DISSOLUTION AND DEGRADATION BEHAVIOUR OF CERTAIN METALS IN GOLD CYANIDATION PROCESS

A thesis Submitted to
Graduate School of Natural and Applied Sciences of
Dokuz Eylül University
In Partial Fulfillment of Requirements for
the Degree of Doctor of Philosophy
in Mining Engineering, Mineral Processing Program

by

Mehmet TANRIVERDİ

September, 1997
İZMİR

Ph.D. THESIS EXAMINATION RESULT FORM

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy

Prof. Dr Üner İPEKOĞLU
(Advisor)

Prof. Dr. Yalçın KAYTAZ
(Committee Member))

Doç. Dr. Hasan MORDOĞAN
(Committee Member))

Approved by the
Graduate School of Natural and Applied Sciences of

Prof. Dr. Cahit HELVACI
Director

ACKNOWLEDGMENT

I would like to express my gratitude to ***Prof. Dr. Üner İPEKOĞLU*** for his kind supervision and valuable suggestion.

I would like to thank ***Assoc. Prof. Dr.Hasan MORDOĞAN*** for his constructive advice and valuable discussions, ***Ass. Prof. Dr. Ferhan ŞİMŞİR*** and ***Mining. Eng. Çağatay PAMUKÇU*** for their help during translation

I must pay tribute to both my wife, ***Arzu TANRIVERDİ***, and my family, who have supported and have suffered appreciably as a result of my commitment to this work.

Finally I would also like to thank to,

- ✓ Eurogold Inc. for financing the Metaliç leaching device
- ✓ Workshop staff of engineering Faculty for constructing the Metaliç device
- ✓ ***Necmettin AYÇELİK*** for reading the results of the chemical analyses
- ✓ ***Assoc Prof. Dr. Uğur KÖKTÜRK*** and ***Hatice YILMAZ,*** who achieved the X-Ray analyses

Mehmet TANRIVERDİ

ABSTRACT

Cyanide leaching is the mostly used method for processing gold and silver-bearing ores for many years. In this study, gold and silver extraction from Gümüşhane-Mastra ore, behaviour of other metals in the ore (Cu, Pb, Zn, Fe), and treatment processes of cyanide containing wastes are investigated theorically and experimentally. By having carried out the tests, optimum leaching conditions are determined, then, natural degradation conditions are investigated.

ÖZET

Altın ve gümüş cevherlerinin zenginleştirilmesinde yıllardan beri en yaygın yöntem olarak siyanür liçi kullanılmaktadır. Bu çalışmada Gümüşhane Mastra cevherinden siyanür liçi ile altın ve gümüşün kazanılması, cevher içerisindeki diğer (Cu, Pb, Zn, Fe) metallerinin davranışları ve siyanürlü çözeltiden siyanür arıtma prosesleri teorik ve deneysel olarak incelenmiştir. Yapılan deneyler sonunda optimal liç şartları tesbit edilmiş daha sonra liç çözeltisinin doğal bozunma koşulları incelenmiştir.

CONTENTS

Contents..........I
List of Tables..........V
List of Figures..........VII

Chapter One
INTRODUCTION

Chapter Two
GENERAL INFORMATION

2.1. Properties of Gold..........3
2.2. Use of Gold..........5
2.3. Gold Potantiel and Production..........5
2.4. Gold Bearing Materials for Production..........10

Chapter Three
GOLD PRODUCTION TECHNOLOGIES

3.1. Gravity Concentrations..........18
3.2. Amalgamation..........19
3.3. Flotation..........20
3.4. Leaching Gold – Bearing Ore..........20
    3.4.1. Pre-Treatments Methods..........20
    3.4.2. Leachants Used In Gold Hydrometallurgy..........25
    3.4.3. Gold Recovery Methods..........27

Chapter Four
CYANIDATION

4.1. Properties of Cyanide Compounds 30
  - 4.1.1. Free Cyanides. 31
  - 4.1.2. Complex Cyanides 32
  - 4.1.3. Insoluble Complexes 32
  - 4.1.4. Other Cyanide Reaction Products 32

4.2. Leaching Kinetics 32

4.3. Other Compounds and Metals their Effects on Leaching 35
  - 4.3.1. Silver 37
  - 4.3.2. Copper 37
  - 4.3.3. Iron 39
  - 4.3.4. Zinc 39
  - 4.3.5. Lead 40
  - 4.3.6. Arsenic and Antimony 41
  - 4.3.7. Mercury 42
  - 4.3.8. Tellurides 42
  - 4.3.9. Carbonaceous Material 42
  - 4.3.10. Nickel 43
  - 4.3.11. Sulphur Material 43

4.4. Leaching Parameters 44
  - 4.4.1. The Effect of Cyanide Concentration 44
  - 4.4.2. The Effect of Alkalinity 46
  - 4.4.3. The Effect of Particle Size 47
  - 4.4.4. The Effect of Temparature 48
  - 4.4.5. The Effect of Agitation Rate 49
  - 4.4.6. The Effect of Oxygen 50

Chapter Five
CYANIDE TREATMENT TECHNOLOGIES

5.1. Natural Degradation 54

- 5.1.1. Chemistry and Rate of Natural Degradation Process 55
  - 5.1.1.1. Form of Cyanide 55
  - 5.1.1.2. pH Depression 56
  - 5.1.1.3. Volatilization 56
  - 5.1.1.4. Dissociation of Metallo – Cyanide 57

5.2. Inco SO_2-Air Process 58

5.3. Hydrogen Peroxide Oxidation 60

5.4. Alkaline Chlorination 61

5.5. Biodegradation 64

5.6. Hemlo-Gold Process 64

5.7. Cyanide Recovery Processes 65

- 5.7.1. AVR 65
- 5.7.2. Ion Exchange Process 66

5.8. Storage of Cyanide Containing Waste and Disposal Design 67

Chapter Six
EXPERIMENTAL STUDIES

6.1. Material and Methods Used in Experimental Studies 71

- 6.1.1. Sample Preparation 71
- 6.1.2. Grinding Conditions 71
- 6.1.3. Leaching Conditions 74
- 6.1.4. Experimental Equipments and Apparatus 76
- 6.1.5. Reagents 83
- 6.1.6. Experimental Procedure 83
- 6.1.7. Analysis Method 84

6.2. Experimental Procedure of Natural Degradation 85

- 6.2.1. Natural Degradation carried out in the Impervious Media 85
- 6.2.2. Natural Degradation carried using the Seeped Solution 86

6.3.Analysis Method and Results 89

- 6.3.1. Results of Fire Assay and ICP Analysis 89
- 6.3.2. X-Ray Analysis and Results 89

6.3.3. Results of Chemical Analysis.. 93

6.4. Size Reduction Method 95

6.4.1. Results of Crushing and Screening.. 95
6.4.2. Grinding Tests. 99

6.5. Experimental Results of Leaching Conditions 105

6.5.1. Effect of Particle Size 105
6.5.2. Effect of Solids Concentration 108
6.5.3. Effect of Alkalinity 111
6.5.4. Effect of Cyanide Concentration 114
6.5.5. Effect of Agitation Speed.. 117
6.5.6. Final Tests 120

6.6. Experimental Results of Natural Degradation.. 124

6.2.1. Results of Natural Degradation carried out on a Non-Seeping Media . 124
6.2.2. Rasults of Natural Degradation carried using the Seeped Solution...... 127

Chapter Seven
CONCLUSION

References

LIST OF TABLES

Page

Table 2.1.World Gold Reserves and Reserve Base (tone) 6
Table 2.2.Gold Reserves And Planning Production of Turkey....................9
Table 3.1. Leaching system for gold 26
Table 4.1. Important Cyanide Species Found in Mining Effluent....................30
Table 4.2 Stability Constant for Metal – Cyano Complex 31
Table 4.3. Properties of simple cyanide compounds....................33
Table 4.4.Cyanides....................36
Table 4.5.Stability constants of some metal cyanocomplexes 36
Table 4.6. Solubility of Copper Minerals in 1 % NaCN Solution 38
Table 4.7. Solubility of Zinc Minerals in Cyanide Solution....................40
Table 4.8.Various Investigators and Their Results Which Demonstrates Maximum..45
Table 5.1.Cyanide Treatment Process Alternatives....................53
Table 5.2. Dissociation Rates (h^{-1}) for Metallo-Cyanide Complexes....................57
Table 5.3. Typical treatment results....................59
Table 6.1. Fire assay and IPC analysis results....................89
Table 6.2 Au and Ag, distribution of the Ore 93
Table 6.3. Screen Analysis of primary crusher product....................95
Table 6.4. Screen analysis of scondary crusher product (-1mm)....................97
Table 6.5. 10 min. grinding of feeding material (-1mm)....................99
Table 6.6. 30 min. grinding of feeding material (-1mm)....................100
Table 6.7. 60 min. grinding of feeding material (-1mm)....................101
Table 6.8. 80 min. grinding of feeding material (-1mm)....................102

Table 6.9. 125 min. grinding of feeding material (-1mm)..103
Table 6.10. Particle Size Distribution by Time 104
Table 6.11. Conditions of experiment 1 105
Table 6.12. Results of Experiment 1 106
Table 6.13 Conditions of Experiment 2...108
Table 6.14. Results of Experiment 2 109
Table 6.15. Conditions of Experiment 3..111
Table 6.16. Results of Experiment 3 112
Table 6.17. Conditions of Experiment 4..114
Table 6.18. Results of Experiment 4 115
Table 6.19. Conditions of Experiment 5..117
Table 6.20. Results of Experiment 5 118
Table 6.21. Conditions of Experiment 6..121
Table 6.22. Results of experiment 6...121

LIST OF FIGURES

.... **Page**

Figure 2.1. Use of gold..5

Figure 2.2. Gold reserves by countries..6

Figure 2.3. Distribution of gold production by countries in1995...................7

Figure 2.4. The geographical distribution of gold mines under condition and ....
will start operating between 1996 – 1999 (Total 479 tone/year) 8

Figure 2.5. Tentative distribution of gold production in Europe including
Turkey's contribution in 1997-1998 9

Figure 2.6. Primary and secondary gold – bearing materials.........................12

Figure 3.1. The technologies used in gold production....................................18

Figure 3.2. General process options for pretreating refractory ores...............22

Figure 4.1. Schematic Representation of The Local Corrosion Cell at a Gold
Surface In Contact With An Oxygen-Containing Cyanide Solution.........35

Figure 4.2. Effect of cyanide concentration on the dissolution rate of Au and Ag.....45

Figure 4.3. Equilibrium concentration of HCN and CN^- as a fun0ction of pH...........46

Figure 4.4. Schematic illustration of relations ship between particle size and gold
recovery...48

Figure 4.5. Effect of temperature on gold dissolution rate...........................49

Figure 4.6. Effect of Agitation Rate...50

Figure 5.1. Concentration Trends in Sallow Barren Bleed Holding Pound at
Dome Mine 55

Figure. 5.2. Inco SO_2- Air process flow diagram...60

Figure 5.3. Hydrogen peroxide treatment process flow diagram..................62

Figure 5.4. Schematic Water Balance for Cyanidation Tailings System 68

Figure 5.5. Typical measures for limiting tailings pond seepage...................70

Figure 6.1. Sample preparation flowchart 72
Figure 6.2. General flow chart of grinding tests 73
Figure 6.3. SIEBTECHNIC vibrating mill 74
Figure 6.4. Flow diagram of the experiments. 75
Figure 6.5. Construction of METALİÇ leach plant 77
Figure 6.6. Table of Metaliç device 78
Figure 6.7. Main body of Metaliç device 78
Figure 6.8. Assembling of FK P204 type bearings. 79
Figure 6.9. Technical data of main shaft 79
Figure 6.10. Technical data of stirring rod 80
Figure 6.11. Metaliç plant 81
Figure 6.12. Metaliç plant 81
Figure 6.13. Metaliç plant 82
Figure 6.14. Agitation jars (leaching tanks) 82
Figure 6.15. Degradation in the impervious media 86
Figure 6.16. Natural Degradation Carried out Using the Seeped Solution 87
Figure 6.17. X-Ray diffraction diagram of used clay 88
Figure 6.18. X – Ray fluoresans diagram of Gümüşhane gold ore 91
Figure 6.19. X – Ray diffraction diagram of Gümüşhane gold ore 92
Figure 6.20. Distribution of Au and Ag grade versus particle size 94
Figure 6.21. Cumulative oversize and undersize after primary crushing 96
Figure 6.22. Particle size distribution after primary crushing 96
Figure 6.23. Cumulative oversize and undersize after secondary crushing 97
Figure 6.24. Particle size distribution after secondary crushing 98
Figure 6.25. 10 min. grinding of feeding material (-1mm) 99
Figure 6.26. 30 min. grinding of feeding material (-1mm) 100
Figure 6.27. 60 min. grinding of feeding material (-1mm) 101
Figure 6.28. 80 min. grinding of feeding material (-1mm) 102
Figure 6.29. 125 min. grinding of feeding material (-1mm) 103
Figure 6.30. Comparison of undersize fractions in various grinding time 104
Figure 6.31. Au Recovery vs Time 106

Figure 6.32. Ag Recovery vs Time 106
Figure 6.33. Cu Recovery vs Time 106
Figure 6.34. Zn Recovery vs Time 106
Figure 6.35. Pb Recovery vs Time 107
Figure 6.36. Fe Recovery vs Time 107
Figure 6.37. Au Recovery vs Particle Size 107
Figure 6.38. Ag Recovery vs Particle Size 107
Figure 6.39. Cu Recovery vs Particle Size 107
Figure 6.40. Free NaCN Variations vs Time 107
Figure 6.41. General assessment of first set of experiments. 108
Figure 6.42. Au Recovery vs Time 109
Figure 6.43. Ag Recovery vs Time 109
Figure 6.44. Cu Recovery vs Time 109
Figure 6.45. Zn Recovery vs Time 109
Figure 6.46. Pb Recovery vs Time 110
Figure 6.47. Fe Recovery vs Time 110
Figure 6.48. Au Recovery vs Solid-Water Ratio 110
Figure 6.49. Ag Recovery vs Solid-Water Ratio 110
Figure 6.50. Cu Recovery vs Solid-Water Ratio 110
Figure 6.51. Free NaCN Variations vs Time 110
Figure 6.52. General assessment of second set of experiments 111
Figure 6.53. Au Recovery vs Time 112
Figure 6.54. Ag Recovery vs Time 112
Figure 6.55. Cu Recovery vs Time 112
Figure 6.56. Zn Recovery vs Time 112
Figure 6.57. Pb Recovery vs Time 113
Figure 6.58. Fe Recovery vs Time 113
Figure 6.59. Au Recovery vs pH 113
Figure 6.60. Ag Recovery vs pH 113
Figure 6.61. Cu Recovery vs pH 113
Figure 6.62. Free NaCN Variations vs Time 113

Figure 6.63. General assessment of experiment 3 114
Figure 6.64. Au Recovery vs Time 115
Figure 6.65. Ag Recovery vs Time 115
Figure 6.66. Cu Recovery vs Time 115
Figure 6.67. Zn Recovery vs Time 115
Figure 6.68. Pb Recovery vs Time 116
Figure 6.69. Fe Recovery vs Time 116
Figure 6.70. Au Recovery vs NaCN Cons 116
Figure 6.71. Ag Recovery vs NaCN Cons 116
Figure 6.72. Cu Recovery vs NaCN Cons 116
Figure 6.73. Free NaCN Variations vs Time 116
Figure 6.74. General assessment of forth set of experiments 117
Figure 6.75. Au Recovery vs Time 118
Figure 6.76. Ag Recovery vs Time 118
Figure 6.77. Cu Recovery vs Time 118
Figure 6.78. Zn Recovery vs Time 118
Figure 6.79. Pb Recovery vs Time 119
Figure 6.80. Fe Recovery vs Time 119
Figure 6.81. Au Recovery vs Agitation Rate 119
Figure 6.82. Ag Recovery vs Agitation Rate 119
Figure 6.83. Cu Recovery vs Agitation Rate 119
Figure 6.84. NaCN Cons.vs Time 119
Figure 6.85. General assessment of fifth set of experiments 120
Figure 6.86. Au Recovery vs Time 122
Figure 6.87. Ag Recovery vs Time 122
Figure 6.88. Cu Recovery vs Time 122
Figure 6.89. Zn Recovery vs Time 122
Figure 6.90. Pb Recovery vs Time 122
Figure 6.91. Fe Recovery vs Time 122
Figure 6.92. NaCN Cons.vs Time 123
Figure 6.93. Results of Experiment 6 by Final Test 123

Figure 6.94. The variation of free cyanide and temperature by time........................124
Figure 6.95.Relationship between temperature and volatilization with time............125
Figure 6.96. Cumulative volatilization by time..126
Figure 6.97. Variation of pH by time...126
Figure 6.98. The variation of free cyanide and temperature by time........................127
Figure 6.99. Relationship between temperature and volatilization with time...........128
Figure 6.100. Cumulative volatilization by time..128
Figure 6.101. Changes of pH by time...129

CHAPTER ONE
INTRODUCTION

The extraction of gold from the earth has been performed since it developed a naturally occurring value early in the history of mankind as a result of its unique physical and chemical properties, its decorative appeal and its scarcity. It has been called noble from earliest times, because it does not oxidize under atmospheric exposure, and that it appeared to the ancients to be insoluble.

In the past century, scientists have found out that gold can be solved in acid mixture comprising of HCl and HNO_3 which called aqua-regia. The later stage has been the discovery of solubility of gold in chlor. Although various processes had been developed regarding this method, no great success were obtained. Firstly Ensler, a German chemist, in 1846, then a group of Scottish scientists in 1887 discovered that gold could be solved rapidly in inorganic cyanide solutions at relative low concentrations (100 mg/lt) requiring no additional pressure and temperature.

The cyanidation process as it is known, was rapidly developed into a commercial process first at Crown Mine (New Zealand) in 1889 and at Robinson Deep Mine (South Africa) in 1890. Over the past hundred years it accounted for a growing propotion of world gold production. In particular, it made possible the exploitation of low grade, fine grained, so called “invisible” gold beyond the reach of gravity separation, and it has helped to eliminate use of a truly harmful reagent, mercury, which has almost disappeared in the world. To be sure, cyanide is not perfect. Its use is interfered with by certain copper and iron minerals, and the presence of naturally occurring carbonaceous minerals can reduce its gold recovery drastically. Elements such as Ag, Cu, Fe, Ni, Co, Zn, Hg, Pb, As, S and Sb are often seen in gold ores.

Some of these elements suffer various degrees of oxidation, and some from stable cyanocomplexes (cyanide consumer or cyanides).The presence and abundance of elements like Hg, Fe, Co, Cu, As, Co in the ore is especially important from cyanide consumption point of wiew. These elements cause excessive cyanide and oxygen consumption during leaching and create difficulties in solution and effluent treatment.

Almost 85 % of world's total gold production is carried out by cyanide leaching showing the importance of this method at gold production. But, however, due to the high toxicity of cyanide, the method is often banished in view of environmental considerations. For this reason, the importance and popularity of cyanide clarification increased steadily.

Leaving the cyanide containing process wastes stored to natural degradation is one of the methods mostly utilized for cyanide clarification. Because the success of this method depends upon many variables and the possibility of being affected by natural events is present, the use of chemical clarification methods has been a must. Up to 1982, the chemical clarification method for cyanide containing wastes was the alkali chlorification method. This method has today been replaced by cheaper and safer methods such as Inco SO_2-Air process and Hydrogen Peroxide Oxidation. Moreover, methods like biodegradation and AVR(Acidification-Volatilization-Reneutralization) are being developed.

In Turkey, since 1986 various foreign companies have initiated large exploration projects for gold and silver mines and as a result of these efforts some epithermal based gold deposits were discovered. Gümüşhane gold mines is one of these new gold mines in Turkey which will employ cyanidation process for the recovery of gold.

This study involves the experimental investigations for the determination of leach and natural degradation conditions of Gümüşhane mastra gold ore.

CHAPTER 2

GENERAL INFORMATION

2.1. Properties of Gold

Gold known as the noble metal of history is yellow coloured and one of the metals does not rush, corrode or tarnish. Use of gold goes back to written history. Gold has been considered a precious metal since ancient times and the search for gold stimulated world exploration and world trade.

Atomic Number	**79**
Atomic Mass	**197**
Atomic radius	**0.1439 NM.**
Density	**19.32 gr/cm^3 (0.698 lb/inç^3) at 20 °C**
Mhos' hardness scale	**2.8**
Brinell hardness scale	**18 HB**
Melting point	**1064 °C**
Boiling point	**2808 °C**
Casting temperature	**1100 - 1300 °C**
Heat Expansion coefficient	**Linear 14.2 m/Mk (at 20 °C)**
Specific heat	**131 Joule/kg.K (at 18 °C)**
Heat conductivity	**300 W/Mk (at 20 °C)**
Electrical conductivity	**45 m/ohm.mm^2**
Electrical resistance	**21.9 nn.m (at 0 °C), 23.5 nn.m (at 20 °C)**

Gold was derived from Latin word "Aurum" meaning shining dawn. A precious substance because it is one of the rarest metals, it has unique physical properties. It exceeds all other metals or alloys in malleability and ductility.

The purity of gold is called carat. Pure gold (100 % gold) is measured over 24 carat, which represents the other metal content rate in gold. For example, 18 carat gold contains 75% gold. This is called blue gold by goldsmiths and contains 750 units' gold and 250 units iron. White gold is an alloy of Cu, Ni, Zn and Pb.

Gold was named as "noble" because it does not react with water, dry or humid air, oxygen(even at high temperature),ozone, nitrogen, hydrogen, fluorine, iodine, sulfur and hydrogen sulfide under normal conditions. Sulfuric acid, hydrochloric acid, hydrofluoric acid, phosphoric acid, halide-free nitric acid (except in very high concentrations),and practically all organic acids have no effect on gold, either in concentrated or dilute solutions and at temperatures up to the boiling point. If a hydrochloric acid is combined with an oxidising agent such as nitric acid ,a halogen, hydrogen peroxide or chromic acid, gold will dissolve.

It is inert to the alkali metal phosphates and borate's, and to the alkali metals salts of the mineral acids, which can therefore be used as slagging agents for removing metallic impurities of gold.

The standard potential of Au/Au(+3) is +1.498V of Au/Au(+1) +1.68V, and of Au(+1)/Au(+3) +1.29V.

Gold alloys readily with mercury at room temperature to form an amalgam. This property is utilized in the amalgamation process and in fire gilding (Hermann&Wark 1992).

2.2. Use of Gold

Gold and Copper were the first metals used by man because of their occurrence in the native state and their malleable and ductile properties, which meant that they could be easily worked with primitive tools.

Nowadays, Gold is used in many fields ranging from jewellery to industrial purposes, the jewellery being the most popular field. .Figure 2.1. shows the various areas of gold. use

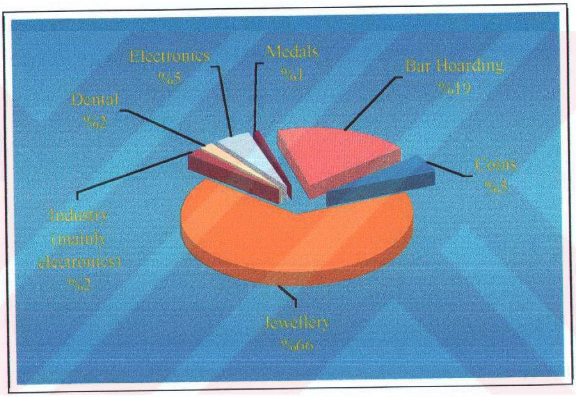


Figure 2.1. Use of gold

2.3. Gold Potential and Production

Total world resources of gold are estimated at 75 000 metric tons, of which 15 % to 20 % are by product resources. The Republic of South Africa has about one-half of world resources, and Brazil and the United States have about 13 % each. (Table 2.1. and Figure 2.2)

Table 2.1. World Gold Reserves and Reserve Base (tone)

(Mineral Commodity Summaries, 1995)

Country	Reserves	Reserve base
United States	5 000	5 500
Australia	3 100	3 400
Brazil	800	1 200
Canada	1 400	3 300
China	NA	NA
Russia	3 100	3 400
South Africa	18 000	29 000
Uzbekistan	3 000	3 300
Other Countries	9 300	11 000
World Total	*44 000	*60 000

*Excludes China and some other countries for which data were not available

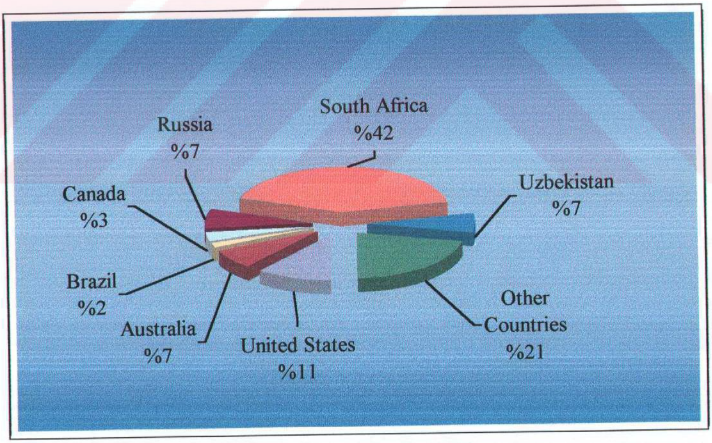


Figure 2.2. Gold reserves by countries (Mineral Commodity Summaries, 1995)

In the 1970's, Industrialised and developing countries have paid much attention to gold mining. As a result in 1980's,a considerable increase in gold production has been observed especially in USA, Canada, Australia, Russia, China, Indonesia, Brazil, and Philippines. Distribution of gold production by countries is given in Figure 2.4.

In 1995 24 % of World's gold production was met by South Africa. The world's total gold production in 1995 increased 50 % compared to 1970's. (Altın ve altın madenciliği, 1997)

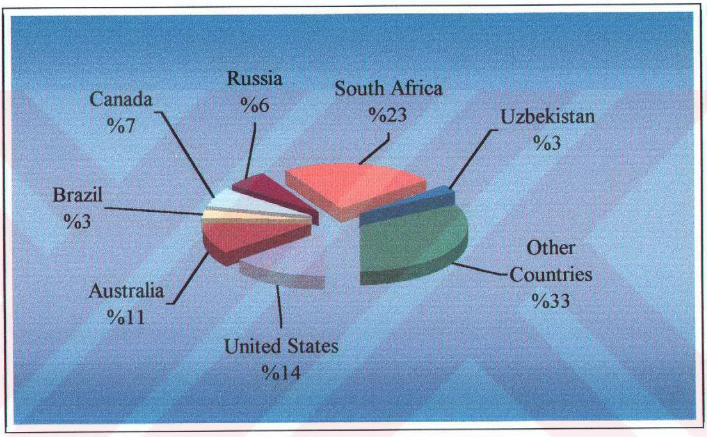


Figure 2.3. . Distribution of gold production by countries in1995 (Altın ve altın madenciliği, 1997)

According to a study carried out by Mining Journal Ltd, to evaluate the trend of today's gold mining industry, the geographical distribution of gold mines which will start operation between 1996 – 1999 is given in Figure 2.4,

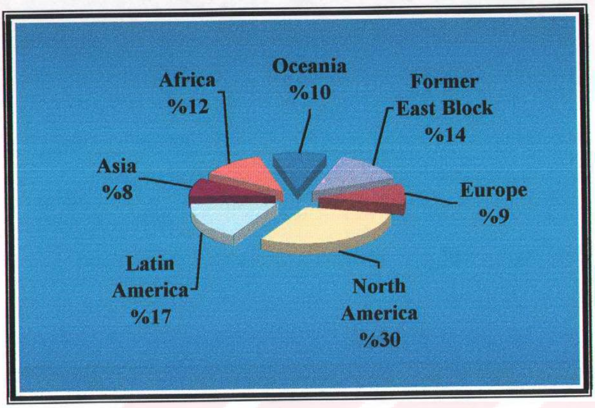


Figure 2.4. The geographical distribution of gold mines under condition and will start operating between 1996 – 1999 (Total 479 tone/year)

In Table 2.2, data about relevant gold mining projects in Turkey which are collected from gold prospecting companies, are given.

Turkey imports 150 – 160 tpy gold. Although Turkey has a gold production potential of 11 tpy, the country has no contribution to world's total production.

If this production is realized Turkey will be one of the leading gold producers of as seen in Figure 2.5.

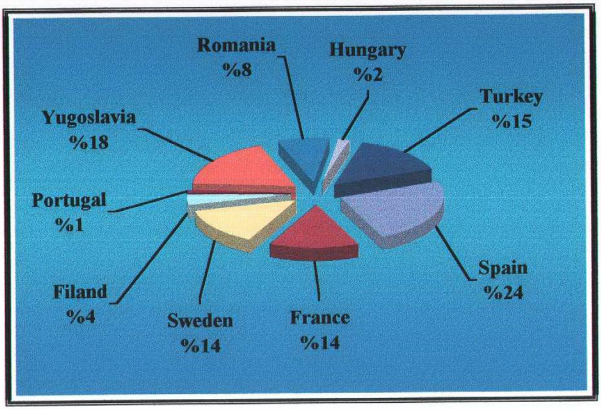


Figure 2.5. Tentative distribution of gold production in Europe including Turkey's contribution in 1997-1998

Table 2.2.Gold Reserves And Planning Production of Turkey(Madencilik bülteni, 1997)

Location	Reserve Tone	Planned production Tone/year	Current situation
Kaymaz-Eskişehir	6	1	Investment permission taken
Efemçukuru	20 (*)	2 (*)	Prospecting continues
Küçükdere-Balıkesir	7,5	1	No permission taken yet
Ovacık-Bergama	24 gold (24 silver)	3	Investment permission taken
Mastra-Gümüşhane	12	1	Prospecting continues
Cerattepe-Artvin	30,3 gold (1,050 silver)	3	Feasibility study continues
Total	99,8 gold (1,074 silver)	11	No production yet.

