDES	K _{sp} (25°C)
Bi ₂ S ₃	1 x 10 ⁻⁹⁷
CdS	7.8 x 10 ⁻²⁷
Cu ₂ S	2 x 10 ⁻⁴⁷
CuS	9 x 10 ⁻³⁶
PbS	8 x 10 ⁻²⁸
MnS	4.8 x 10 ⁻¹⁶
CoS	5.4 x 10 ⁻²²
HgS	4 x 10 ⁻⁵³
NiS	3 x 10 ⁻¹⁹
Ag ₂ S	2 x 10 ⁻⁴⁹
ZnS	1 x 10 ⁻²¹

The values of the solubility product allow us to distinguish very insoluble sulphides (i.e. Bi₂S₃) vs. more soluble sulphides (i.e. MnS). The table indicates the thermodynamic potential of selective precipitation of some sulphides (i.e. Zn, Ni, Cu, Co) vs. others (MnS).

A better idea of the process is provided by presenting the data as shown in Figure 1, that also provides the effect of pH on sulphide precipitation.

3.2. SELECTIVE ALKALINE PRECIPITATION

The removal of metals from solution by hydroxide precipitation can be described by the reaction:



The solubility products of most common hydroxides are presented in Table 2.

Table 2: Solubility Products at 25°C of Common Metal Hydroxides (3,4)

METAL HYDROXIDE	K _{sp} (25°C)
Al(OH) ₃	2 x 10 ⁻³²
Bi(OOH)	4 x 10 ⁻¹⁰
Cd(OH) ₂	5.9 x 10 ⁻¹⁵
Ca(OH) ₂	5.5 x 10 ⁻⁶
Cr(OH) ₂	1.0 x 10 ⁻¹⁷
Cr(OH) ₃	6 x 10 ⁻³¹
Co(OH) ₂	2 x 10 ⁻¹⁶
Co(OH) ₃	1 x 10 ⁻⁴³
Cu(OH) ₂	3.7 x 10 ⁻⁴⁷
Fe(OH) ₂	8 x 10 ⁻¹⁶
Fe(OH) ₃	4 x 10 ⁻³⁸
Mg(OH) ₂	1.2 x 10 ⁻¹¹
Mn(OH) ₂	1.9 x 10 ⁻¹³
Ni(OH) ₂	6.5 x 10 ⁻¹⁸
Zn(OH) ₂	1.2 x 10 ⁻¹⁷

The table indicates a large solubility difference between some hydroxides (i.e. Cu(OH)₂, Co(OH)₃) relatively insoluble, and more soluble hydroxides (i.e. Ni(OH)₂). From a thermodynamic point of view, there is little difference between the solubility of the hydroxides of cobalt (II), zinc, nickel (II), and manganese (II).

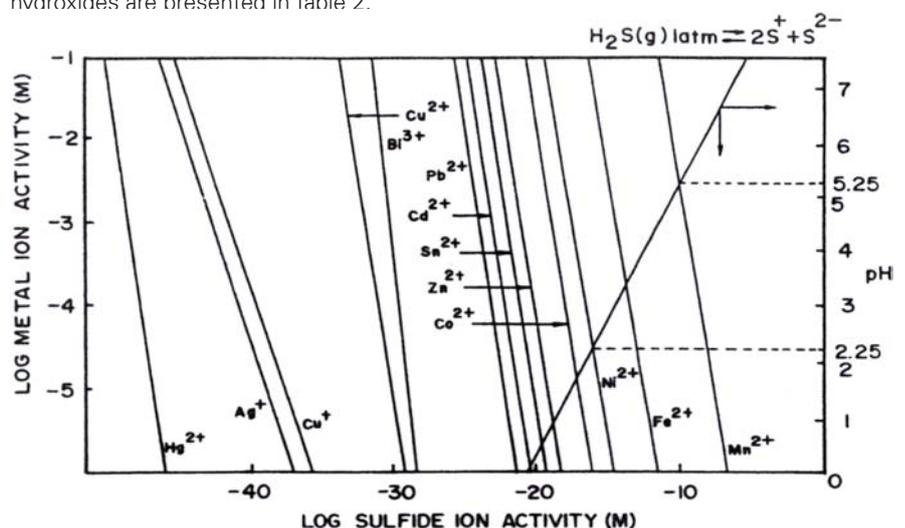


Figure 1: Precipitation of Metal Sulphides (25°C) (Ref. 1)

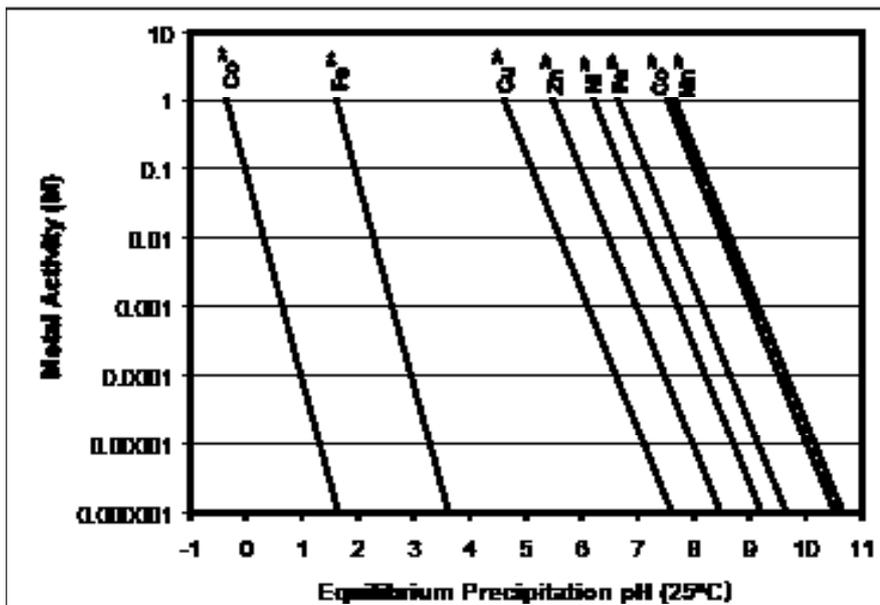


Figure 2: Metal Hydroxides Formation at 25°C

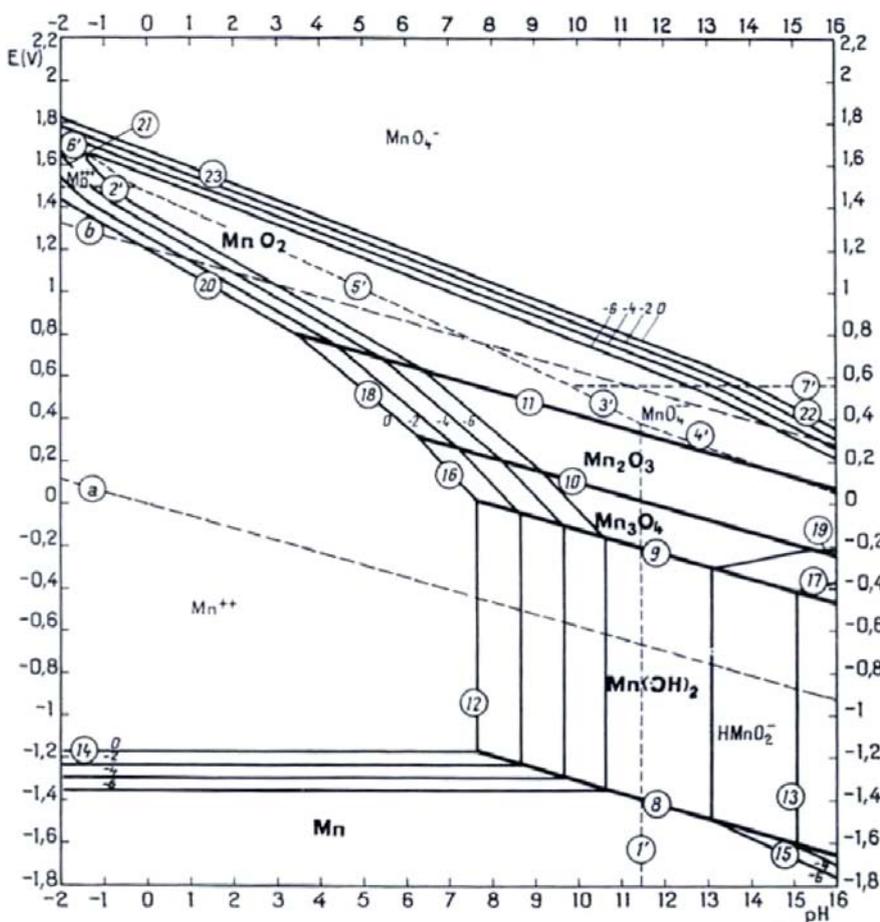


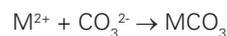
Figure 3: Pourbaix Diagram of Mn at 25°C

As indicated in the reaction shown above, pH has a significant effect on hydroxide formation. This effect is better represented as in Figure 2, using data from (5).

Figure 4 confirms the ease of precipitating hydroxides of Cu and Al selectively from the group of zinc, nickel, cobalt and manganese, but the separation between these latter will be difficult.

The Eh-pH diagram (Pourbaix diagram) of manganese at 25°C is presented in Figure 3. Those of Cu, Fe, Zn, Ni and Co are appended.

Similar reactions can be written for carbonate precipitation:



Various bases are available to raise the pH of the metal solution and complex the anion (SO_4^{2-} or Cl^-). Typical bases are $Ca(OH)_2$, $Mg(OH)_2$, $NaOH$ for hydroxide precipitation and $CaCO_3$, $MgCO_3$, Na_2CO_3 for carbonate precipitation.

The choice will depend on costs, availability, the fate of the metal sulphate by-product (Na_2SO_4 , $CaSO_4$, $MgSO_4$) and the downstream processing of the metal hydroxide.

A severe complication of alkaline precipitation is that the reactions shown above are oversimplifications, and in fact, mixed precipitates (hydroxide-sulphate, hydroxidecarbonate) are usually formed.

A closer look at the Eh - pH diagrams indicates that the higher oxidation states of manganese undergo hydrolysis at lower values of the pH; precipitation selectivity certainly exists (at least from a thermodynamics point of view at 25°C) between zinc and manganese and also likely between manganese and nickel, the window of selectivity being larger for the higher valency states.

From a thermodynamic point of view, the oxidation of Mn^{2+} to Mn^{4+} at 25°C and unit activity requires high potential, ranging from 0.8 and 1.2 V (SHE) when pH varies from ~3.5 to 0. As a comparison, under the same conditions (25°C, unit activity of iron ions), the potential required to oxidise Fe^{2+} to Fe^{3+} ranges from 0.75 to 0.05V when pH varies from ~6.5 to 0. Strong oxidants are therefore required to oxidise Mn^{2+} , and oxidants such as ozone, Caro's acid and hypochlorite have all been proven efficient, as will be discussed later.

The use of these oxidants presents a few problems

- these reagents are quite expensive.
- some introduce a foreign ion (Cl⁻) that is normally undesirable
- these oxidants are so strong that they also oxidise nickel and cobalt and, therefore, the selectivity is not excellent.

Another oxidant has been proposed in recent years by SGS Lakefield to selectively oxidize/precipitate Mn from various acidic leach solutions: these are SO₂/O₂ mixtures.

The oxidizing power of SO₂/O₂ mixtures (under certain conditions) was discovered in the 1920's by the USBM when working on the system Fe²⁺/Fe³⁺/H₂SO₄ (6). Most of the subsequent work on the SO₂/O₂ system was dedicated to oxidize ferrous (7,8,9,10,11,12), but also other ions (13,14,15), and the only known commercial application of the SO₂/O₂ process to date is the Inco's process for cyanide destruction.

SGS Lakefield's contribution to the study of the SO₂/O₂ system initiated in the late 1980's, and in 1991, the following rate expression was proposed for ferrous oxidation (16):

$$\frac{dFe^{2+}}{dt} = k \exp [-E/RT] \frac{[SO_2]^a [SO_3]^{1-b}}{[H_2SO_4]^c}$$

for % SO₂ between 0 and 5% vol and with E, a,b, and c respectively of 6.65 kJ/mole, 2.1, 1.1 and 2.5.

The use of SO₂/O₂ mixtures to oxidize ferrous solutions (sulphates or chlorides) has been applied at Lakefield on various projects and was piloted three times. Also tested were SO₂/O₂ mixtures to oxidize thiosalts, arsenic (III) and manganese.

Typical results for ferrous sulphate oxidation using SO₂/O₂ mixtures are illustrated in Figure 4.

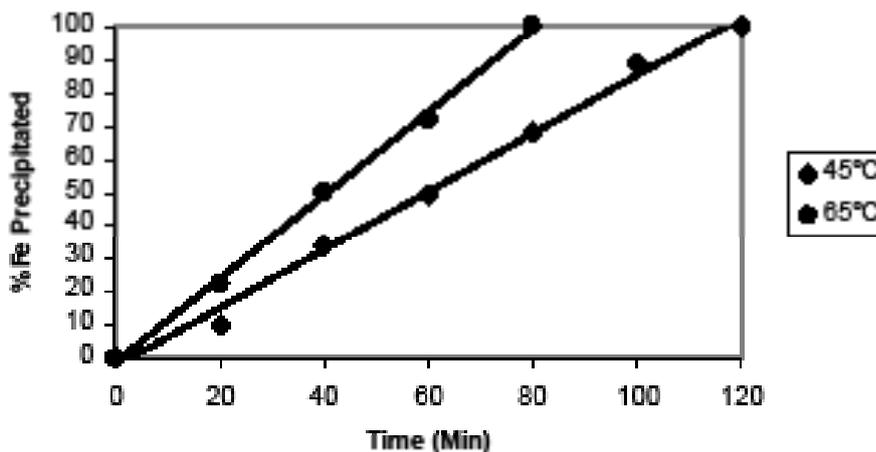


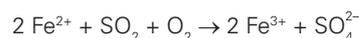
Figure 4: Oxidation/Precipitation of Ferrous Sulphate using SO₂/O₂ Mixtures.

Specific oxido-precipitation rates are typically 5-10 g Fe²⁺/L/hr, and, under some conditions, can be pushed towards ~40 g Fe²⁺/L/hr (17).

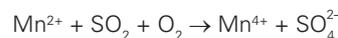
The use of SO₂/O₂ mixtures had been briefly mentioned in the past for the oxidation of manganese (II) but for neutral or near-neutral solutions under conditions not conducive to selective precipitation from nickel (18). It had still to be demonstrated that these mixtures of SO₂/O₂ could selectively oxidize/precipitate manganese under more acidic conditions. Initial work was started on leach solutions from a Central African commercial plant in 1994; these studies culminated in 1996-1997 with the complete laboratory development of a process for the removal of Mn from Co solutions, followed by a pilot plant demonstration. Since then, work has continued on the use of SO₂/O₂ mixtures

for the removal of Mn from zinc sulphate solutions, and from laterite leach solutions.

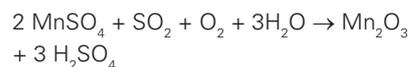
In the case of iron, the reaction involving SO₂/O₂ has been shown to be:



By similarity, it is suggested that the oxidation of Mn²⁺ occurs as per one of the following reactions:



and, at higher pH's:



Typical results of Mn oxidation/precipitation, using oxygen or SO₂/O₂ mixtures, are presented in Figure 5.

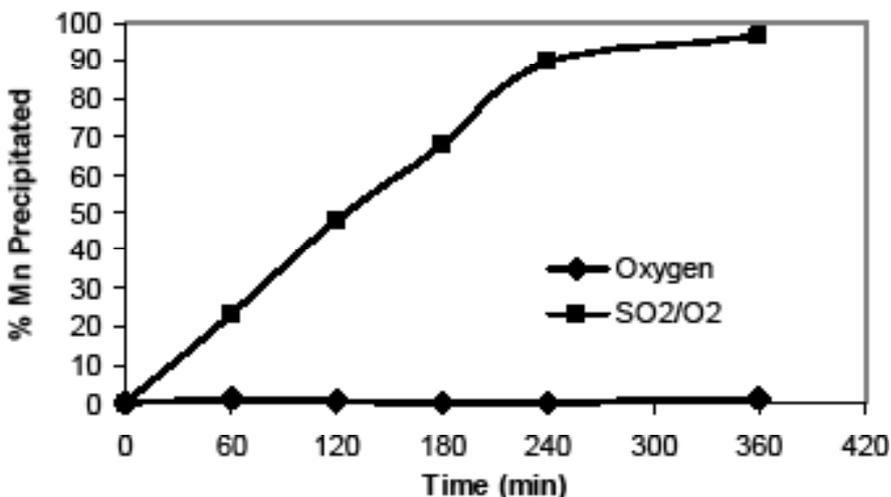


Figure 5: Oxido-Precipitation of Mn with O₂ and with SO₂/O₂ pH = 4.0. 2 L/min Oxygen in both cases. Temperature = 80°C. 2% SO₂ in mixture.