(*) Expected

2.4. Gold Bearing Materials for Production

Gold is inert at ambient temperatures and pressures and consequently there are very few naturally occurring compounds of the metal. The average concentration of gold in the earth's crust is 0,005 g/t.

The low concentration of gold in primary rocks means that up grading by a factor of 3000-4000 is usually required during ore formation processes to achieve commercials concentrations.

Primary and secondary gold-bearing materials can be classified into 15 mineral processing-based categories, defined Figure 2.4.

Placer deposits are formed by the liberation of gold and hydraulic transport of gold particles away from a primary old deposit. There are several clusses of placer ores which relate to means of gold concentration and the distance from the primary gold deposits.

Eluvial(or residual) placers consist of wheathered rock from which some of the finer and lighter minerals have been washed away, leaving gold at a higher concentration. Colluvial(or deluvial) placers have been transported some distance from the parent deposit Fluvial(or alluvial) placers are those in which gold occurs in stream or river systems.

The amount of gold present in placer ores is usually low compared with the associated primary hard rock deposit . However, due to the ease of operation and low costs, placers are often commercially significant and may be the forerunner to further underground mining. The capital and operating costs of placer operations can be very low, allowing economic mining of ores containing as little as 0.2 g Au t^{-1} . However, the contribution of placer gold (excluding palaeo-placers) to annual world production is now small, between 2 and 5 %. (Marsden & House, 1992)

Placer ores has been recovered by gravity treatment units such as Knelson concentrators that are in use for gold recovery. (Tükel Ç., 1996)

Free Milling Ores are defined as those from which cyanidation can extract approximately 95 % of the gold when the ore is ground to a size of 80 % < 75 micron, as commonly applied in industrial practice, without incurring prohibitively high reagent consumption. Two main classes of free milling ores are palaeo-placers and quartz vein gold ores. Some epithermal deposits may be free milling but more commonly contain significant concentrations of sulphides and are therefore considered in subsequent classes.

Palaeo-placers are literally fossilized placers, the most famous being the Witwatersrand lake bed reefs in South Africa.

From a mineral processing point of view paleau-placers differ from young alluvial placers as the gold is unliberated and the ore is consolidated. Crushing and grinding is therefore required to librate to gold to an extent, which allows efficient gold extraction. . Palaeo-placer gold deposits have been mined at depths of up to 3 km and therefore both mining and mineral processing costs are generally more than an order of magnitude greater than those for young placer deposits (Marsden & House, 1992).

Quartz/gold veins or lodes comprise a variety of deposits which are essentially hydrothermal veins of quartz and gold that either replace wall rock or fill open spaces along fractures zones. Most of them are pre-cambrian or tertiary in age and can occur to depths in excess of 1 km.

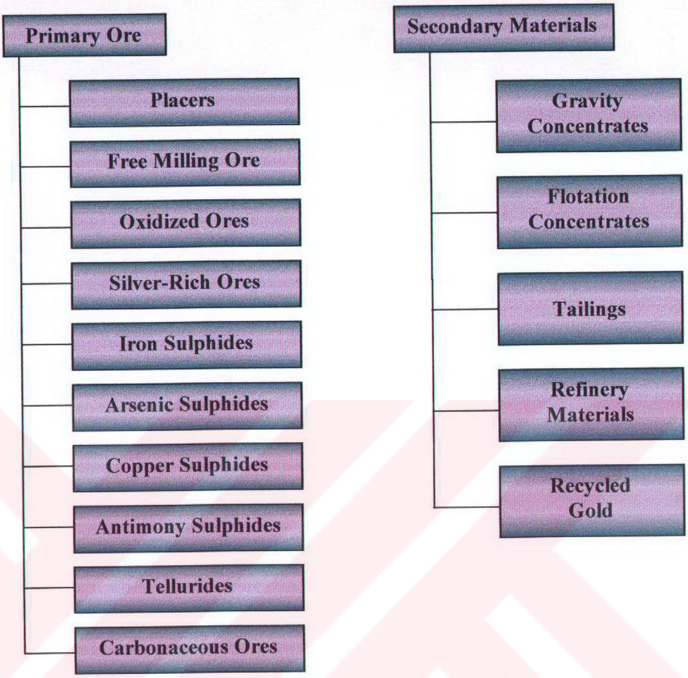


Figure 2.6. Primary and Secondary Gold – Bearing Materials

An oxidized ore is defined as ore in which the ore material has been oxidized or weathered, posibily in a zone that is a typical of the primary sulphide deposit, and for which some special processing may be required. Oxidation and other hydrothermal alteration process lead to the breakdown of rock structure, resulting in increased permeability. This often allows high leaching extractions to be achieved by heap leaching of run-of-mine ore even though the ore particle size is very coarse.

Oxidized ores differ from primary ores as a large proportion of fines are often generated on grinding, or during heap leaching and minerals such as clays are more abundant. The presence of clays, such as pyrophyllite ($Al_2Si_4O_{10}(OH)_2$), tale

($Mg_3Si_4O_{10}(OH)_2$), kaolinite ($Al_4Si_4O_{10}(OH)_8$) and montmorillonite ($Al_4Si_8O_{20}$ $(OH)_4 . nH_2O$) can have important process implications, for example ;

- decreased heap leach pad permeability,
- increased slurry viscosities in processing (e.g. cyanidation or CIP) and hence increased energy required for slurry mixing,
- blinding of activated carbon, in CIP or CIL.

Although gold is almost always associated with ***silver***, when the silver grade is high(10 gr/t) and/or the gold is present as electrum the precessing may need to be modified. The greater reactivity of silver particularly influences the behaviour of gold in flotation, leaching and/or recovery processes. Silver has a value of about one-hundredth that of gold, but tends to occur at higher grades and therefore may be a significant source of revenue to a gold operation. The drawback is that the larger volume or mass of recovered product may cause reduced gold recovery (e.g. in Cıp circuits and recovery section) if the gold circuit design has not adequately taken into accont the silver mineralization.

Electrum readily tarnishes in the presence of sulphide ions to form a silver sulphide layer of 1-2 μm thickness, which can limit the access of cyanide solution, thereby decreasing dissolution kinetics and,possibly, reducing the gold and silver extraction (Mardsen & House, 1992)

Iron sulphide minerals which is most important are: Pyrite, Marcasite and Pyrrhotite. Arsenopyrite also has similar charecteristics, though it is sufficient distinctive to warrant separate consideration.

The most significiant arsenic minerals are arsenopyrite, orpiment and realgar. Arsenopyrite is common sulphide host for gold, second only pyrite.It is marginally less hard though more brittle than pyrite, which results in preferential grinding and finer product size than pyrite. This can lead to higher flotation recoveries of pyrite over arsenopyrite.Orpiment contains 61 % As and very minor component in several commerical gold ore deposits.Realgar is associated with orpiment to which it alters on weathering.Realgar is less soluble than orpiment in alkaline cyanide solution and has less significant effect on cyanidation.

Ores containing gold associated with ***copper sulphide*** minerals which affect process selection or operating conditions are considered at part 4.3.2.. It is relatively oncommon for gold to be associated solely with copper minerals and there is almost always some pyrite present. In base metal sulphide processing gold generally reports with copper minerals,e.g. chalcopyrite or bornite, in process stream. This can be attractive from a metallurgical point of wiev, as there is some selectivity against pyrite and the possibility of selling a gold-rich copper concentrate for which a credit is received(typically 90-97 % of gold value).Although gold grades in copper ores may be low (usually < 1 gt^{-1}) gold production as a by-product of copper is relatively large due to the high tonnages of material processed. About 80 % of by-product gold comes from copper ores; the remainder being accounted for by Pb-Zn_cu ores (Marsden & House, 1992).

Antimony sulphides are Aurostibnite($AuSb_3$) and Stibnite(sb_2S_3). Aurostibnite can present problem in gold ore treatment due to its low solubility in cyanide solution and poor amalgamarion properties. Stibnite is main source of antimony metal and occurs in quartz veins and with Pb-Zn sulphide assemblages.

Tellurides are the only gold minerals other than metallic gold and Au-ag which are of economic significance. There is a wide range of Au/Te and mixed metal tellurides.Gold tellurides usually contain some native gold, together with other metal tellurides, often with complex intergrowths. One of the best known telluride deposits is Cripple Creek (Colorado, USA).

Carbonaceous ores are those containing carbonaceous components which adsorb dissolved gold during leaching thereby reducing gold extractions by cyanidation. These gold ores sometimes require oxidative pre-treatment prior to cyanide leaching.

Effect of copper ores, iron ores, arsenic ores, antimony ores gold tellurides etc. in cyanide leaching are discussed part 4.3.

Gravity concentrates are a special class of material due to their unusual contents; principal coarse (ie. >50 μm<2 cm) gold and high concentrations of dense oxide and sulphides. Gravity concentrates are recovered using a variety of equipment e.g. sluices, jigs, spiral concentrators and shaking tables and contain primarily heavy mineral oxides such as magnetite, ilmenite and zircon possibly with lesser amounts of sulphides, usually pyrite. The majority of gold present or quartz may be present and some gold may be coated with Ca, Fe or Mg oxides or carbonates. Fine unliberated gold grains can also occur in ilmenite and rutile and would be recoverable by amalgamation.

Flotation concentrates contain gold and other hydrophobic minerals resulting from flotation of a primary ore or preconcentrated material. These concentrates have a high sulphide content. In sulphide flotation concentrates gold can be present as either free gold, which floats readily or gold locked in sulphides. Slurries of sulphide flotation concentrates have the unusual characteristics of being strongly hydrophobic and rapidly setting. This often leads to difficulties in handling and treatment by gravity concentration or cyanidation.

Tailings are materials, which have been discharged from either currently operating or disused gold plants. This class of material can result from any of several extraction processes (e.g. cyanidation, flotation, gravity concentration or amalgamation.)

Refinery materials are considered to be the gold bearing products of hydrometallurgical or pyrometallurgical process eg. Calcine precipitates, anode slimes and slags.

Recycled gold is that which is produced from gold bearing materials resulting from a fabrication process, eg. jewellery scrap or electrical components.

CHAPTER 3

GOLD PRODUCTION TECHNOLOGY

Process selection is the systematic development of the optimum metal extraction route for a particular feed material using the most appropriate technology.

In the case of gold this procedure has two main objectives:

- To optimize project economics, principally a function of gold recovery, through put rate and processing costs.
- To develop a process that satisfies all of the project requirements, including, for example political and environmental considerations.

The chemical response of a particular gold ore to the various process options plays a key role in achieving these objectives. (See figure 3.1.) At present over 85 % of the world's gold production involves chemical processing. Process selection is playing an increasingly important role as the complexity of chemical processing techniques increases with the exploitation of lower grade and more complex gold ores.

Process selection is an iterative procedure, which usually starts as soon as exploration has established the presence of gold mineralization in sufficient grade and tonnage for the ore body to be considerable a potentially economic reserve.

The amount of effort devoted to process selection is related to the degree of certainly of the grade and reserve estimations and their absolute values, i.e. the overall attractiveness of the deposits.

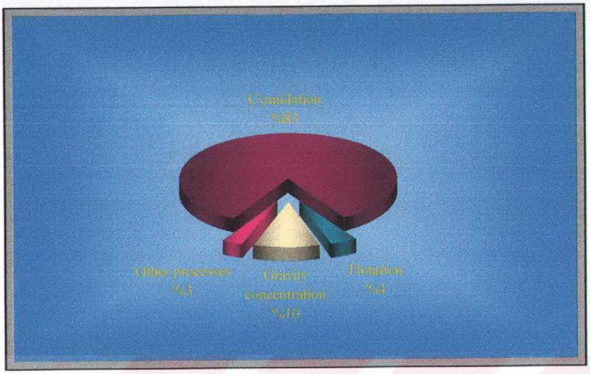


Figure 3.1. The technologies used in gold production
(Altın ve Altın Madenciliği, 1997)

3.1. Gravity Concentrations

Gravity concentrations are used widely for the recovery of free gold and gold associate with heavier minerals. e.g. sulphides and titanium minerals. A variety of equipment is available for this and recent developments have enabled the recovery of free gold down to about 10 micron. Concentrates may be treated by direct cyanidation, smelting, amalgamation, flotation or intensive leaching, depending on their mineralogy. (Marsden & House, 1992)

There are two main types of gravity concentration process.

- ✓ The first type is separation in current of liquid (usually water) (jigs, tables, sluices, vanners, buddles etc.)
- ✓ The second type is Dense Medium Separation (DMS) or Heavy Medium Separation (HMS).

New devices have been put on the market with the aim of achieving lower capital and capital cost and of extending to finer size of gold. Such as, belt concentrations, spirals, cone concentrators, Knelson concentrators, Falcon concentrators, jigs and multi gravity separators (MGS).

3.2. Amalgamation

Concerns over the health hazard associated with mercury have reduced the application of amalgamation in the industry. However, it is still used for the treatment of gravity concentrates since there are few suitable alternatives. The amalgam that is produced is retorted and smelted for gold and mercury recovery(Marsden & House, 1992)

The gold concentrate and mercury are usually conducted for several hours under mildly agitated conditions, e.g. using a rotating dram with a Au: Hg ratio of 1:10 (batch process), or by passing a slurry over mercury coated plates or mercury pools. The gold loaded amalgam may be separated from the waste minerals by elutriation or sedimentation prior to removal of excess mercury by filtration and retorting in which process the amalgam is placed in a mercury retort and heated until the mercury has been distilled off.

The following criteria are necessary for efficient precious metal recovery by amalgamation.

- ✓ Gold and silver should be the metallic components in the ore
- ✓ The gold grains must be wettable by mercury
- ✓ The surface tension of gold Hg-water must be high enough for the mercury wetted gold to be included in the mercury bulk. (Tükel, 1996).

3.3. Flotation

The flotation process separates minerals of varying surface chemistry and has two important applications in gold ore processing These are;

- ✓ The separation of constituents of the ore, mentioned above, from the free milling part so that they may receive separate treatment
- ✓ The recovery of gold values where cyanidation or gravity concentration are not applicable

Another less important application in case where it is possible to recover flotation concentrate containing the gold and to produce a tailing which is sufficiently low grade to be discarded. The subsequently cyanide plant can then be much smaller than when the entire ore is leached. This can effect considerable capital savings (Srewart, 1984).

3.4. Leaching Gold-Bearing Ore

All hydrometallurgical gold extraction routes use a leaching step to produce a gold solution as an intermediate product. Two important elements in leaching are complexant and oxidant. In gold processing, limited number of leachants from complex of sufficient stability for use in gold extraction. Cyanide is universally used to due to low cost and great effectiveness for gold. Dissolved oxygen have been the major oxidant, supplied from air, which contributes to effectiveness of the process.

3.4.1. Pre-treatment Methods

World demand for gold has continued to be buoyant and this has resulted in relatively high and stable prices for the metal. The need to treat increasingly low grade and/or refractory gold ores and the continuing search improvements in the economic of existing operations, has led to a wide variety of developments and innovations in gold benefication technology. (Wall, Hornby & Sethi, 1987).

Some investigators determined treatment of gold refractory ores and concentrates that respond poorly to conventional cyanidation techniques due to the complex mineralogy of the ore.

Worldwide investigations have shown that possible reason for poor response of gold-bearing material to cyanidation include;(McDonald, Johnson & Sandberg,1990)

- ✓ Physical locking in sulphides, oxides, silicates etc
- ✓ Chemical locking as gold alloys or compounds e.g. electrum, gold tellurides, $AuSb_2$ (aurostıbnite), Au_2Bi (muldonite) etc
- ✓ Gold substitution in the sulphide lattice e.g. "solid solution" gold in arsenopyrite
- ✓ Gold surface passivation due to formation of a chemical layer (Brooy, Linge & Walker, 1994)

A common technique to treat refractory ore has been roasting of flotation concentrates prior to cyanidation. Other techniques include fine grinding, pressure oxidant of sulphides, bacterial digestion, chemical pretreatment and hypochlorite or chlorine oxidation.

These pretreatment options for dealing with refractory ores are illustrated in Figure 3.2. Pressure oxidation is a particularly aggressive pretreatment method for highly refractory gold ores and concentrates(Wall, Hornby & Sethi, 1987).

Typical operating conditions are temperatures of 170-225°C with a retention time of 1-3h in a 4 or 5 compartment autoclave. Operation at around 200°C minimizes construction cost of autoclaves. Temperatures need to be above 160°C to ensure irreversible oxidation of sulphur to sulphate, as molten sulphur can occlude gold and consume cyanide in subsequent cyanidation-CIP/CIL. In the autoclave, pyrite and arsenopyrite initially dissolve to form ferric, sulphate and arsenate ions which are transformed by hydrolysis into solids such as scorodite, haematite, basic iron (III) sulphates and jarosites.

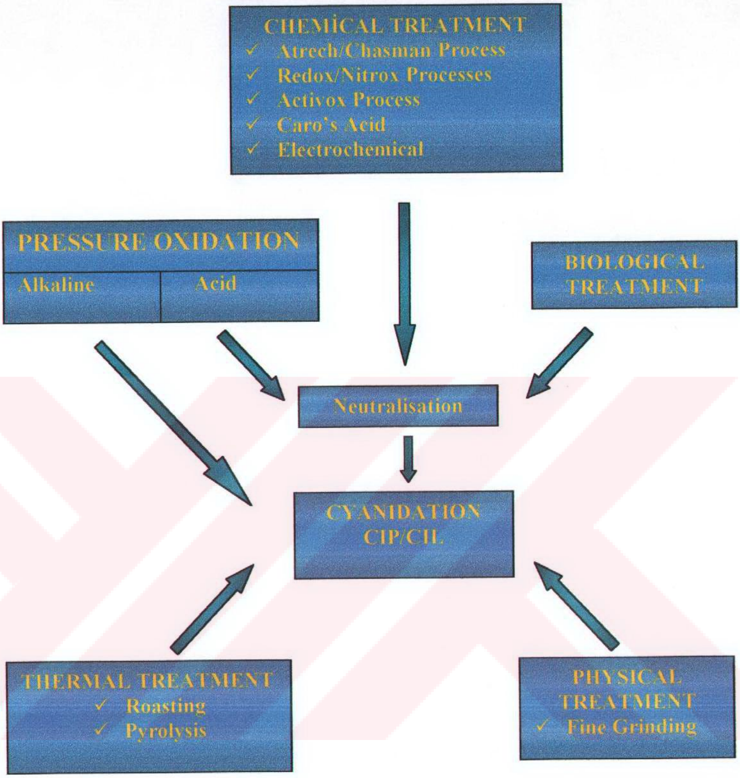


Figure 3.2. General process options for pretreating refractory ores (Brooy, Linge & Walker, 1994)

Alkali pressure oxidation is also used for high carbonate (>10 % CO_3) and low sulphur ores (< %2). This process operates at 220°C with an oxygen partial pressure of 140-180 kPa and 3300 kPa total pressure and dissolves pyrite to form iron oxides/hydroxides and sulphuric acid.

The pressure cyanidation technique has been applied to cyanidation of stibnite containing ores or concentrates. Which give poor gold recovery under atmospheric conditions. The reaction can ba carried out in an autoclave or pipe reactor. The problem has been ascribed to oxygen depletion associated with the formation of antimonites and thioanatimonites, with stibnite decomposition being grater at pH>10. (Brooy, Linge & Walker, 1994).

Bio-oxidation is now an accepted technology for the pretreatment of refractory sulphide gold ore which can be retrofitted to conventional cyanidation-CIP/CIL operation. Thiobacillus ferrooxidans and sulpholobus which are types of bacteria can be used in the biooxidation step. (15). Thiobacillus are the most suitable for the oxidation of gold-bearing sulphide ores and concentrates since they thrive under close to ambient temperatures (35-40°C) and feed on un-pathogenic inorganic compounds. The bacteria derive energy from the oxidation of sulphur and iron species but they also require oxygen, carbon and nitrogen to support oxidation reactions and for cell growth. These chemicals must be supplied either from the ore, from nutrient reagent and/or air additions. The bacteria operate best within a pH range 1,0-1,8. (Marsden & House, 1992)

Bacterial oxidation is only process that can be operated to achieve controlled partial oxidation of sulphides. This is not practically possible with roasting and is more difficult for aqueous pressure oxidation, although in the latter case it is possible that the feed rate might be controlled to maintain partial oxidation for a feed material which has a consistent composition. Partial oxidation not only reduces the oxygen and heat transfer requirements of the system, but also has the added benefit of producing less acid with correspondingly lower neutralization requirements, al of which can have a significant effect on capital and operating cost.

The major factors affecting the kinetics of biological oxidation ore as follows;

- ✓ Ore mineralogy
- ✓ Solution chemistry and conditions (temperature, pH, potential, pulp density)

- ✓ Dissolved oxygen concentration
- ✓ Particle size

All these variables above can have a controlling effect on bacterially assisted oxidation reactions and must be optimized and controlled to maximize bacterial activity, and consequently, the oxidation rate.

The only option in physical pretreatment is to grind finer. Fine grinding with a conventional mill (100 % < 38 micron) or ultrafine grinding with different types of mill producing particles with sizes in the range of 1-20 μm. There are three types of mills for ultrafine grinding, namely: vibtatory mills, stirred mills and jel mills of these the stirred mills are the most cost effective in terms of the energy in put required to produce a given grain size with main application the semi refractory materials. (Brooy, Linge & Walker, 1994).

Roasting can be applied to a wide variety of sulphide, carbonaceous and telluride ores and concentrates. Single-stage roasting is applied to feed materials which have low arsenic content, typical <3 %As and which show good response to the direct oxidation process. Two-stage roasting is preferred for high arsenic materials and for some iron sulphide feeds, even in the absence of arsenic. In these case, the increased gold recovery which result from more efficient two-stage roast more than compensates for increased capital and operating costs. This route is not always justified, and each refractor material must be considered individually. (Marsden & House, 1992).

Pyrite roasting is normally carried out in the range 650-700°C as a " dead roast". The procedure convents the pyrite in stage to hematite (Fe_2O_3) which is in soluble in cyanide solution and sufficiently porous to expose the gold particles.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

but the actual reaction take place two stages. Firstly, pyrrhotite is formed and the pyrrhotite is then converted to hematite. The sulphur is volatilised as SO_2.

3.4.2 Leachants Used in Gold Hydrometallurgy

In the context of gold extraction, leaching is the dissolution of a metal or mineral in a liquid. Only a limited number of leachants from complexes of sufficient stability for use in gold extraction process. Cyanide is universally used because of its relatively low cost and great effectiveness for gold dissolution.

Chlorine-chloride leaching was applied commercially in the 19 th century, but its use diminished following the introduction of the cyanide process in 1889.

Thiourea, thiosulphate, thiocyanate and a variety of other halide solutions have been investigated extensively in the laboratory and several potential process have been developed. But none of them were commercially applied on a large scale.

Examples of some leachants, together with the complex formed, the oxidants used, and other data are shown in table 3.1.

Cyanidation chemistry and mechanism are well known. It was explained in detail in chapter 4. Also, despite some concerns over the toxicity of cyanide, it can be applied with little risk to health and the environment.(Marsden & House, 1992)

Acid thiourea solutions (pH 1-2) can be used as a solvent for gold. The anodic reaction follows the equation:

$$Au + 2CS(NH_2)_2 \rightarrow Au(CS(NH_2)_2)_2 + e^-$$

Although this reagent has low acute toxicity and the gold dissolution is rapid, commercial adsorption of the process has been hindered by three factors;

- ✓ Thioure is more expensive than cyanide
- ✓ Consumption is high due to easy degradable property
- ✓ The gold recovery step requires more development (Brooy, Linge & Walker, 1994)

Gold dissolves in ***alkaline thiosulphate*** ($S_2O_3^{-2}$) solution, using dissolved oxygen as the oxidant, to from the Au(I) complex, as follows

Table 3.1. Leaching System for Gold.

Leaching Reagent	**Oxidant Used**	**Gold Complex in solution**	**General conditions**
Alkaline Systems			
Cyanide	O_2	$Au(CN)_2^-$	pH>10
Ammonia-cyanide	O_2	$Au(CN)_2^-$	pH>10
Organic nitrilles	O_2	$Au(CH(CN)_2)_2^-$	pH>7
Alpha-hydroxynitriles	O_2	$Au(CN)_2^-$	pH>10
Calcium cyanamid	O_2	$Au(NCN)_2^-$	pH>10
Alkali cyanaform	O_2	$Au(C(CN)_3)_2^-$	pH>10
Neutral Systems			
Thiosulphate	O_2	$Au(S_2O_3)_2^{3-}$	pH>7, 60°C
Bromocyanide	BrCN	$Au(CN)_2^-$	pH>7
Bromine	Br_2	$AuBr_4^-$	pH>7
Acid Systems			
Chlorine (aqueous)	Cl_2	$AuCl_4^-$	pH<2, Cl^-
Aqua regia	HNO_3	$AuCl_4^-$	pH<2, Cl^-
Ferric chloride	Fe^{3+}	$AuCl_4^-$	pH<2, Cl^-
Thiocynate	Fe^{3+}, H_2O_2	$Au(SCN)_4^-$	pH<3
Thiourea	Fe^{3+}, H_2O_2	$Au(NH_2CSNH_2)_2^+$	pH 1-2

$$4Au + 8S_2O_3^{-2} + O_2 + 2H_2O \rightarrow 4Au(S_2O_3)_2^{-3} + 4OH^-$$

The rate of dissolution is dependant on thiosulphate and dissolved oxygen concentrations and temperature (60°)

Chlorine is able to dissolve gold as outlined at following equation:

$$Au + 4Cl^- \rightarrow AuCl^-_4 + 3e$$

Main problem encountered with chlorine are that if any oxidisable materials are present reagent consumption will be high, and if there are any dissolved sulphide present the dissolved gold will be reduced to back to metallic form. There are, also, environmental problems associated with chlorine including dangerous handling.

Other halide systems, such as bromine-chloride are capable of dissolving gold at very fast rates by the electrode potentials of the relevant reduction for example:

$$Au + 2Br^- + Br_2 \rightarrow AuBr_4^- + e$$
$$Au + 2I^- + I_2 \rightarrow AuI_4^- + e$$

These systems are capable of dissolving many sulphide minerals and bromine-chloride solution has been used commercially for leaching of refractory gold-bearing materials.

Unfortunately, the commercial application of bromine and iodine solutions for gold leaching is restricted by the high cost of the reagents, the high cost of materials of construction to withstand the severe conditions and health risks associated with their use. (Marsden & House, 1992).

3.4.3. Gold Recovery Methods

After gold have been taken into solution by forming complexes with various reagents as mentioned above, it is important to recover it from solution. To recover gold from complex, a number of methods have been developed and used widely. Selection of method depends on gold concentration and impurities in solution.

Zinc precipitation, Merill Crow process, is traditional method of gold recovery from pregnant cyanide solutions. Effectiveness of the precipitation is enhanced by dearating the solution by vaccum prior to zinc addition. The overall zinc precipitation reaction is as follows;

$$2Au(CN)_2^- + Zn \rightarrow 2Au + Zn(CN)_4^{-2}$$

Gold will adsorb onto activated carbon from a pregnant solution. The use of this principle has received considerable attention in recent years and three important processes have been developed. These are;

- ✓ Carbon In Pulp (CIP)
- ✓ Carbon In Leach (CIL)
- ✓ Carbon In Column (CIC)

These methods are based on the adsorption of gold ions in the saturated cyanide solution onto the activated carbons.

In CIP process, activated carbon flows countercurrently to the pulp stream of leached solids and pregnant solution. Here, gold ions in the solution are loaded onto the carbon particles by adding activated carbon into the adsorption tanks.

The CIL process differs from CIP in that instead of contacting the carbon and dissolved gold in separate vessels, contact takes place in the leaching vessels. As leaching is a slower process than adsorption it is preferable to commence leaching before adding the carbon. The CIL process has advantages than CIP where the ore is low grade and the leach rate is high.

CIC involves the contacting of activated carbon with relatively clean pregnant solution. Contact normally takes place in vertical column pertitined horizontally with the carbon being moved countercurrently and intermittently to the flow of solution (Steward, A.L., 1984)

One of the emerging technologies deserving attention involves the recovery of precious metals from pregnant solution by ion exchange resin. Either strong or weak base resin may be used as presented in the following loading and stripping equation.

$$RCl + NaAu(CN)_2 \rightarrow RAu(CN)_2 + NaCl$$

Where R is an anion exchanger.

In general, the stripping of the loaded gold and silver values from the resin has proved to be somewhat difficult.

Solvent extraction of gold and silver from pregnant solution is another alternative technique and worthly of consideration. The loading stage reaction is as follows;

$$R_2NH + H^+ + Au(CN)_2^- \rightarrow (R_2NH_2\ )\ (Au(CN)_2)$$

Where R= $C_{10} - C_{12}$ alkali group.

Additional research and development activities in the future should provide the SX alternate to be quite attractive practically and economically.

CHAPTER 4

CYANIDATION

4.1. Properties of Cyanide Compounds

In solid and liquid wastes of gold extraction plants, many cyanide compounds and some derivatives of these are found (Table 4.1). Stability constants of these are given in Table 4.2.