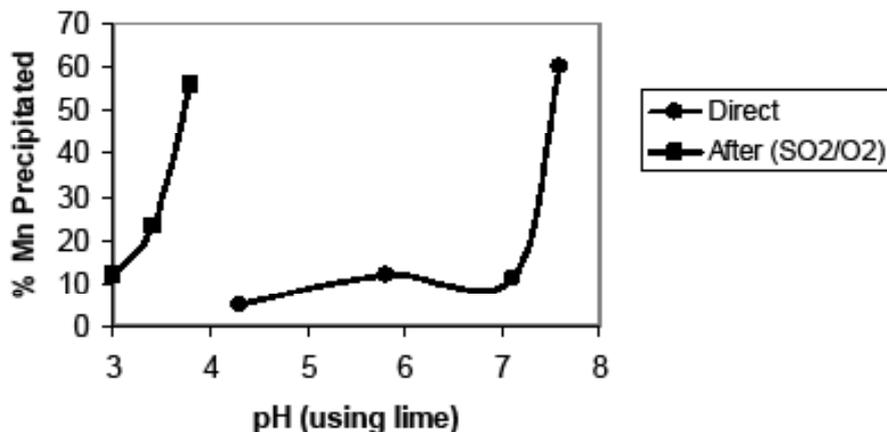


Figure 6: Lime Precipitation of Mn Directly or after Oxidation with SO₂/O₂

Results clearly indicate the SO₂/O₂ mixture is a much better oxidant than oxygen alone.

The effect of pH when using SO₂/O₂ mixtures for the Mn oxidation and hydrolysis is indicated in Figure 6.

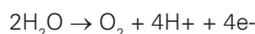
3.3. ELECTRO OXIDATION OF MANGANESE

The electrolytic oxidation of manganous ion Mn²⁺ to MnO₂ is well known, and the production of electrolytic manganese dioxide (EMD) is commercially practiced, both from sulphate or from chloride electrolytes.

The oxidation of manganese follows the reaction:



The standard potential for that reaction is 1.23V, nearly identical to the standard potential for the water decomposition reaction (oxygen evolution reaction), which is the typical anodic reaction for most electrowinning processes:



Therefore, both reactions will normally occur together to a certain extent which will depend on concentration in solutions, anodic material, temperature, acidity, ...

In the case of EMD, other factors are also critical to the marketability of the MnO₂ produced; in particular, the MnO₂ must be of the γ variety to be used in dry cells. Also, anodic current efficiency has to be maximized, while maintaining product specification. These constraints

do not necessarily apply to processes removing manganese as an impurity.

3.4. SOLVENT EXTRACTION SEPARATION OF MANGANESE FROM Cu, Zn, Ni AND Co

As we all know, solvent extraction is an extremely powerful process to separate metals from solution. Its application is now general for acidic copper liquors; it is very popular to process acidic liquors of cobalt and nickel, and it starts gaining acceptance for acidic zinc liquors.

In the case of acidic copper liquors, manganese is normally not co-extracted to the best of our knowledge. Table 3 presents data for the metal extractions of a typical copper extractant.

Table 3: Relative Extraction Power of LIX 84-I for Metals at pH 2.0 (Ref 19)

METAL	RELATIVE EXTRACTION POWER
Cu(II)	Very strongly extracted
Fe(III)	Slightly extracted
Mo(VI)	Somewhat strongly extracted*
V(V)	Slightly extracted*
Zn(II)	Nil
Sn(II)	Nil
Ca(II)	Nil
Mg(II)	Nil
As(III)	Nil
Al(III)	Nil
Fe(II)	Nil
Si(IV)	Nil
Co(II)	Nil
Ni(II)	Nil

Typical pH isotherms for the same copper extractant is presented in Figure 7.

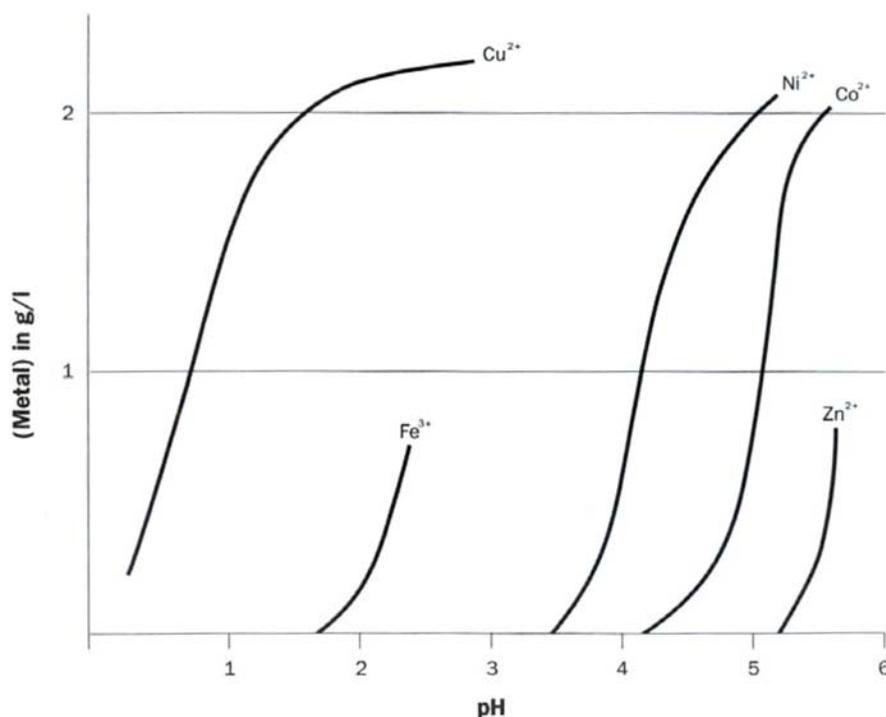


Figure 7: Typical pH isotherms for LIX 84-I (Ref 19)

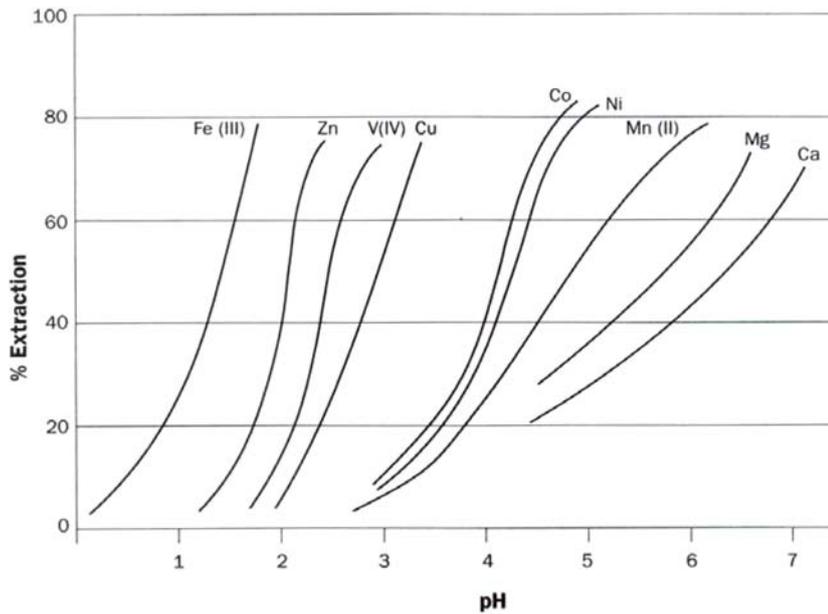


Figure 8: Extraction of Metals from Sulphate Solutions using D2EHPA (Ref 19)

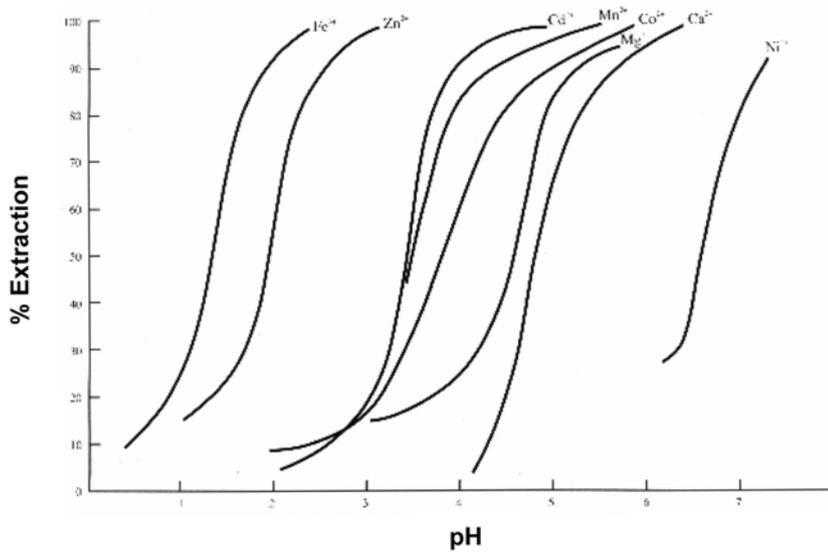


Figure 9: pH Isotherms for Cyanex 272 (Ref 20)

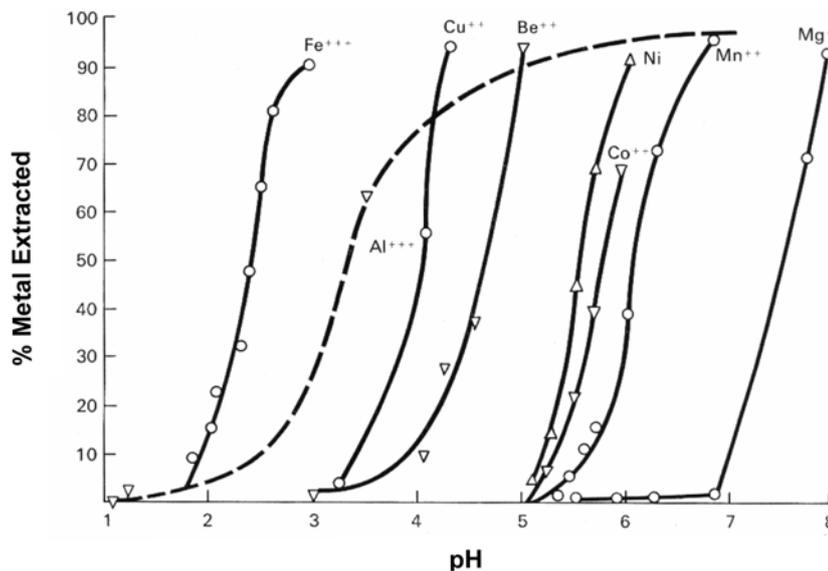


Figure 10: pH isotherms for Versatic 10

Even if we assume Mn^{2+} is extracted by LIX 84-I similarly to Ni, Co, Zn, it would likely occur at a much higher pH than copper and therefore, would not interfere with copper extraction.

One of the solvent extractants commercially used for zinc extraction is di-2-ethylhexyl phosphoric acid (DEHPA).

Typical pH isotherms of the most common metals extracted with DEHPA are presented in Figure 8.

It appears that the selectivity of zinc extraction versus manganese is good, and the selectivity between Co, Ni and Mn is probably sufficient, but will depend on other factors (relative concentrations).

The extractant most commonly used to solvent extract cobalt from acidic leach liquors is Cytec's Cyanex 272.

Standard pH isotherms for the extraction of major metals of interest by Cyanex 272 are presented in Figure 9.

It can be seen clearly that the selectivity of Cyanex 272 between Mn and Co is not sufficient.

Carboxylic acids, in particular Versatic 10, have been used to extract nickel from acidic/neutral liquors. Typical pH isotherms for the main metals of interest are presented in Figure 10.

Using Versatic 10, nickel is extracted just before manganese, but the window of selectivity might not be sufficient.

4. CASE STUDIES

The following chapter reviews the application of the manganese separation processes described previously to specific cases. Whenever possible, examples of commercial application are reviewed, as well as proposed procedures.

4.1. THE COPPER-MANGANESE SEPARATION

The occurrence of manganese in copper leach circuits is not rare, and it could cause operating problems. Significant amounts of manganese are present in the Gecamines (DRC, ex-Zaire)

copper electrowinning circuits, and in Girilambone (Australia), for example.

Manganese could originate from Cu-Mn Wads and Cu-Co-Mn Wads, and other manganiferous minerals that undergo some solubilization under Cu leach conditions.

The presence of manganese could have noticeable effects on the operation of the plant:

- the manganese does not plate with copper, but it could be physically entrapped into the copper deposit and contaminate the Cu cathode if the Mn level in solution is too high (LME Grade A copper specification is 1 g/t Mn).
- the manganese gets plated at the anode, forming a MnO₂ layer; this layer could peel off and some MnO₂ flakes could be incorporated within the cathode, contaminating it. The other potential problem with MnO₂ coating the anode arises for plants planning to use reactive inert anodes (i.e. DSA anodes) to replace conventional lead anodes (21): in that case, the reactive anode being coated with MnO₂ behaves like a MnO₂ anode, therefore negating some of the energy savings advantages of the reactive anodes.

The manganese in solution is also partially converted to permanganate at the anode, and if the spent electrolyte is used as stripping solution in a conventional Cu solvent extraction circuit, severe degradation of the organic extractant will occur (22). This is the situation at Girilambone, where the spent electrolyte Eh is measured and controlled to less than 750 mV (NHE). The control mechanism in that plant is to maintain a Fe²⁺/Mn ratio of at least 10 (23). The possibility also exists to reduce the permanganate prior to SX.

In the case of plants not using SX and where Mn build up would jeopardise cathode quality (i.e. Gecamines, for example), the Mn is controlled through the circuit bleed (24,25), as illustrated in Figure 11.

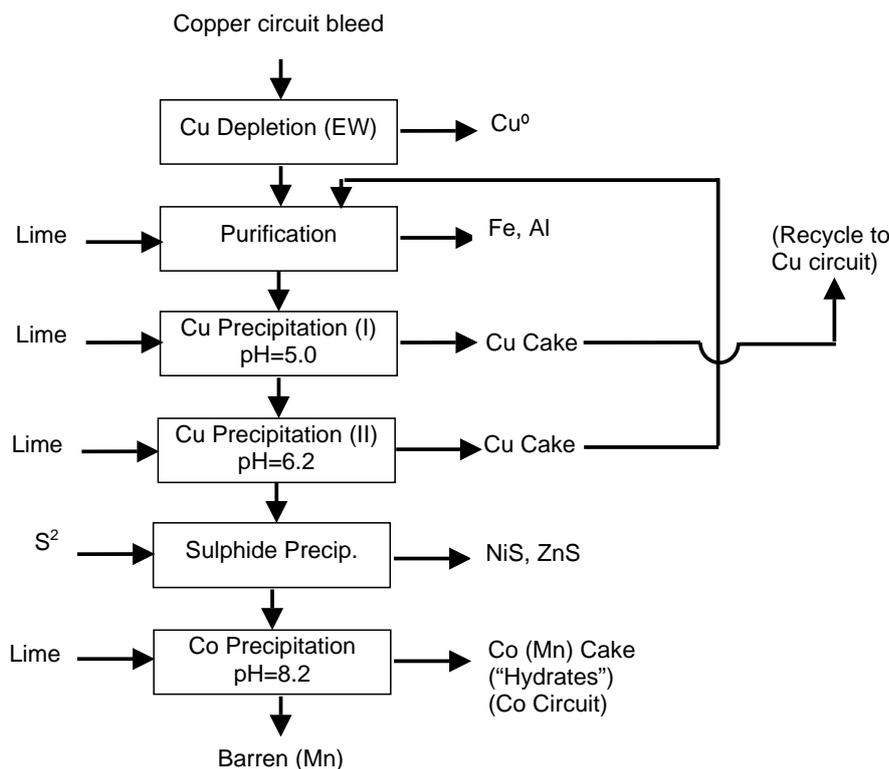


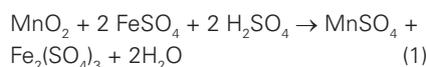
Figure 11: Manganese Control in the Copper Bleed Treatment

Copper from the bleed is recovered, first by EW down to a certain concentration, and then by stage lime precipitation where care is taken to let most of the manganese exit the copper circuit via the cobalt cake and the final barren.

4.2. THE ZINC-MANGANESE SEPARATION

Zinc and manganese are commonly associated in commercial sulphate electrolytes. The association of zinc and manganese in sulphide concentrates is not uncommon, and the typical example is that of the Gamsberg deposit in South Africa (26). The Zn/Mn association in oxidic minerals (for example franklinite [(Zn, Mn)O.Fe₂O₃] (27) or in recycled products (28) (Leclenche batteries, EAF dusts,...) is also frequent.

In addition, typical practice calls for adding MnO₂ to oxidise ferrous prior to jarosite precipitation:



The manganese sulphate follows the zinc sulphate to the cell house; part of the manganese is then re-oxidised back to MnO₂ at the anode, and accumulates at the bottom of the cell to be periodically

removed and recycled to the ferrous oxidation stage.

Most commercial plants operate with 5 - 6 g/L Mn in the electrolyte to protect lead anodes from corrosion and insure the quality of the electrowon zinc.

Steady-state levels of Mn in the electrolyte are normally easily maintained, except when substantial amounts are introduced to the system via the calcine.

In those cases, excess manganese must be removed from the system.

Dimensionally stable anodes (DSA) prepared by coating a titanium blank with a precious metals mixture (Pt-Ir, Ir,...) have been proposed and investigated as a replacement of lead anodes for the electrowinning of copper, cobalt, zinc. In the particular case of zinc electrowinning from sulphate solutions, it has been shown that the manganese present in the electrolyte would coat the DSA anode and increase the overpotential for oxygen evolution, negating therefore one of the main advantages of these anodes.

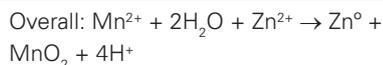
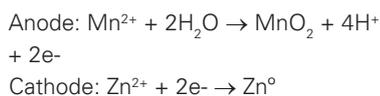
Various options have been considered to accommodate high manganese zinc solutions.

4.2.1. CO-RECOVERY OF MnO_2 AND ZINC METAL

The possibility of replacing the oxygen evolution reaction, which has high overvoltage, by a more favourable anodic reaction has always attracted researchers, since it would lead to substantial energy savings.

Methanol oxidation (zinc electrolysis), and ferrous oxidation (copper electrolysis) have been proposed in the past (21), and the latter is still being investigated.

In the case of high manganese zinc sulphate solutions, researchers have proposed (29,30,31) a process by which manganese oxidation replaces the oxygen evolution reaction at the anode, and produces MnO_2 (EMD) for sales, while the cathodic reaction remains the zinc reduction.



Conditions favouring the electrodeposition of MnO_2 are diametrically opposite to those for zinc metal. MnO_2 deposition is favoured at high temperatures (>90°C), low anodic current densities (<100 A/m²), relatively low acid concentrations (~0.2M), and high manganese concentrations.

The deposition of zinc, on the other hand, is favoured by lower temperatures (<40°C), higher current densities, higher acid concentrations (~0.5M) and low manganese concentrations.

The overpotential for the MnO_2 deposition has been measured to be

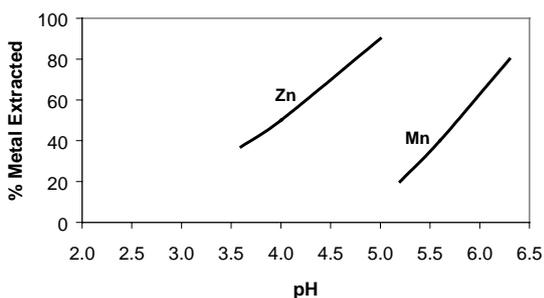


Figure 12: Extraction pH isotherms of Mn and Zn using Cyanex 272. Mn, Zn = 0.01M; 5% TBP in Kerosene; Cyanex 272 (Na form): 0.03 M (Ref.)

very small, and therefore the cell voltage is significantly lower (2.3 - 2.7 V at 90°C, 300 A/m² cathodic current) as compared to traditional zinc plants (3.43 V at 526 A/m²).

The system requires the use of an anode material that will promote manganese dioxide deposition, and the material proposed by the researchers is graphite.

4.2.2. ELECTROLYTIC REMOVAL OF MN AS MnO_2 ANODIC SLUDGE

The Argentinian zinc producer Sulfacid (Rosario) has been operating for years a process by which manganese well in excess of the typical 5-6 g/L is removed as a MnO_2 anodic sludge in a sacrificial cell, and this allows the rest of the plant to operate normally (32). This process has been retained by Anglo American for the treatment of the Gamsberg concentrate (33).

4.2.3. SEPARATION OF MN AND ZN BY SOLVENT EXTRACTION

The extraction pH isotherms of Mn and Zn using some common extractants have been shown in a previous chapter. Examination of the published data indicates that both metals are easily extracted in the acidic range but usually zinc is extracted at lower pH's than manganese (34). Typical example is presented in Figure 12 for the use of Cyanex 272 to separate Mn from Zn.

Such results are indicative of a process suitable to remove traces of zinc from a manganese solution, but not to purify a zinc electrolyte. However, solvent extraction of Zn from other impurities, including manganese, using Cyanex 272, has been demonstrated to produce SHG zinc metal (35).

4.2.4. SEPARATION OF MN AND ZN BY SULPHIDE PRECIPITATION

The equilibrium lines for selective sulphide precipitation have been presented earlier. Here too, data indicate that zinc sulphide can be precipitated selectively from manganese sulphate solutions at lower pH's and with low partial pressure of H_2S .

Published data confirmed that zinc (and other impurities such as Cu...) are indeed removed by sulphide precipitation from

manganese solutions (36) and from a manganese electrolytic plant in South Africa.

4.2.5. SEPARATION OF MN AND ZN BY OXIDATION/PRECIPITATION

If one considers the Eh-pH diagrams of zinc and manganese, one finds that it would be difficult, from a thermodynamic point of view, to separate Mn and Zn by simple hydrolysis, when starting from the plus 2 oxidation states Mn^{2+} and Zn^{2+} . In fact, zinc hydroxide will precipitate first. The same occurs when using sodium carbonate to precipitate zinc and manganese instead of lime. Typical results are presented in Figure 13, where a solution containing 5 g/L Mn (as $MnSO_4$) and 50 g/L Zn (as $ZnSO_4$) were contacted at 70°C with various amounts of sodium carbonate.

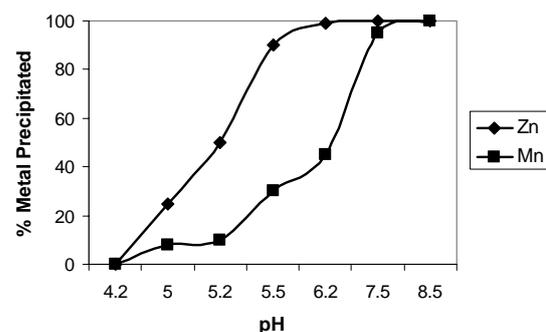


Figure 13: Precipitation of Mn, Zn using Na_2CO_3

That procedure can only be used to remove zinc impurity from a Mn solution.

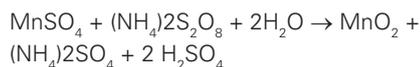
Fortunately, zinc has only one oxidation state while manganese can be oxidized to the 3rd and 4th oxidation states, and, when oxidized, manganese can be precipitated as Mn_3O_4 (mixture of oxidation state +2 and +3), Mn_2O_3 (oxidation state +3) and MnO_2 (oxidation state +4). Examination of the Pourbaix diagrams of zinc and manganese indicates that under oxidizing conditions, manganese can thermodynamically be precipitated while zinc remains in solution.

There are several oxidants capable of oxidizing manganous ion into insoluble manganese dioxide, the choice depending mainly on economic factors and the undesirability of introducing deleterious elements into the zinc sulphate solution.

Examples are provided of oxidants recommended for manganese oxidation and removal from zinc solutions.

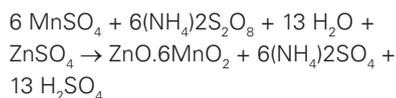
a. Newmont process (37)

A patent was awarded in 1976 to Newmont Exploration Limited for a process using ammonium persulphate to separate Mn from Zn, as per the reaction:



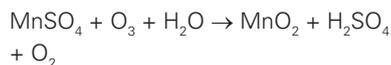
The hydrolysis was conducted at a pH of approximately 5.3.

According to the patent, care must be taken not to overdose the persulphate, to avoid coprecipitation (and therefore losses) of zinc as per the reaction:



b. Sherritt process (38):

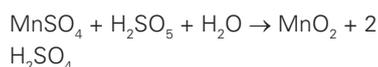
Another patent was awarded to Sherritt Gordon Mines Limited in 1979 for a process using ozone to separate Mn from Zn, as per the reaction:



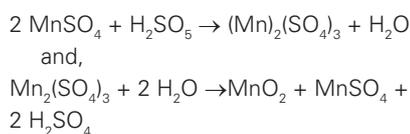
The reaction can be effected on spent electrolyte as well as on a slightly acidic solution.

c. Imperial college (39):

Researchers described a process that uses peroxymonosulphuric acid (Caro's acid) to separate Mn from Zn, as per the overall reaction:



The authors indicated that the reaction proceeded in two steps, i.e.:



which combine to the overall reaction above. The use of Caro's acid to separate Mn from Zn solutions had been patented

by Hudson Bay Mining in 1957 (40), and by Vieille Montagne in 1978 (41).

d. Lakefield's SO₂/O₂ process:

Based on the experience acquired with the SO₂/O₂ system for the oxidation of iron and manganese in cobalt solutions, the process was expanded to oxidise/precipitate Mn from Zn solutions, and at the present time, the process has been tested on 3 different projects, including the Gamsberg project.

Typical manganese precipitation tests from a representative zinc solution are presented in Figure 14.

The oxido-precipitation appears linear (within the range tested). The specific rate of Mn removal (= slope of the line) depends on the acidity level (pH), as indicated in Figure 15.

These results are consistent with the effect of acid on the kinetics of ferrous oxidation using SO₂/O₂ mixtures. Higher pH's result in increased co-precipitation of zinc due to local spikes in pH, and therefore it is suggested to include a step of acid washing the manganese precipitate, if the water balance in the circuit allows it: under those conditions, at pH = 4.5 and precipitate repulping at pH = 2.5, zinc losses were minimum (<0.1% Zn).

4.3. THE COBALT-MANGANESE SEPARATION

Cobalt and manganese are frequently associated in nature.

In Central Africa, Democratic Republic of Congo (ex Zaire), cobalt is found primarily as carrollite (CuCO₂S₄) in the sulphide zones, and as heterogenite (CoOOH) in the oxide zone, together with a weathered compound named cobalt wad, a soft manganese oxide of low density. The cobalt oxide rich layer, named BOMZ (Black Ore Mineralized Zone) is characterized by its black MnO₂ component.

Another famous Co-Mn association is that represented by ocean manganese nodules, which contain significant amounts of cobalt. Similar land manganese "nodules" are also known, in Australia for example (42).

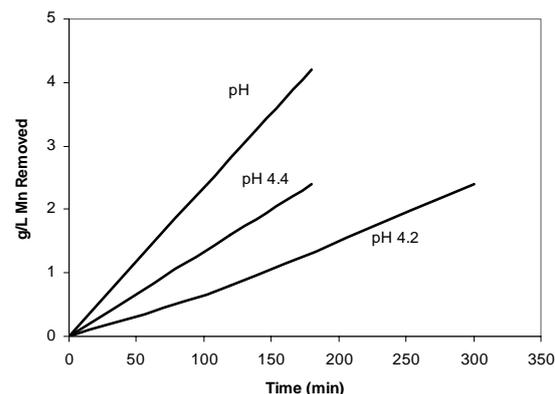


Figure 14: Manganese Oxido-Precipitation Tests using SO₂/Air (0.4% Vol SO₂). 60°C; 150 g/L Zn, 7.8 g/L Mn. Effect of pH (lime)

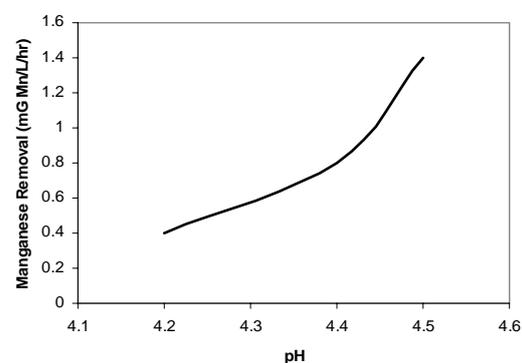


Figure 15: Effect of Acidity on the Kinetics of Mn Oxido-Precipitation from a Zinc Electrolyte

The limonitic laterites have been touted in recent years as a major source of nickel. The cobalt component of these laterites are normally associated with manganese (43), as indicated in Figure 16.

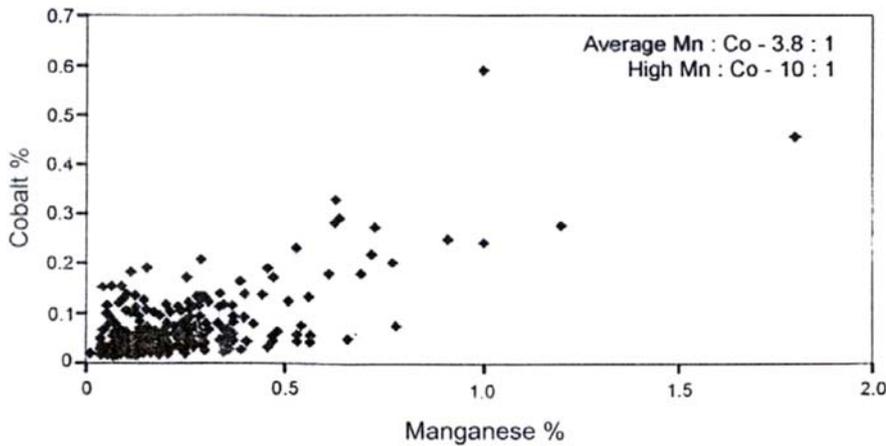


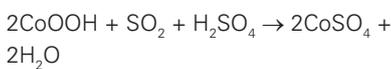
Figure 16: Correlation Between Co and Mn in Bulong Laterite

Specific Co-Mn mineral identified (44,45,46,47) in these laterites is asbolan $(Co, Ni)_{1-y}(MnO_2)_{2-x}(OH)_{2-2y-2x}$ (48).

Studies of the Ramu project asbolan composition indicated that the limonitic variety contained up to 8.4% Co and 5.2% Ni, while the saprolitic variety contained up to 5.6% Co and 15.1% Ni.

Work by Inco indicated that the asbolite contained up to 12% Ni and 9% Co. At Weda Bay, the asbolan also displayed a variable composition and was present as two varieties, a nickeliferous and a cobaltiferous, and could assay up to 11.8% Co and 6.7% Ni.

Because of that mineralogical association, cobalt dissolution will require manganese dissolution. Under atmospheric conditions, the recovery of cobalt normally requires the use of a reductant, for example SO_2 (49), and the reaction will proceed as per the reaction:



Under those conditions, manganese dioxide will also be reduced, as indicated

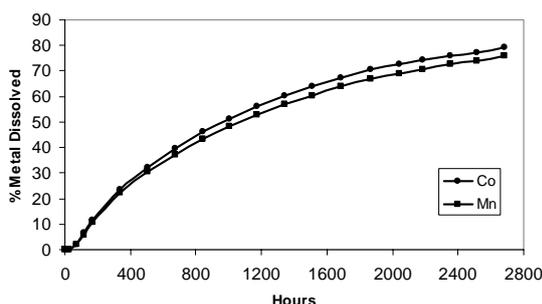


Figure 17: Kinetics of Cobalt and Manganese Dissolution. Room Temperature. pH=1.5, with SO_2 : 0.55% Co, 2.96% Mn

in Figure 17 comparing the kinetics of dissolution of manganese and cobalt when column leaching a West African upgraded laterite at 90°C.

Due to the mineral constituents containing both cobalt and manganese, cobalt and manganese are frequently together in acidic liquors, and, therefore, cobalt-manganese has always been an issue for the cobalt metallurgist.

4.3.1. HYDROXIDE PRECIPITATION

Until recently, Gecamines and ZCCM were by far the major producers of cobalt in the world.

At Gecamines, cobalt is recovered from the copper circuit bleed as hydrates (24,25), which are repulped (re-leached) before going to electrowinning. A certain selectivity vs. Mn is obtained at Gecamines because during hydrates precipitation, cobalt precipitation is carried out at a pH allowing for some selectivity. This is also made possible due to the fact that the Co/Mn ratio in solution is much higher than what would be expected from processing oxide ores only, since the leach circuit at Gecamines also processes calcined Cu-Co sulphide concentrates where the Co/Mn ratio is much higher. This process would not work as efficiently on other feed samples (i.e. laterites), where the Co/Mn ratio is lower.

At Gecamines older cobalt plant (Shituru), the cobalt hydrates were leached in pulp in the electrowinning cells to maintain pH at a value of 7.0 and cobalt concentration at 25 g/L (50, 51). Cobalt cathodes were only 95% Co and

800-1500 g/t Mn; the cathodes were fire refined to 99% Co, and the Mn content reduced to 50 g/t.

At the newer cobalt plant (Luilu), the purified cobalt solution was treated with lime to pH=8.2 to precipitate the cobalt hydrates. These were re-leached with spent cobalt electrolyte at a pH of 6.5, and the rich electrolyte assayed about 45 g/L Co and 4 g/L Mn. The final cathode assayed 99.95% Co.

At the Chambishi cobalt plant, the purified Co solution prior to hydroxide precipitation at pH = 8.5 assays 7 g/L Co and 0.3 g/L Mn. After re-dissolution of the hydrates at a pH of 5.8 - 6.4 (87% cobalt redissolved), the rich electrolyte assays 30-40 g/L Co, 2 g/L Mn.

Typical hydroxide precipitation curves for Co-Mn sulphate solutions are presented in Figure 18 where it can be seen that the cobalt precipitation occurs at slightly lower pH's than manganese precipitation. Similar results are obtained when using sodium carbonate as a precipitant, as illustrated in Figure 19. These results are consistent with the data presented in a previous chapter.