In general, cyanide compounds can be grouped as follows;

- ✓ Free cyanides
- ✓ Complex cyanides
- ✓ Insoluble complexes
- ✓ Other cyanide reaction products

Table 4.1. Important Cyanide Species Found in Mining Effluent (Staunton, 1991)

Free Cyanide	HCN, CN^-
Simple Cyanide Compounds a-Readily soluble b-Relatively insoluble	 $NaCN$, KCN, $Ca(CN)_2$, $Hg(CN)_2$, NH_4CN, $Zn(CN)_2$, $CuCN$, $Ni(CN)_2$, $AgCN$, $Cd(CN)_2$,
Weak metal cyanide complexes	$Zn(CN)_4^{-2}$, $Cd(CN)_3^{-2}$, $Ni(CN)_4^{-2}$, $Ag(CN)_2^-$
Moderately strong complexes	$Cu(CN)_2^-$, $Cu(CN)_3^{-2}$, $Ni(CN)_4^{-2}$, $Ag(CN)_2^-$
Strong Complexes	$Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$, $Co(CN)_6^{-4}$, $Au(CN)_2^-$, $Hg(CN)_4^{-2}$
Other Cyanide Reaction Products	SCN^-, CNO^-

Table 4.2 Stability Constant for Metal – Cyano Complex (Jones & Staunton, 1991)

n=	1	2	3	4	5	6
Cd^{+2}	5.5	10.6	15.2	18.4		
Co^{+2}	2.7					19.1
Co^{+3}						64.0
Cu^{+}	6.5	15.3	19.0	21.6		
Cu^{+2}	5.7	16.0	26.5	28.7		
Au^{+}		38.3				
Au^{+3}				56.0		
Fe^{+2}					32.8	37.0
Fe^{+3}						42.0
Pb^{+2}					10.3	
Hg^{+2}	18.0	34.7	38.5	41.4		
Ni^{+2}				26.0		
Ag^{+}	7.9	18.7	19.4	18.3		
Zn^{+2}	6.0	10.4	15.6	19.2		

4.1.1. Free Cyanides

These are in the form of HCN and CN^- ions. Free cyanides are obtained using inorganic salts such as NaCN, KCN, $Ca\ (CN)_2$. These salts decompose in aqueous solutions and release the active compound cyanide ion (CN^-). CN^- ion produces HCN by hydrolysis in neutral or near neutral solutions (İpekoğlu & Mordoğan, 1993).

In aqueous solutions

$$NaCN + H_2O \rightarrow Na^+ + CN^-$$

In acidic conditions

$$CN^- + H_3O^+ \rightarrow HCN + H_2O$$

In neutral or near neutral conditions

$$CN^- + H_2O \rightarrow HCN + OH^-$$

HCN and CN^- concentrations in the solutions are equal (% 50 each) at pH = 9.36.

4.1.2. Complex Cyanides

In gold extraction plants, cyanide solves not only gold but also other metals in the ore such as Cu, Ni, Zn, Fe in form of complex cyanides. The metal cyanide complexes occurring are classified by their stability.

Weak Complexes: Such complexes decompose easily during leaching and release free CN^- ions into the solution.

Moderate Complexes: decomposition depends upon complex stability.

Strong Complexes: These complexes release the cyanide ion not easily from the compound. Although they are not toxic, some problems appear at degradation of or regeneration from waste solutions (İpekoğlu & Mordoğan, 1993).

4.1.3. Insoluble Complexes

Such complexes can settle onto the solid part of the solution during the extraction process. So, they are likely to occur in wastes -ferri-ferro cyanides and ferro-ferro cyanides solve giving the solution cyanide at a total concentration of 5-10 ppm. In alkaline solutions, resolving at a considerable extent can be seen.

4.1.4. Other Cyanide Reaction Products

During leaching, cyanide reacts with non metallic minerals in the ore and forms other compounds then metal cyanides which are called OCN^- and SCN^- ions. are non toxic.

4.2. Leaching Kinetics

Simple cyanide salts, such as sodium, potassium and calcium cyanides, dissolve and ionise in mater to form their respective metal cation and free cyanide ions;

$$NaCN \rightarrow Na^- + CN^-$$

The solubilities and relative cyanide content of the different cyanide salts are given in Table 4.3 All these salts have been used effectively on a commercial scale as source of cyanide for leaching. Sodium and potassium cyanide are more readily soluble than calcium cyanide.

Table 4.3. Properties of Simple Cyanide Compounds(Marsden & House, 1992).

Compound	**Available cyanide (%)**	**Solubility in water At 25⁰C (g/100⁰C)**
NaCN	53.1	48
KCN	40.0	50
$Ca(CN)_2$	56.5	Decomposes

Sodium cyanide is also widely available in solution in some regions of the world. Thus, the choice of cyanide type depends on the method of applications, cost and availability free cyanide form complexes with many metal species, principally the transition metals, which vary widely in stability and solubility:

$$M^{X+} + y\ CN^- \rightarrow M(CN)_y^{(y-x)-}$$

The mechanism of cyanidation can be demonstrated as reactions below (Hedley& Tabachnick 1968)

$$O_2 + 2H_2O+2e^- \rightarrow 2OH^- +H_2O_2$$

$$Au \rightarrow Au^+ + e^-$$

$$Au^+ + CN^- \rightarrow AuCN$$

$$AuCN +CN^- \rightarrow Au(CN)_2^-$$

Dissolution of gold can be explained in two reactions anodic and cathodic reactions.

In anodic reaction, gold is oxidised and to form Au(I) cyanide complex, $Au(CN)_2^-$ in aqueous and alkaline cyanide solution. Cyanide complex passes into the solution. In this stage, the reaction is;

$$Au\,(CN)_2^- + e \rightarrow Au + 2CN^-$$

This reaction gives 2 electron to the cathodic reaction area. In the cathodic reaction, these two electrons are taken and lead to reduction of oxygen. The experimental investigation of the stoichiometry of gold dissolution has shown the major reaction to be;

$$2O_2 + 2H_3^+O + 2e \rightarrow 3H_2O_2$$

These two products are given to the solution-Hydrogen peroxide decomposes to oxygen and water as follows.

$$H_2O_2 + 2e \rightarrow 2OH^-$$

Only hydrogen peroxide is not a very effective oxidant for gold leaching. Too much hydrogen peroxide can passivate gold surface by oxide layer formation. Finally oxygen may be directly reduced to hydroxide ions, rather than H_2O_2

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

This reaction proceeds slowly and limited extend. The overall dissolution of gold in aerated, alkaline cyanide solutions, considering both the anodic and cathodic half reactions, is most accurately described by the following reaction equations, which proceed in parallel,

$$2Au + 4CN^- + O_2 + 2H_2O \rightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^-$$

$$2Au + 4CN^- + H_2O_2 \rightarrow 2Au(CN)^-_2 + 2OH^-$$

The major reactions are illustrated schematically in Figure 4.1.

4.3.Other Compounds and Metals their Effects on Leaching

Cyanides are those substances found in ores, concentrates and tailings that cause a loss of CN ions from the leach solution and thus result in excessive consumption of cyanide. Table 4.4.shows examples of such cyanides. Their presence results in high reagent consumption and low gold recoveries (Shulze, 1985)

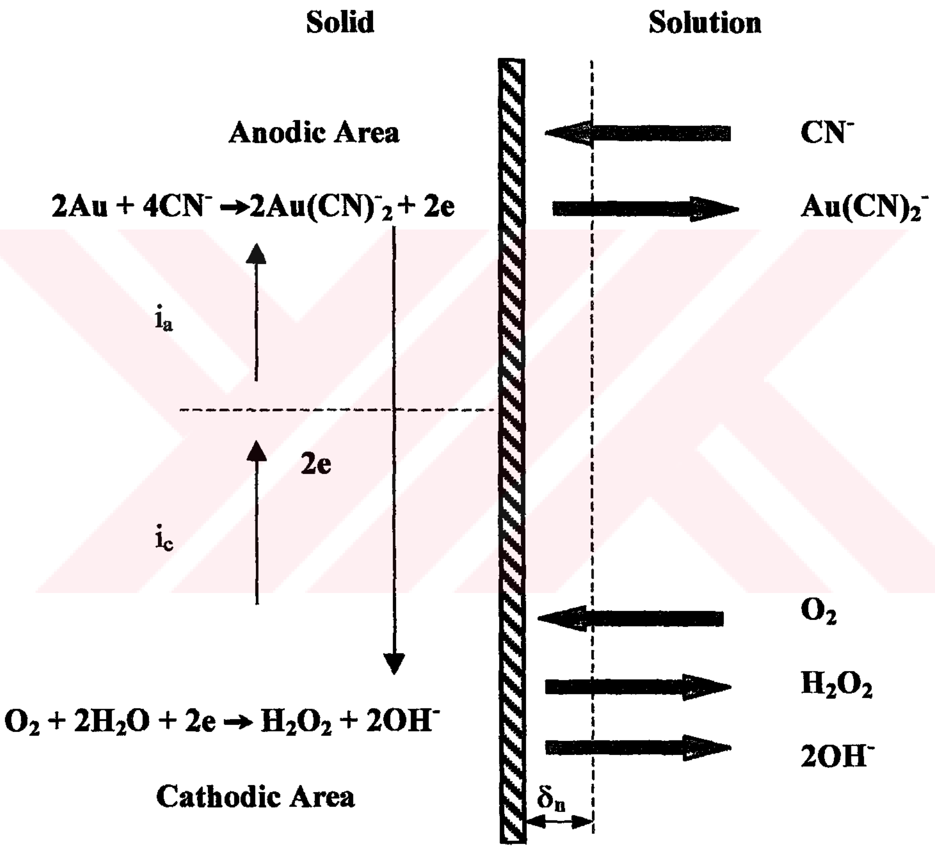


Figure 4.1. Schematic Representation of The Local Corrosion Cell at a Gold Surface In Contact With An Oxygen-Containing Cyanide Solution (Marsden & House, 1992).

Ia is the anodic current
Ic is the cathodic current

Among all the elements present Ag, Cu, Fe, Ni, Co, Zn, Hg, Pb, As, S and Sb are the common. Some of these elements suffer various degrees of oxidation, and some form stable cyanocomplexes (cyanide consumer or cyanides). Table 4.5.shows stability constant data of the cyanocomplex of some of these metals. The data in Table 4.5.indicate that the cyanocomplex of Hg^{+2},$Fe^{+3}$and Co^{+2} have higher stability constants than gold cyanocomplex.

Table 4.4.Cyanides

Metals	
Fe, Cu, Ni, Zn	Complex Cyanides
Sulphides	
Pyrrhotite (FeS)	
Zinc Blend (ZnS)	Cyanide--->Thiocyanate
Coppersulfides (Cu_2S, uS)	
Arsenides, Antimonides	
Arsenopyrite (FeAsS)	
Stibnite (Sb_2S_3)	Cyanide--->Thiocyanate
Tetrahedrite (Cu_3SbS_3)	Cyanate
Tennannite (Cu_3AsS_3)	
Pyrargyrite (Ag_3SbS_3)	(Metals--->Complex Cyanides)

Table 4.5.Stability Constants of Some Metal Cyanocomplexes (Haque, 1992).

Metal Ion	*Complex*	*Stability constant: Log B*
Zn^{+2}	$Zn(CN)_4^{-2}$	16.7
Ag^{+}	$Ag(CN)_2^{-}$	21.1
Au^{+}	$Au(CN)_2^{-}$	38.3
Cu^{+}	$Cu(CN)_4^{-3}$	30.3
Ni^{+2}	$Ni(CN)_4^{-2}$	31.3
Fe^{+2}	$Fe(CN)_6^{-4}$	35.4
Hg^{+2}	$Hg(CN)_4^{-2}$	41.5
Fe^{+3}	$Fe(CN)_6^{-3}$	43.6
Co^{+3}	$Co(CN)_6^{-3}$	64.0

The presence of these metals would lead to higher consumption of cyanide and oxygen, difficulties in solution purification operation and in the control of cyanide level in the solution effluent for disposal.

4.3.1. Silver

Silver frequently occurs with gold in economically significant quantities and therefore its behaviour in cyanide solutions is most important. Metallic silver behaves similarly to gold in aqueous cyanide solution and anodically dissolves as follows;

$$Ag(CN)^{-}_{2}+e \rightarrow Ag + 2CN^{-}$$

The reaction for the dissolution of metallic silver in cyanide solutions is analogous to that for the dissolution of gold. The occurrence of metallic silver in ores , however, is not common; the silver is more likely to occur in the sulphide form either as the plain sulphide or in combination with sulphides of copper, arsenic, antimony and lead. The reactions involved for the dissolution of such minerals are somewhat different from the reaction, which takes place when metalic silver is dissolved in cyanide and conditions have to be regulated accordingly (Hedley & Tabachnick, 1968).

One of the most refractory forms of silver occurs as an oxide intimately associated with oxides of manganese. Cyanide solutions have practically no dissolving effect on silver of these types. Special leaching or roasting techniques have to be employed to liberate the silver before it will dissolve in cyanide solutions.

4.3.2. Copper

One of the most frequent sources of trouble in cyanidation is the presence of copper minerals in an ore. The copper content may be less than 0,10% but its effect on both the dissolution and precipitation of gold can be very pronounced. Not only do copper minerals dissolve in cyanide and cause excessive consumption of this chemical, but also, the copper cyanogen complexes thus formed indirectly affect the dissolution of the gold. In addition, the copper in solution influences the precipitation of gold by zinc. The resulting gold precipitate contains copper which in turn frequently presents a problem in the subsequent melting operation (Hedley & Tabachnick, 1968).

The majority of copper minerals are highly soluble in cyanide solution expect chalcopyrite which has limited solubility (5.6.%).Table 4.6. Copper is one of the major cyanide consumers because it forms various cyanocomplex (e.g. $Cu(CN)^{-}_2$,$Cu(CN)^{-2}_3$,$Cu(CN)^{-3}_4$) .Among all these complexes, tricyonocomplex is the prominent ore further more, copper passes through all stages of gold recovery processes into the dore bullion.

Table 4.6. Solubility of Copper Minerals in 1 % NaCN Solution (Hedley & Tabachnick, 1968).

Mineral	Formula	Percent Total Copper Dissolved	
		At 23 °C	At 45 °C
Azurite	$2CuCO_3.Cu(OH)_2$	94.5	100.0
Malachite	$CuCO_3.Cu(OH)_2$	90.2	100.0
Cuprite	Cu_2O	85.5	100.0
Chrysocolla	$CuSiO_3$	11.8	15.7
Chalcocite	Cu_2S	90.2	100.0
Chalcopyrite	$CuFeS_2$	5.6	8.2
Bornite	$FeS.2Cu_2S.CuS$	70.0	100.0
Enargite	$3CuS.As_2S_5$	65.8	75.1
Tetrahedrite	$4Cu_2S.Sb_2S_3$	21.9	43.7
Metallic Copper	Cu	90.0	100.0

Copper sulphides when react with cyanide form copper cyano complexes and soluble sulphide (S^{-2}) (equation 1). Sulphide ion (S^{-2}) undergoes oxidation and finally forms sulphate. Further more, sulphide ion reacts with cyanide in the presence of oxygen and forms thiocyanate.(equation 2 to 4) .In addition to all these chemical transformations sulphide ion (S^{-2}) may form protective coating on the surface of the gold particle and thus recard the cyanidation process. However, excess oxygen demand and surface passivating can be reduced by removing sulphide ion (S^{-2}) by treatment with a soluable lead or mercury salt (Haque, 1992)

$$Cu_2S + 6CN^{-} \rightarrow 2Cu(CN)_3^{-2} + S^{-2}$$

$$2S^{-2} + 2O_2 + H_2O \rightarrow S_2O_3^{-2} + 2OH$$

$$S_2O_3^{-2} + 2OH^{-} + 2O_2 \rightarrow 2SO_4^{-2} + H_2O$$

$$S^{-2} + CN^{-} + H_2O + \tfrac{1}{2}O_2 \rightarrow CNS^{-} + 2OH^{-}$$

4.3.3. Iron

Iron in the form of oxides and sulphides is commonly present in gold ore. Cyanide reacts readily with iron and with various iron minerals.FeS_2 is the most common iron sulphide mineral occurring in gold ore, but it seldom interferes with cyanidation of gold.

Marcasite and pyrrhotite readily react with cyanide and form iron cyanocomplexes and soluble sulphide.(Equations 5 to 9).Soluble sulphide (S^{-2}) undergoes oxidation and forms various oxidation products. Reactive iron sulphides, like the reactive copper sulphides, are both cyanide and oxygen consumers. The deleterious effect of the soluble sulphide on gold cyanidation could be removed or at least be minimised by preparation and /or by treatment with a soluble salt of lead or mercury (Haque, 1992).

$$Fe_5S_6 + CN^- \rightarrow CNS^- + 5FeS$$

$$FeS + 2O_2 \rightarrow FeSO_4$$

$$FeSO_4 + 6CN^- \rightarrow Fe(CN)_6^{-4} + SO_4^{-2}$$

$$FeS + 6CN^- \rightarrow Fe(CN)_6^{-4} + S^{-2}$$

$$2Fe(CN)_6^{-4} + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Fe(CN)_6^{-3} + 2OH^-$$

4.3.4. Zinc

Most zinc minerals are moderately soluble in the cyanide lixiviant. Table 4.7.Among various zinc minerals, sphalerite is commonly present in the gold ore or concentrate. Sphalerite reacts with cyanide and form water soluble zinc cyano complex ($Zn\ (CN)^{-2}_4$) and sulphide ion (S^{-2}).The zinc cyano complex has a much lower stability constant than the gold cyano complex:

In practice, the adverse effect of zinc are of limited significance mostly because of lower stability of zinc cyano complex with respect to aurocyano complex(Haque, 1992).

$$Zn + 4NaCN + 2H_2O \rightarrow Na_2Zn(CN)_4 + 2NaOH + H_2$$

$$ZnS + 4NaCN \rightarrow Na_2Zn\ (CN)_4 + Na_2S$$

$$Na_2S + 2NaCN + 2H_2O + O_2 \rightarrow 2NaSCN + 4NaOH$$

$$ZnO + 4NaCN + H_2O \rightarrow Na_2Zn\ (CN)_4 + 2NaOH$$

$$ZnCO_3 + 4NaCN \rightarrow Na_2Zn\ (CN)_4 + Na_2CO_3$$

$$Zn_2SiO_4 + 8NaCN + H_2O \rightarrow 2Na_2Zn(CN)_4 + Na_2SiO_3 + 2NaOH$$

Table 4.7. Solubility of Zinc Minerals in Cyanide Solution
(Hedley & Tabachnick,1968).

Mineral	*Formula*	*Percent Extraction of Zinc*
Sphalerite	ZnS	18.4
Willemite	Zn_2SiO_4	13.1
Hydrozincite	$3ZnCO_3, 2H_2O^*$	35.1
Calamine	$H_2Zn_2SiO_5$	13.4
Franklinite	$(Fe, Mn, Zn)O. (Fe, Mn)_2O_3$	20.2
Zincite	ZnO	35.2
Smithsonite	$ZnCO_3$	40.2

*Formula usually given for hydrozincite is $2ZnCO_3.3Zn(OH)_2$

4.3.5. Lead

Among various lead minerals galena (PbS) is the most common one encountering gold ore. Galena is not so reactive for cyanide but often surface oxidation takes place forming lead sulphate($PbSO_4$).In highly alkaline solution lead sulphate can form a soluble plumate which may react with cyanide forming sparingly soluble basic lead cyanide

$$PbS + 2O_2 \rightarrow PbSO_4$$

$$PbSO_4 + 4NaOH \rightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O$$

$$3NaPbO_2 + 2NaCN + 2O_2 \rightarrow Pb(CN)_22PbO + 8NaOH$$

Ores containing anglesite ($PbSO_4$) should be cyanided at low alkalinity to minimise the formation of soluble plumate. Lead minerals may cause problems during roasting by forming an insoluble oxide coating on precious metals. This problem may be overcome by washing the calcine with brine solution prior to cyanide leaching.

4.3.6. Arsenic and Antimony

Arsenic in the form of realgar (As_2S_3) and orpiment (As_2S_3) and antimony as stibnite (Sb_2S_3) present serious problems in cyanidation. They do not form complex cyanides as far as is known but they do dissolve in alkaline solutions of the strength used in cyanidation to form compounds such as thioarsenites and thioantimonites. These compounds react with the oxygen in the cyanide solution to form the corresponding arsenites and antimonites. The result is that practically no oxygen is available for the dissolution of gold, the extraction of which falls off accordingly (Hedley & Tabachnick, 1968).

$$2As_2S_3 + 12OH^- \rightarrow 2AsO_3^{-3} + 2AsS_3^{-3} + 6H_2O$$

$$2AsS_3^{-3} + 12OH \rightarrow 2AsO_3^{-3} + 6S^{-2} + 6H_2O$$

$$2S^{-2} + 2O_2 + H_2O \rightarrow S_2O_3^{-2} + 2OH^-$$

$$2S^{-2} + 2CN^- + \frac{1}{2}O_2 + H_2O \rightarrow 2CNS^- + 2OH^{-2}$$

$$2As\ S_3^{-3} + 6CN^- + 3O_2 \rightarrow 6CNS^- + 2AsO_3^{-3}$$

$$2AsO_3^{-3} + O_2 \rightarrow 2AsO_4^{-3}$$

The adverse effect of these minerals on gold dissolution can be eliminate or be minimized by through preaeration of the leach slurry followed by cyanidation at low alkalinity (< pH 10).

4.3.7. Mercury

Gold ores containing mercury are not common, but mercury is moderately reactive with cyanide. Mercury is a not cyanide consumer because it forms stable cyano complex (Hg $(CN)^{-2}{}_4$) .Usually, dissolved mercury passes through the carbon absorption and stripping processes with cold. It is usually removed by retorting at the smelting stage. Dissolved mercury can be removed by treating the leach liquor with sodium or calcium sulphide. In this treatment mercury is precipitated as mercuric sulphide (HgS) (Haque, 1992).

4.3.8. Tellurides

Gold bearing tellurides dissolve slowly in alkaline cyanide solution. Tellurides do not form stable complexes with cyanide. Generally, tellurides do not cause any problem in the cyanidation of gold. However, If there is a problem then a mild oxidative pretreatment (e.g. oxidation with $Ca(COCl)_2$ is sufficient for efficient cyanidation of gold.(Haque, 1992).

4.3.9. Carbonaceous Material

Many ores contain carbonaceous material, sometimes in amounts varying form a few hundredths of a percent to several percent. In some forms this carbonaceous material has no effect on cyanidation; in other form it is an active precipitant for gold in cyanide solutions. It is always difficult in practice to determine whether all the gold in a cyanidation residue can be attributed to a refractory form of gold in the ore or whether some of it was first dissolved by the cyanide solution and than precipitated by carbonaceous material present. If the latter were the case, it would be possible to prevent this gold loss, at least to some extent.

When cyanides are present in the cyanidation system appropriate steps must be taken to reduce the cyanide consumption and increase gold recoveries these steps are;

- ✓ Neutralisation of soluble salts with lime
- ✓ Intense pre-aeration of the pulp with alkalinity control.
- ✓ Use of lead salts
- ✓ Bleeding of barren solution
- ✓ Roasting if economically applicable
- ✓ Regeneration of cyanide.(Bhappu, 1986)

4.3.10. Nickel

It has been suspected in practice that a small amount of nickel a pregnant solution has a very detrimental effect on the precipitation of gold but it apparently has little effect on the dissolution of gold. The reason for this is not definately known, nor is cure. The detrimental effect of nickel on the precipitation of gold can be controlled, however, by keeping the nickel content of the pregnant solution below a certain danger percentage. This is done by discarding barren solution at regular intervals. Although this procedure circumvents the problem, provided that the amount of nickel dissolved in one cyanidation cycle is not in excess of the critical amount, it does not solve the problem.

4.3.11. Sulphide Minerals

When sulphide minerals such as covellite, pyrrhotite, sphalerite etc are decomposed by or dissolved in cyanide solutions, some of the products of the reactions, in addition to cyanide complexes, are alkaline sulphides, thiosulphates, thiocyanates. Some of these affect adversely the dissolution and precipitation of gold.

4.4.Leaching Parameters

4.4.1.The Effect of Cyanide Concentration

The dissolution rates of gold in cyanide a maximum in passing from concentrated (0,25 %NaCN). For all partial purpose, solution weaker than 0,001 % NaCN does not dissolve gold efficiently (Tükel, 1996).

As gold atoms undergo oxidation with the dissolved oxygen, cyanide must be in the vicinity to stabilize the gold aurocyano complex (Au (CN^-_2). The rate of formation of this complex mainly depends on the concentration of cyanide $(CN^-)$and oxygen (O_2) in the Nernst's boundary layer (Figure 4.1).In other words the rate of cyanidation depends on the rate of diffusion of CN and O_2 through this boundary layer.(Haque, 1992).

It is reported in the literature that the rate of gold cyanidation increases linearly with increase of cyanide concentration until the maximum is reached beyond which any further increase of cyanide concentration has some retarding effect in gold dissolution rate.(.Haque, 1992).

According to the following reaction

$$4Au + 8\,NaCN + O_2 + 2H_2O = 4NaAu(CN)_2 + 4NaOH$$

There would be no advantage in having more than 392 parts by weight of NaCN for every 32 parts by weight of oxygen in the cyanide solution.(Hedley & Tabanich 1965). Under ideal conditions of aeration and agitation, maximum cyanidation rate of gold could be obtained with 0,0098 % of NaCN in the lixiviant. Effect of cyanide concentration was illustrated in Figure 4.2.

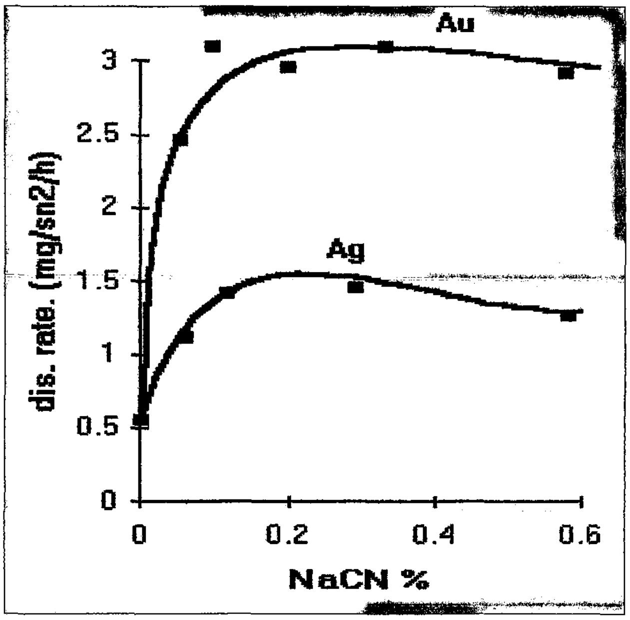


Figure 4.2. Effect of cyanide concentration on the dissolution rate of Au and Ag. (Marsden & House, 1992).

Various investigators have studied the dissolution of gold and found different results. These results were listed in Table 4.8. The cause of variations in the solution strength found by various investigators to give maximum rate of gold dissolution probably lies in the variety of techniques used in determining these Figures: These variations include such factors as the ratio of volume of solution to gold surface, agitation rate, rate of aeration.

Table 4.8.Various Investigators and Their Results Which Demonstrate Maximum and Minimum Dissolution of Gold.

Max. Dis. Rate at NaCN%	*Min. Dis. rate at NaCN%*	*Investigator*
0.25		Maclaurin
0.020*		White
0.050		Barky, Swainson, Hedley
0.080		Julian, Smart
	0.008	Christy

* When saturated with O_2.

Cyanide concentration that gives maximum dissolution of gold at 8,2 mg/l (25 °C and at sea level) is approximately 0,005 % or 0,002 % CN^-, equivalent to 0,01 % NaCN.

4.4.2 The Effect of Alkalinity

High alkalinity of cyanidation solution is an important factor not only to maintain maximum concentration of cyanide (CN^-) but also to obtain favourable oxidation potential for the oxidation of gold. Lime (CaO) is the most commonly applied base for the control of pH in the cyanidation slurry. Lime provides a number of operational advantages over NaOH or KOH, such as coagulator in thickening and filtering operations and in removaling CO^-_3 and HCO^-_3 ions from the leach liquor as precipitates.

Cyanide ions hydrolyse in water to form molecular hydrogen cyanide (HCN) and (OH^-) as in reaction below.

$$CN^- + H_2O \rightarrow HCN + OH^-$$

Figure 4.3. Shows the equilibrium concentration of HCl and CN as a function of pH:

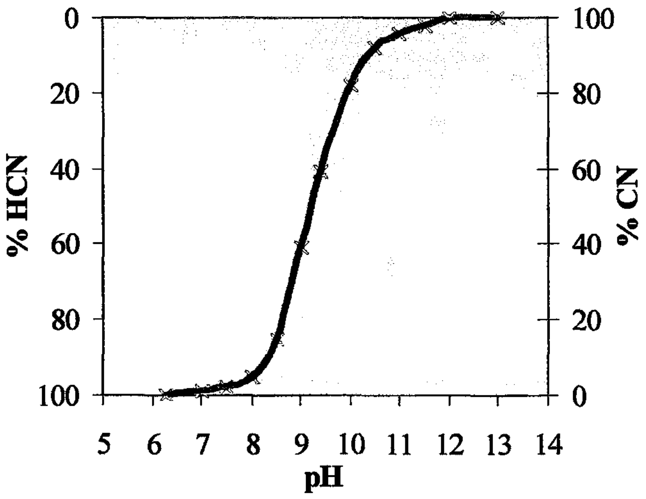


Figure 4.3.Equilibrium concentration of HCN and CN^- as a function of pH.

At approximately pH 9,3, half of the total cyanide exists as hydrogen cyanide and half as free cyanide ions. At pH 10,2 more than 90 % the total cyanide is free cyanide (CN^-),while at pH 8,4 over 90 % exists as hydrogen cyanide.

Calcium hydroxide (CaOH) , sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) are the other modifiers used for specific purposes. Many investigators have strated that alkalies such as NaOH, especially CaOH retart the dissolution of gold in cyanide solution.

4.4.3.Effect of Particle Size

The rate of cyanidation of gold depends on the surface area of the gold particle actually exposed to chemical reaction. Gold particles of 75 micron or above are separated by gravity separation processes, while the size of the cyanidation feed ranges from 75 micron to 45 micron with total retention time of 30 to 48 hours. Irregular shape and partial exposure of the gold surface to cyanide reaction require longer dissolution time.(.Haque, 1994)

With an actual ore and under plant conditions the rate of dissolution is affect by such factors as the association of the gold, coatings on the and the efficiency of the cyanide solution.(Hedley & Tabachnick, 1968)

Particle size versus gold recovery for two different ore is given in Figure 4.4.Although the rate generally increases with the decreasing particle size due to an increase in gold liberation, sometimes dissolution rate from ore containing cyanides may decrease with the decreasing particle size.

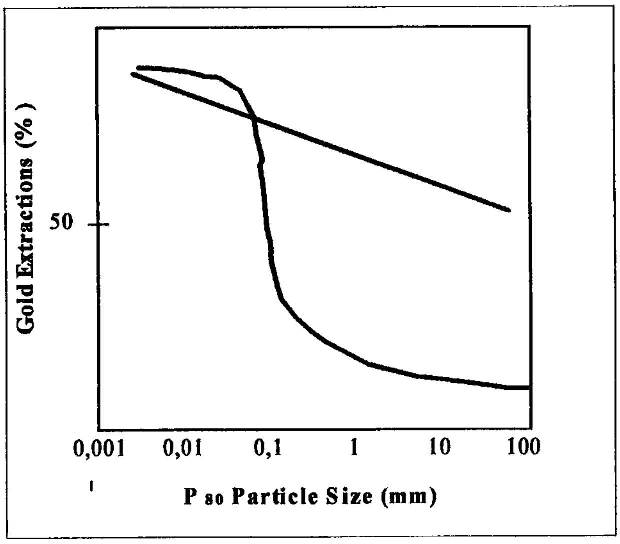


Figure 4.4. Schematic illustration of relationship between particle size and gold recovery.

A.Gold fine dispersed in non-porous matrix, grinding required.

B.Gold located in cracks and fissures of rock structures, some degree of liberation achieved at coarse size.

4.4.4.Effect of Temperature

When heat is applied to a cyanide solution containing metallic gold, two opposing factors affect the rate of dissolution. The increase in temperature would be expected to increase the activity of the solution and thus increase the rate of dissolution of gold. At the same time the amount of oxygen in the solution would decrease because the solubility of gases decreases with increasing temperature.

Julian and Smart determined the solubility of gold in 0,25 % KCN solution at temperatures between 0 °C and 100 °C. Figure 4.5. The rate of dissolution increased to a maximum at 85 °C although the oxygen content of the solution at this temperature was less than half of than at a temperature of 25 °C. It is only a 20-25 % increase in dissolution rate is achieved by elevating the temperature from 25°C to 85°C

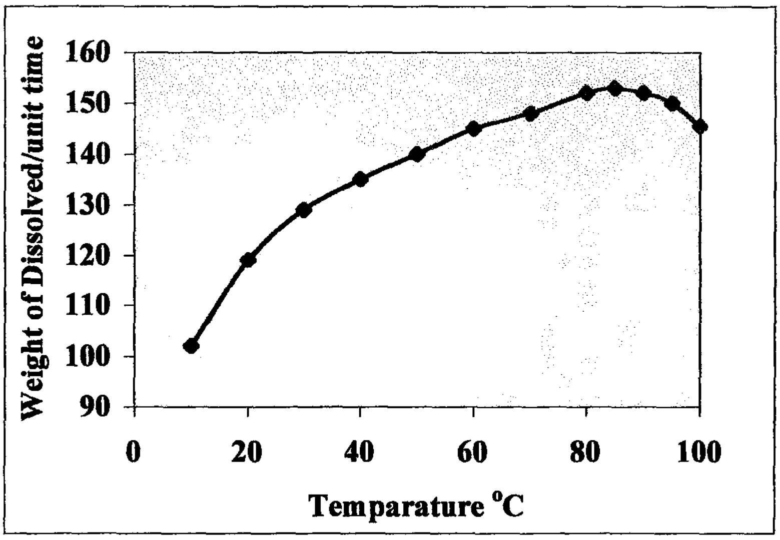


Figure 4.5.Effect of temperature on gold dissolution rate

In practice the use of hot solutions for the extraction of gold from an ore has many disadvantages, such as the cost of heating the ore and solution, the increased decomposition of cyanide due to heat, the increased consumption of cyanide due to the accelerated reaction between cyanides in the ore such as sulphides of copper, iron, etc. and cyanide.

4.4.5.Effect of Agitation Rate

Gold dissolution is usually mass transport controlled under conditions normally applied for cyanide leaching, and therefore the rate depends on the diffusion layer thickness and mixing characteristics of the bulk solution. Increasing agitation increases the dissolution rate up to a maximum, above which agitation has little or no further benefit.(Mardsen & House, 1992)

Dissolution of gold was illustrated in Figure 4.6. Agitation, up to 150 rpm, has a favourable effect on the rate of gold dissolution (Haque, 1992).

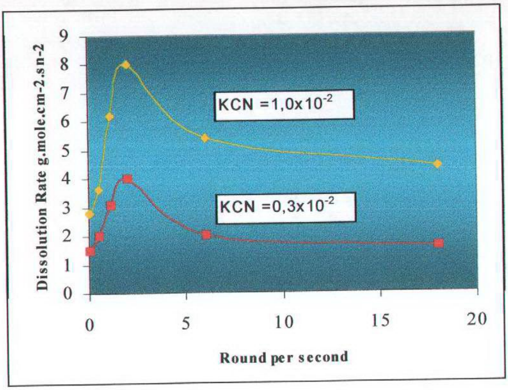


Figure 4.6. Effect of Agitation Rate

4.4.6.The Effect of Oxygen

Oxygen (O_2) or an oxidizing agent (Na_2O_2, CaO_2,$KmnO_4$,Cl_2 or Br_2) is an essential component of cyanide lixiviant. Commonly oxygen or air is applied in plant scale cyanidation of gold ore. Oxidizing reagents and process complications in handling have fallen into disuse. Aeration under the right condition will often give as gold results as chemical oxidizers.

According to Elsner's reaction. Figure 4.1. 1mg gold requires 0.04 mg oxygen. The solubility of oxygen water at 20 °C is approximately 8 mg/l, therefore a gold ore sample containing 20 mg Au/kg of solids would require 0,8 mg oxygen. At 50 % solids a leach pulp contains ample oxygen for the oxidation of all the gold present in one kilogram of ore (Haque, 1992).

Although cyanide concentration is relatively easy to control by addition of concentrated cyanide solution, or a solid cyanide solution compound, control of the oxidant concentration (ie. dissolved O_2) is not easy because of low solubility of oxygen in water under atmosphere condition. Dissolution of oxygen is affected by the conditions of temperature and pressure. At sea level and 25 °C, the saturated concentration of dissolved oxygen in solution is 8,2 mg/l.

- Operation under pressure, using air as the oxidant
- Pure oxygen, oxygen enriched air, hydrogen peroxide or another oxygen source can be used in place of air to supply oxygen to the solution.

Both methods are expensive and can usually be justified for treatment of ores containing significant amounts of oxygen-consuming species.

CHAPTER 5

CYANIDE TREATMENT TECHNOLOGY

This chapter provides information on the technological processes that currently available to treat cyanide wastes. It describes the main commercial processes used in the mining industry and some of the alternatives currently under development or having site-specific applications.

Table 5.1. Presents a summary of the existing treatment process alternatives for cyanide-bearing waste streams.

These methods are;

- ✓ Natural Degradation
- ✓ Inco SO_2-Air process
- ✓ Hydrogen peroxide
- ✓ Alkaline chlorination
- ✓ Acidification-volatilization-regeneration (AVR)
- ✓ Homestake biodegradation
- ✓ Helmo Gold process

Beside these, Vitrokele, MNR Degussa process and ion exchange (in combination with AVR) are used in pilot scale

Potential processes are electrolytic decomposition, ozonation, activated carbon, Noranda SO_2 process, kastone peroxide, Celec process and ferrous sulphide adsorption.

Table 5.1.Cyanide Treatment Process Alternatives (Higgs, 1995)

Treatment Process	stage	Applications	Comments
Natural Degradation			
Neutralization by CO_2 Absorption HCN Volatilization Metal Cyanide Complex Dissociation Metal Cyanide Precipitation	C	TPO, B, S	Universal application to treatment of slurries, barren bleed and tailings pond overflows. Application is often limited by site-specific factors associated with TP and regulations.
Oxidation Processes			
Alkaline Chlorination	C	S, B, TPO	Displaced by SO_2 –Air and H_2O_2 due the cost, inability to remove iron cyanide and Cl_2 residual concerns.
Inco SO_2 – Air Process	C	S, B,	Universal application-slurry treatment can result in elevated reagent consumption
Hydrogen Peroxide	C	TPO	Not applicable to slurries due to reagent consumption.
Ozonation	D	B, TPO B	Energy intensive. On-site generation of O_3 required.
Adsorption/ Precipitation			
Hemlo Process (Cuprous Process)	C	B	
Cominco Ferrous Sulphide Adsorption	C	B	Not in use.
Neville Process-Ferrous Iron Bisulphite	D	B	
Activated Carbon Adsorption	D	TPO	Limited to low CN concentrations. Site-specific.
Biological Treatment			Limited to low CN concentrations.
Biodegradation	C	TPO	May require supplemental heat. Site-specific.
Cyanide Recycle			
Canment Modified AVR	D	B	May be applicable to reduce cost for NaCN. Safety concerns and capital costs limit application.
Electrolytic Recovery	D	B	Site-specific
Ion Exchange	D	B	Site-specific
Resin in Pulp	D	S	

Legend

C-Commercial stage

D-Development

S-Mill waste slurry from CIP/CIL or repulped Merrill Crowe

B-Barren Bleed from Merrill

TPO-Tailings pond overflow or reclaimed water

TP- Tailings pond

5.1.Natural Degradation

Natural degradation involves the removal of cyanide associated cyanide-metal complexes from wastewater by naturally occurring processes while the wastewater are retained for extended periods in holding ponds, usually tailings ponds. The degradation of cyanide and metal-cyanide complexes results from a combination of physical, chemical and biological processes(Kilborn Inc, 1991).

The major removal mechanisms responsible for natural degradation are the following;

- ☐ pH depression due to CO_2 absorption
- ☐ Volatilization of hydrogen cyanide gas (HCN).
- ☐ Chemical and photochemical decomposition.
- ☐ Precipitation of metal complexes.
- ☐ Chemical and biological oxidation.
- ☐ Hydrolysis and adsorption.

Natural degradation is influenced by a number of variables including cyanide species and their concentrations in solution, pH, temperature, sunlight (UV), aeration, pond conditions (area, depth, turbidity, turbulence, ice cover, retention) and presence of bacteria.(Kilborn Inc, 1991).

In a study carried out by WTC (Wastewater Technology Centre), the degradation kinetics and the change in the concentrations of Cu, Ni, and 22 at the waste disposal of Dome Mine, Ontario, have been investigated.(Figure 5.1).

The study results showed that cyanide concentration decreased from 63,5 to 0,008 mg/l over a 15 week period.

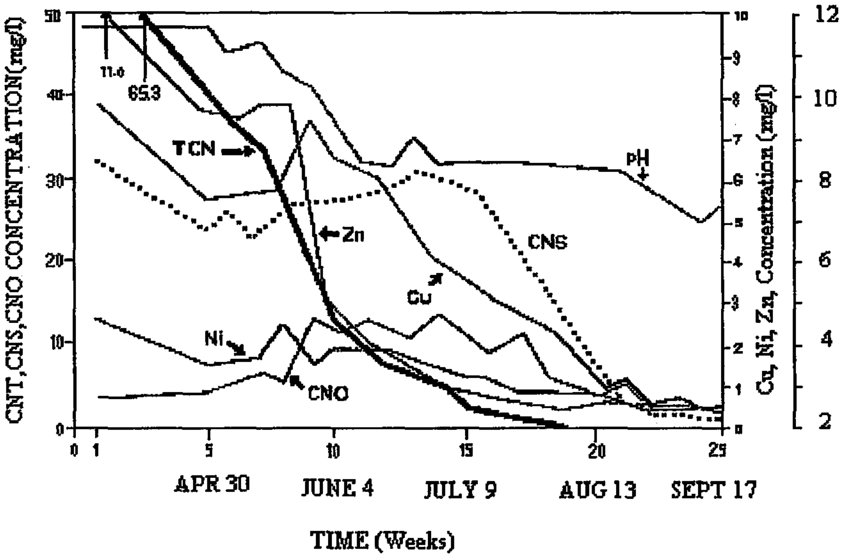


Figure 5.1. Concentration Trends in Sallow Barren Bleed Holding Pond at Dome Mine.(Bayraktar, 1996)

Although cyanide removal by natural means is rapid during warmer months it is extremely slow or perhaps non-existent during the late fall and winter months. Consequently, it appears that a stand-alone natural degradation system requires a retention time of 9-10 moths since the tailings pond must have the capacity to stone water form October through to the following July or August. Advantage should be taken of maximizing tailings pound water recycle is order to reduce the need to store a large volume of mill effluent during the October to July period.(Scott,1989).

5.1.1. Chemistry and Rate of Natural Degradation Process.

5.1.1.1. Form of Cyanide.

They are many natural activities occurring in leach waste and effecting free cyanide concentration after leaching. Hydrolysis of cyanide ion is done by CO_2 absorption and so pH value degreases. The hydrolysis reaction is as follows;

$$CN^- + H_2O \rightarrow HCN + OH^-$$

In the other hand, concentration of cyanide ion (CN^-) and molecular hydrogen cyanide (HCN), are stable dependent upon the pH value of the solution. Figure 4.3.At pH 9,36 the concentrations of HCN and CN^- ion are equal. Thus, pH should be below 9,0 to ensure that a substantial percentage of cyanide is present as HCN (Cambazoğlu.1995).

5.1.1.2. pH Depression

The cyanide process uses high pH conditions (ie, pH> 10,5) to reduce the loss of cyanide during milling. Mill tailings are therefore characterised by high pH and a low percentage of HCN.

In tailing ponds system where lime has been used in the mill pH control, the pH of the pond supernatant will drop as CO_2 is absorbed from the air as follows;

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

In this reaction, alkalinity in the form of calcium hydroxide reacts with absorbed CO_2 to form insoluble calcium carbonate, which precipitates form solution. Hydroxide ions (OH^-) are consumed by the reaction, which in turn lowers pH.

The rate of CO_2 absorption is influenced directly by the degree of contact between the air and the solution.

5.1.1.3.Volatilization

The volatilization rate is enhanced by providing good contact between air and the solution, identical to the circumstances that enhance pH depression. Mechanical aeration and mixing can also be used to enhance volatilization; however, limitations to the use of aeration would be expected at low cyanide concentrations because of high solubility of HCN and reduced driving force. The actual rate of volatilization can be expressed as a mass transfer coefficient.

5.1.1.4.Dissociation of Metallo-cyanide

Dissociation Mechanism: Cyanide forms a variety of metal complexes of varying stability, as discussed in section.4.1.2.These metal cyanide complexes equilibrate with cyanide ion CN^- in solution, for example with copper;

$$Cu(CN)_3^{-2} \leftrightarrow Cu(CN)_2^- + CN^- \leftrightarrow CuCN + 2CN^-$$

Depending on the pH of the solution, the cyanide ion released from the complex can then combine with hydrogen ion to form molecular HCN, with volatilizes from solution. As CN^- ion is lost from solution due to volatilization of HCN, the $Cu(CN)_3^{-2}$ complex will release additional CN^- ion in an attempt to maintain the equilibrium. Naturally, dissociation is affected by pH, as this influences the form of free cyanide. Tricyanocuprate is stable in the presence of sufficient CN^- ion.

Dissociation Rate: Dissociation rates of the metallo-cyanide complex are given in table 5.2. The data in this table are volatilization mass transfer constant of these complexes at various temperature and pH values using these value approximations of regarding the plant can be done.

Table 5.2. Dissociation Rates (h^{-1}) for Metallo-Cyanide Complexes(Higgs, 1995).

Complex	*pH: 7 4°C*	*pH: 7 20°C*	*pH: 10.5 4°C*	*pH: 10.5 20°C*
$Cu(CN)_3^{-2}$	0.0018	0.0055	0.000071	0.00022
$Zn(CN)_4^{-2}$	0.023	0.049	0.001	0.0022
$Ni(CN)_4^{-2}$	0.00042	0.00097	0.000051	0.00012
$Fe(CN)_6^{-2}$	0.000031	0.00009	0.000003	0.0000097
HCN Volatilization Coefficient (cm/h)	0.0294	0.04175		

5.2.Inco SO_2-Air process

The Inco SO_2-Air process for cyanide treatment employs a combination of sulphur dioxide and air in the presence of a copper catalyst to oxidize both free cyanide and metal cyanide complexes to cyanate. The optimum pH range is 8 to 10. Retention times of 60 to 90 minutes are required for mill tailings, while lower retention times of 30 to 45 minutes may be applicable for tailings pond overflow. The process is sensitive to the provision of adequate aeration and pH (Higgs, 19954).

The overall reaction for cyanide oxidation is given as

$$CN^- + SO_2 + O_2 + H_2O \rightarrow CNO^- + H_2SO_4$$

Based on this reaction the stoichiometric requirement of reagent is 2.47 kg SO_2 per. Kg CN^-.Sulphur dioxide may be supplied as liquid SO_2, roaster gas if readily available, or additions of sodium sulphite (Na_2SO_3), bisulphite ($NaHSO_3^-$) or metabisulphite ($Na_2S_2O_5$). Sulphur dioxide concentrations in the range 1-3 % in air provides optimum oxidation efficiency.(Staunton, 1995).

Oxygen needed for the reactions is supplied by blowing air at a sufficient amount into the tanks. Metal cyanide complexes decomposable with weak acids release H_2SO_4 and metal ions when oxidizing to cyanides according to the reactions given below..

$$Me(CN)_4^{-2} + 4SO_4 + 4O_2 + 4H_2O \rightarrow 4OCN^- + 4H_2SO_4 + Me^{+2}$$

$$(Me^{+2} = Zn^{+2}, Cu^{+2}, Ni^{+2}, Cd^{+2} \text{ etc.})$$

Strong ferro cyanide complexes oxidizing after the above reaction are settled as insoluble ferro-cyanide salts by metal ions (especially Cu ions) being released.

$$2Me^{+2} + Fe(CN)_6^{-4} \rightarrow Me_2Fe(CN)_6$$

Other metal ions remaining in the solution settle as hydroxide compounds.

$$Me^{+2} + Ca(OH)_2 \rightarrow Me(OH)_2 + Ca^{+2}$$

To neutralise the acid (H_2SO_4) occurring as a result of the oxidisation reaction, lime is fed into the reactor at the same time. Wherefrom, gypsum is produced by the reaction is given below (Çelik, Mordoğan & İpekoğlu, 1997).

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O$$

As seen in this reaction, the process does not produce any toxic intermediaries.

These typical treatment results are given in table 5.3.

Table 5.3. Typical Treatment Results (Robins & Devuyst, 1995)

	Cyanide (total) mg/lt	
Gold and Silver Milling	Initial	After treatment
Barren solution	420	0,11
Leach tails slurry	240	0,30
Plating wastes		
Copper rinse-water	405	0,03
Zinc rinse-water	147	0,12
Cyanide rinse	1460	0,50

The **advantage and disadvantage** of the Inco/SO_2 purification processes are as follows.

- At clarifying cyanide and metal containing wastes, it is a proven method
- The process can operate continuously or discontinuously.
- All compounds of cyanide (incl. ferro cyanides) can be clarified
- Investment and operating costs are lower than other chemical processes
- Heavy metals can be removed by settling in form of metal hydroxide
- Precautions are to be taken against SO_2 to be used in the process.
- Cost and consumption of reagent can be higher
- Cyanide is not recoverable
- $CaSO_2$ can be at an undesired amount

- When CN_T, thiosulphate, cyanate, metal and ammonium concentrations outside of the clarifying plant exceed environmental protection limits, additional clarification may be required.
- Process parameters must be controlled frequently which may cause an increase in operating cost.

Figure 5.2. shows a typical Inco/SO_2 air clarifying process.

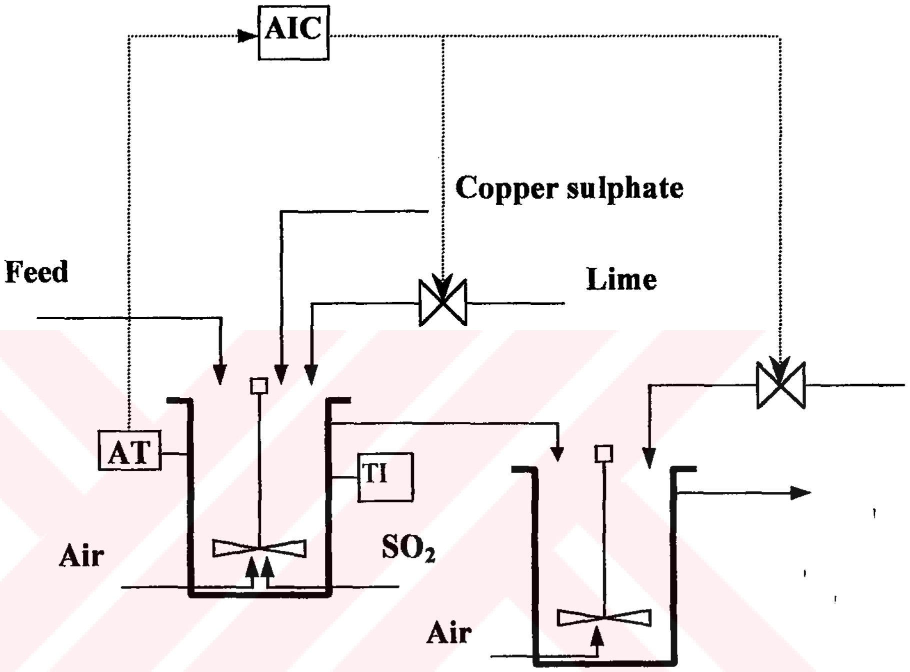


Figure. 5.2. Inco SO_2- Air process flow diagram(Higgs, 1995).

5.3.Hydrogen Peroxide Oxidation

This process is used to eliminate the cyanide in the waste water occurring after gold – silver production. The process description and chemistry is as follows; In the presence of a copper catalyst, hydrogen peroxide (H_2O_2) will oxidize cyanide and metal complexes. The overall reaction for the oxidation of cyanide ion is as follow;

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O$$

Cyanate formed by oxidation of cyanide in turn hydrolysis to ammonia and carbonate(Higgs, 1995).

$$OCN^- + 2H_2O \rightarrow NH_4^+ + CO_3^{-2}$$

Heavy metals such as copper, zinc and cadmium are simultaneously precipitated as hydroxides;

$$2Cu(CN)_3^{-2} + 7H_2O_2 + 2OH^- \Rightarrow 6OCN^- + 2Cu(OH)_2 \downarrow + 6H_2O$$

Iron cyanide complexes can also be easily removed in a subsequent treatment step according to the following reaction.(Norcross & Steiner, 1995)

$$2Cu^{+2} + Fe(CN)^{-4}_6 \rightarrow Cu_2Fe(CN)_6 \downarrow$$

The process has an optimum pH range of 9,5 to 10 .However, after the removal of cyanide, pH value is determined to be between 9 – 9.5 for the metals to be precipitated. Nevertheless, the most eligible pH value is < 9 for the ferrous cyanide compound to be precipitated (Önal, Yüce & Karahan, 1995).

Theoretically, one mole of hydrogen peroxide will oxidise one mole cyanide. In practice, the efficiency of the reaction depends on various process parameters such as temperature, initial cyanide concentration, residual cyanide target and the presence of decomposition catalysts (metals, suspended solids).In order to achieve very low residual cyanide concentrations, a higher molar ratio is required due to the retardation of the reaction rate and increasing H_2O_2 losses through decomposition:

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$

This process flow diagram is given in figure 5.3.

5.4. Alkaline Chlorination

Alkaline Chlorination is a chemical process involving the oxidation and destruction of free and weak acid dissociable under extremely alkaline conditions (pH = 10,5-11,5).The chlorine is supplied either in liquid form or as solid sodium or calcium hypochlorite which are made into concentrated solutions prior to their use. (Smith &. Mudder, 1995).

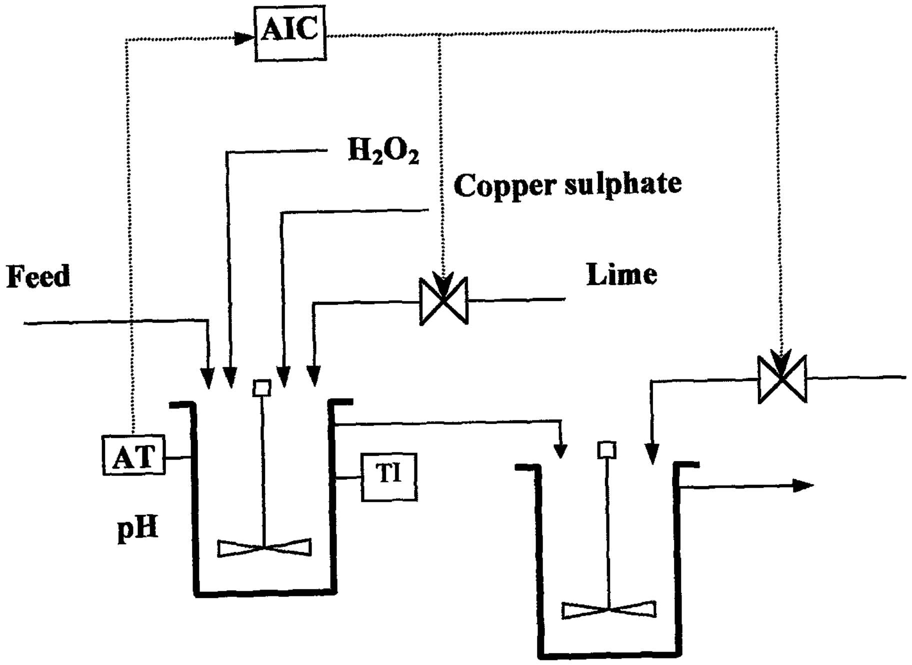


Figure 5.3. Hydrogen peroxide treatment process flow diagram(Higgs, 1995)

The reaction is a two step process, the cyanogen chloride formed as an intermediate is converted to cyanate as shown in the following exudations (Staunton, 1991).)

$$CN^- + OCl^- + H_2O \rightarrow CNCl + 2OH^-$$

$$CNCl + 2OH^- \rightarrow CNO^- + Cl^- + H_2O$$

In this process both free and metal-complexes cyanides (expect for iron cyanide) are oxidised to cyanate (CNO). Simplified process chemistry is illustrated by the following equations (Scott, 1989).

$$Zn(CN)_4^{-2} + 4Cl_2 + 10(OH)^- \rightarrow 4CNO^- + 8Cl^- + Zn(OH)_2 + 4H_2O$$

Excess hypochlorite results in further oxidation to nitrogen and carbonate:

$$2CNO^- + 3OCl^- + 2OH^- \rightarrow N_2 + 2CO_3^{-2} + 3Cl^- + H_2O$$

Cyanogen chloride is volatile and highly poisonous, so conditions must be maintained to ensure its rapid conversion to cyanate;

The stoichiometric chlorine requirement is 2,73 kg of chlorine per kilogram of cyanide. In practice however, consumption is usually much greater due to the presence of reduced sulphur species and other oxidisable material. Thiocyanate reacts to form cyanate as shown following reaction.

$$SCN^- + 4OCl^- + 2OH^- \rightarrow CNO^- + SO_4^{-2} + 4\,Cl^- + H_2O$$

Organic material may also react with the chlorine, raising consumption to unacceptable levels. The by products of these reactions may be chlorinated organic species which are more harmful than the cyanide. (Staunton. 1991).

According to Ritcey and Mc Namara, the advantage and disadvantages of alkaline chlorination are given below (Kaya, at all, 199*).

Advantage

- Very widely-used method, expertise available
- Reactions complete rapid to (CN_T) 0,1 ppm
- Toxic metals removed
- Chlorine readily available
- Suitable for continuous/batch operation
- Easy/trouble free control
- Low capital cost
- CNS is decomposed and thio-salts are oxidized.

Disadvantages

- Reagent costs are high
- Requires very careful control of pH ($pH > 11$) and final free Cl_2 level
- Cl_2 demand increase if plant water contains ammonia, Cu and Ni
- If mixing is inadequate, MeCN very rapidly precipitate
- Cyanide and metal content are not recovered
- Ferro/ferricyanide are not usually decomposed.