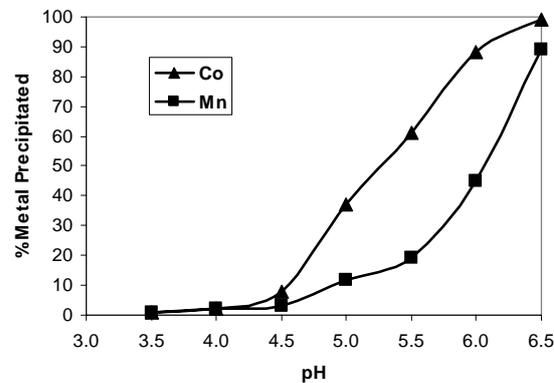


Figure 18: pH Hydrolysis Curves for Co, Mn at 85°C using Lime. Co: 7 g/L; Mn: 0.6 g/L

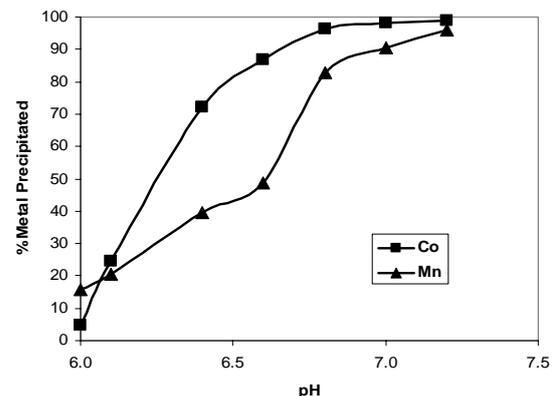


Figure 19: pH Hydrolysis Curves for Co, Mn at 65°C using Sodium Carbonate. Co: 7.8 g/L; Mn: 0.7 g/L

4.3.2. SULPHIDE PRECIPITATION

As indicated in the data presented in an earlier chapter, sulphide precipitation should offer a window of selectivity between cobalt and manganese.

Selective precipitation of cobalt sulphide away from manganese liquors is more suited to high Mn low cobalt solutions, such as Mn leach solutions for the production of electrolytic manganese metal, and leach solutions from processing sea nodules. In the case of high cobalt, low manganese solutions, that procedure does not always make sense.

This selectivity was confirmed on two leach solutions.

The first leach solution was generated during a reductive acid (H₂SO₄) leach of a West African Co-Mn ore. The results of atmospheric batch sulphide precipitation tests are presented in Figure 20.

The sulphide precipitate, from a solution with a Co/Mn ratio of 0.2, assayed 20% Co and 1.1% Mn (Co/Mn = 18).

The second leach solution was the result of an hydrochloric leach of a cobalt manganese catalyst. The cobalt and manganese were separated in a two-stage process, as shown in Figure 21.

The selectivity achieved during that precipitation is best exemplified in Figure 22, where the pulp potential was monitored throughout Na₂S additions. During CoS precipitation, a potential plateau is observed at around 110 mV (Ag/AgCl); as soon as the Co is precipitated, the potential drops to about -40 mV (Ag/AgCl), where a new plateau corresponding to MnS precipitation starts to be observed. This good correlation between Co precipitation and pulp potential opens the door to an easy control strategy.

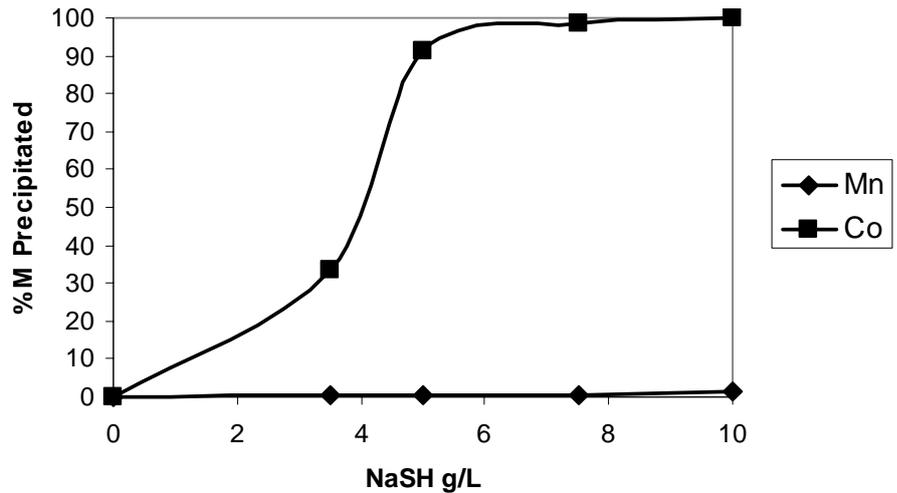


Figure 20: Selective Cobalt Sulphide Precipitation. Feed Solution: 0.4 g/L Co, 2 g/L Mn

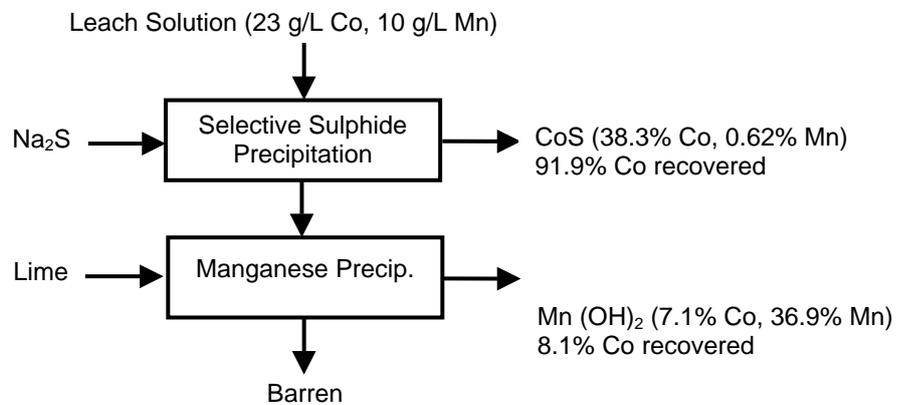


Figure 21: Selective Cobalt Sulphide Precipitation from a Chloride Leach Solution

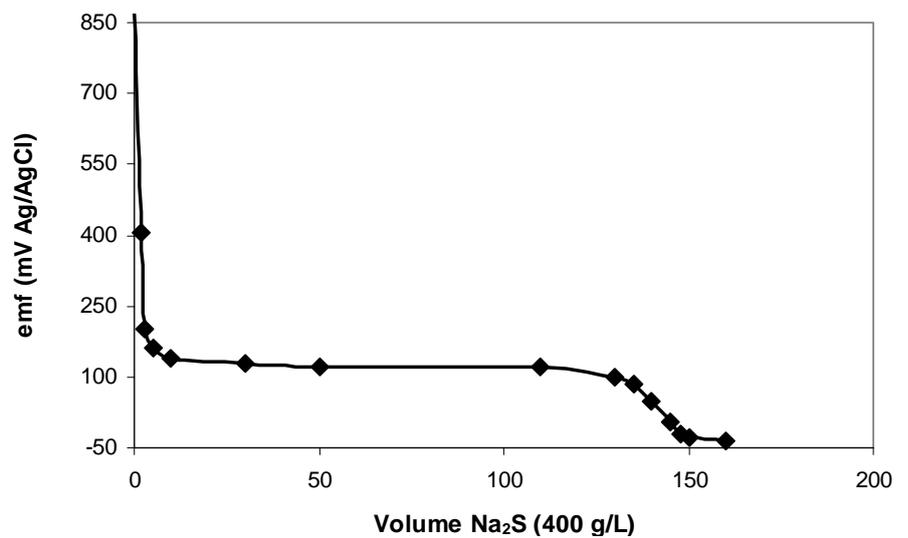


Figure 22: Selective Cobalt Sulphide Precipitation - Emf Variation

4.3.3. CO-MN SEPARATION BY SOLVENT EXTRACTION

Data shown in previous chapters and published data indicate that the selectivity between Mn and Co is difficult to achieve with Cyanex 272. In fact, Cytec recommends removing Mn prior to cobalt SX with Cyanex 272 (52).

However, a few other extractants have been proposed to effect such separation.

DEHPA

Data presented in a previous chapter hinted to a possible separation of Mn from Co using DEHPA. Recent work at the AJ Parker CRC for Hydrometallurgy confirmed these theoretical data (53). Some of their results are summarized in Table 4 below.

Table 4: Manganese/Cobalt Separation Factors; Ni: 3 g/L, Mn: 2 g/L; Co: 0.3 g/L. Temp: 23°C

A/O	β Mn/Co	
	pH = 3.0	pH = 3.5
1:2	119.3	116.4
1:1	133.4	128.8
2:1	132.9	147.0
5:1	93.9	98.4
10:1	340.6	90.4

Data indicated also that the Mn/Co separation factor was normally lower at higher temperatures. These results obtained on solutions of composition similar to that of a laterite leach liquor are promising.

Other results, in particular of a continuous mixer-settler trial (54), confirmed the separation was possible: from a synthetic feed solution assaying 4 g/L Mn and 2.2 g/L Co (no other elements) and 4 extraction stages at pH = 4.2, all manganese was extracted very selectively from cobalt.

DS 6001

The development reagent DS 6001 is based on a tetra - substituted dithiophosphoramidate structure (55).

This experimental reagent, developed by Zeneca, indicated that cobalt could be extracted selectively from manganese. pH isotherms produced by Zeneca are presented in Figure 23.

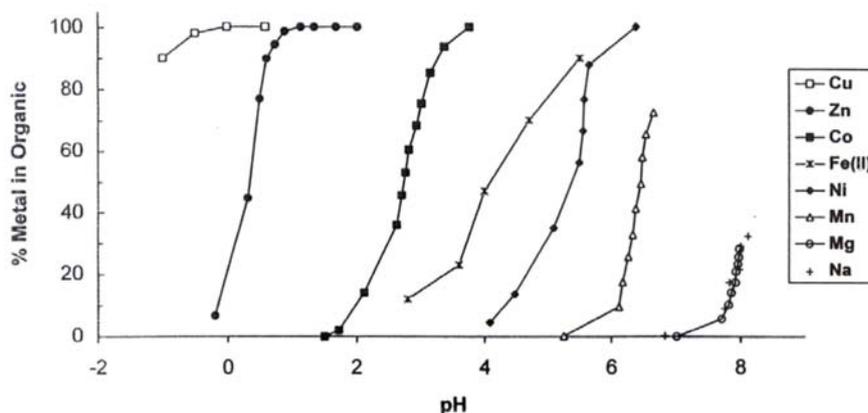


Figure 23: pH Isotherms for Zeneca Development Reagent DS 6001. (From Ref. 55)

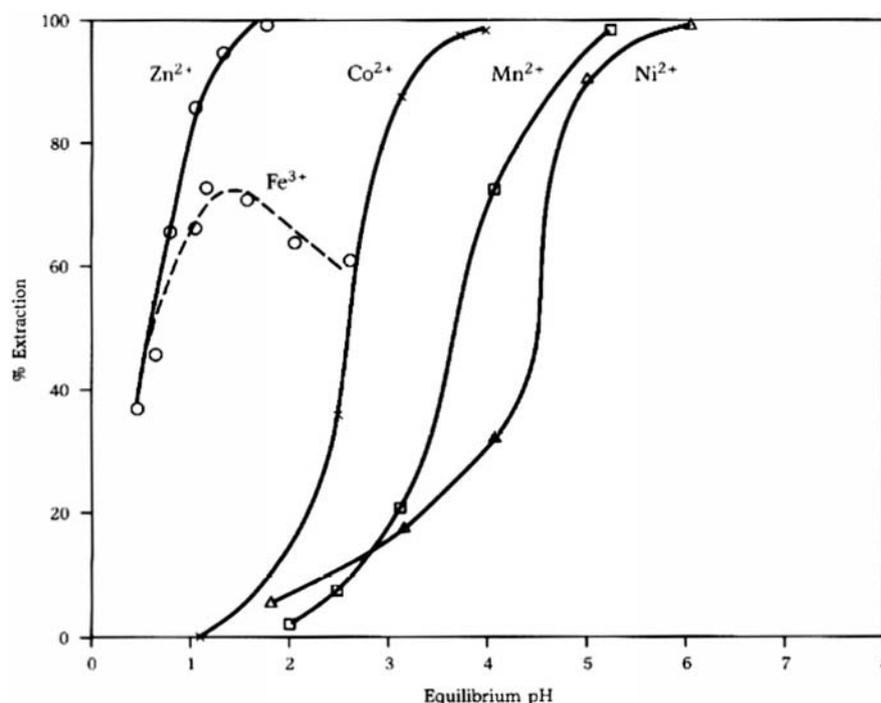


Figure 24: pH Isotherm for Cytec Cyanex 302

There appears to be about a 4 pH units difference between the isotherms for Co and Mn and this should allow a good separation between the 2 metals. These results were confirmed by other research institutions (56).

Unfortunately, the study of this promising extractant was terminated due to instability problems.

Cyanex 302

Cyanex 302, a monothiophosphinic acid commercialized by Cytec, displays a good selectivity window between Co and Mn, as illustrated in Figure 24 (57): Cobalt can be extracted below pH = 3.0, while manganese is extracted above pH = 4.0. These data are interesting but there could be issues with the reagent

stability. In addition, cobalt stripping will require high acidity, incompatible with an EW circuit.

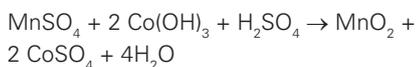
Mintek process

While working on a Co tailing sample from the DRC, Mintek developed a solvent extraction process to remove Mn from cobalt sulphate solutions assaying ~2.9 g/L Co and ~1 g/L Mn (58). The process was piloted during 440 hours and average Mn extraction was 75-80% in 3 extraction stages, leaving 0.2-0.3 g/L Mn in the raffinate. No detail was given on the type of extractant used. Typical composition of the cobalt EW feed was still 22 g/L Mn, and, therefore, an average of 12.8% of the total Mn was still removed as an anodic sludge, assaying from 55.3-57.5% Mn, 1.7 - 2.1% Co (~0.17% overall cobalt lost).

4.3.4. SELECTIVE MN OXIDATION/PRECIPITATION (59)

Sumitomo Process (Niihama Cobalt refinery).

Sumitomo Metal Mining Ltd. (SMM) purified the leach solution generated while processing mixed sulphide precipitates from the Marinduque Surigao Nickel Refinery, and the manganese sulphate impurity was oxidized/precipitated using cobaltic hydroxide. The cobaltic hydroxide was produced by blowing chlorine gas through the cobalt anolyte. The oxidation/precipitation of manganese with cobaltic can be described by the reaction:

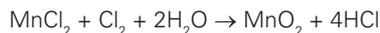


Similar reaction can be written for nickelic Ni(OH)₃ to remove Mn from nickel sulphate solutions.

Métaux Spéciaux S.A. (Pechiney Group) (Pomblière plant) (60)

This French cobalt producer used to process cobalt arsenides from Morocco (Bou-Azzer) after calcination in Marseille.

The leach solution was hydrochloric acid, and manganese was removed from spent electrolyte by oxidation/precipitation, using chlorine as oxidant, as per the reaction:



Lakefield SO₂/O₂ Process

Based on the experience acquired in the late 1980's on the use of SO₂/O₂ mixtures to oxidize/precipitate iron, the process was applied to the selective oxidation/precipitation of Mn from cobalt sulphate solutions. The development culminated in 1997 in a pilot plant demonstration (60 L/hour) that confirmed the technical feasibility of the process.

Pilot plant manganese removal test results are illustrated in Figure 25: the cobalt leach solution, after iron purification, was contacted with SO₂/Air at 60°C, and, in less than 2 hours, >95% of the manganese had been removed, leaving a solution with less than 10 mg/L Mn to be fed to solvent extraction.

As soon as the mixture was sparged through the solution, the manganese started to precipitate, and in 2 hours, more than 95% was precipitated out.

A few additional points were observed:

- kinetics of manganese removal were lower than those of iron
- kinetics of manganese removal was improved with higher pH; this is similar to iron removal
- in mixed iron-manganese systems, iron was oxidised first (at a potential of ~650 mV (Ag/AgCl) and when all iron has been removed, manganese was oxidised at a potential of 1000-1200 mV (Ag/AgCl).
- The system proved to be quite selective versus cobalt, and cobalt losses in the manganese precipitate were less than 0.5%. As a comparison, using stronger oxidants such as persulphate, cobalt losses of 25% have been cited in the literature (61), from a solution assaying ~1.4 g/L Mn and 0.9 g/L Co.

5. MANGANESE CONTROL IN LATERITE LEACH LIQUORS

The cobalt-manganese association in laterites is well documented, as shown as an example in Figure 16 where the correlation Co/Mn is clearly visible for the Bulong laterite project.

Presently, four commercial plants are processing limonitic laterites using the pressure acid leach (PAL) process. These are Moa Bay, Murrin Murrin, Cawse and Bulong. Different processes are used to recover cobalt and nickel from the autoclave liquors, and, therefore, these plants have various means of controlling the manganese. The manganese control procedure will be reviewed first for the commercial plants and, then, for several other projects to be coming on stream in the near future.

5.1. COMMERCIAL OPERATIONS

5.1.1. MOA BAY (62,63)

Moa Bay in Cuba was the first commercial plant to use PAL to process limonitic Ni/Co laterites. The process involves the recovery of nickel and cobalt as an intermediate sulphide concentrate using H₂S precipitation; under those conditions, the selectivity of precipitation versus manganese is excellent and very little Mn, if any, appears to coprecipitate (See Table 6). The sulphide concentrate is shipped to Fort Saskatchewan, Canada, for further treatment.

5.1.2. MURRIN MURRIN (67,68,69)

The plant at Murrin Murrin also uses sulphide precipitation to recover nickel and cobalt in a mixed precipitate, that is reprocessed on site. Here too, selectivity versus manganese during precipitation is not an issue.

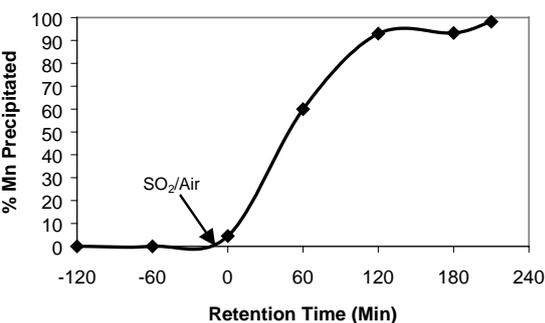


Figure 25: Pilot Plant Manganese Removal from Cobalt Leach Solution using SO₂/Air at 60°C

Table 5: Summary of Sulphide Precipitates Composition

SULPHIDE PRECIPIT.	FEED (g/L)			BARREN (g/L)			PRECIPITATE (%)			REF.
	Ni	Co	Mn	Ni	Co	Mn	Ni	Co	Mn	
Moa Bay	3.9-4.35	0.33-0.37	1.0-1.5	0.066	0.010	1.0-1.5	<50	<4.5	-	63
Amax	3.8	0.28	1.6	-	-	-	55.7	3.9	0.002	64
Ambatovy	3.04	0.30	1.98	-	-	-	HT:56.1	5.74	0.01	65
							LT:55.9	5.66	0.01	
Panda*	-	1.63	1.44	-	<0.05	1.34	-	45-48	0.38	66

*Not a laterite

ELEMENT	HYDROXIDE PRECIPITATE ASSAYS (%)							
	WEDA BAY	CAWSE	RNO	RAMU	SGS LAKEFIELD	HYDROMETALS		CESL
Precipitant	MgO	MgO	MgO	CaO	MgO	MgO	CaO	CaO
Ni	37-38	30	42.9	15.4	35.3	38	19	11
Co	1.35-1.45	8	1.47	1.4	5.8	1.4	0.8	1.1
Mg	3.5-4.5	-	2.7	0.4	-	4	0.7	0.6
Mn	2.4-2.5	12	3.03	3.2	4.11	2.5	2.1	8
SO ₄	-	-	9.17	-	-	-	-	-
Cl*	-	-	0.3-0.5	-	-	-	-	-
Fe	-	-	0.17	0.1	-	-	-	0.03
Zn	-	-	0.34	0.4	-	-	-	0.01
Reference	Alta 1998	Alta 1999	Alta 2001	Alta 1999	LR - Intern'l	Alta 1999		Alta 2001

Table 6: Summary of MHP Composition from Various Projects

5.1.3. CAWSE (67,70,71,72)

The plant at Cawse recovers nickel and cobalt as a mixed hydroxide precipitate (MHP) using magnesia MgO as a precipitant. As expected, the selectivity of precipitation is not great versus manganese (See Table 6).

Manganese co-precipitation is significant if high cobalt recoveries are desired. Ammonia re-leach is more selective versus manganese, and the ammonia re-leach solution assayed 15 g/L Ni, 3.7 g/L Co and 0.04 g/L Mn during the pilot plant trial, for a 90% Co re-leach recovery.

5.1.4. BULONG (67,43)

The plant at Bulong recovers Ni and Co from the autoclave leach liquor directly by SX, without going through

the precipitation of a mixed Ni/Co intermediate.

The simplified process is illustrated in Figure 26.

The manganese is first co-extracted with cobalt using Cyanex 272 (Cyanex 272 raffinate: <1 mg/L Co, Mn, 3 g/L Ni), and then is separated from the cobalt by sulphide precipitation (Target 99% Co precipitation, 0.5% Mn, Mg co-precipitation), and eventually, the (design) composition of the cobalt advance electrolyte is 50 g/L Co, 160 mg/L Ni, 530 mg/L Mg and 300 mg/L Mn. The process is technically sound but results in using an expensive reagent (Cyanex 272) to carry along impurities, in particular Mn and this results in a large

inventory of extractant. Published results indicate that more than 2/3 of the organic is used to load Mg + Mn (73).

5.2. UPCOMING PROJECTS

5.2.1. GORO PROJECT (74,75)

Published information by Inco on the process to be used for the Goro project (plant under construction and thoroughly demonstrated) points towards a radically new process to recover Ni/Co from the leach liquor. The process can be shown in a simplified form in Figure 27.

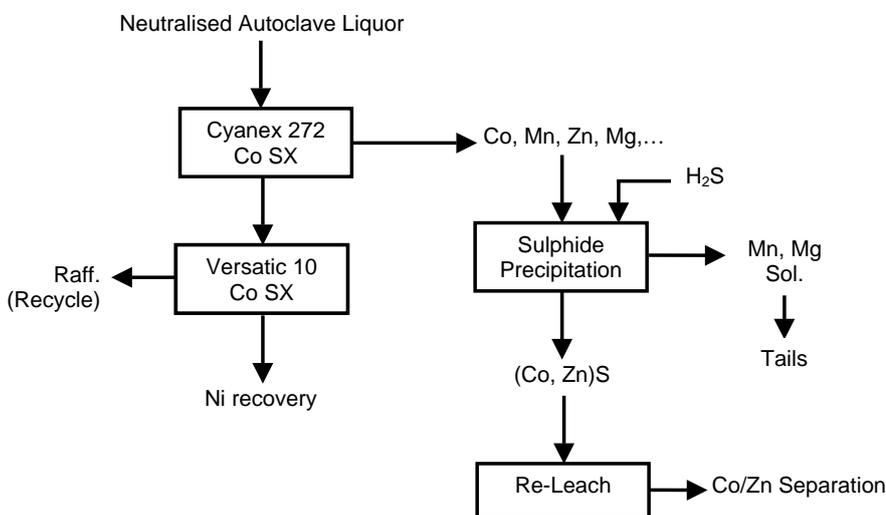


Figure 26: Manganese Behaviour During Treatment of Laterite Liquor at Bulong

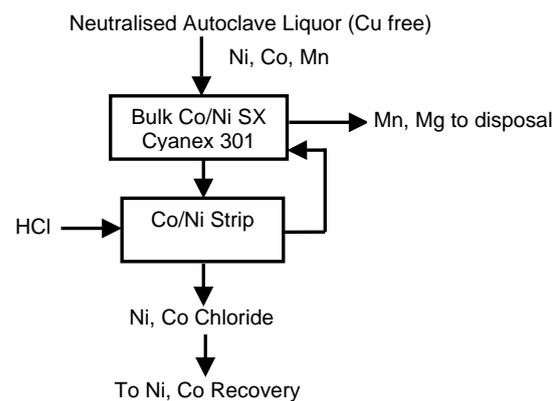


Figure 27: Mn Behaviour During the Treatment of Goro Laterite Project

Using Cytec 301, Ni + Co are directly separated from Mn (and Mg).

5.2.2. RAMU ISLAND (46)

The process developed by Highlands Pacific involves the production of a mixed hydroxide precipitate, using lime as precipitant. The process was piloted at Lakefield, and a two stage precipitation process, as illustrated in Figure 28, was demonstrated.

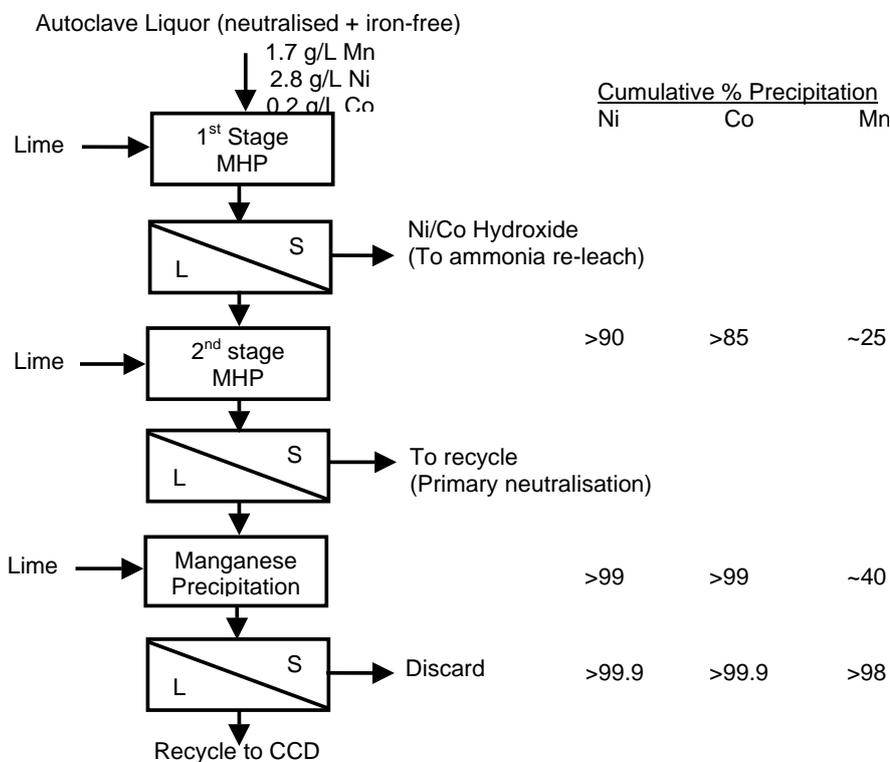


Figure 28: Two-Stage Hydroxide Precipitation for Manganese Control for the Ramu Project

The manganese in the MHP was only slightly dissolved during the ammoniacal re-leach circuit and final PLS assays ranged from 2 to 14 mg/L Mn in the feed to the Ni solvent extraction; in practice Mn dissolves at the beginning of the re-leach circuit, but is then oxidized to MnO₂ and precipitated throughout the circuit.

The residual manganese was removed during the Manganese Removal (MR) stage where the solution was aerated and maintained at pH ~9.0 using hydrated lime. The precipitate, containing the remainder of the Mn, Ni and Co was discarded, while the overflow was reused in the CCD circuit as wash water, with some being bled off for Mg control.

5.2.3. RAVENSTHORPE NICKEL OPERATIONS (RNO) (76)

The process developed by RNO to recover nickel and cobalt from the autoclave liquor is hydroxide precipitation using MgO. The process was thoroughly piloted at Lakefield, and a typical product analysis is shown in Table 7.

5.2.4. WEDA BAY (INDONESIA) (77, 78)

The Weda Bay laterite project in Indonesia is being developed and the final process has not been completely decided upon.

Table 7: Typical MHP Analysis (before caustic washing) for the RNO Project (Ref.)

ELEMENT	ANALYSES
Ni	4.29
Co	1.47
Mg	2.71
Fe	0.17
Si	1.05
Al	0.11
Mn	3.03
Zn	0.34
SO ₄	9.17

Published information indicated that the recovery of Ni, Co from PAL liquors was by MgO precipitation of a mixed precipitate MHP. Data indicated that the neutralised liquor (after iron removal) would assay 5.1 g/L Ni, 0.19 g/L Co, 1.08 g/L Mn and 34 g/L Mg. The precipitate analysis is shown in Table 6, with a Mn assay of 2.4-2.5%.

5.2.5. AMBATOVY PROJECT (MADAGASCAR) (65,79)

Phelps Dodge has been developing a laterite project in Ambatovy, East-Central Madagascar. The project has reached the pre-feasibility stage and has been piloted at Hazen Research in 1997 and 1998. The recovery of nickel and cobalt from autoclave liquors was investigated using sulfide precipitation, both at low and high temperatures.

As expected, the sulphide precipitation was very selective versus manganese, as indicated in Table 8 below

Table 8: Sulphide Precipitation Pilot Plant Results

PRODUCTS	ASSAYS								
	Ni	Co	Cu	Zn	Fe	Al	Mn	Mg	S
Feed Solution (g/L)	3.04	0.30	0.03	0.08	0.39	3.77	1.98	0.65	-
Sulphide Precipitation									
High Temp.	56.1	5.74	0.41	1.31	0.5	0.17	0.01	0.01	36.5
Low Temp.	55.9	5.66	0.48	1.47	0.24	0.05	0.01	0.01	36.6

5.2.6. THE CESL PROCESS (80)

The CESL process was initially developed to treat chalcopyrite concentrates, but was later expanded to treat laterites. In the laterite - CESL process, the partially neutralized liquor is purified in two stages, at pH = 3.5 to remove Al, Cr, Fe, and then at pH ~4.5-6.5 to remove Zn, Cu and Fe. The purified solution is then submitted to a mixed hydroxide precipitation in two stages, at pH = 7.0-7.5 to produce the final precipitate containing significant amounts of manganese, and at pH ~8.0-8.5 to scavenge the nickel/cobalt, the scavenger precipitate being recycled to the first stage precipitation.

The mixed precipitate is then leached in ammonium sulphate solution, selectively versus manganese. Results are summarized in Table 9.

Table 9: Lime Precipitation of Laterite Liquor. CESL Process

PRODUCT	ASSAYS				
	Ni	Co	Mg	Mn	Ca
Feed Solution (g/L)	3.0	0.3	1.85	1.85	-
Precipitate (%)	11	1.1	0.6	8	15

5.2.7. THE AMAX PROCESS (81)

In the late 1970's, Amax developed a PAL process applicable to a broad range of oxide nickel ores. The process was piloted, and the recovery of nickel and cobalt from the PAL liquor was by sulphide precipitation, and therefore, the selectivity versus manganese was not an issue, as indicated from published results included in Table 5.

5.3. NEW PROCESSES TESTED TO TREAT LATERITE LIQUORS

Besides the processes briefly described in the previous chapters, a few others have been tested and recommended to process laterite liquors to improve the

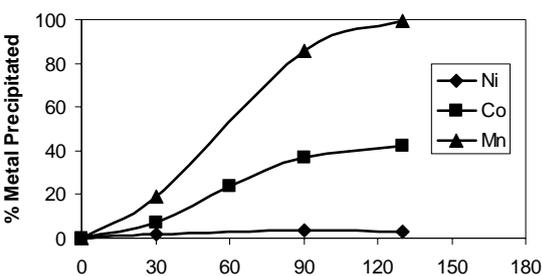


Figure 29: Oxido-Precipitation of Mn from Laterite Liquor (Brine); NaClO: 110% Stoichiometric

separation between nickel + cobalt and the impurities.

5.3.1. RESIN-IN-PULP (RIP)

Resin-in-pulp processes have been used in the gold industry (for example South Africa and CSSR) to recover gold from cyanide pulp. Besides better selectivity and faster kinetics over activated carbon, the use of resin eliminates the need for CCD circuits, and this could have a significant impact on capital costs for laterite projects, especially with pulps with rheological challenges.

The use of resin-in-pulp has been recommended recently to treat laterite pulps (82). The resin has been selected for adsorption of Ni and Co over competing ions. The resin, Clean TeQ R-604 is a high mechanical strength, macroporous and chelate-based. From a PAL liquor assaying 4.1 g/L Ni, 15 g/L Mg, 0.3 g/L Co and 1.5 g/L Mn, a purified

solution assaying 21 g/L Ni, 1.5 g/L Co and 10 mg/L Mn was produced.

Excellent selectivity of the Clean TeQ proprietary resin Clean-ix™ was demonstrated on the Young (Jervois Mining) High Grade Composite leach Slurry (83).

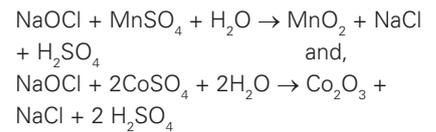
The use of IX for laterite liquor has also been patented by BHP Minerals (84).

5.3.2. SELECTIVE OXIDATION/PRECIPITATION OF MN

Based on the success of the SO₂/O₂ process developed by Lakefield to selectively remove manganese from cobalt and zinc sulphate solutions, the same process was tested for laterite liquors, in which the Co/Mn ratios are usually lower.

At the start, tests were aimed at removing Mn selectively from the cobalt and the nickel, but initial results indicated that the selectivity versus cobalt was not as good as expected. An example of initial results is presented in Figure 29.

Sodium hypochlorite NaClO has been used (85) to oxidize/precipitate manganese and cobalt from zinc sulphate solutions, as per the reaction:



Similar results were obtained with SO₂/O₂ mixtures. The reasons for such a loss of selectivity when treating some laterite liquors is not yet fully understood. It appears that the presence of chloride played a role. It is not clear either whether the loss of cobalt is due to unselective oxido-precipitation of cobalt or to another phenomenon, such as adsorption of cobalt to the manganese precipitate (86).

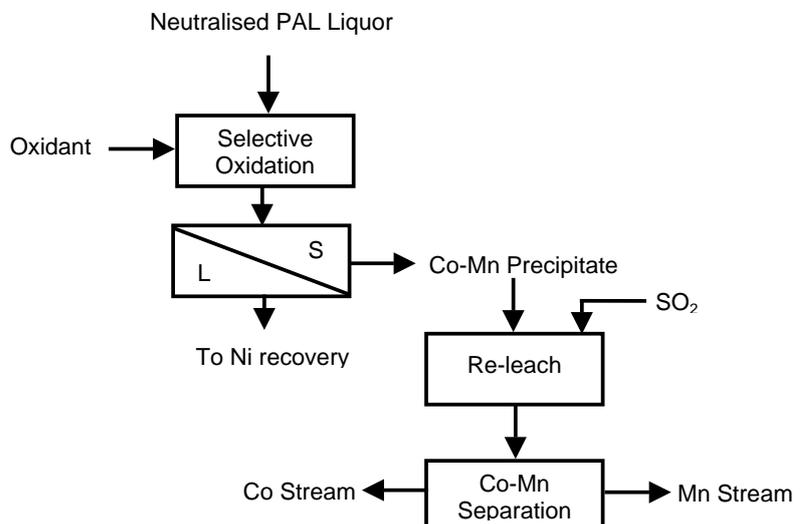


Figure 30: Modified Purification Process to Treat PAL Liquors

This was not a fatal flaw, since the manganese-free solution (containing all of the nickel and part of the cobalt) could be processed by any standard route; however, it meant that cobalt had to be recovered at two different steps of the process.