5.5 Biodegradation

This operation employs mechanized biological removal of cyanide and thiocyanate from a blend of mine water and tailings pond decants. Treatment involves to steps. Cyanide and thiocyanate (SCN) are converted in the first step to carbondioxide and ammonia by microorganisms acclimatised to increasing cyanide and thiocyanate levels, while sulphur is oxidized to sulphate. The second step involves nitrification whereby ammonia is converted first to nitrite and then to nitrate by bacteria that grow spontaneously in the presence of ammonia. Metals, including ferrocyanide, are absorbed by the bacteria. Flocculated sludge is subsequently removed in clarifiers and filters and disposed of in the tailing area. Temperature and feed concentrations vital to the organisms are quite critical and it is uncertain whether the process could be successfully employed in Canada.

Principal advantages/disadvantages

- ☐ Temperature sensitive
- ☐ Only demonstrated on dilute solutions
- ☐ Principal advantage is the conversion of ammonia to nitrate and nitrite
- ☐ High capital and operating costs. (Scott, 1989).

5.6. Hemlo-Gold Process

This process consists of adding a premixed solution of $CuSO_4$ and FeSO4 to the tailings pond decant. The premix solution is added at a controlled pH of 6-7, following which it is believed that ferrousion is oxidized immediately to form ferric hydroxide and cupric ion is simultaneously reduced to cuprous, according to the following equation.

$$Cu^{+2} + Fe^{+2} + 3OH^{-} \rightarrow Cu^{+} + Fe(OH)_3$$

The resulting cuprousion ion removes free cyanide as an insoluble cuprous cyanide precipitate. The removal of free cyanide results in the dissociation of copper, nickel and zinc cyanide complex leading to the removal of further cyanide by cuprousion. These reactions are represented by the following equations;

$$2Cu^{+} + 2CN^{-} \rightarrow Cu_2(CN)_2$$

$$Cu_2(CN)_4^{-2} \rightarrow Cu^{+2} + 4CN^{-}$$

Ferrocyanide precipitates as cupric ferrocyanide. The heavy metals copper, nickel and zinc, and antimony and molybdenum are co-precipitated from solution with the ferric hydroxide formed upon addition of the $CuSO_4$- $FeSO_4$ solution (Scott, 1989).

5.7. Cyanide Recovery Processes

Several processes have been developed to recover and recycle cyanide. The basic processes are AVR (acidification-volatilization, reneutralization) and ion exchange with AVR and electrolytic recovery.

5.7.1. AVR (Acidification- Volatilization- Reneutralization)

The AVR process consists of acidifying waste cyanide-bearing solutions or slurries to pH 2-3 with H_2SO_4, volatilizing the resulting HCN by intense air stripping and recovering the HCN by absorption in an alkaline solution.

The recovered HCN is recycled to the cyanidation circuit. Some cyanide containing solids, $CuCN_2$, $Cu_2Fe(CN)_6$, ...ie. remain the acidified solution. Dissolved metals, Cu, Ni, Zn also remain.

In solution are precipitated as hydroxides in a subsequent step by neutralisation with lime (Scott, 1989).

The AVR reactions are shown as follows;

Acidification $Ca(CN)_2 + H_2SO_4 \rightarrow CaSO_4 + 2HCN$

Absorption $2HCN + Ca(OH)_2 \rightarrow Ca(CN)_2 + 2H_2O$

Advantage/Disadvantage

- Costly and complex installation
- Safety considerations related to HCN gas handling
- Primarily effective on free cyanide only, and where high concentrations of cyanide present
- Cyanide recovered for resue

5.7.2. Ion Exchange Process

Two processes of interest use ion exchange resin for cyanide recovery and recycle. Resource Technology Associates (RTA) process consist of an ion-exchange step to remove metal-cyanide complexes from barren solution using a weak-base anion exchange resin, concentrating the cyanide by eluding with a calcium hydroxide solution, followed by cyanide volatilization and recovery by the AVR process. In order to remove free cyanide in solution by the ion-exchange resin the cyanide must first be complexed by the addition of cupper(Higgs, 1995).

A second process combining IX-AVR, similar in many respects to the ore described above was being marketed by Canadian Company called CY-TECH. In this process metal-cyanide complexes were adsorbed on a strong- base resin. The resin once loaded was elutred with a dilute solution of H_2SO_4. The elute from ion exchange was sent to a standard AVR process (Scott, 1989).

Principal **advantage and disadvantage** of the process.

- High capital and operating costs
- Safety considerations related to HCN gas handling
- Cyanide recovered for reuse

5.8. Storage of Cyanide Containing Waste and Disposal Design

Due to the characteristics of gold ores, considerably high volumes of waste occurs in plants. Generally disposal dams that are built in order to render the fine – grained waste coming out of the plant in a state of poor leaching solution, to be stored and/or to make possible the liquid part to be sent back to the plant, form an important part of the whole project. With the increasing environmental awareness, it's clear that much more serious restrictions should be bought to this part of the plants (McLeon, Lighthall & Broughton, 1989)

The tailing disposal area is a key element, in the overall system in that it must safety contain the tailings and optimise natural degradation of cyanide in the pond. Natural degradation in the pond will assist in reducing the need for chemical treatment of excess water. Safety of the tailing impoutment requires consideration of;

- Dam design and stability
- Water balance allowances to prevent spills
- Control of groundwater seepage from the pond.

The parameters effecting natural degradation and the degradation mechanism is given in part 5.1. in detailed.

Water balance must be determined as apart of the impoundment design. Where degradation of a large volume of supernatant is desirable to take advantage of naturel cyanide degradation, this additional storage must be accommodated in the tailings detention area. The typical components of a tailings system water balance are shown on figure 5.4

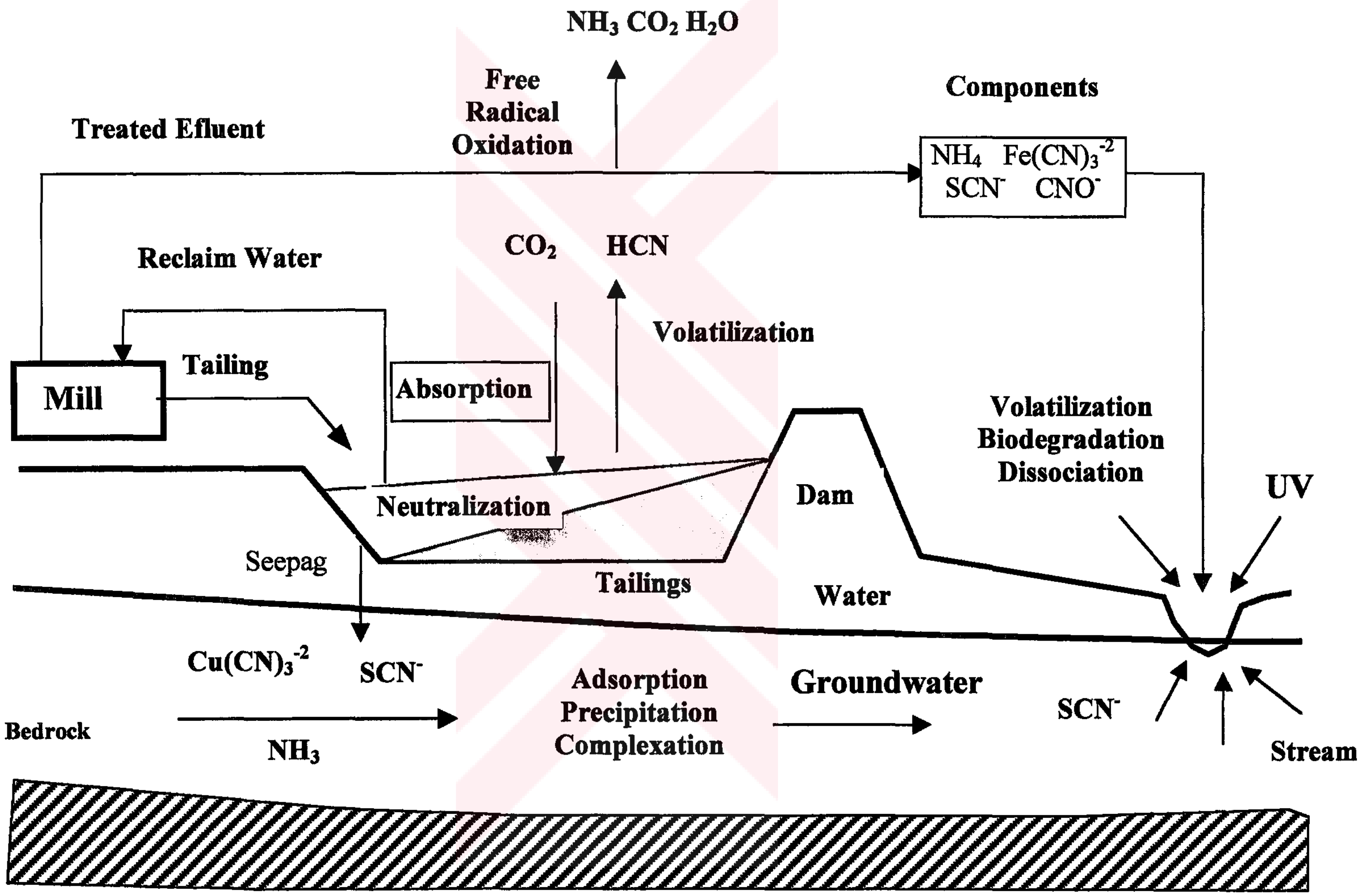


Figure 5.4. Schematic Water Balance for Cyanidation Tailings System(Higgs, 1995)

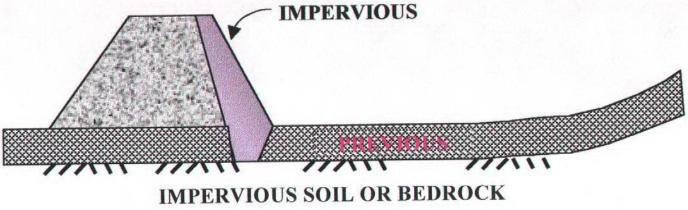
For conservative design, impoundment should usually be sized to include;

- ☐ Tailings and supernatant water storage up to the next stage of completed dam construction
- ☐ Storage for a design flood
- ☐ Storage for the excess run off from a wet year
- ☐ One meter of freeboard

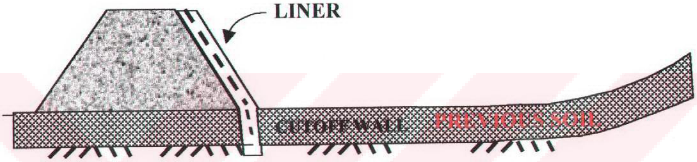
The degree of "imperviousness" required is dependent on the following factors;

- ☐ Regulatory guidelines for CN levels
- ☐ Aquatic resource values downstream of the pound
- ☐ Hydrogeologic properties and geology of the site
- ☐ Seepage travel times and rates of cyanide degradation in the groundwater system.

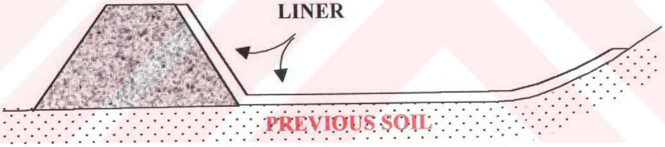
Figure 5.5. Shows a number of typical measures used to limit seepage from tailings pond (McLeon, Lighthall & Broughton, 1989).



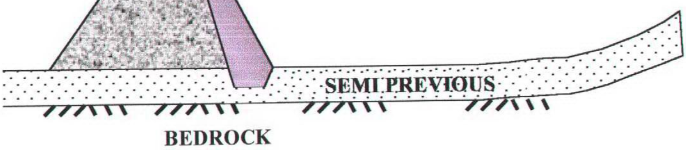
Shallow previous foundation in confined valley-cutoff trench to impervious formation



Deeper previous formation in confined valley - concrete cutoff wall combined with membrane liner on up stream face of dam



Deep previous formation – full lined reservoir



Partial speeage cutoff with pumpback collector wells

Figure 5.5. Typical measures for limiting tailings pond seepage.

CHAPTER 6

EXPERIMENTAL STUDIES

6.1. Materials and Methods Used in Experimental Studies

6.1.1 Sample Preparation

Bore samples to be used in the experiments were taken from Gümüşhane Gold ore deposit. Approximately 50 kg of sample was collected, mixed and blended to form representative experimental samples. Sample preparation flowchart is shown in Figure 6.1.. In order to prepare the samples for analysis and leach tests, the samples were subjected to comminution.

Samples to be used in the tests were ground to 150,106,75,53 and 38 micron size fractions according to grindability characteristics. Flowchart of these experimental studies are given in Figure 6.2. and results are given part in 6.4..

6.1.2.Grinding Conditions:

Sample amount	: 4 kg
Ball charge	::5 kg
Charging Ratio:	: 1/5

Ball charging ratio:

Ball diameter(mm)	38	25	20	-20
Weight %	15	50	20	15

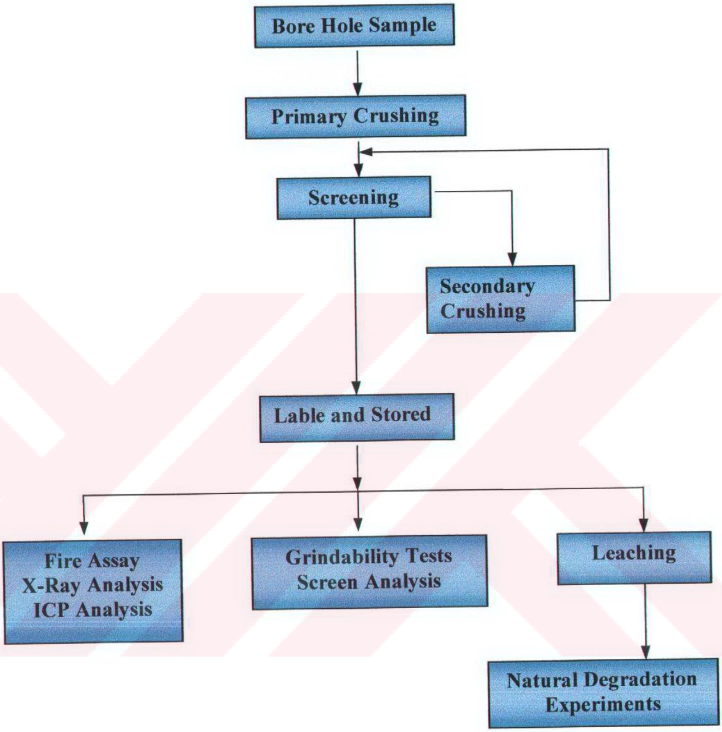


Figure 6.1.Sample preparation flowchart

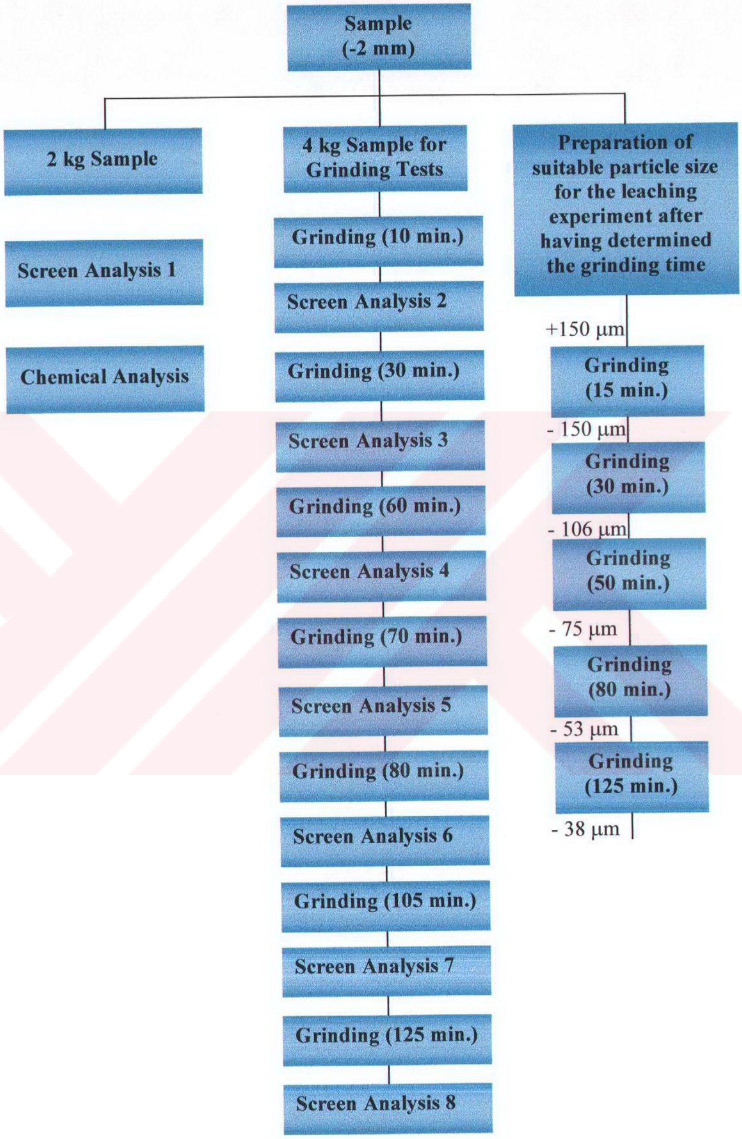


Figure 6.2.General flow chart of grinding tests

At grinding tests, SIEBTECHNIC's vibrating type mills have been used. .Figure 6.3..

Number of mill : 4
Dimensions of mill : 200x200mm

The aim of these tests was to determine the required time to grind the ore below 150, 106, 75, 53 and 38 microns. There fore other parameters have not been considered at this stage.

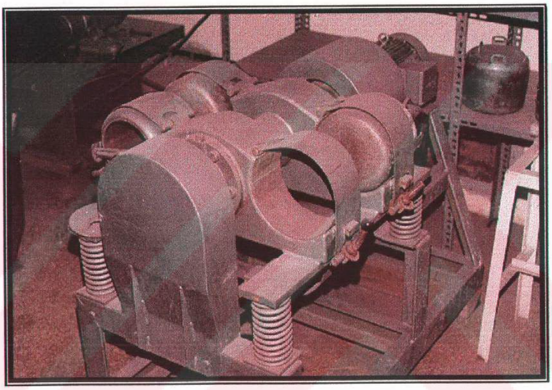


Figure 6.3.SIEBTECHNIC vibrating mill

6.1.3.Leaching Conditions

Flow diagram of the experiments are given in figure 6.4. and leaching conditions are as follows;

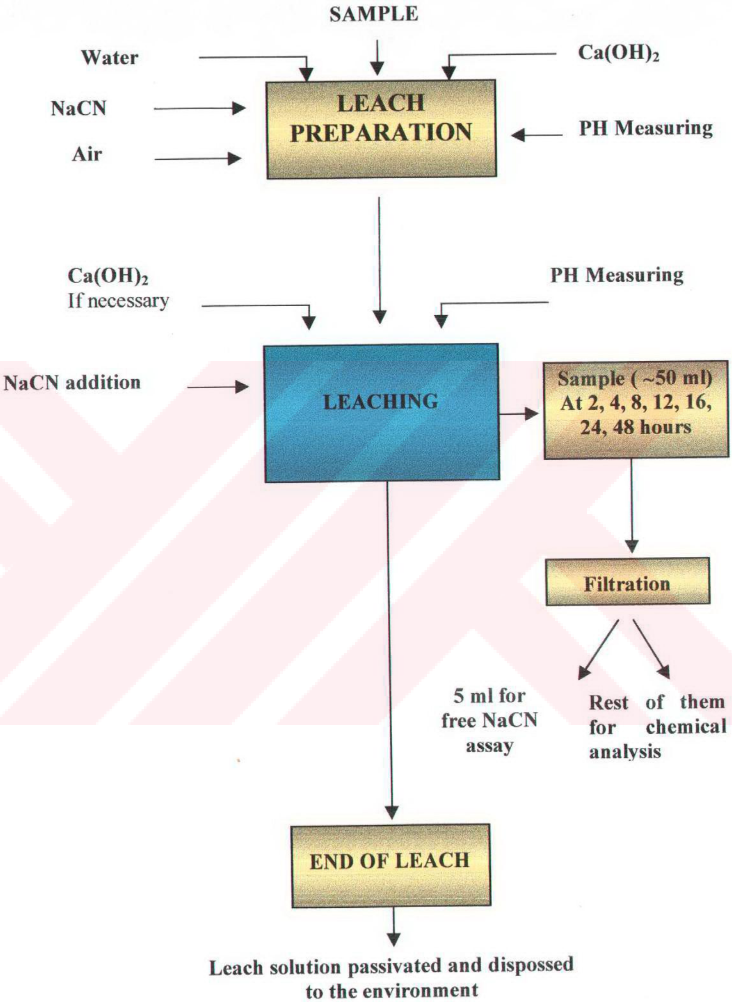


Figure 6.4.Flow diagram of the experiments.

Water	Top water
Sample Weight	300,400,600,800,1000gr.
Particle size	80 % under, 150,106,75,53, and 38 micron
Pulp density	20 %,30%,40 %,50 %,60 %
pH	10,10.5, 11,11.5 (regulated with $Ca(OH)_2$)
NaCN	0,5, 1,2,3,4 (Kg/t)
Temperature	Ambient, 15-25 °C
Time	2-48
O_2	6-8 mg/lt
Agitation Rate	300,460

As seen above; the effect of particle size, solid ratio, pH value, amount of NaCN, agitation rate and amount of O_2 versus time have been evaluated for the determination of experimental leaching conditions.

6.1.4 Experimental Equipment and Apparatus.

Metaliç Plan

While investigating about leaching procedure for carrying out the laboratory studies in optimal conditions, it was observed that a leach experiment was carried out in a single cell driven by a motor in Etibank Kütahya Gümüşköy Plant laboratories. But, it was considered that using such a set-up would slow down the work and would not provide fast experimental studies under the same conditions. Having been inspired by this, the possibility of carrying out a series of experiments in optimal conditions has been searched. As a result , the structure plan of the leaching experiments shown in figure 6.5 was drawn. As seen from the figure, two motors were planned to draw 6 leaching jars. After a detailed work, a leach experiment device called ***Metaliç*** has been developed.

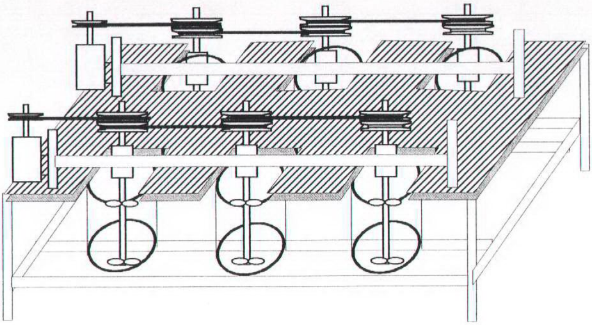


Figure 6.5 Construction of METALİÇ leach plant

The ***Metaliç*** device was constructed in laboratories of Dokuz Eylül University Engineering Faculty, Mechanical Engineering Department. During the construction of the device, the cost was kept at a minimum level due to the economical limitations. As seen in figure 6.6, a table was first designed and constructed from 50 x 50 mm L profiles. Later, the main body to be laid on to the table has been designed using 40 x 60 mm rectangular profiles. Properties of the body are given in figure 6.7, Between the table and main body, a 20 mm thick wooden plate measuring 1200 x 920 mm has been installed after preparing the gaps for the leaching jars. As can be seen in figure 6.8, FK P204 type bearings have been installed onto the main body for the main stirring shafts of which technical data are given in figure 6.9, Because the experiments were to carried out at speeds of 460 and 300 rpm, revolution of electric motors and the diameter of belt - pulley to be installed onto the strings haft were defined by calculation. The reason of selecting a belt - pulley system was due to economic considerations.

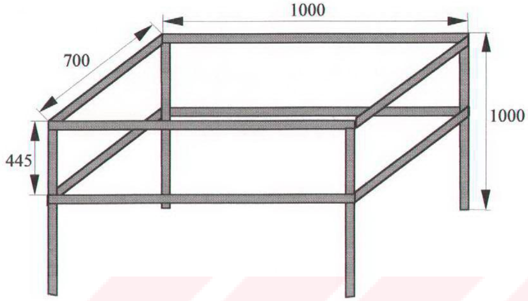


Figure 6.6. Table of Metaliç device

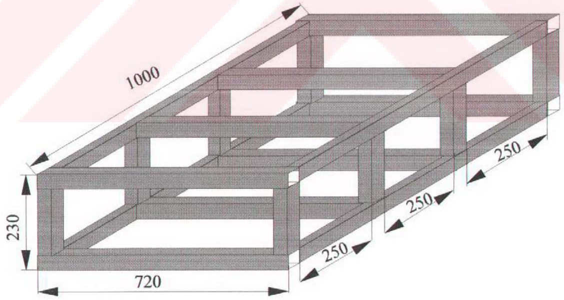


Figure 6.7. Main body of Metaliç device

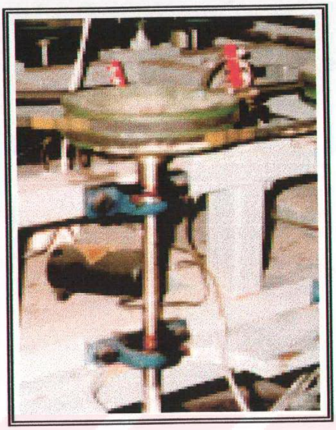


Figure 6.8. Assembling of FK P204 type bearings.

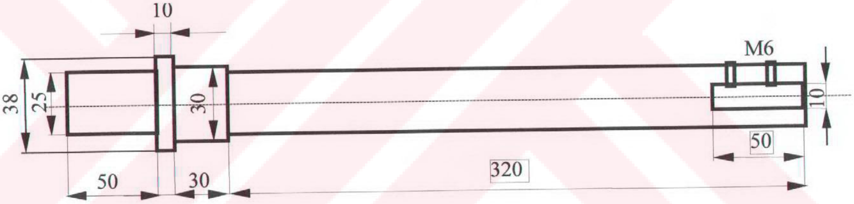


Figure 6.9. Technical data of main shaft

During the calculations it has been found out that the motor type capable of running 48 hours continuously is the squirrel-cage type motor. Then the diameter of belt pulley has been calculated for the agitation speed of 460 rpm when using a motor of type QU 80 M4 B having 0.75 kw at 1400 rpm;

Motor speed (D_1) : 1400 rpm.
Diameter of Motor pulley (r_1) : 60 mm
Agitation speed (D_2) : 460 rpm.
Diameter of stirring belt - pulley (r_2) :

$D_1.2\pi r_1 = D_2.2\pi r_2$

$1400.2.\pi.60 = 460.2.\ \pi.\ r_2$

$r_2 \cong 180$ mm.

In the same way, using a 180 mm diameter belt - pulley it has been obtained that the stirring speed will be 300 rpm with a AGM 90 S G type motor having 0.75 kW at 910 rpm. This is calculated as follows;

$D_1.2\pi r_1 = D_2.2\pi r_2$

$910.2.\pi.60 = D_2.2.\ \pi.180$

$D_2 \cong 300$ rpm.

After the motors and 2 canal belt - pulleys measuring 180 mm were installed, 13 x 1150 mm V type belts were stretched between the motor and stirring belt - pulleys. In order to avoid a reaction of stirring rods (figure 6.10) with the solutions, they are manufactured using stainless steel (steel type 316), and the stirring wings on the rods form 2 mm thick Cr-Ni plates and are then plated with synthetic material.

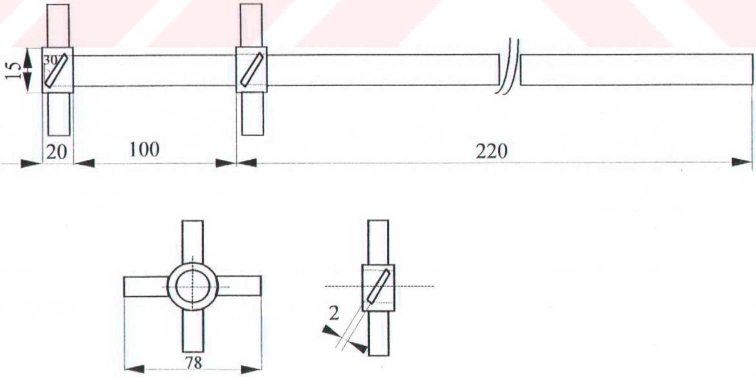


Figure 6.10. Technical data of stirring rod

At the device, 3 and 5 l jars were used as stirring cups and these were installed on a system that was vertically movable. This vertical movement was provided by a rod with square teeth. The movable system was manufactured using 30 x 30 mm L-shaped profiles, as shown in figures 6.11-13.