This partial loss of selectivity towards cobalt could actually be advantageously used to significantly modify the approach used during the solution treatment process. The need for a modified purification process better capable of handling Mn has been recently declared (87).

The oxidation/precipitation process could be modified to remove, selectively versus nickel, the manganese and cobalt in the PAL liquors, as per the flowsheet presented in Figure 30 below:

The main points of this process are:

- the nickel solution is separated from manganese and cobalt at the very beginning and can be processed to Ni final product in any conventional way: Ni SX or Ni precipitation, with the advantage that the Ni/Co separation has already been accomplished.
- the cobalt can be recovered from a sidestream by re-dissolving the precipitate (reductive leach) and separating the cobalt from the manganese using any conventional processes (SX, sulphide precipitation, IX,...), but on a much smaller stream.

The oxidant to effect the precipitation of Co/Mn must be selective towards Ni. Tests at Lakefield have indicated that SO₂/O₂ mixtures, and sodium hypochlorite could be used, the choice being determined by economics and other factors (such as the acceptance of chloride in the process). Figure 31 presents results of tests conducted at Lakefield on an Australian laterite PAL liquor.

This approach could be useful to plants using the Bulong process and plants using the hydroxide precipitation process.

In the case of Bulong-type plants, the new purification process would conceptually be as shown in Figure 32.

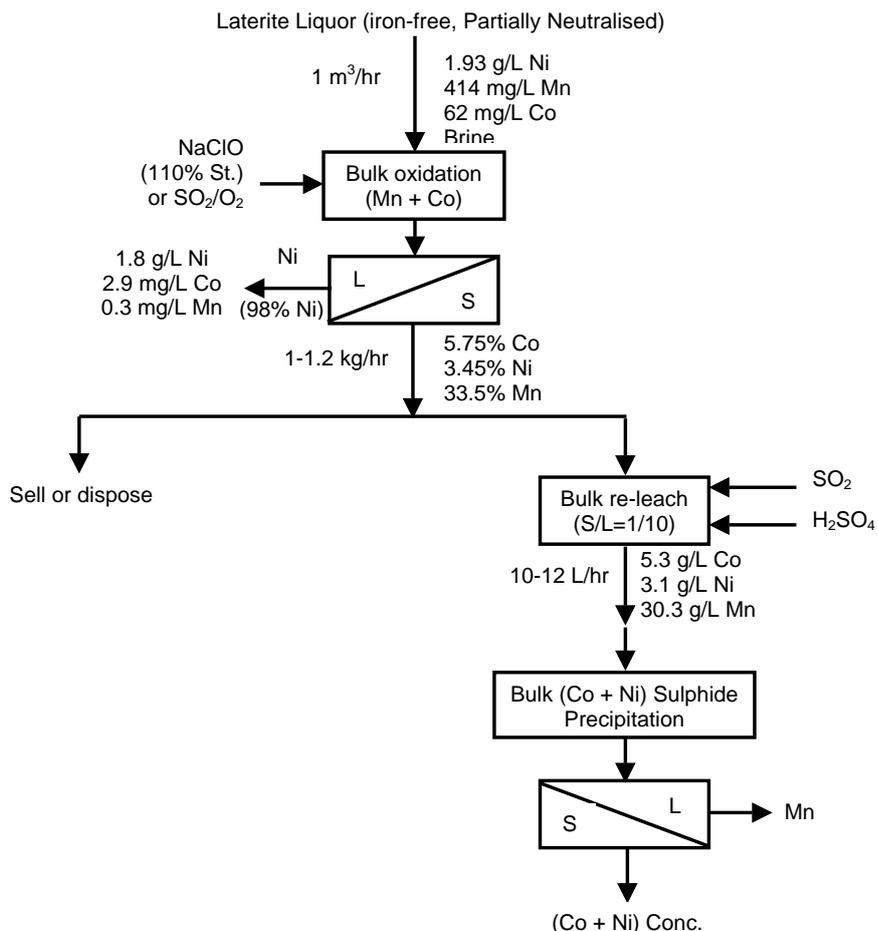


Figure 31: New Laterite Liquor Purification Process. Batch Data. Australian Laterite (with Cl⁻)

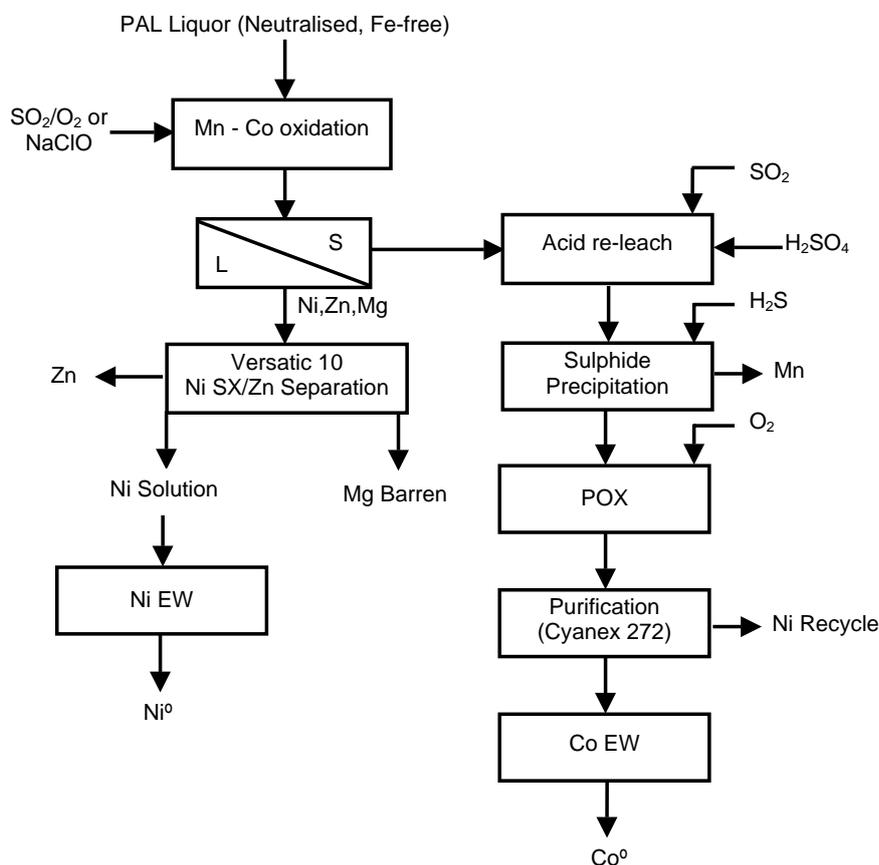


Figure 32: A new Purification Process for Bulong-type Plants

The main advantage of this modification would be that the Cyanex 272 circuit is much smaller since there are much less Mg, Mn in the solution to cobalt SX.

In the case of a hydroxide precipitation plant, the new purification process would conceptually be as shown in Figure 33.

The advantage of this new approach would be that cobalt and nickel are generated as separate high grade products containing little Mn, the cobalt circuit is relatively small, and that the final Mn removal stage occurs on a smaller stream.

6. CONCLUSIONS

Control of manganese in acidic leach liquors is certainly not a new issue and various options are available to the metallurgist to raise to the challenge.

Obviously, besides metallurgical performance and economic factors, the choice between the various process options will depend on other factors, such as solution composition (in particular the ratio of manganese to the pay metal(s)) and the type of pay metal compound that is being targeted (metal, sulphide, oxide, carbonate, ...).

In the case of copper-manganese acidic solutions with high Mn/Cu ratios (manganese electrolyte, for example), copper can easily be removed selectively from manganese by sulphide or hydroxide precipitation. If the ratio Mn/Cu is lower (for example, copper leach solutions), and no copper solvent extraction process is practiced, as in the Central African Copper Belt), manganese is controlled through a bleed, and copper is separated by a two-stage hydroxide precipitation with recycle of the second stage Cu-(Mn) precipitate. The issue arises when copper is recovered by SX/EW, because of organic degradation by permanganate ions formed at the anode. Solutions to that problem are to maintain a Fe²⁺/Mn ratio of at least 10 in the electrolyte (Girilambone), or to reduce the Mn in the spent electrolyte prior to contacting the loaded organic.

In the case of zinc manganese acidic liquors, excess manganese can be

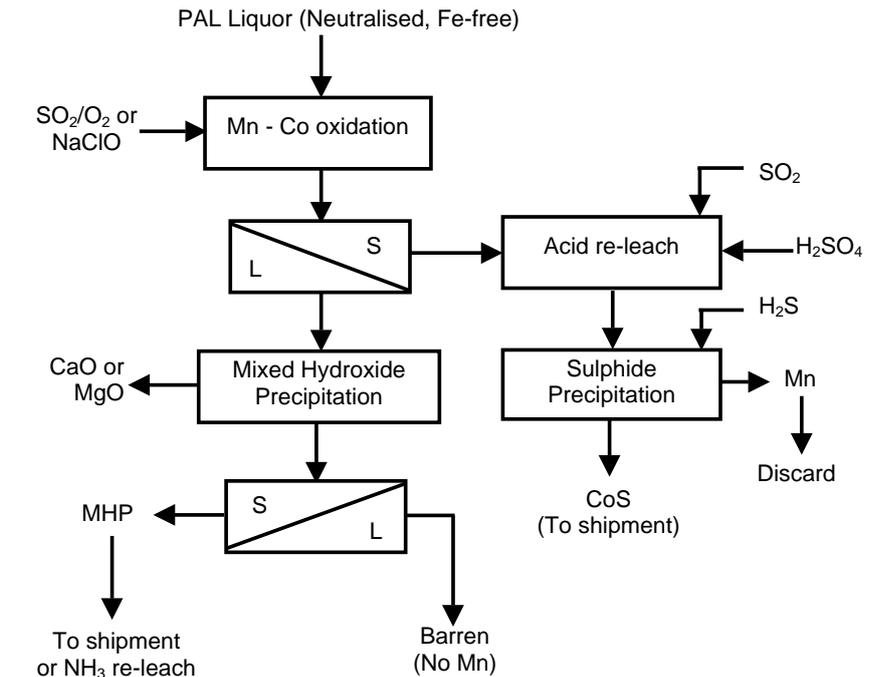


Figure 33: New Purification Process for Mixed Hydroxide Precipitation Plants

controlled by electrolytic oxidation to MnO₂ in a sacrificial cell, or by selective oxidation/precipitation. Normally, strong oxidants (ozone, Caro's acid, hypochlorite) have been suggested for manganese removal, but, recently, Lakefield developed a process using SO₂/O₂ mixtures to remove Mn from zinc electrolytes from the Gamsberg project. The possibility also exists to selectively solvent extract zinc from manganese and produce SHG grade zinc, as demonstrated for the Boleo project during a pilot plant at Lakefield.

Cobalt is well separated from manganese by sulphide precipitation; on the other hand, the selectivity of cobalt hydroxide precipitation ahead of manganese is not great. The main cobalt solvent extractant, Cyanex 272, displays little selectivity between cobalt and manganese.

Removal of manganese away from cobalt using oxidation/precipitation normally requires strong oxidants and, therefore, cobalt losses in the manganese precipitate are usually high. Removal of Mn from cobalt solutions using SO₂/Air mixtures was also piloted successfully at Lakefield, and cobalt losses were low (<0.5% Co).

Laterite liquors contain significant amounts of Mn, usually several times

higher than cobalt. Of the 4 commercial plants using PAL to treat limonitic laterites, two (Moa Bay, Murrin Murrin) are using sulphide precipitation to produce an intermediate Co/Ni sulphide concentrate, and, in that case, Mn is not an issue. At Bulong, Mn is extracted with Co and Zn using Cyanex 272, and the Co-Mn separation is effected later by sulphide precipitation. At Cawse, hydroxide precipitation is used to prepare an hydroxysulphate Co/Ni concentrate, and some manganese is co-precipitated with the Co/Ni.

A new purification process, based on bulk removal of (Mn + Co) using oxido-precipitation techniques (hypochlorite, SO₂/O₂, ...) could result in a significant simplification of the nickel recovery circuit and shows promise, in particular for Bulong-type or Cawse-type laterite plants.

7. REFERENCES

1. GUPTA, C.K., MUKHERJEE, T.K., "Hydrometallurgy in Extraction Processes," CRC Press, Vol II, 1990, pp. 167-169.
2. DIJKMAN, H., BUISMAN, C.J.N., BAYER, H.G., "Biotechnology in the Mining and Metallurgical Industries: Cost Savings Through Selective Precipitation of Metal Sulphides," in Copper '99, Volume IV, Ed. Young, Dreisinger, Hackl, Dixon, Phoenix 1999, pp. 113-126.
3. FISCHER, R.B., PETERS, D.G., "Quantitative Chemical Analysis," W.B. Saunders Co, 3rd Ed. 1968.
4. GARRELS, CHRIST, "Solutions, Minerals and Equilibria," Freeman, Cooper and Co, San Francisco, 1965.
5. POURBAIX, M., "Atlas of Electrochemical Equilibria in Aqueous Solutions," NACE - Cebelcor, Houston, 1974.
6. RALSTON O., MAIER, C.G., "The Ferric Sulphate - Sulphuric Acid Process," USBM Bull 260, 1927.
7. TIWARI, B.L., KOLBE, J., HAYDEN, H.W. JR., "Oxidation of Ferrous Sulfate in Acid Solution by a Mixture of Sulfur Dioxide and Oxygen," AIME TRANS, Volume 10B, Dec. 1979, pp. 607- 612.
8. KRAUSE, E., "The Oxidation of Ferrous Sulfate Solutions by Sulfur Dioxide and Oxygen.", PhD Thesis, University Waterloo, Canada 1988.
9. WALLIS, A.E., WEST, D.H., "Process of Removing Ferrous Sulfate from Sulfate Solutions Containing Nickel and/or Cobalt," US Patent 2,816,819, Dec. 1957. 2002-2 37
10. LEGGE, D.I., LIPWORTH, M., "Treatment of Uranium Ores for Recovery of the Uranium Content Thereof," US Patent 3,092,447, June, 1963.
11. ZHANG, W., SINGH, P., MUIR, D.M., "Iron (II) Oxidation by SO_2/O_2 in Acidic Media: 1. Kinetics and Mechanism," Hydrometallurgy, Volume 55 (2000), pp. 229-245
12. ZHANG, W., MUIR, D.M., SINGH, P., "Iron (II) Oxidation by SO_2/O_2 in acidic Media - Part II. Effect of Copper," Hydrometallurgy, Volume 58, (2000) pp. 117-125.
13. ETTTEL, V.A., MOSOIU, M.A., DEVUYST, E.A., "A Novel Oxidant for Nickel," Hydrometallurgy, Volume 4 (1979), pp. 247-257.
14. DEVUYST, E.A., MOSOIU, A., KRAUSE, E., "Oxidizing Properties and Applications of the $\text{SO}_2\text{-O}_2$ System" in Hydrometallurgy Research Development and Plant Practice, Ed. Osseo- Asare, Miller AIME/TMS, Atlanta 1983, pp. 391-403.
15. ZHANG, W., SINGH, P., MUIR, D.M., " SO_2/O_2 as an Oxidant in Hydrometallurgy," Minerals Engineering, Volume 13, No. 13, 2000, pp. 1319-1328.
16. FERRON, C.J., KWATENG, D.O., DUBY, P.F., "Kinetics of the Precipitation of Goethite from Ferrous Sulphate Solutions using Oxygen-Sulphur Dioxide Mixtures," AIME/TMS Annual Meeting, New Orleans, 1991, EPD, 1991, pp. 165-177.
17. FERRON, C.J., "Atmospheric Leaching of Zinc Sulphide Concentrates using Regenerated Ferric Sulphate Solutions" in Lead-Zinc 2000," Ed. Dutrizac, Gonzalez, Henke James, Siegmund, TMS 2000, Pittsburgh.
18. KNIPRATH, E., "Redox Precipitation of Non-ferrous Heavy Metals from Aqueous Solutions," Canadian Patent No. 935650, October, 1973.
19. HENKEL, "The Chemistry of Metals Recovery using LIX Reagents," MID Red Book.
20. Cytec Technical Brochure - Cyanex 272
21. FERRON, C.J., "Investigation of the Behaviour of an Iridium Oxide Coated Anode in Copper Electrowinning," Ph.D. Columbia University, NY, 1989
22. CHENG, C.Y., HUGHES, C.A., BARNARD, K.R., LARCOMBE, K., "Manganese in Copper Solvent Extraction and Electrowinning," Hydrometallurgy, Volume 58 (2000)., pp. 135-150.
23. HOLLE, H., "Process Innovations at Girilambone Copper Company's Heap Leach SX/EW Operation," Randol at Vancouver, 1996, pp. 289-294.
24. LENOIR, P., VAN PETEGHEM, A., FENEAU, C., "The Extractive Metallurgy of Cobalt," in International Conference on Cobalt: Metallurgy and Uses, ATB Metallurgie, Brussels, 1981, Volume I, pp. 51-62.
25. VERNEY, L.R., "Overview of Cobalt Supply and Production," in Extractive Metallurgy of Nickel and Cobalt, Ed. Tyroler, Landolt, TMS 1988, Phoenix, pp. 135-185.
26. HEARNE, T.M., HAEGELE, R., BECK, R.D., "Hydrometallurgical Recovery of Zinc from Sulphide Ores and Concentrates" in "Zinc and Lead Processing," Ed. Dutrizac, Gonzalez, Bolton, Hancock, CIM/METSOC, Calgary 1998.
27. VAN WEERT, G., BOERING, M., "Selective Pressure Leaching of Zinc and Manganese from Natural and Man-made Spinels using Nitric Acid," Hydrometallurgy, Volume 39, (1995) pp.201-213.
28. DE SOUZA, C.C.B.M., TENORIO, J.A.S., "Study of the Batch Purification Process of Solutions from Leaching of used Alkaline Batteries," TMS, EPD Congress 2001, Ed. Taylor, 2002-2 38 pp. 681-687.
29. PANDE, A.M., GUPTA, K.N., ATELKAR, V.A. "Single Cell Extraction of Zinc and Manganese Dioxide from Zinc Sulfide Concentrate and Manganese Ores," Hydrometallurgy, Volume 9, (1982), pp. 57-68.