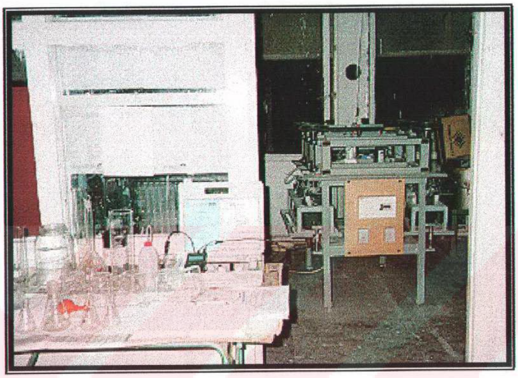


Figure 6.11.Metaliç plant

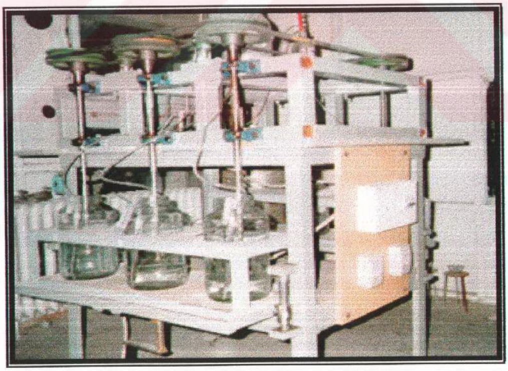


Figure 6.12.Metaliç plant

To obtain a well – stirring action in the jars (leaching tanks), plates of 20 mm in width were located vertically and plastic tubes were connected to blow air into the jars. This system can be seen in Figure 6.14

Figure 6.13.Metaliç plant

Figure 6.14.Agitation jars (leaching tanks)

A pH-meter of WTW Ph320 type was also used for pH measurements with following features.

- The calibration system has been arranged according to DIN 19266 standards.
- The intervals and susceptibility of measurements –2.00 16.00/0.01Ph –5 +99,9 °C/0.1 °C

6.1.5. Reagents

NaCN : Reagent grade
$Ca(OH)_2$: Powder
Wash solution : Tap water adjusted to pH 11 with $Ca(OH)_2$
Ph butter solution : Ph 7-11

6.1.6. Experimental Procedure

Required amount of water was put into the agitation jars according to the solid ratio. The ground and weighted sample was added and agitation was allowed for 10 minutes. Then, pH was regulated with the addition of $Ca(OH)_2$ ($pH \approx 10$). After the regulation of pH, NaCN was added and stirred for 5-10 minutes to dissolve NaCN. An air tube was inserted into the slurry to aerate at 6-8 mg/lt. After 2,4,8,12,16,24 and 48 hours, pH level was measured and $Ca(OH)_2$ was added when required to regulate pH. Approximately 50 ml of sample was taken at the end of every time period and then filtered. Of the filtered liquid, 5 ml was used for the determination of free NaCN and the rest for chemical analysis. After determining the free cyanide, the more NaCN was added to compansate the consumed amount. The determination of free cyanide and other chemical methods are given below.

At the end of leach test the slurry containing free cyanide was treated with sodiumhypocholoride in order to protect any harmful effect. After 8 hours, passivated slurry was disposed to the environment.

6.1.7.Analysis Method

Determination of free cyanide in leach solution

5 ml sample from the leach solution was taken into a 200 ml erlene cup, then, 5 ml of 0.1N NaOH, 20-25ml distilled water and 4 drops 0.2 % grade metil amino benzol rodanin as indicator were added. The solution prepared was titrated with 0,02 M $AgNO_3$ and the value read was placed in the equation formula to find out the free NaCN..

$$\text{FreeNaCN}(g/l) = \frac{\text{AgNO}_3(\text{value read}(\text{ml}))\,\text{x}\,1.96\ g/l}{\text{Sample amount}\ (\text{ml})}$$

Amount of NaCN to be added during the experiments was calculated using the formula given below;

$$\text{NaCN to be added}(\text{ml}) = \frac{\text{NaCN necassary}(g/l) - \text{FreeNaCN}(g/l)}{0.1(10\%\ \text{NaCN solution})}\ \text{x Volume of liquid}(l)$$

Determination of Au and Other Metals in Cyanide Leach Solution

20 ml from the cyanide-containing leach solution was taken and 1 gr $KMnO_4$ was added to solve the gold by chloridization then, 30 ml HCl was added and heated to solve the gold. When the color got bright the heating was stopped. After the solution got cold, it was completed to 100 ml by adding distilled water. Half of this solution (50 ml) was used to define gold concentration, the other half for other metals (Ag, Cu, Pb, Zn, Fe). The concentration of these metals in the solution was defined as percentage using Atomic Absorption Spectrophotometer (AAS) method. To calculate gold concentration, 50 ml solution was given to separation cones, then, 20 ml Methyl Iso Butiyl Ketone (MIBK) and 2 ml 10 % HBr were added to take the gold into the ketone phase. This phase was filled up to 25 ml with MIBK and the concentration value was read by the AAS device.

Determination of Dissolved O_2 in Leach Solution

Dissolved O_2 in solution was titrated with $Na_2S_2O_3$ solution. Starch was used as indicator in titration.

6.2. Experimental Procedure of Natural Degradation

In this part of the experimental studies, cyanide leaching were performed under optimal conditions and the pulp solution obtained has been used for the experiments. The experiments have been conducted in 2 different types. These are;

- ✓ Natural degradation experiments carried out in an impervious media.
- ✓ Natural degradation experiments carried out by using the solution obtained from the seepage.

6.2.1. Natural Degradation carried out in the Impervious Media

The pulp was taken into a jar and left for degradation in a non – seeping media for 2 months as seen in Figure 6.15. By taking sample every 10 day periods, free cyanide, volatilization amount and pH measurements were carried out under the weather conditions (in a closed room and no sunshine) which is unfavourable for the natural degradation. The results of the experimental studies are given is section 6.6..

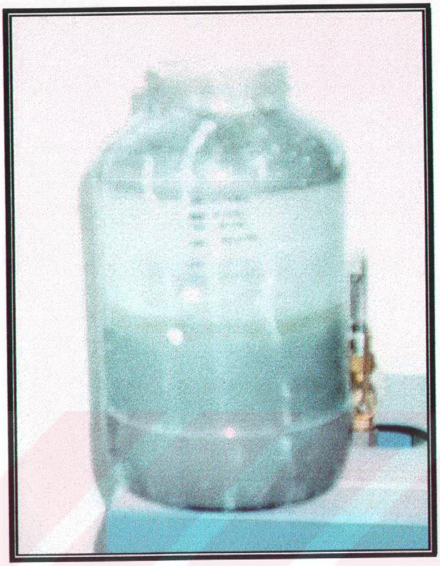


Figure 6.15. Degradation in the impervious media

6.2.2. Natural Degradation Carried out Using the Seeped Solution

These tests were performed by taking the pulp material into a 20 lt container as seen in Figure 6.16. Iilmenite type clay, whose properties are given in Figure 6.17, was used to provide a ground within the container.The thickness of this layer was about 15 cm.

The leach pulp whose initial free cyanide and pH values determined was poured on thid layer and was left about ten days to seep through. The seepage was then tested for every 10 days with regard to free cyanide, pH and volatilization values for about 2 months. The resultsand discussion of these experiments are given in section 6.6.

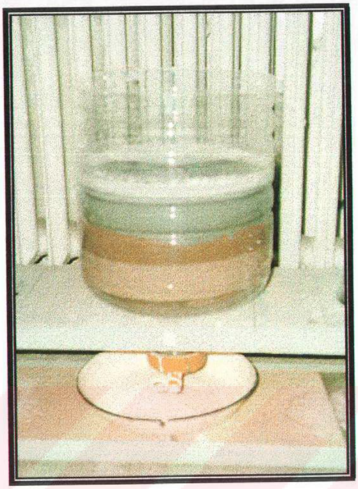


Figure 6.16. Natural Degradation Carried out Using the Seeped Solution

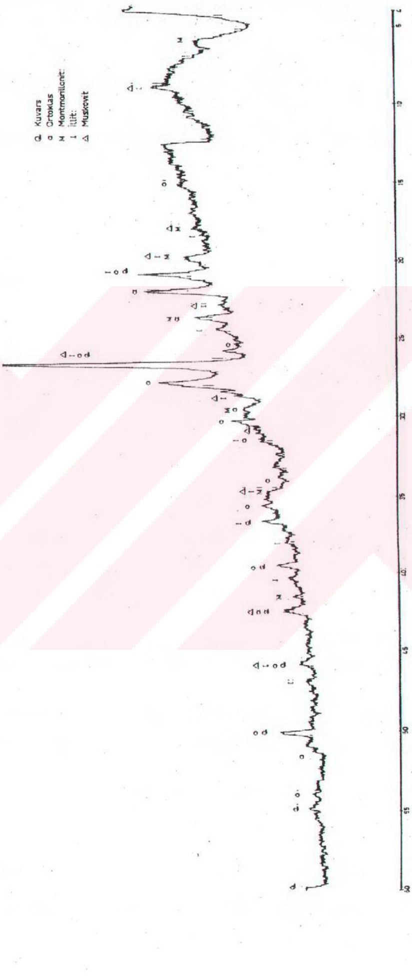


Figure 6.17. X-Ray diffraction diagram of used clay

6.3. Analysis Method and Results

6.3.1. Results of Fire Assay and ICP Analysis

Fire assay and ICP analysis of the ore sample were carried out by İzmir Branch of international SGS company. The results of the analysis are given in Table 6.1., Concentrations of Pb, Cu and Zn were above the reading values of the analysing device. Therefore the analysis of these elements and other elements for controlling purposes were repeated at the laboratories of the Mining Engineering Department., The results of these tests are given in Section 6.3.3

Table 6.1. Fire assay and IPC analysis results

Ag	ppm	18,7
Al	%	0,634
As	ppm	211
Au	ppm	18.7
Ba	ppm	52
Be	ppm	1,6
Bi	ppm	4
Ca	ppm	0,225
Cd	ppm	308
Co	ppm	24
Cr	ppm	31
Cu	ppm	>10000
Fe	%	5,97
K	%	0,095
La	ppm	6
Li	ppm	4
Mg	%	0,305

Mn	ppm	425
Mo	ppm	<1
Na	%	0,016
Ni	ppm	2
P	%	0,03
Pb	ppm	>10000
Sb	ppm	44
Sn	ppm	<3
Sr	ppm	50
Ti	%	<0,005
Tl	ppm	<1
V	ppm	20
W	ppm	952
Y	ppm	2
Zn	ppm	>5000
Zr	ppm	5

6.3.2. X – Ray Analysis and Results

X – Ray Analysis were done by using x – ray spectrophotometer (Joel – Sax – 100 S_4). The samples for x – ray analysis were pressed to form tablets. In order to assist wet chemical analysis, x – ray fluoresans spectrum was traced for qualitative determination of the sample as shown in figure 6.18 Si, S, Mg, Al, K, Ca, Ti, Fe, Cu, Zn, Pb, Ba were determined by peaks in the spectrum. As wolfram tube was out of service during analysis chrominum tube had to be used. This resulted in low detecting sensitivity and metals such as Au, As, Ag were not able to be determined as only responses above 30 ppm could be detected. But all elements in the ore were determined by ICP analysis as shown in Table 6.1.

For minerological assessment of the ore X – Ray diffraction was performed. Figure 6.19

It was found out that the ore contained mainly of quartz, chalcopyrite, sphalerite galena and pyrite. The distributions of these minerals in the ore was calculated as follows;

SiO_2 : %65.24 $CuFeS_2$: %3.33 ZnS : %3.90 PbS : %1.93
FeS_2 : %12.92 Other : %12.68

The following points can be drown after microscopic investigations.

- The major components of the sample are FeS_2, $CuFeS_2$, ZnS, and PbS
- Gangue minerals are SiO_2 and fine muscovite.
- Sulfhur minerals were found as fine dissemination of massive sulfide particles and silicatic gangue
- While pyrite tends to be finer and disseminated, ZnS and PbS are found mainly as separate coarse particles or as composite masses. $CuFeS_2$ is found with both fine FeS_2, and coarse Pb – Zn mineralization.
- Three types of gold occurrences have optically been observed that are found with both fine and coarse sulfur minerals, and within the gang. An almost liberate 100micron particle with a small silicate inclusion and two smaller (8 and 15 micron) particles associated with PbS and FeS_2.

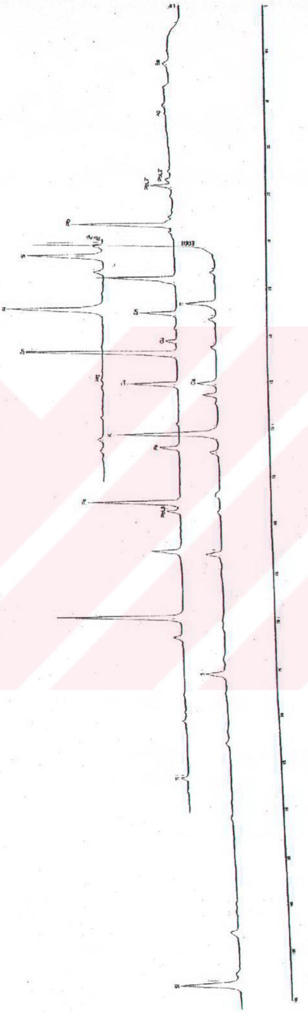


Figure 6.18. X – Ray fluoresans diagram of Gümüşhane gold ore

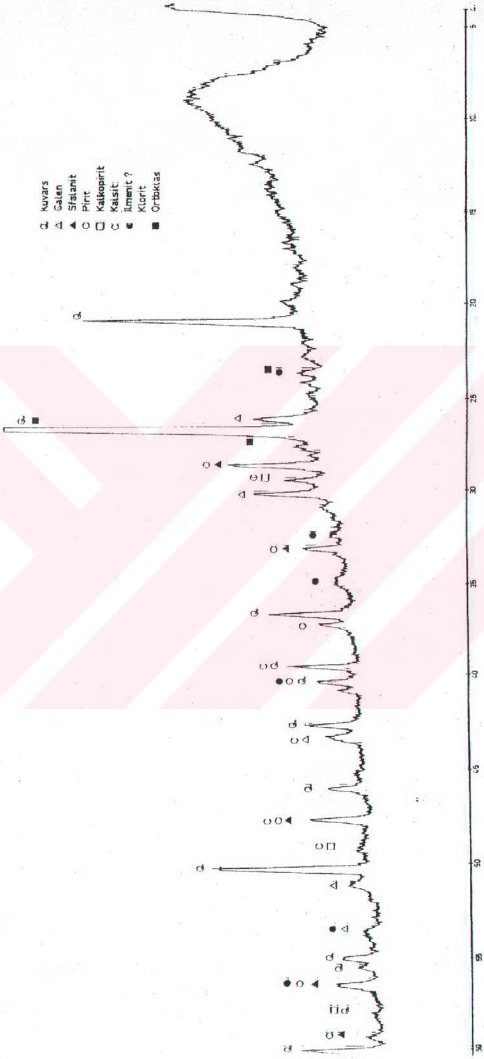


Figure 6.19. X – Ray diffraction diagram of Gümüşhane gold ore

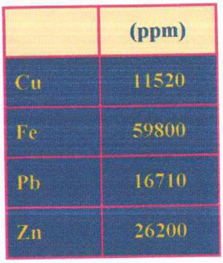
6.3.3. Results of Chemical Analysis

Sample taken from secondary crushing were ground under 150 micron to determine Au, and Ag distribution. The ground samples were screened and each fraction was subjected to chemical analysis. Results are given in Table 6.2.

Table 6.2 Au and Ag, distribution of the Ore

Particle size (mm)	Wt %	Au		Ag	
		ppm	content	ppm	content
3,000-2,000	17,60	17,05	300,08	17,50	308,00
2,000-1,000	15,38	13,60	209,17	17,08	262,69
1,000-0,500	13,35	11,85	158,20	14,84	198,11
0,500-0,300	6,19	13,35	82,64	14,70	90,99
0,300-0,212	2,92	12,90	37,67	14,98	43,74
0,212-0,150	4,45	13,70	60,97	15,68	69,78
0,150-0,106	3,71	14,95	55,46	14,42	53,50
0,106-0,075	3,27	18,15	59,35	21,98	71,87
0,075-0,053	4,57	19,90	90,94	18,34	83,81
0,053-0,038	3,27	18,30	59,84	19,32	63,18
0,038-0,000	25,29	29,05	734,67	25,48	644,39
	100,00	18,49	1848,99	18,90	1890,07

Results of Chemical analysis of other metals :



	(ppm)
Cu	11520
Fe	59800
Pb	16710
Zn	26200

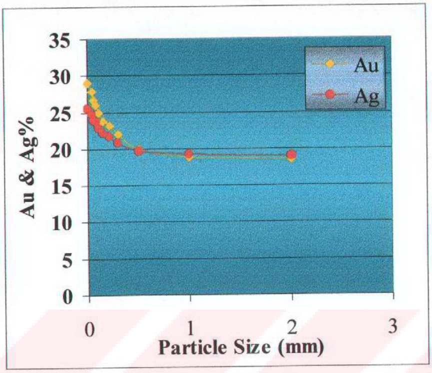


Figure 6.20.Distribution of Au and Ag grade versus particle size

6.4. Size Reduction Method

6.4.1. Results of Crushing and screening

A primary jaw crusher (Retsch – Germany) with 50 mm opening and 3 mm discharge gap was used for a primary crushing. After being crushed the sample was subjected to screen analysis. Table 6.3 and Figure 6.21-22

Table 6.3. Screen Analysis of primary crusher product

Particle Size (mm)	Wt %	Cum. Undersize	Cum. Oversize	Wt%/ΔD
3,000-2,000	17,60	100,00	17,60	7,04
2,000-1,000	15,38	82,40	32,99	10,26
1,000-0,500	13,35	67,01	46,33	17,79
0,500-0,300	6,19	53,67	52,52	15,46
0,300-0,212	2,92	47,48	55,44	11,41
0,212-0,150	4,45	44,56	59,89	24,60
0,150-0,106	3,71	40,11	63,61	29,00
0,106-0,075	3,27	36,39	66,88	36,17
0,075-0,053	4,57	33,12	71,45	71,34
0,053-0,038	3,27	28,55	74,71	71,83
0,038-0,000	25,29	25,29	100,00	1330,87
	100,00			

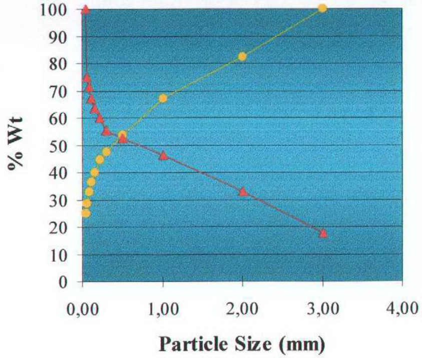


Figure 6.21. Cumulative oversize and undersize after primary crushing

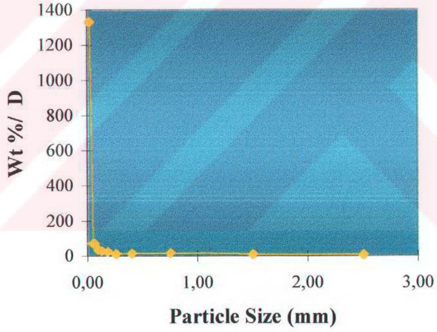


Figure 6.22. Particle size distribution after primary crushing

After primary crushing the sample was screened under 1 mm. To crush the material above 1 mm, an impactor with a screen (Kreuzmühle) of 1 mm gap was used. The result of this study is given in table 6.4 and figure 6.23-24.

Table 6.4. Screen analysis of secondary crusher product (-1mm)

Particle Size (mm)	Wt %	Cum. Undersize	Cum. Oversize	Wt%/ΔD
2,000-1,000	0,00	100,00	0,00	0.00
1,000-0,500	19,59	100,00	19,59	26.12
0,500-0,300	10,55	80,41	30,14	26.37
0,300-0,212	6,32	69,86	36,46	25.70
0,212-0,150	6,68	63,54	43,15	37.92
0,150-0,106	7,29	56,85	50,43	57.93
0,106-0,075	6,20	49,57	56,63	68.46
0,075-0,053	6,47	43,37	63,10	101.11
0,053-0,038	6,85	36,90	69,95	151.60
0,038-0,000	30,05	30,05	100,00	1581.40
	100,00			

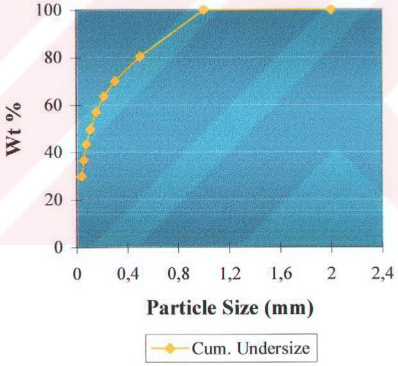


Figure 6.23. Cumulative oversize and undersize after secondary crushing

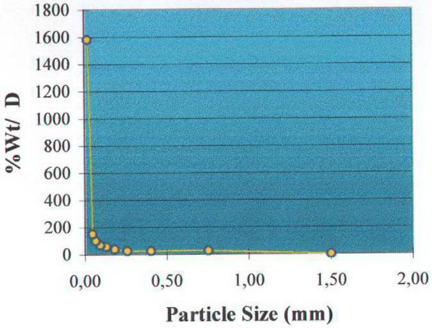


Figure 6.24. Particle size distribution after secondary crushing

6.4.2. Grinding Tests

The samples of Gümüşhane ore were ground with Retch laboratory type vibratory mill and screen analysis were performed to determine the grinding time as shown in Table 6.5 and Figure 6.25 for 10 min.

Table 6.5. 10 min. grinding of feed material (-1mm)

Particle Size (mm)	Wt %	Cum. Undersize	Cum. Oversize
1,000-0,500	0,00	100,00	0,00
0,500-0,300	0,00	100,00	0,00
0,300-0,212	13,53	100,00	13,53
0,212-0,150	13,78	86,47	27,30
0,150-0,106	11,87	72,70	39,17
0,106-0,075	11,49	60,83	50,66
0,075-0,053	10,06	49,34	60,73
0,053-0,038	5,49	39,27	66,21
0,038-0,000	33,79	33,79	100,00
	100,00		

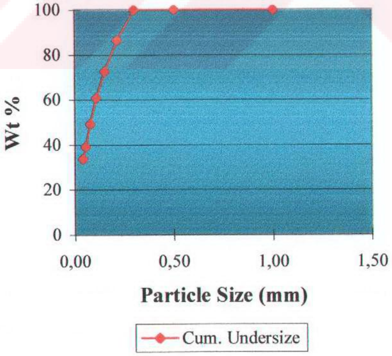


Figure 6.25. 10 min. grinding of feed material (-1mm)

As seen in the Table 6.5.and Figure 6.25.after 10 minutes of grinding time, 72 % of the ore was reduced under 150 micron size. Grinding results after 30 minutes are given in Table 6.6. and Figure 6.26. 80 % of the sample was found to be under 106 micron particle size. This is sufficient time to grind the sample material.

Table 6.6. 30 min. grinding of feed material (-1mm)

Particle Size (mm)	Wt %	Cum. Undersize	Cum. Oversize
1,000-0,500	0,00	100,00	0,00
0,500-0,300	0,00	100,00	0,00
0,300-0,212	0,53	100,00	0,53
0,212-0,150	4,40	99,47	4,93
0,150-0,106	15,70	95,07	20,63
0,106-0,075	13,59	79,37	34,22
0,075-0,053	12,81	65,78	47,03
0,053-0,038	9,58	52,97	56,61
0,0380,000	43,39	43,39	100,00
	100,00		

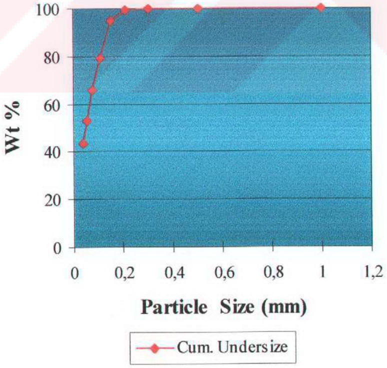


Figure 6.26. 30 min. grinding of feed material (-1mm)

In order to grind the sample to –75 micron particle size, grinding time was increased to 60 minutes and 88,56 % of the material was found to be under 75 micron particle size(Table 6.7 and Figure 6.27).

Table 6.7. 60 min. grinding of feed material (-1mm)

Particle Size (mm)	Wt %	Cum. Undersize	Cum. Oversize
1,000-0,500	0,00	100,00	0,00
0,500-0,300	0,00	100,00	0,00
0,300-0,212	0,00	100,00	0,00
0,212-0,150	0,18	100,00	0,18
0,150-0,106	2,24	99,82	2,43
0,106-0,075	9,02	97,57	11,44
0,075-0,053	14,64	88,56	26,08
0,053-0,038	13,75	73,92	39,83
0,0380,000	60,17	60,17	100,00
	100,00		

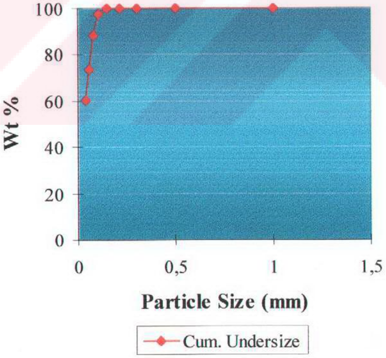


Figure 6.27. 60 min. grinding of feed material (-1mm)

After 80 minutes grinding period, 80.15 % of the sample was determined to be under 53 micron particle size. Results of this analysis are given in Table 6.8 and Figure 6.28.

Table 6.8. 80 min. grinding of feed material (-1mm)

Particle Size (mm)	Wt %	Cum. Undersize	Cum. Oversize
1,000-0,500	0,00	100,00	0,00
0,500-0,300	0,00	100,00	0,00
0,300-0,212	0,00	100,00	0,00
0,212-0,150	0,00	100,00	0,00
0,150-0,106	0,55	100,00	0,55
0,106-0,075	5,43	99,45	5,98
0,075-0,053	13,87	94,02	19,85
0,053-0,038	12,35	80,15	32,21
0,0380,000	67,79	67,79	100,00
	100,00		

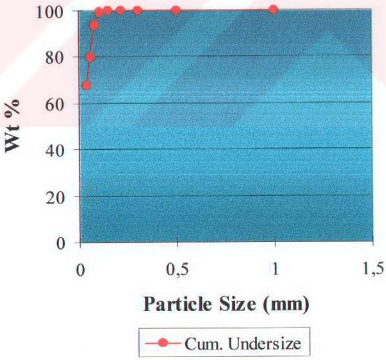


Figure 6.28. 80 min. grinding of feed material (-1mm)

As the final grinding test, sample was ground for 125 minutes and 80.52 % of the sample was found to pass under 38 micron size.(Table 6.9 and Figure 6.29).

Table 6.9. 125 min. grinding of feed material (-1mm)

Particle Size (mm)	Wt %	Cum. Undersize	Cum. Oversize
1,000-0,500	0,00	100,00	0,00
0,500-0,300	0,00	100,00	0,00
0,300-0,212	0,00	100,00	0,00
0,212-0,150	0,00	100,00	0,00
0,150-0,106	0,00	100,00	0,00
0,106-0,075	1,02	100,00	1,02
0,075-0,053	6,90	98,98	7,91
0,053-0,038	11,57	92,09	19,48
0,038-0,000	80,52	80,52	100,00
	100,00		

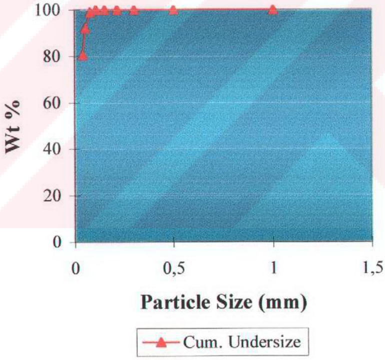


Figure 6.29. 125 min. grinding of feed material (-1mm)

Data taken from the grinding tests are summarised in Figure 6.30. The optimum grinding time under the conditions given in the chapter 6.1.2. was determined in the light of cumulative under size curves. The results of grinding periods are given in Table 6.10.

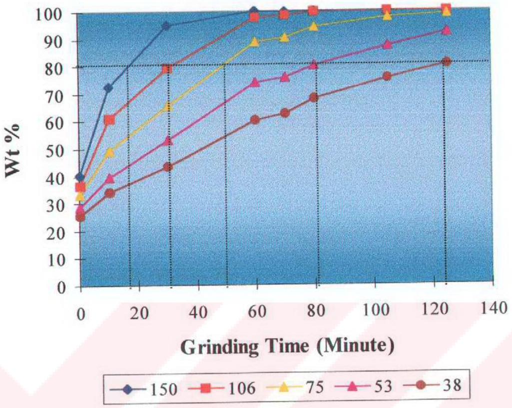


Figure 6.30. Comparison of undersize fractions in various grinding time

Table 6.10. Particle Size Distribution by Grinding Time

Particle Size(µm)(-% 80)	*Time(minute)*
-150	18
-106	30
-75	55
-53	80
-38	125

6.5. Experimental Results of Leaching Conditions

6.5.1. Effect of Particle Size

Five sets of experimentes were carried out in order to see the effect of particle size. Test conditions and results are given in Table 6.11 and 12. As seen from Table 6.11 five fraction of –150,-106,-75,-53 and –38 microns were used in the experiments. At 150 and 106 micron size fractions, recovery of gold and silver were found lower compared to 75,53 and 38 microns particle size were a high recovery of approximately 86 % Au was obtained.

It was observed that beside gold and silver copper was also taken into the solution with a recovery of 14 %. Dissolution of Zn, Pb and Fe, were very low.

NaCN and time variations at these particle size fractions were also studied and the results are given in Figure 6.31-41.

Table 6.11. Conditions of Experiment 1

Experimental Conditions	*1*	*2*	*3*	*4*	*5*
Solid – Water Ratio (%)	30	30	30	30	30
Amount of Sample(g)	400	400	400	400	400
Water Used (ml)	934	934	934	934	934
Particle Size (-80%) µm	150	106	75	53	38
pH	11	11	11	11	11
NaCN(kg/tone)	3	3	3	3	3
O_2 (mg/l)	6	6	6	6	6
Rotation Speed (rpm)	300	300	300	300	300

Table 6.12.Results of Experiment 1.

	1	*2*	*3*	*4*	*5*
NaCN Used /kg/t)	4.33	4.36	4.26	4.16	3.95
Lime Used (kg/t)	2.30	2.45	2.55	2.80	2.75
Au Recovery (%)	63.95	72.67	86.18	86.79	86.95
Ag Recovery (%)	40.63	42.19	47.31	48.74	49.42
Cu Recovery (%)	11.50	13.67	14.67	14.89	15.19
Zn Recovery (%))	0.67	0.94	1.05	1.18	1.43
Pb Recovery (%)	0.02	0.02	0.02	0.02	0.05
Fe Recovery (%)	0.02	0.01	0.01	0.01	0.03

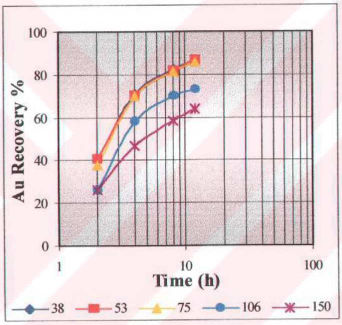


Figure 6.31. Au Recovery vs Time

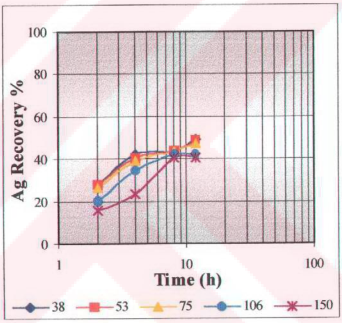


Figure 6.32. Ag Recovery vs Time

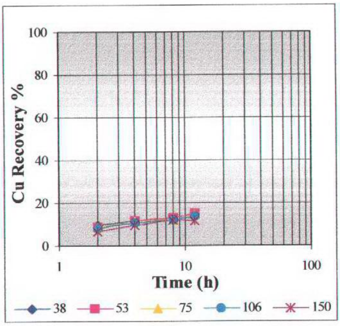


Figure 6.33. Cu Recovery vs Time

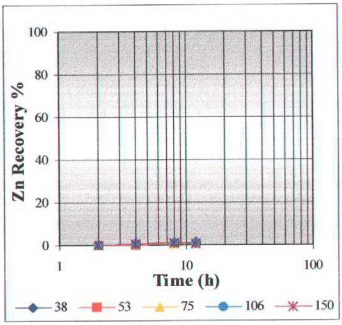


Figure 6.34. Zn Recovery vs Time

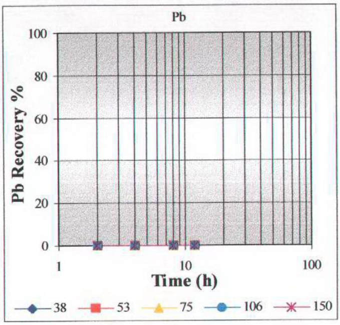


Figure 6.35. Pb Recovery vs Time

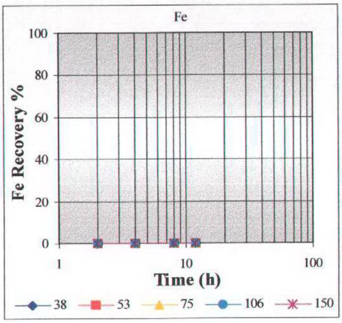


Figure 6.36. Fe Recovery vs Time

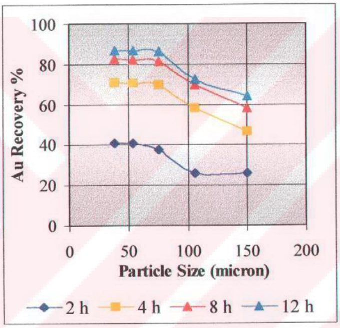


Figure 6.37. Au Recovery vs Particle Size

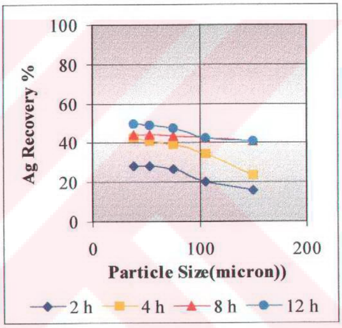


Figure 6.38. Ag Recovery vs Particle Size

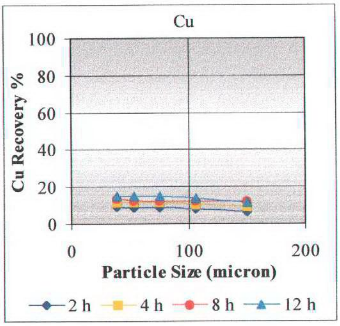


Figure 6.39. Cu Recovery vs Particle Size

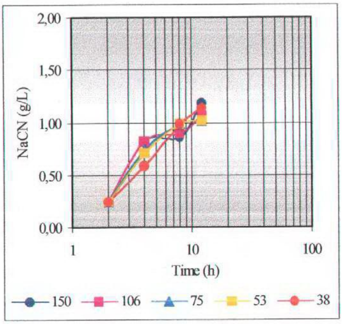


Figure 6.40. Free NaCN Variations vs Time

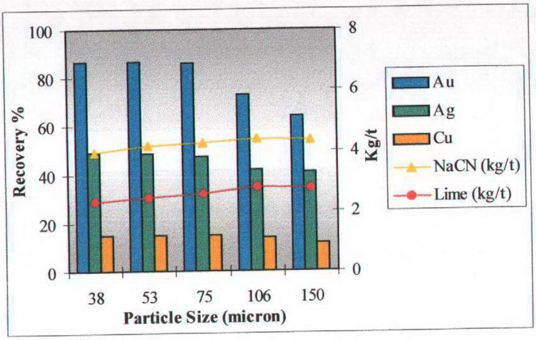


Figure 6.41. General assessment of first set of experiments

6.5.2.Effect of Solids Concentration

In order to determine the effect of solid-water ratio on gold dissolution, five sets of experiment were performed. The experimental conditions and the test results are given in the Table 6.13-14. and in Figure 6.42-6.52 As seen from the data , cyanide consumption decreases with increasing solid ratio as less reagent is required for the reactions. The highest gold and silver recoveries were obtained at 30 % solids concentration

Table 6.13 Conditions of Experiment 2.

Experimental Conditions	*1*	*2*	*3*	*4*	*5*
Solid – Water Ratio (%)	20	30	40	50	60
Amount of Sample(g)	300	400	600	800	1000
Water Used (ml)	1200	934	900	800	667
Particle Size (-80%) µm	75	75	75	75	75
pH	11	11	11	11	11
NaCN(kg/tone)	3	3	3	3	3
O_2 (mg/l)	6	6	6	6	6
Rotation Speed (rpm)	300	300	300	300	300

Table 6.14. Results of Experiment 2.

	1	*2*	*3*	*4*	*5*
NaCN Used /kg/t)	4.83	4.74	4.66	4.13	3.44
Lime Used (kg/t)	2.60	2.50	2.30	2.80	2.95
Au Recovery(/%)	72.44	87.33	83.11	82.67	81.47
Ag Recovery (%)	47.22	47.83	42.36	36.98	36.25
Cu Recovery (%)	10.62	14.53	14.00	14.27	14.33
Zn Recovery (%))	0.54	0.98	0.83	0.86	0.57
Pb Recovery (%)	0.03	0.01	0.01	0.01	0.01
Fe Recovery (%)	0.04	0.03	0.02	0.03	0.03

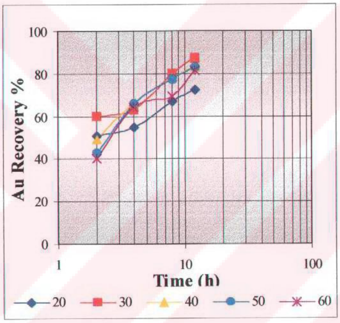


Figure 6.42. Au Recovery vs Time

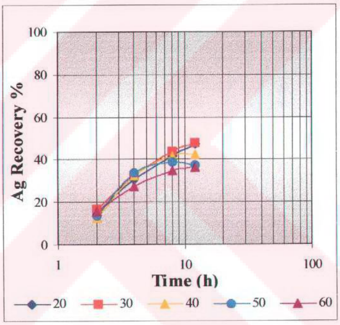


Figure 6.43. Ag Recovery vs Time

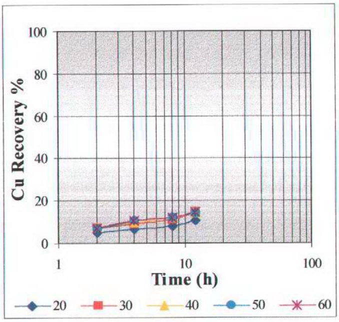


Figure 6.44. Cu Recovery vs Time

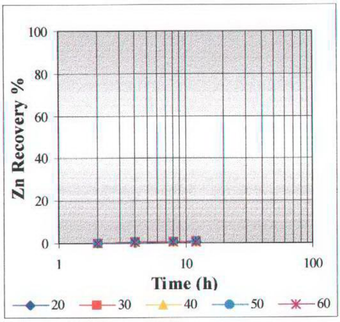


Figure 6.45. Zn Recovery vs Time

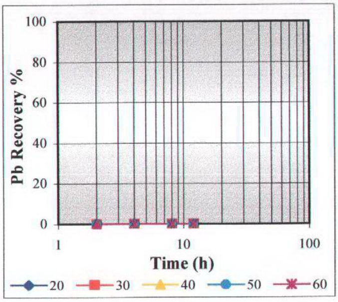


Figure 6.46. Pb Recovery vs Time

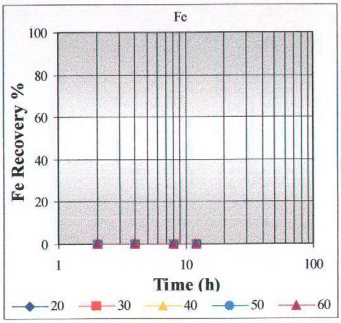


Figure 6.47. Fe Recovery vs Time

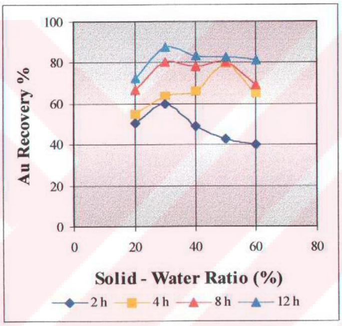


Figure 6.48.Au Recovery vs Solid-Water Ratio

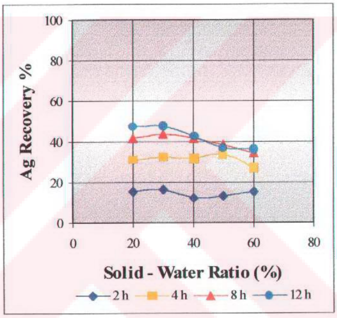


Figure 6.49 Ag Recovery vs Solid-Water Ratio

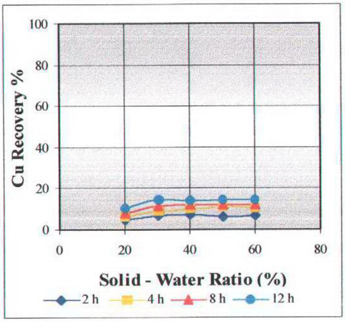


Figure 6.50. Cu Recovery vs Solid-Water Ratio

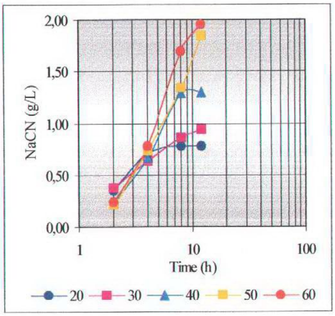


Figure 6.51 Free NaCN Variations vs Time

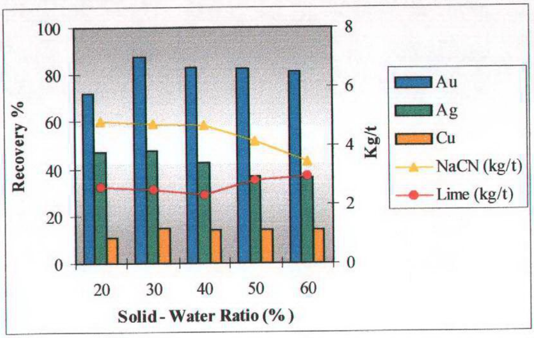


Figure 6.52. General assessment of second set of experiments

6.5.3.Effect of Alkalinity

In these four sets of experiment, effect of pH were tested. Experimental conditions and results are given in Table 6.15-16 and Figure 6.53-63.As shown in related Table and Figures pH at pH 10.5 the highest recoveries were obtained. Recoveries are not dominantly dependant on pH variations. High NaCN consumption at pH 10 and 10.5 can be explained due to formation of HCN as shown Figure 4.3.

Table 6.15. Conditions of Experiment 3

Experimental Conditions	*1*	*2*	*3*	*4*
Solid – Water Ratio (%)	30	30	30	30
Amount of Sample(g)	400	400	400	400
Water Used (ml)	934	934	934	934
Particle Size (-80%) μm	75	75	75	75
pH	10	10.5	11	11.5
NaCN(kg/tone)	3	3	3	3
O_2 (mg/l)	6	6	6	6
Rotation Speed (rpm)	300	300	300	300

Table 6.16. Results of Experiment 3

	1	*2*	*3*	*4*
NaCN Used /kg/t)	5.19	5.08	4.70	4.69
Lime Used (kg/t)	2.20	2.60	2.90	3.00
Au Recovery (%)	84.75	88.25	86.00	79.50
Ag Recovery (%)	39.84	49.53	52.38	38.28
Cu Recovery (%)	15.99	15.92	15.59	15.13
Zn Recovery (%))	0.86	1.02	1.04	0.97
Pb Recovery (%)	0.03	0.03	0.03	0.04
Fe Recovery (%)	0.02	0.03	0.02	0.04

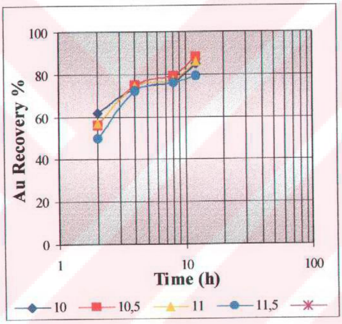


Figure 6.53. Au Recovery vs Time

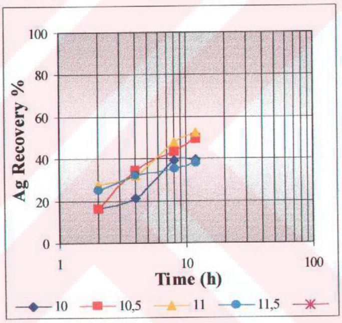


Figure 6.54. Ag Recovery vs Time

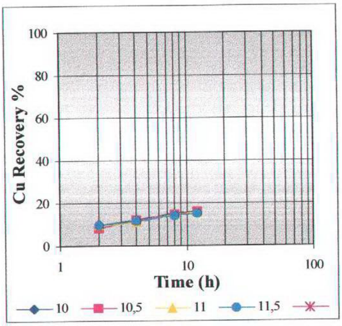


Figure 6.55. Cu Recovery vs Time

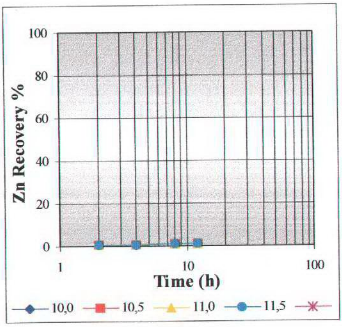


Figure 6.56. Zn Recovery vs Time

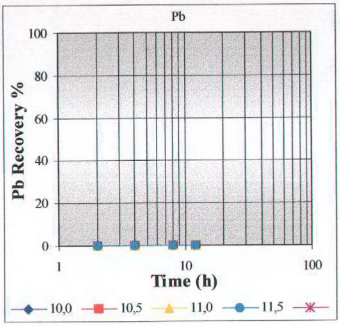


Figure 6.57. Pb Recovery vs Time

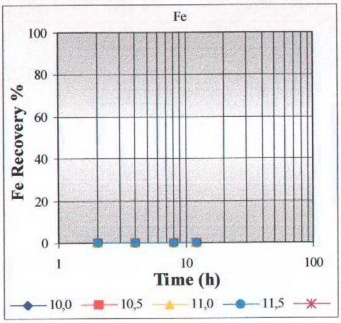


Figure 6.58. Fe Recovery vs Time

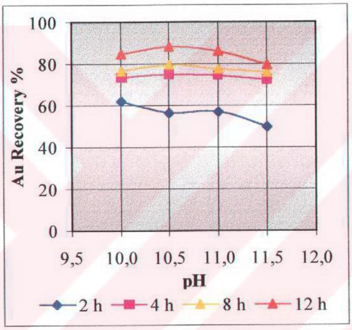


Figure 6.59. Au Recovery vs pH

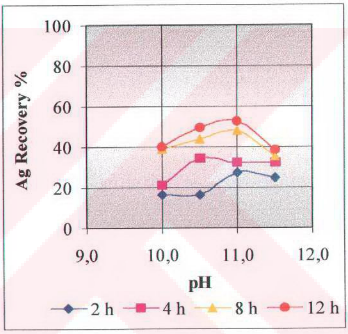


Figure 6.60. Ag Recovery vs pH

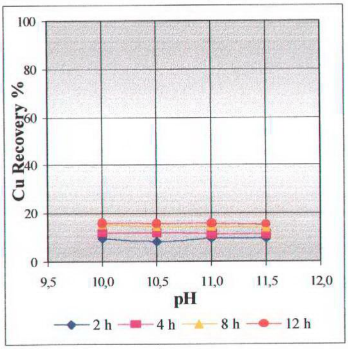


Figure 6.61. Cu Recovery vs pH

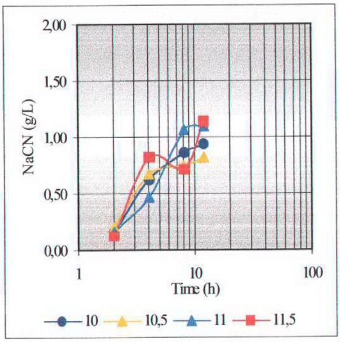


Figure 6.62. Free NaCN Variations vs Time

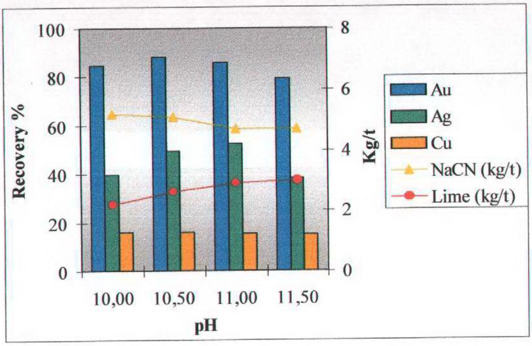


Figure 6.63. General assessment of experiment 3

6.5.4.Effect of Cyanide Concentration

Cyanide concentration is known to have a significant effect on gold dissolution. Recovery of gold and silver increases with increasing cyanide concentration. In order to see this effect 0.5 kg/t,1 kg/t,2 kg/t,3 kg/t and 4 kg/t NaCN were used. In this set of experiments, as shown in Figure 6.64-74. it was observed that gold and silver recoveries decrease highly at low NaCN concentration, the best recoveries of 87 % Au was obtained at 3 kg/t cyanide concentration and this was taken as an optimum value at the following experiments.

Table 6.17. Conditions of Experiment 4.

Experimental Conditions	*1*	*2*	*3*	*4*	*5*
Solid – Water Ratio (%)	30	30	30	30	30
Amount of Sample(g)	400	400	400	400	400
Water Used (ml)	934	934	934	934	934
Particle Size (-80%) µm	75	75	75	75	75
pH	10.5	10.5	10.5	10.5	10.5
NaCN(kg/tone)	0.5	1.0	2.0	3.0	4.0
O_2 (mg/l)	6	6	6	6	6
Rotation Speed (rpm)	300	300	300	300	300

Table 6.18. Results of Experiment 4.

	1	*2*	*3*	*4*	*5*
NaCN Used /kg/t)	0.53	2.01	3.91	4.55	4.77
Lime Used (kg/t)	2.00	2.25	2.40	2.50	2.80
Au Recovery (%)	52.67	64.33	76.00	87.17	86.17
Ag Recovery (%)	15.45	25.19	46.82	51.36	53.18
Cu Recovery (%)	5.86	6.67	12.28	15.37	15.70
Zn Recovery (%))	0.07	0.12	0.48	0.96	1.04
Pb Recovery (%)	0.01	0.02	0.01	0.03	0.04
Fe Recovery (%)	0.03	0.03	0.05	0.06	0.09

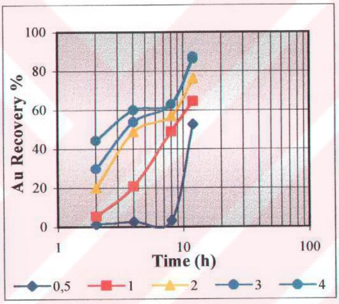


Figure 6.64. Au Recovery vs Time

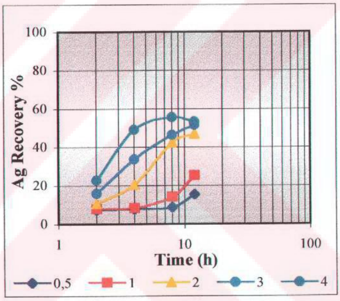


Figure 6.65. Ag Recovery vs Time

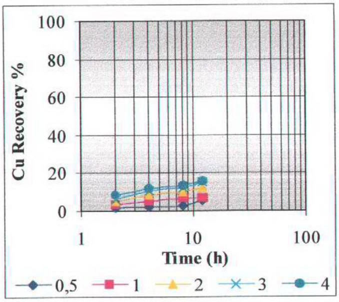


Figure 6.66. Cu Recovery vs Time

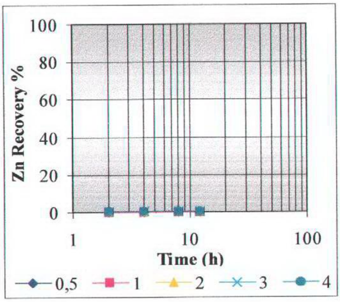


Figure 6.67. Zn Recovery vs Time

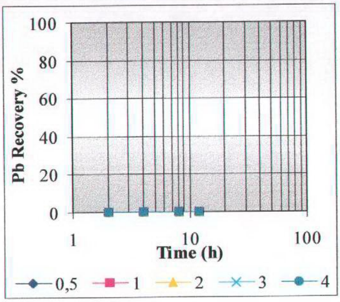


Figure 6.68. Pb Recovery vs Time

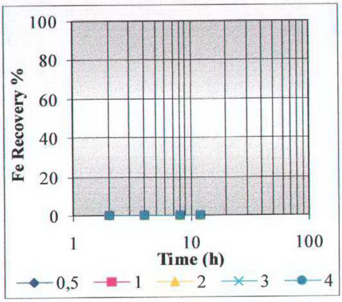


Figure 6.69. Fe Recovery vs Time

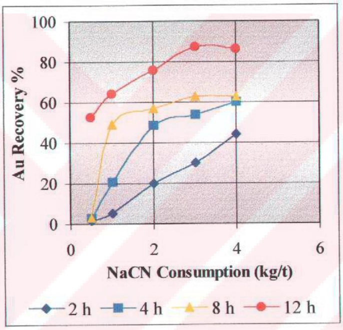


Figure 6.70. Au Recovery vs NaCN Cons.

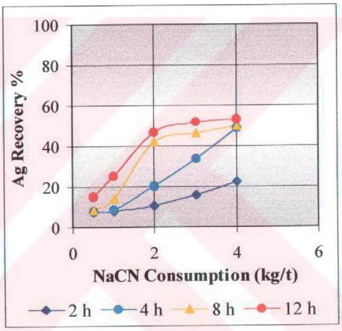


Figure 6.71. Ag Recovery vs NaCN Cons.

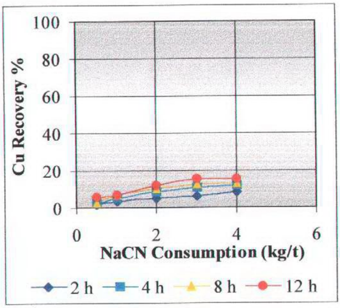


Figure 6.72. Cu Recovery vs NaCN Cons

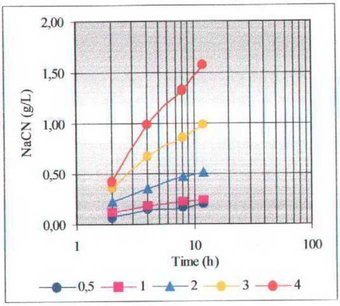


Figure 6.73. Free NaCN Variations vs Time

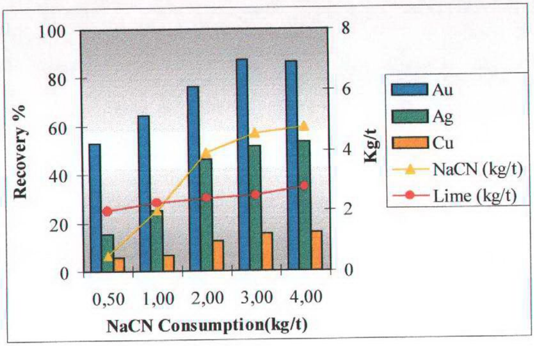


Figure 6.74. General assessment of forth set of experiments

6.5.5.Effect of Agitation Speed

At this stage of the experiments, the effect of two different agitation rates (300 rpm, 460 rpm) on cyanide leaching were tested. The conditions and results of the experiments are given in Table 6.19 and 20. Moreover, efficiencies of Au, Ag, Cu and other metals at these rates are given in Figure 6.75-6.83, cyanide consumption in Figure 6.84 and the overall evaluation in Figure 6.85. The recoveries of Au and Ag were found about 87 % and 54 % at 460 rpm.

Table 6.19. Conditions of Experiment 5

Experimental Conditions	*1*	*2*
Solid – Water Ratio (%)	30	30
Amount of Sample(g)	400	400
Water Used (ml)	934	934
Particle Size (-80%) μm	75	75
pH	10.5	10.5
NaCN(kg/tone)	3	3
O_2 (mg/l)	6	6
Rotation Speed (rpm)	300	460

Table 6.20.Results of Experiment 5

	1	*2*
NaCN Used /kg/t)	4.01	3.94
Lime Used (kg/t)	2.55	2.20
Au Recovery(/%)	87.35	85.51
Ag Recovery (%)	53.94	50.14
Cu Recovery (%)	15.72	15.09
Zn Recovery (%))	1.03	1.01
Pb Recovery (%)	0.04	0.03
Fe Recovery (%)	0.03	0.02

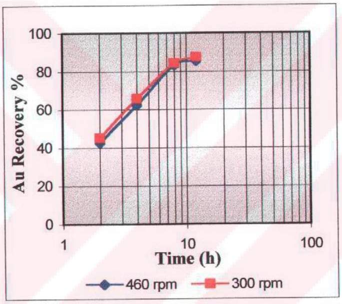


Figure 6.75. Au Recovery vs Time

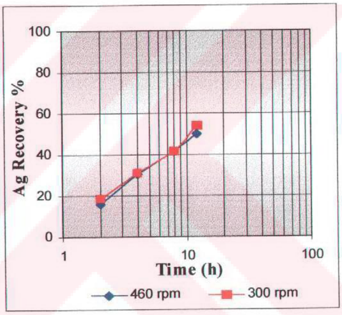


Figure 6.76. Ag Recovery vs Time

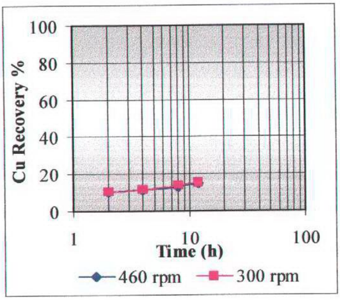


Figure 6.77. Cu Recovery vs Time

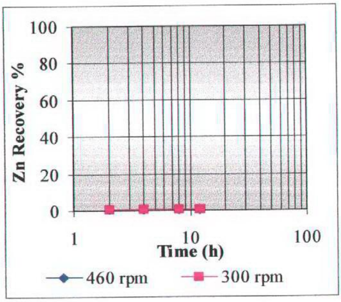


Figure 6.78. Zn Recovery vs Time

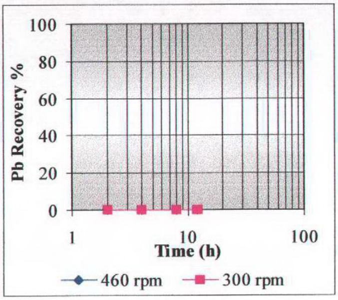


Figure 6.79. Pb Recovery vs Time

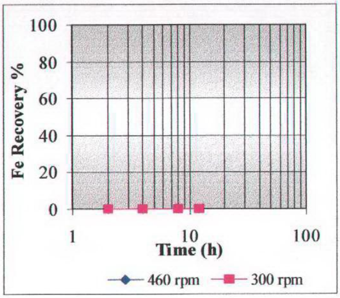


Figure 6.80. Fe Recovery vs Time

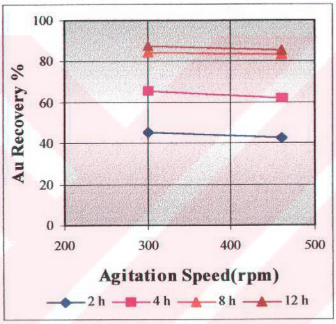


Figure 6.81. Au Recovery vs Agitation Rate

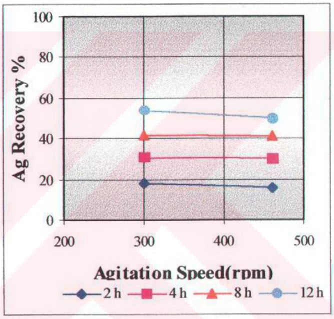
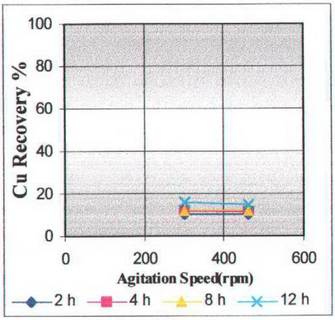


Figure 6.82. Ag Recovery vs Agitation Rate



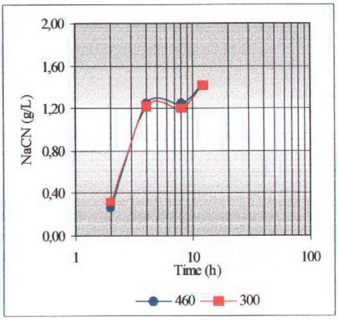


Figure 6.83. Cu Recovery vs Agitation Rate Figure 6. 84. NaCN Cons.vs Time

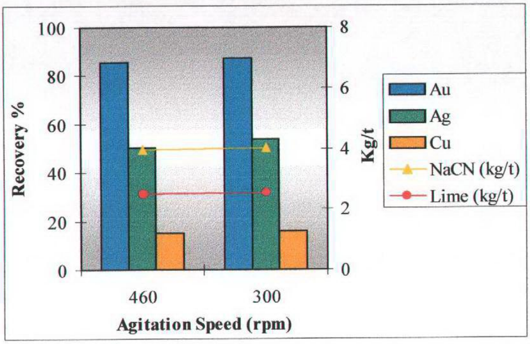


Figure 6.85. General assessment of fifth set of experiments

6.5.6 Final Tests

Last experiment was performed in order to see the leach conditions in 48 hours. In this test, the optimum conditions determined in previous tests (Table 6.21) were followed. Results of this experiments are given in Table 6.22. As can be seen from the Table, NaCN and lime consumption were 4.10 kg per tone and 2.60 kg per tone respectively.