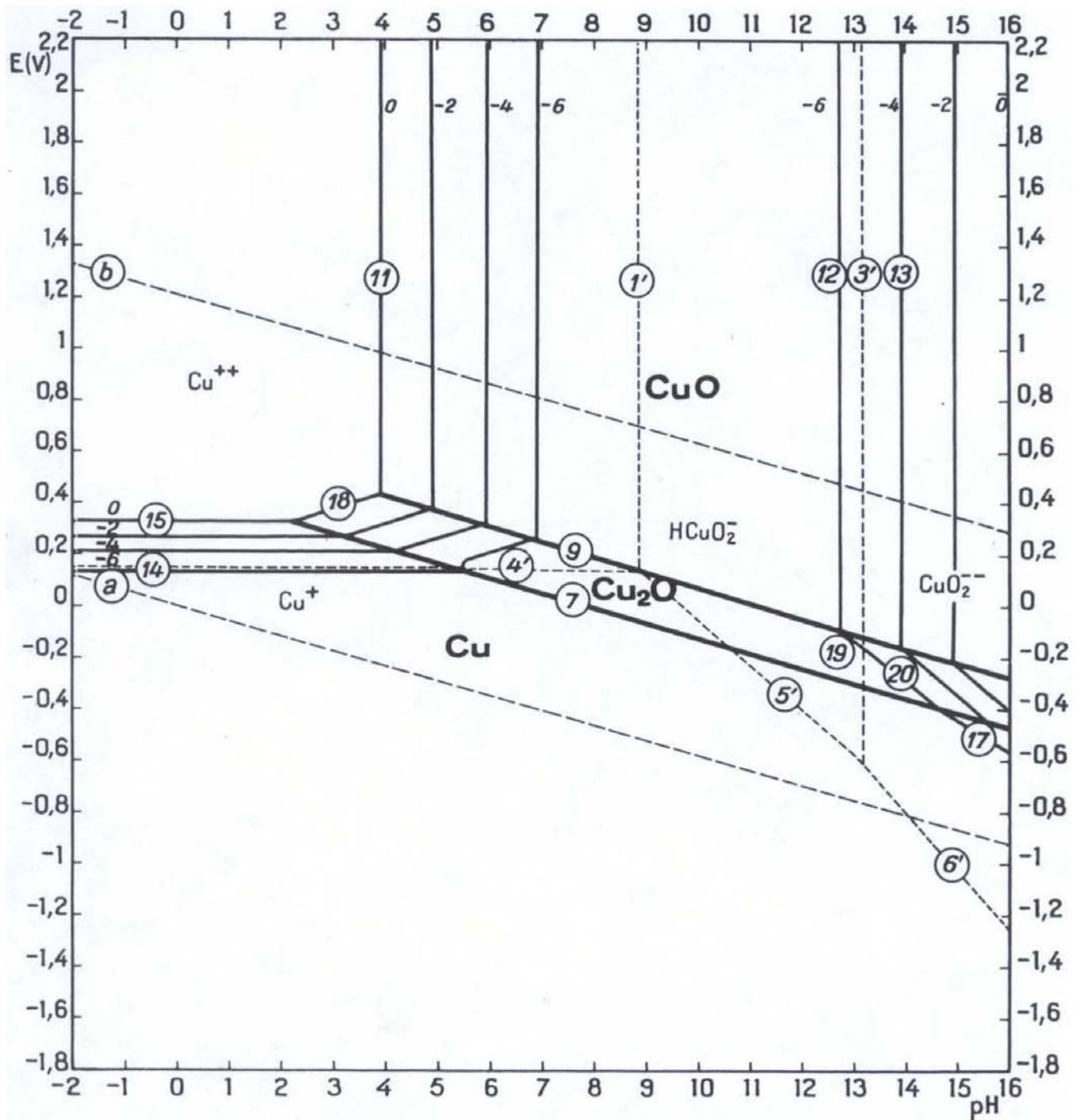
30. VERBAAN B., MULLINDER, B. "The Simultaneous Electrowinning of Manganese Dioxide and Zinc from Purified Neutral Zinc Sulfate at High Current Efficiencies", *Hydrometallurgy*, Volume 7, (1981), pp. 339-352.
31. RODRIGUES, J.M.S., DRY, M., "The Production of Particulate Manganese Dioxide during Zinc Electrowinning, in *Electrometallurgical Plant Practice*, Ed. Claessens, Harris, Pergamon Press, Montreal 1990, pp. 199-220.
32. FUSSI, J.L., QUINTERO, O., CORNAGLIA, A., MOROSINI, C., "Electrowinning of High Purity Zinc Metal From a Mn-Containing Leach Solution Preceded by Cold Electrolytic Demanganization", Patent #00885976/EP B1, March 2002.
33. MATTHEW, S.P., BOWES, K.G., BENTLEY, M.D., "Process Selection for the Gamsberg Zinc Refinery", SAIMM Conference, Pretoria Falls, 2001.
34. DEVI, N.B., NATHSARMA, K.C., CHAKRAVORTY, V., "Extraction and Separation of Mn(II) and Zn(II) from Sulphate Solutions by Sodium Salt of Cyanex 272", *Hydrometallurgy*, Volume 45 (1997), pp. 169-179
35. TOMLINSON, M., LOMMEN, J., MOLNAR, R., "Solvent Extraction and Direct Electrowinning of Zinc from a Cobalt-Bearing Solution", in *Zinc and Lead Processing*, Ed. Dutrizac, Gonzalez, Bolton, Hancock, CIM, 1998, pp. 733-747.
36. PAIXÃO, J.M.M., AMARAL, J.C., MEMÓRIA, L.E., FREITAS, L.R., "Sulphation of Carajas Manganese Ore", *Hydrometallurgy*, Volume 39 (1995), pp. 215-222.
37. HARRIS, L., HANSON, A.K. JR., "Process for Manganese Removal from Zinc Metal-Bearing Solutions", US. Patent 4,067,789, January 1978.
38. BOLTON, G.L., SEFTON, V.B., ZUBRYCKY J.N., "Removal of Manganese Ions from Zinc and Manganese Containing Solutions", US. Patent 4,290,866, September 1981.
39. BURKIN, A.R., CHOUZADJIAN, K.A., "Precipitation of Manganese Dioxide from Zinc Electrolyte Solution using Peroxymonosulphuric Acid" in *Hydrometallurgy Research Development and Plant Practice*, Ed. Osseo-Asare, Miller AIME/TMS, Atlanta 1983, pp. 603-615.
40. HUDSON BAY MINING AND SMELTING CO., "Process for the Purification of Aqueous Solutions of Zinc Sulphate", Canadian Patent 550,346, Dec. 17, 1957
41. VIEILLE MONTAGNE S.A., "Process for the Removal of Impurities Contained in Zinc and Cadmium Sulphate", US Patent, 4,096,233, June 20, 1978
42. CANTERFORD, J.H., "Cobalt Extraction and Concentration from Manganese Wad by Leaching and Precipitation", *Hydrometallurgy*, Volume 12 (1984), 00. 335-354.
43. RESOLUTE LTD., "Bulong Nickel Laterite Project", Cobalt 2001 Conference, CDI, Toronto.
44. BURGER, P., "Implication of Geological and Mineralogical Aspects of Laterite Deposits for Metallurgical Plant Design", *Alta* 1998, Perth.
45. KRAUSE, E., BLAKEY, B.C., PAPANGELAKIS, V.G., "Pressure Acid Leaching of Nickeliferous Laterite Ores", *Alta* 1998, Perth. 2002-2 39
46. MASON, P., "Ramu Nickel Process Piloting", *Alta* 1998, Perth.
47. HELLMAN, P.L., "Mineralogical and Geochemical Studies - Key Elements in Evaluating Nickel Laterites", *Alta*, 2001, Perth.
48. FLEISCHER M., MANDARINO, J.A., "Glossary of Mineral Species - 1991", *The Mineralogical Record*, Tucson, 1991.
49. BOLLES, T, McELROY, R., GRIFFITHS, D., "Process Development for International Curator's El Boleo Copper-Cobalt Project", in *Nickel Cobalt '97 - Hydrometallurgy and Refining of Nickel and Cobalt*, Volume 1, Ed. Cooper, Mihaylov, CIM, Sudbury 1997, pp. 71-83.
50. SHUNGU, T., CHARLES, P., "Recent Improvements in Metallurgical Processing at the Metallurgical Plant of Shituru", in *International Conference on Cobalt: Metallurgy and Uses*, ATB Metallurgie, Brussels, 1981, Volume I, pp. 73-78.
51. LOUIS, P., KALALA, B., SHUNGU, T., "Quality of the Cobalt Produced by Gecamines. Discussion on the Mechanism of Electrodeposition of Most Impurities", in *Extractive Metallurgy of Nickel and Cobalt*, Ed. Tyroler, Landolt, TMS 1988, Phoenix, pp. 531-541.
52. RICKELTON, W.A., NUCCIARONE, D., "The Treatment of Cobalt/Nickel Solutions Using Cyanex Extractants:, in *Nickel Cobalt 97 - Hydrometallurgy and Refining of Nickel and Cobalt*, Volume, 1, Ed. Cooper, Mihaylov, CIM, Sudbury 1997, pp. 275-292.
53. CHENG, C.Y., "Separation of Manganese from Nickel and Cobalt by Solvent Extraction", *Alta* 1999, Perth.
54. HOH, Y-C, CHUANG, W-S, LEE, B-D, CHANG, C-C, "The Separation of Manganese from Cobalt by D2EHPA", *Hydrometallurgy*, Volume 12 (1984), pp. 375-386.
55. COX, M.A., LAWSON, J.R., "Cobalt Extraction using Zeneca Development Reagent DS 6001", *Alta* 1997, Perth.
56. FERRON, MOLNAR, R., WILLIAMSON, R.G., "High Temperature Acidic Pressure Leaching: An Omnivorous Process to Treat Nickel-Cobalt Feedstocks", in *Nickel Cobalt '97 - Hydrometallurgy and Refining of Nickel and Cobalt*, Volume 1, Ed. Cooper, Mihaylov, CIM, Sudbury 1997, pp. 427-440.
57. CYTEC - Technical Brochure - Cyanex 302
58. DRY, M., IRIO, G., JACOBS, D.F., COLE, P.M., FEATHER, A., SOLE, K., ENGELBRECHT, J., MATCHETT, K.C., CILLIERS, P.J., O'KANE, P.T., DREISINGER, D.B., "Cu/Co Tailings Treatment Project, Democratic Republic of Congo", *Alta* 1998, Perth.

59. ONO, N., ITASAKO, S., FUKUI, I., "Sumitomo's Cobalt Refining Process", in International Conference on Cobalt: Metallurgy and Uses, ATB Metallurgie, Brussels 1981, Volume I, pp. 63-71
60. GRAVEY, G., PEYRON, F., "A French Producer of Cobalt: Métaux Spéciaux S.A.", in International Conference on Cobalt: Metallurgy and Uses, ATB Metallurgie, Brussels, 1981, Vol I, pp 79-84.
61. BHASKARA SARMA, P.V.R., SRINIVASA RAO, K., NATHSARMA, K.C., ROYCHOUDHURY, G., "Processing of Nickel and Cobalt-Containing Leach Liquors Obtained from Different Raw Materials", Hydrometallurgy, Volume 19 (1987), pp. 83-93.
62. CHALKLEY, M.E., TOIRAC, I.L., "The Acid Pressure Leach Process for Nickel and Cobalt Laterite. Part I: Review of Operations at Moa", in Nickel-Cobalt '97, Hydrometallurgy and Refining of Nickel and Cobalt, 27th Annual CIM Meeting, Volume 1, August, 1992, Sudbury, pp. 341-353. 2002-2 40
63. MATOS, R.R., "Industrial Experience with Ni/Co Sulphide Precipitation Process", Nickel- Cobalt 97, Hydrometallurgy and Refining of Nickel and Cobalt, 27th Annual CIM Meeting, Volume 1, August 1992, Sudbury, pp. 371-378.
64. JHA, M.C., MEYER, G.A., WICKER, G.R., "An Improved Process for Precipitating Nickel Sulfide from Acidic Laterite Leach Liquors", AIME/TMS Annual Meeting, 1981, Paper A81-67.
65. CHOU, E.C., ROOKE, P.M., HANKS, J.T., "Development of Nickel/Cobalt Sulfide Precipitation Process from Laterite Pressure Acid Leach Liquor", Alta 1999, Perth.
66. DUNN, G.M., JOHN, C., "Recovery of Copper and Cobalt from mixed Oxide-Sulphide Tailings Dumps in the Democratic Republic of Congo (DRC)", Alta 1999, Perth.
67. MAYZE, R., "An Engineering Comparison of the Three Treatment Flowsheets in WA Nickel Laterite Projects", Alta 1999, Perth.
68. MOTTERAM, G., RYAN, M., BEREZOWSKY, R., RAUDSEPP, R., "Murrin-Murrin Nickel/Cobalt Project - Project Development Overview", Alta 1996, Perth.
69. MOTTERAM, G., RYAN, M., WEIZENBACH, R., "Application of the Pressure Acid Leach Process to Western Australia Nickel/Cobalt Laterite", Nickel-Cobalt 97, Hydrometallurgy and Refining of Nickel and Cobalt, 27th Annual CIM Meeting, Volume 1, August 1992, Sudbury, pp. 391-407.
70. KYLE, J.H., FURFARO, D., "The Cawse Nickel/Cobalt Laterite Project Metallurgical Process Development", Nickel-Cobalt 97, Hydrometallurgy and Refining of Nickel and Cobalt, 27th Annual CIM Meeting, Volume 1, August 1992, Sudbury, pp. 379-389.
71. BURVIL, D, WHITE, D, "Engineering Aspects of the Cawse Nickel/Cobalt Laterite Project", Alta 1999, Perth.
72. HELLSTEN, K.J., LEWIS, C.R., "Cawse Nickel Laterite Deposit", Alta 1996, Perth.
73. SOLDENHOFF, K., HAYWARD, N., WILKINS, D., "Direct Solvent Extraction of Cobalt and Nickel from Laterite Acid Pressure Leach Liquors", TMS, EPD Congress 1998, Ed. Mishra, pp. 153-165.
74. BACON, G., "Goro - The World's Most Promising Limonitic Laterite Project", CIM Luncheon, Toronto, 2002.
75. MIHAYLOV, I., KRAUSE, E., COLTON, D.F., OKITA, Y., DUTERQUE, J.P., PERRAUD, J.J., "The Development of a Novel Hydrometallurgical Process for Nickel and Cobalt Recovery from Goro Laterite Ore", Mining and Millenium 2000, March 2000, Toronto.
76. MILLER, M., SKEPPER, I., DRY, M., TODD, I., "Observations from the RNO Pilot Plant at Lakefield Research, 2000 AD", Alta 2001, Perth.
77. CLINTON, L.A., BAILLIE, M.G., "Weda Bay Laterite Project, Indonesia", Alta 1999, Perth.
78. BAILLIE, M., COCK, G.C., "Weda Bay Laterite Project, Indonesia", Alta 1998, Perth.
79. HANKS, J.T., "Phelps Dodge Laterite Project in Madagascar", Alta 1998, Round Table.
80. JONES, D., MOORE, R., "The Application of the CESL Nickel Process to Laterites", Alta 2001, Perth.
81. DUYVESTYEN, W.P.C., WICKER, G.R., DOANE, R.E., "An Omnivorous Process for Laterite Deposits", 108th AIME Annual Meeting, New Orleans, 1979.
82. ZONTOV, N., "Potential Benefits of Resin-in-pulp for PAL Plants", Alta 2001, Perth. 2002-2 41
83. JANSEN, M., TAYLOR, A., "Jervois Mining - Young Ni/Co Laterite Prefeasibility Study Testwork Review", Alta 2001, Perth.
84. BHP Minerals U.S. Patent , 6,312,500
85. FONSECA, J.C., COELHO, M.C., CARVALHO, F.G., "Removal of Cobalt and Manganese from Zinc Sulphate Solutions", in Electrometallurgical Plant Practice, Ed Claessens, Harris, Pergamon Press, Montreal, 1990, pp. 191-197.
86. STEEMSON, M., "The Selection of a Hydroxide Precipitation/Ammoniacal Releach Circuit for Metal Recovery from Acid Pressure Leach Liquors", Alta 1999, Perth.
87. NESS, V.H., HAYWARD, N.L., "Nickel Laterite Processing Second Generation Design Considerations", SME Annual Meeting, Denver, 2001, Preprint 01-65.

8. APPENDICES (REF. 5)

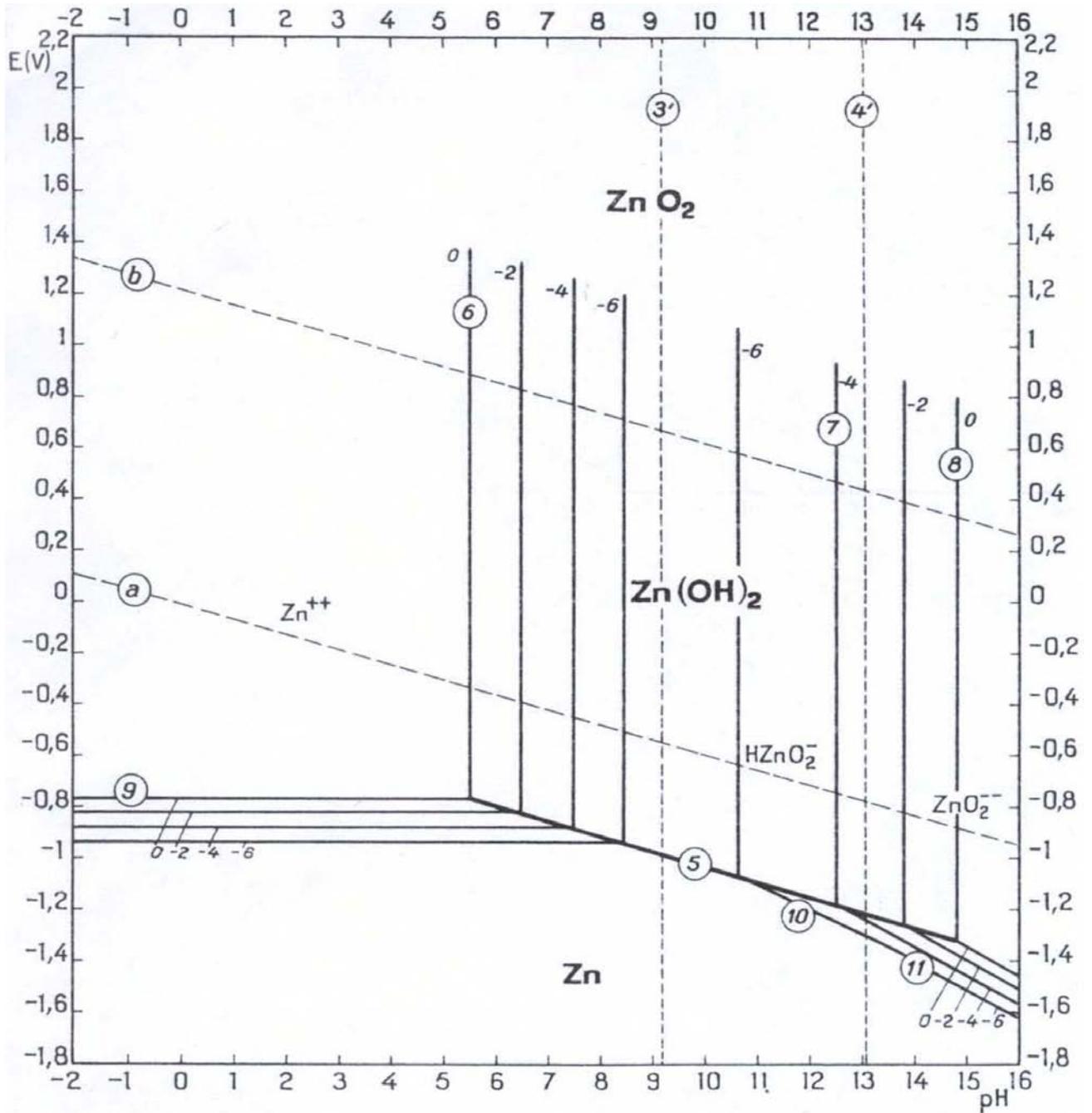
1. Eh-pH Diagram of Cu
2. Eh-pH Diagram of Zn
3. Eh-pH Diagram of Co
4. Eh-pH Diagram of Ni
5. Eh-pH Diagram of Fe

APPENDIX 1



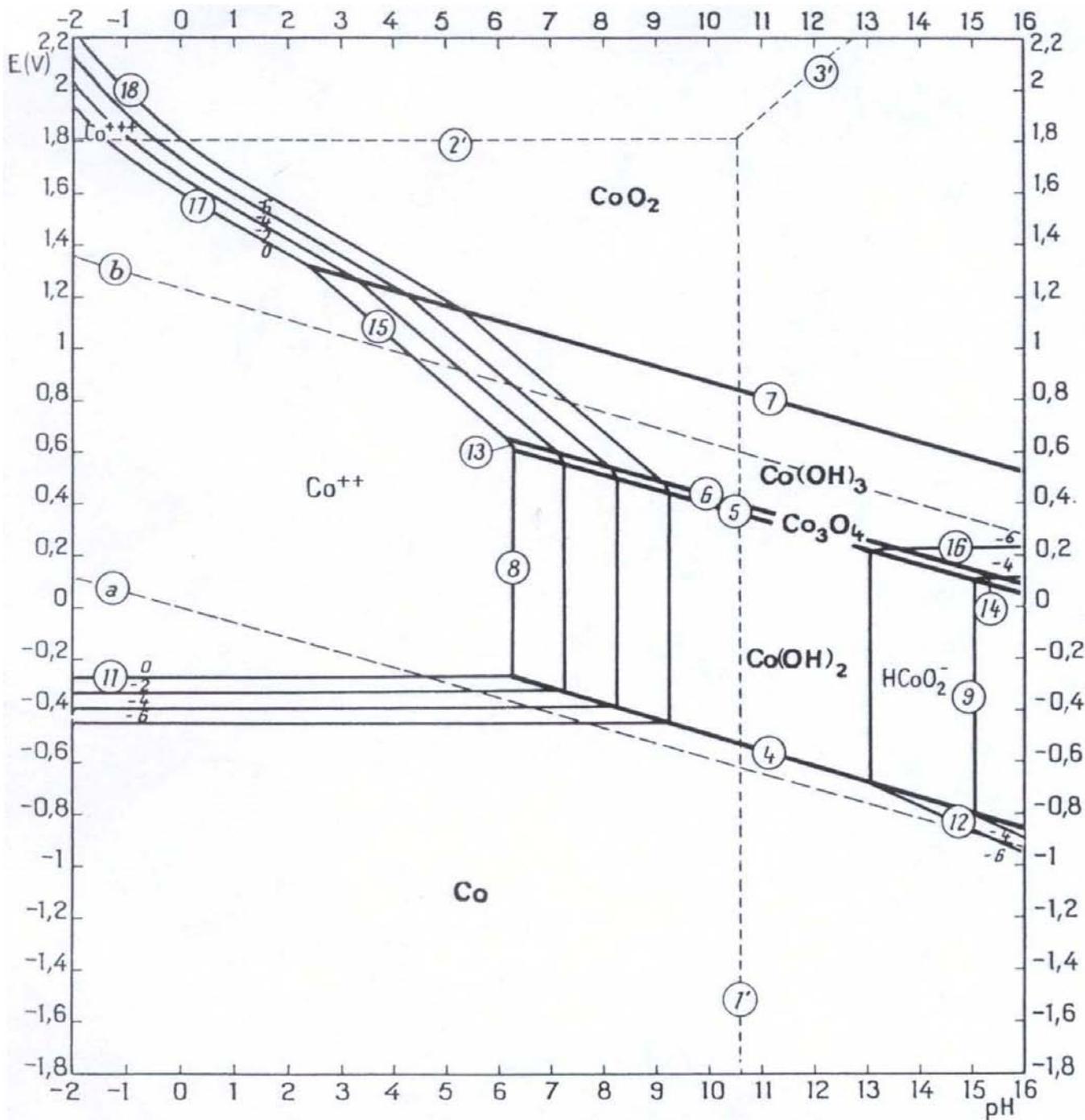
Potential-pH equilibrium diagram for the system copper-water, at 25°C.
 [Considering the solid substances Cu, Cu_2O and CuO . $\text{Cu}(\text{OH})_2$ is not considered.]

APPENDIX 2



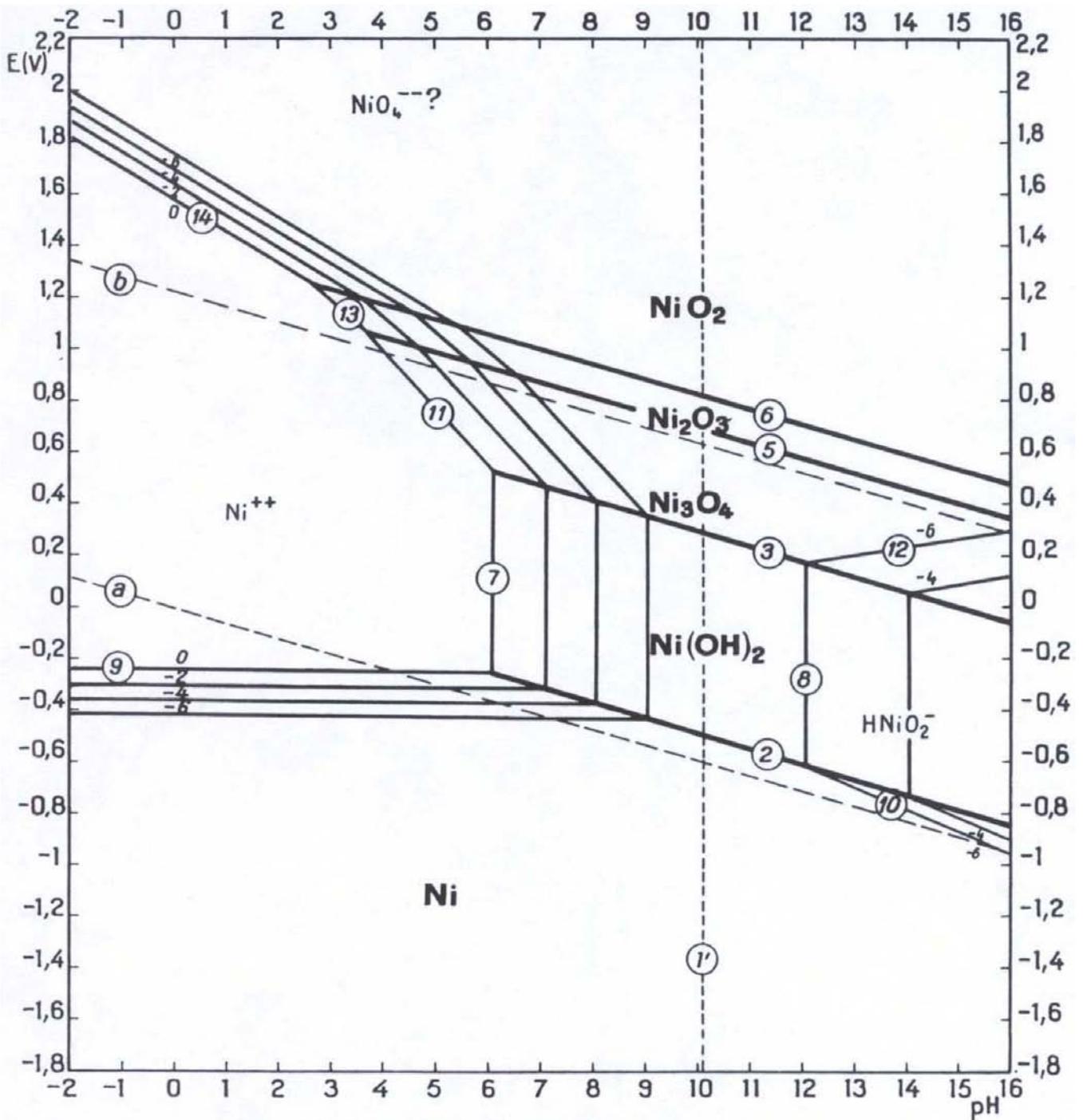
Potential-pH equilibrium diagram for the system zinc-water, at 25°C.
 [Established by considering ε-Zn(OH)₂.]

APPENDIX 3



Potential-pH equilibrium diagram for the system cobalt-water, at 25°C.

APPENDIX 4



Potential-pH equilibrium diagram for the system nickel-water, at 25°C.

APPENDIX 5

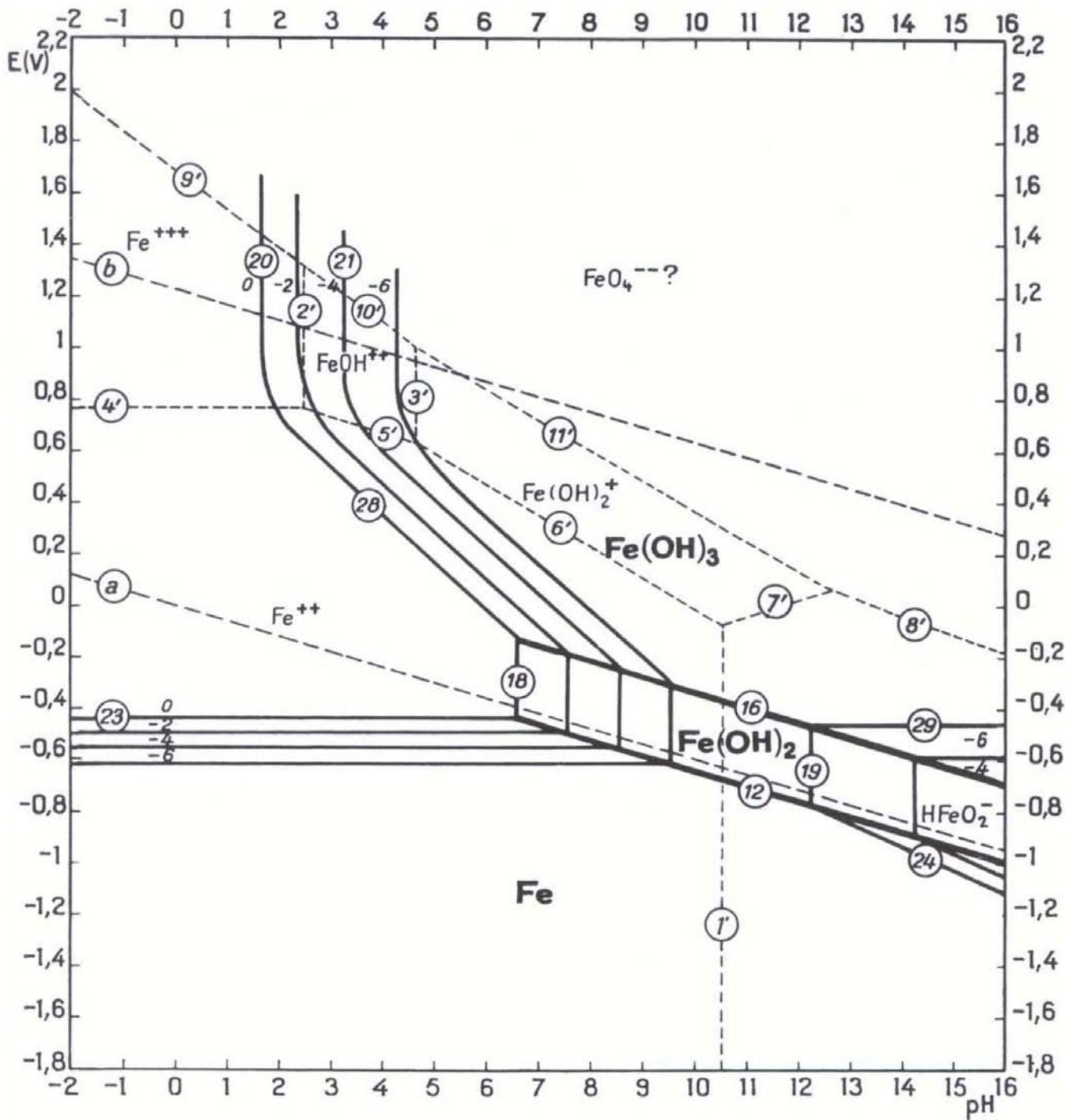


FIG. 5. Potential-pH equilibrium diagram for the system iron-water, at 25°C [considering as solid substances only Fe, Fe(OH)₂ and Fe(OH)₃].

CONTACT INFORMATION

Email us at minerals@sgs.com

WWW.SGS.COM/MINERALS

© 2011 SGS. All rights reserved. The information contained herein is provided "as is" and SGS does not warrant that it will be error-free or will meet any particular criteria of performance or quality. Do not quote or refer any information herein without SGS' prior written consent. Any unauthorized alteration, forgery or falsification of the content or appearance of this document is unlawful and offenders may be prosecuted to the fullest extent of the law.