Compared to recoveries at 24 hours leach time of 89,23 % for gold and 52.19 % for silver, gold and silver recoveries increased to 93.62 % for Au and 60.27 % for Ag. As can be observed from the Table Zn dissolution was very low. Pb and Fe practically did not dissolve in cyanide solution.

Table 6.21. Conditions of Experiment 6

Experimental Conditions	*1*
Solid – Water Ratio (%)	**30**
Amount of Sample(g)	**400**
Water Used (ml)	**934**
Particle Size (-80%) µm	**75**
pH	**10.5**
NaCN(kg/tone)	**3**
O_2 (mg/l)	**6**
Rotation Speed (rpm)	**300**

Table 6.22.Results of experiment 6

	1
NaCN Used /kg/t)	**4.10**
Lime Used (kg/t)	**2.60**
Au Recovery (%)	**93.62**
Ag Recovery (%)	**60.27**
Cu Recovery (%)	**16.80**
Zn Recovery (%))	**1.71**
Pb Recovery (%)	**0.01**
Fe Recovery (%))	**0.03**

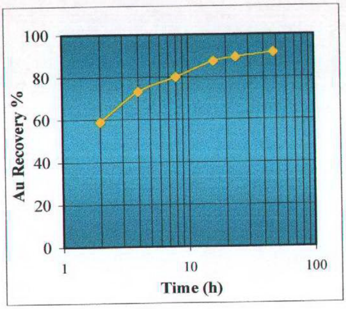


Figure 6.86. Au Recovery vs Time

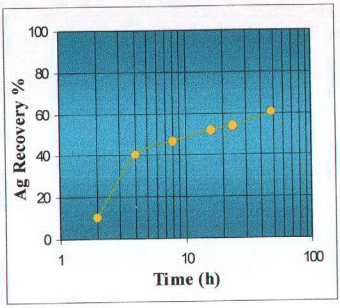


Figure 6.87. Ag Recovery vs Time

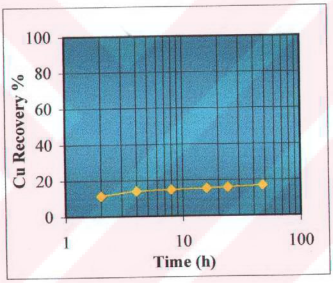


Figure 6.88. Cu Recovery vs Time

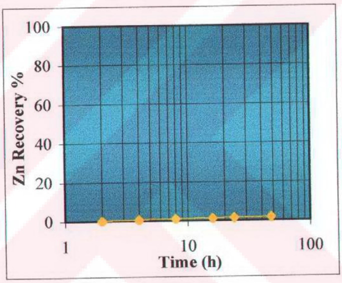


Figure 6.89. Zn Recovery vs Time

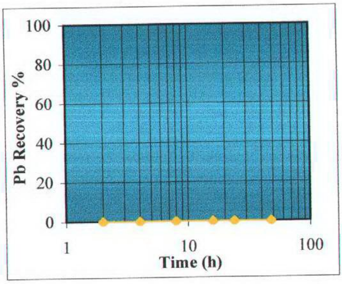


Figure 6.90. Pb Recovery vs Time

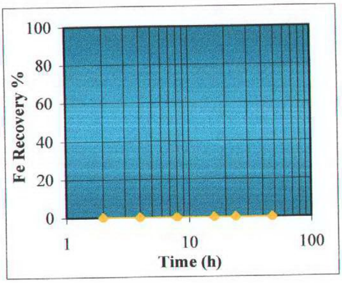


Figure 6.91. Fe Recovery vs Time

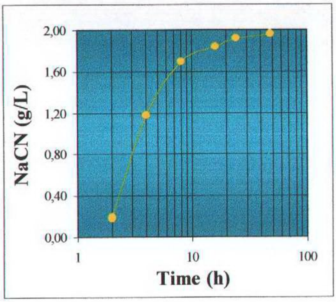


Figure 6.92. NaCN Cons.vs Time

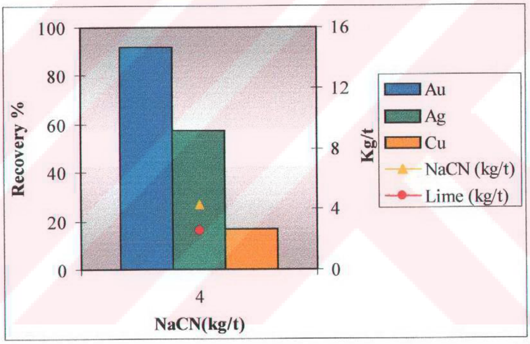


Figure 6.93. General assessment of final experiments

6.6. Experimental Results of Natural Degradation

Conditions of Natural Degradation had been given in Section 6.2.

6.6.1. Experimental Results of Natural Degradation carried out on a Non-Seeping Media

The solution, which was leached under optimal conditions, was left about 70 days (between 1 st June – 9 th of August) for natural degradation on an impervious medium. Free cyanide, pH and temperature variations and volatilization rate of the leach solution were measured every ten day intervals.

Figure 6.94 shows the variation of free cyanide and temperature by days. As can be seen from the graph free cyanide concentration shows a rapid decrease within 30 days and continues to decay slowly after about a month. Considerable drops were observed at points of increased temperatures

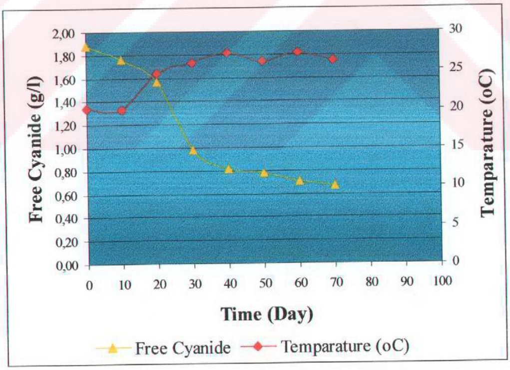


Figure 6.94. The variation of free cyanide and temperature by time

In Figure 6.95 temperature and volatilization rate of free cyanide with time is evaluated. Volatilization increases with increasing temperature. Cumulative volatilizaition amount versus time is shown in Figure 6.96. It can be noted that 50 % of the solution is volatilized after a period of 60 days in a closed room with no sunlight.

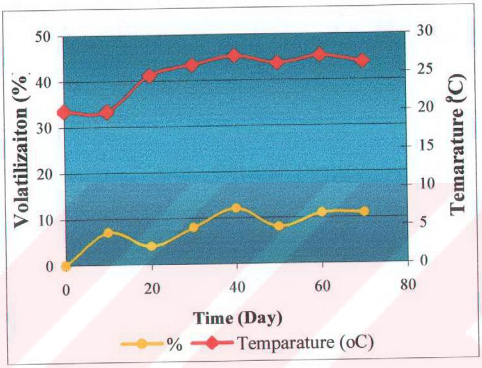


Figure 6.95.Relationship between temperature and volatilization with time

If the experiment would have carried out in the open atmosphere in the presence of sunlight volatilization and eventual degradation of free cyanide would be quicker.

pH of the leach solution is lowered from 10.51 to 9.13 within a period of 70 days. Figure 6.97..

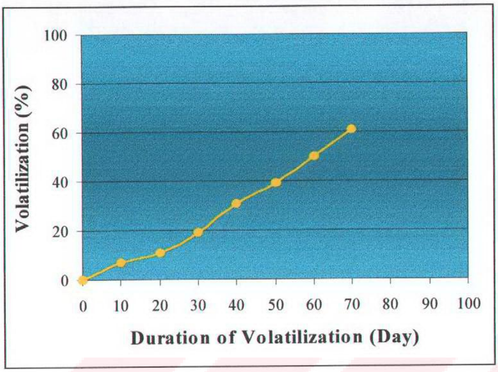


Figure 6.96. Cumulative volatilization by time

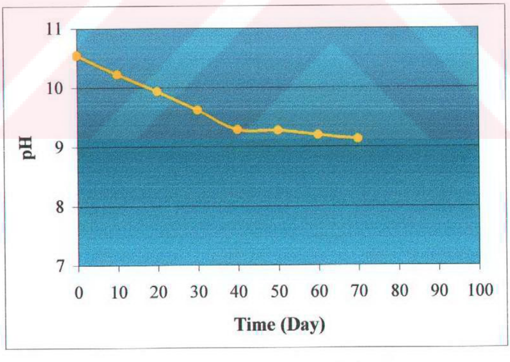


Figure 6.97. Variation of pH by time

6.6.2. Results of Natural Degradation carried out using the Seepage Solution

In the second stage of the natural degradation experiments, leach solution which was passed through a clay layer was used. The composition of clay material is given in Figure 6.17. Experiments were carried out between 1 st. June – 9 th. August 1997.

Free cyanide concentration, temperature and pH variations and volatilization rate of the seepage solution were tested and shown in Figures 6.98 – 101.

As can be seen from the related figures free cyanide and pH values of the seepage from clay layer showed a noticeable drop compared to previous non-seeping tests. Concentration of free cyanide decreased from 1,88 gr/Lt to 1,18 gr/Lt in a period of 10 days time while seepage took place. Free cyanide concentration continued to decrease sharply following at the end of 70 days period, it reached a value of 0,2 gr/Lt.

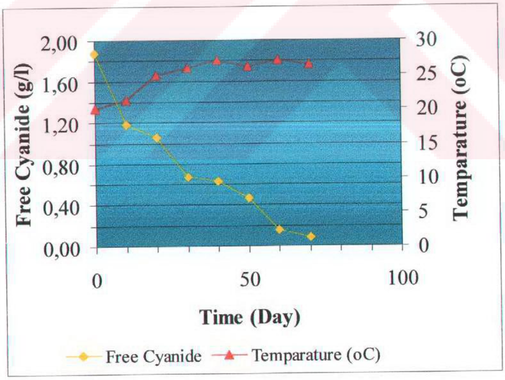


Figure 6.98. The variation of free cyanide and temperature by time

It is worth emphasising that 50 % of the solution volatilized within 60 days of degradation period.

pH value of the seepage solution was measured as 8,27 compared to 10,54 at the beginning of the test.

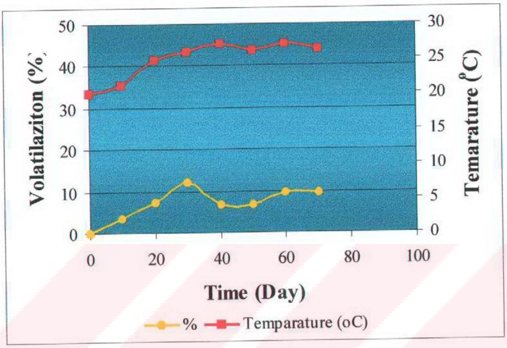


Figure 6.99. Relationship between temperature and volatilization with time

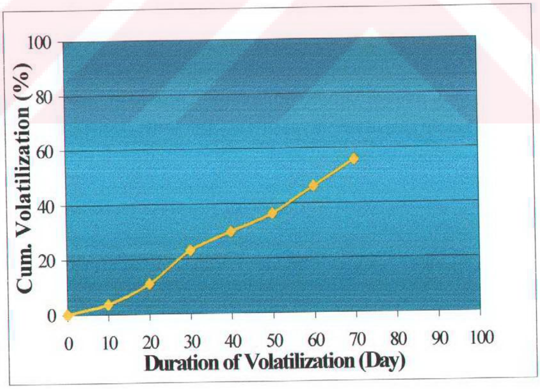


Figure 6.100. Cumulative volatilization by time

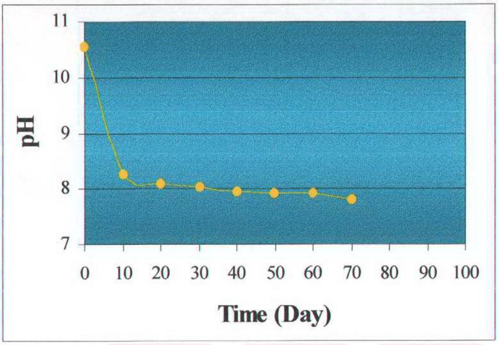


Figure 6.101. Changes of pH by time

CONCLUSION

Microscopic and X-Ray analysis of Gümüşhane Mastra ore indicated that, gold and silver are very finely disseminated in the ore. According to the XRD investigations, the ore consisted of mainly FeS_2 (12.92 %), $CuFeS_2$ (3.33 %), ZnS (3.90 %) and PbS (1,93 %) minerals together with SiO_2 (65,24 %), fine muscovite, calcite and orthoclase as gangue minerals. XRF, ICP and chemical analysis performed on the ore pointed out the presence of Au, Ag, Cu, Fe, Zn, Pb, Sb, As, Mn, elements in amounts of 18.7 ppm Au, 18,9 ppm Ag, 11520 ppm Cu, 59800 ppm Fe, 26200 ppm Zn, 16710 ppm Pb, 211 ppm As, 44 ppm Sb and 425 ppm Mn in the ore.

Sieve analyses of minus 3 mm ore sample and fractional Au, Ag distributions have been determined. Au grade was found to be around 18 ppm for – 150 micron size fraction. There fore the comminution of mastra ore sample to minus 150 micron was targeted for leach conditions.

A vibrating mill with a charge ratio of 1/5 was utilized for dry grinding tests and grinding time for various size fractions was determined as follows;

Time (Minutes)	**Particle Size (μm)**
18	-150
30	-106
55	-75
80	-53
125	-38

In the first part of the leach tests, after determining the mineralogical, chemical and physical characteristics of the ore, the effect of particle size on leach recovery was investigated. Leach tests were carried out for size fractions of -150, -106, -75, -53 and -38 microns. The tests after indicated that about 86 % Au recovery could be achieved for the size fractions below 75 micron. Considering the energy consumption in finer grinding, sufficient liberation and similar recovery values, the optimum size for grinding was decided as 75 micron for further tests.

In the second set of experiments the effect of solids concentration on recovery was investigated. The leach pulps containing – 75 micron particle size fraction at 20 %, 30 %, 40 %, 50 % and 60 % solid concentrations were used and the best result was obtained at 30 % solid concentration coinciding 87 % gold and 47 % silver recoveries in 12 hours leach time. In industrial applications high solid concentrations in leach tanks are preferred to increase the capacity, even though a slight drop in leach recoveries are recorded. This is usually compensated by using a series of leach tanks.

pH value in cyanide leaching is important from the points of leach kinetics and environmental effects and is usually kept between 10 and 11.5. The effect of pH on leach recovery was investigated by adjusting the pH value at 10, 10.5, 11, and 11.5 respectively. Optimum pH was determined as 10.5 and Lime (CaO) consumption as 2.60 kg/ton.

It is known that various cyanide concentrations are used according to the character of gold ores in cyanidation. In the fourth set of experiments 0.21 g/L, 0.43 g/L, 0,86 g/L, 1,2 g/L 1,7 g/L cyanide concentrations (coinciding 0.5 kg/t, 1kg/t, 2 kg/t, 3 kg/t and 4 kg/t NaCN) were used to see the effect of cyanide concentration on leach recovery. During these tests, high cyanide consumption was observed especially within the first two hours of the runs. In low concentrations, the consumption was even more noticeable. At the and of 12 hours leach period, gold recovery showed a decay parallel to lowering concentration below 1.2 g/L (3 kg/t) consumption rate.

The highest recovery (87 % Au)) was at 1,2 g/L cyanide concentration. Dissolution rate was observed to be slower at high cyanide concentration of 1.7 g/L.

As a results of fourth set of experiments 3 kg/t NaCN was found to be optimum concentration for this particular ore sample. Due to batch nature of laboratory leach tests, the amount of NaCN to be added was calculated higher than 3 kg/t, in order to keep a constant concentration within the jars. However in an actual operating plant NaCN consumption would be much less than this amount, due to continuously recirculating solution. It is just to say that dissolution rate of gold, increases with increasing CN concentration up to a maximum point. Addition of more cyanide after this point has no positive effect on gold leaching, on the contrary it slows down the dissolution. This conclusion is in accordance with the general literature.

In the experiment where the effect of agitation speed on dissolution rate was investigated, the best figure was found as 300 rpm. Higher speeds (460 rpm) caused a marked reduction in dissolution recovery. It is known that a small amount of creates a contact between fine particles and solvent and enhances the mass transfer from solid surface into solution. Therefore dissolution rate reaches a maximum point at a reasonable agitation speed.

Leach tests were carried out at room temperature. It was noticed that solution temperature raised about 4-5 °C compared to initial degrees. This is mainly due to exothermic nature of chemical reactions occurring within the solution.

After a series of tests the optimum conditions were obtained as follows;

Particle size (µm) (-80%) : - 75
Solid-Water Ratio (%) : 30
pH : 10.5
NaCN (g/L) : 1,2
(kg/ton ore) : 3
Rotation speed (rpm) : 300

48 hours leach test was performed under these conditions and following Au and Ag recoveries were achieved;

	12h	**24h**	**48h**
Au Recovery (%)	87.35	89.23	93.62
Ag Recovery (%)	51.94	54.19	60.27

The highest extraction rate was obtained after 48 hours leaching time. Cyanide and lime consumption under the conditions was calculated as 4.10 kg/t and 2.60 kg/t respectively. As known from the industrial applications of agitation leaching, maximum 48 hours leach time is allowed due to limitations regarding capacity and plant design.

During cyanidation, depending on the mineralogy of the gold ore, various minerals bearing Ag, Cu, Fe, Ni, Co, Zn elements also dissolve in the form of metal cyanide complexes. The minerals containing As and Sb are both oxygen and cyanide consumer. Some of the oxidation products such as thioarsenite (AsS_3^{-3}), thioantimonite (SbS_4^{-3}) may form a passivating film on gold. Some of these elements suffer various degrees of oxidation, and some from stable cyano complexes in the order of their solubility constant. The presence of these metals would lead to higher consumption of cyanide and oxygen, difficulties in solution purification operations and in the control of cyanide level in effluent solution.

Behaviour of Cu, Fe, Zn and Pb elements have closely observed during leach tests while copper was extracted with a recovery of 16 %, dissolution of other metals could be detected at a negligible level. Solubility of certain sulphide minerals such as ZnS, $CuFeS_2$, FeS_2 and PbS in cyanide solution is known to be quite low and in the order of 18% to 1 %. These solubilities however may show noticeable changes depending on the oxidation conditions on mineral. High cyanide consumption calculated during the experiments can be explained by the existence of cyanides in the ore sample and their oxidation and reactions during leaching. On the other hand these metals were not detected in clear leach solution. This may be explained by the formation of insoluble metal ferro cyanides and precipitation of metal hydroxides due to dissociation of metal cyanide complexes.

Natural degradation of cyanide and metal-cyanide complexes result from a combination of physical, chemical and biological processes. The major removal mechanisms are pH depression due to CO_2 absorption, volatilazition of HCN gas, chemical and photochemical decomposition, precipitation of metal complexes, hydrolysis and adsorption, chemical and biological oxidation.

Natural degradation experiments carried out have been performed in two stages. In the set of experiments the original leach solution, in the second set of experiments the seepage solution, passed through a clay layer, were subjected to natural degradation tests. Free cyanide concentrations of both solutions were 1.81 g/L CN^- and 10.51. After 70 days of retention time cyanide concentration decreased 0.63 g/L and the pH of the solution was recorded as 9.13. Free cyanide degradation was enhanced at periods of increasing temperature. Below pH 9.5 free cyanide concentration showed a significant attenuation due to volatilization of HCN gas.

In the second set of natural degradation experiments, CN^- concentration and pH value were measured immediately after the leach solution was passed through a clay liner. Cyanide concentration decreased to 1.18 g/L and pH value was recorded as 8.27. It is believed that clay layers have a natural cyanide degradation capacity. Measurements carried out at later periods indicated that both CN^- and pH values dropped more rapidly compared to previous solution. Eventual CN concentration and pH were measured as 0.08 g/L and 7.80 at the end of the test period.

50 % of the solution volatilized within 60 days of degradation period. If the experiment would have been carried out in the open atmosphere in the presence of sunlight, volatilization and eventual degradation of free cyanide would be quicker.

In the cyanidation of this particular epithermal type gold ore containing significant amounts of sulphite minerals, high cyanide consumption was recorded during leach process. Negligible amount of heavy metals (Cu, Pb, Fe, Zn etc.) were detected in the leach solution due to naturally-occurring physical and chemical mechanism such as dissolution, complexation and precipitation.

Under the least favorable atmospheric conditions, the CN^- concentration in degraded from 1800 ppm to 80 ppm within 70 days of retention time. Natural degradation capacity of the clay layer could also be deduced from the experiments.

For the attenuation and degradation of cyanide down to acceptable limits for the environmental a 2 stage pond system is recommended. Each pound will receive mill discharge for 12 months, the first pond is continuously filled expect when being emptied into the second pond

Another alternative is to utilize tailing pond for natural degradation and to treat the pond decant in chemical treatment systems.

As a result of this experimental work further research is recommended for the following areas;

- ✓ The effect of temperature and pressure on the leach kinetics.
- ✓ Heap leaching experiments for the remaining gold in the leach residue.
- ✓ Pre-treatment experiments (such as roasting) for determination of optimum leach conditions.
- ✓ Investigation of the behavior of copper and other heavy metals during natural degradation.
- ✓ Investigation of alternative leach reagents for this particular ore.

REFERENCES

1. Altın, Altın Madenciliği, Dünya ve Türkiye (1997), Ankara.

2. Bayraktar, I. (1996). Çevre ve Altın Üretimi, 21.Yüzyıla Girerken Türkiye Madenciliği, pp63-83, Sivas.

3. Kilborn Inc., (1991). Best Available Pollution Control Technology, Report of Ontorio Ministry of Environment Metal Mining Sector, wp/3763-15, Canada.

4. Bhappu, B.R., (1986). Hydrometallurgical Advances in Precious Metals Extraction, in Samasundaran R. (Ed.), Advances in Mineral Processing, a Half Century of Progress in Application of Theory to Practice, (AIME).

5. Brooy, S.R., Linge, H.G., & Walker, G.S., (1994). Rewiev of Gold Extraction from Ores, Mineral Engineering, v7, n10, pp1213-1241.

6. Canbazoğlu, M., (1996). Altın ve Gümüş Madenciliğinde Kullanılan Sıvı Atık Arıtma Tekniklerinden Doğal Arıtmanın Oluşum Mekanizmaları ve Güney Africa Uygulamaları, 21.Yüzyıla Girerken Türkiye Madenciliği, pp85-95, Sivas.

7. Çelik, H., Mordoğan, H. & İpekoğlu, Ü. (1997). Siyanürle Altın Üretim Tesisi Atıklarının Arıtma Yöntemleri, Madencilik Dergisi,pp33-45, Ankara.

8. Haque, K.E., (1992). The Role of Oxygen in Cyanide Leaching of Gold Ore, Canadian Mineral Processors Division of CIM, v85, n963.

9. Hedley, N., & Tabannick, H., (1958). Chemistry of Cyanidation, Mineral Dressing Notes 23, American Cyanamid Company, New York.

10. Herman, R., & Wark, W.J.,(1992). Gold, Gold Alloys and Gold Compounds, ULLMANN Encylopedia, pp 500-505, v A12

11. Higgs, T.W., (1995). Technical Guide for the Environmental Management of Cyanide Mining, British Columbia Technical and Research Committee Reclamation Cyanide Sub-Committee, pp7-(1-17), pp8-(1-7).

12. İpekoğlu, Ü., & Mordoğan, H., (1993). Altın Üretim Tesislerindeki Siyanürün Türleri, Toksik Etkileri ve Atık Barajındaki Davranışı, Madencilik Dergisi, n1, pp37-46, Ankara.

13. Jones, K., & Staunton, W., (1991). Basic cyanide chemistry, Fate of Cyanide in the Environment Near Mine Tailings, Australia Mineral Industries Research Association Limited (AMIRA), P227, Canada.

14. Kaya, M. Kurama, H. & Öz, D. (1996). Comparasion of the Current Cyanide Destruction Method, The First International Symposium on Mine Environmantal Engineering, pp275-282. Kütahya

15. Lucas, M.J., (1995). Gold, Mineral Commodity Summaries, USA.

16. Mardsen, J., & House, I., (1992). Chemitry of Gold Extraction, Ellis Horwood Ltd Publication.

17. McDonald, W.R., Johnson, J.L., & Sandberg, R.G., (1990). Treatment of Alaskan Refractory Gold Ores, Engineering & Mining Jornual, pp. 48-53.

18. McGuire, J., & Schulz, R., (1991). Treatment of Gold Mine Waste Containing Cyanide, Fate of Cyanide in the Environment Near Mine Tailings, Australia Mineral Industries Research Association Limited (AMIRA), P227, Canada.

19. McLeod, H.N.,Lightholl, P.C., & Broughton, L, (1989). Control of Groundwater Impacts from Cyanide Leach Tailings Ponds, Proceeding of Gold Mining Effluent Treatment Seminar Compte-Rendu, pp186-198, Ontario, Canada

20. Smith, A., & Mudder, T., (1995). Alkaline Chlorination, Mining Environmental Management,. pp 12

21. Norcross, R., & Steiner, N., (1995). Degussa's Peroxide Process, Mining Environmental Management pp7-8.

22. Önal, G., Yüce, A.E., & Karahan, S., (1995). Türkiye'de Altın Madenciliği Yurt Madenciliğini Geliştirme Vakfı. Ankara

23. Robbins, G., & Devuyst, E. (1995). Inco's SO_2/Air Process, Mining Environmental Management, pp7-8.

24. Scott, J.S., (1989). An Overwiew of Gold Mill Effluent Treatment, Proceeding of Gold Mining Effluent Treatment Seminar Compte-Rendu, pp1-22, Ontario, Canada.

25. Sparrow, G.J.,& Woodcock,J.T.,(1988). Cyanide Concentrations, Degradation and Destruction in Mineral Processing Plants and Effluents, Commonwell Scientific and Industrial Research Organization (CSIRO). MPC/M-035.

26. Staunton, W., (1991). Fate of Cyanide in the Environment, Fate of Cyanide in the Environment Near Mine Tailings, Australia Mineral Industries Research Association Limited (AMIRA), P227, Canada.

27. Stewart, A.L., (1984). Gold Processing Today, International Mining, pp21-28.

28. TMMOB Maden Mhendisleri Odası, (1997). Dünyada Altın Madenciliği, Madencilik Bülteni, n53, pp-3-9.

29. Tükel, Ç., (1996). Determination of Certain Parameters in Cyanide Leaching of Ovacık Gold Ore, D.E.U. Eng. Faculty, Master's Tesis

30. Wall, N.C., Hornby, J.C., & Sethi, J.K., (1987). Gold Benefication, Mining Magazine, 156. 393-399.