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## **Cyan-ara Final Presentation**

## **Cyanide Treatment Using Pure SO**<sub>2</sub>

#### **Group P1**

Kiavash Bakrani, Satvik Chandar, Joshua Donaldson, Vishnu Jayaprakash, Alex Lee, Jaideep Mullick, Vitorio Sambatti, Adam Wiebe

Introduction

**Process Overview** 

Safety

**Environmental Analysis** 

**Economic Analysis** 

## Introduction

Scope, Goals and Benefits, Market



### **The Solution**

#### Cyanide Destruction

Ensure destruction to < 1 ppm cyanide [3]



Recover Free Cyanide to re-use in leaching process, recover metal in leach solution.

Cyanide

Recovery

#### Cyan-ara

- 1. Cyanide treatment using combined process utilizing pure Sulphur Dioxide
- Production and Sale of Sulphur Dioxide and Recovery By-Products

#### **Goals and Benefits**



**Reduce** social, economical and environmental impacts caused by untreated tailings



Reduce overall plant size leading to lower capital costs and operational costs



**Recycle** cyanide from leach solution to reduce costs of purchasing new cyanide

# Treatment Capacity 730,000 m<sup>3</sup>/year



#### Location: Sonora, Mexico

7

## **Process Overview**



#### **Recovery Section**



10

#### **Destruction Section**



### **General Reaction Schemes**

Leach Component	Processing Agent	Processing Section	Removal Reaction
Metal/Cyanide Complexes	Sulphide	Recovery	$2Cu(CN)_3^{2-} + HS^- + 5H^+ \rightarrow Cu_2S + 6HCN$
Metal/Cyanide Complexes	Sulphuric Acid	Recovery	$Zn(CN)_4^{2-} + SO_4^{2-} + 4H^+ \rightarrow ZnSO_4 + 4HCN$
Metal/Cyanide Complexes	Sulphur Dioxide/ Cu <sup>2+</sup> Catalyst	Destruction	$Ni(CN)_4^{2-} + 4SO_2 + 4O_2 + 4H_2O \rightarrow 4OCN^- + 4H_2SO_4 + Ni^{2+}$
Cyanate (OCN <sup>-</sup> )	Sulphuric Acid	Destruction	$OCN^- + H^+ + 2H_2O \rightarrow HCO_3^- + NH_4^+$
Strong Complexed Cyanide (Fe <sup>2+</sup> and Co <sup>3+</sup> )	Sulphur Dioxide	Destruction	$2Fe(CN)_{6}^{3-} + SO_{2} + 2H_{2}O \rightarrow 2Fe(CN)_{6}^{4-} + 4H_{2}SO_{4}$ $2Cu^{2+} + 2Fe(CN)_{6}^{4-} \rightarrow Cu_{2}Fe(CN)_{6 (s)}$

[2] [4]



#### P&ID, Control Narrative, HAZOP,

Plant Layout, Cause & Effect Matrix

#### P&ID A-01-300



#### **Floor Layout**



### HAZOP: Oxy-Furnace

Node	Deviations	Risk Rating
Inlets and outlets of the Oxy-Furnace	Total of 11 deviations in the defined node	Risk Ratings of 2, 3 and 4 are determined in this node:
This Node is used to show the main control scheme of the most dangerous unit of the plant	Range of mechanical, pressure, temperature, control and maintenance problems are discussed	<ul> <li>Two 2's</li> <li>Seven 3's</li> <li>Two 4's</li> </ul>

## **Example of a Major HAZOP Deviation**

Deviation	Consequence	Cause	Safeguard	RR
1.1 Temperature Runaway	Damage to refractory. Damage to piping.	1.1.1.1 Insufficient sulphur dioxide recycle flow rate due to valve failure.	19 Interlock to stop fuel injection and flush system with pure oxygen	
	Explosion risk. Pressure buildup.	1.1.1.2 Insufficient sulphur dioxide recycle flow rate due to compressor failure.	19 Interlock to stop fuel injection and flush system with pure oxygen	
		1.1.1.3 Increase in sulphur dioxide production	20 TIC 301 controller to increase/decrease how much recycle sulphur dioxide is fed into Furnace F-301.	4
		1.1.1.4 Deviation from target fuel to	1 FIC 301 Ratio Controller	
			2 Sufficient maintenance	
			3 Oxygen Inlet Flow interlock	

## **Major Control Loops**

#### Oxy-Sulphur Furnace Temperature

- Recycle cooled sulphur dioxide to furnace to control temperature
- Ensure temperature does not exceed 1500 degrees Celsius

#### **Feed Ratios**

- Ensure 3% excess oxygen is maintained in furnace
- Interlock sulphur flow in case temperature reaches High-High level

#### Liquid Level in Waste Heat Boiler

- Ensure sufficient water is supplied to cool gas from Oxy-Sulphur furnace
- Ensure water level is not too high to prevent overflow

### **Cause and Effect Matrix**

			FV-301	FV-303	PV-302
			Sulphur Flow Control Valve	Temperature Recycle Flow Valve	Sulphur Dioxide Pressure Valve
Tag Number	P&ID	Description			
F-301	A-01-300	High High Temperature in Furnace	I	I	I

#### Start-up / Shut-down

#### Plant

- Addresses a general Start-up and Shut-down for the entire plant
- Every part of the plant still needs a detailed plan

#### P&ID

- Addresses Start-up and Shut-down in detail for PFD-300
- Main concern is pre-heating of Oxy-Sulphur furnace

## Environmental Analysis

### **Air Emissions**



Main Gas Emissions

HCN and SOx gas generation

Pollutant	Expected Pollutant Generation	Emission Limit
HCN	1 -11 ppm	4.7 ppm [5]
SO <sub>2</sub>	Negligible	0.7 ppm [6]

## **Liquid Permitting**

Main Concerns - Cyanide (all forms), Ammonia/Ammonium, Copper (and other metals)

Tailings Ponds are not regulated but any discharge to the natural environment has federally imposed limits.

Effluent requires further processing in conventional treatment units for non-cyanide species.

Substance	Expected Discharge to Pond (mg/L)	Tailings Pond Limit (mg/L)	Environmental Limit (mg/L)
Cyanide	31.96	50 [3]	1 [7]
NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	660	-	24.3 - 1450* [8]
Copper	38.30	-	0.3 [7]

\*Discharge limit dependent on effluent pH. A range of 6 - 8 was considered.

### **Solid Storage and Disposal**



Solids for the process will be transported in a truck and stored in closed, dry containers



Proper handling and disposal of solids such as sodium hydrosulphide, sulphur and the copper catalyst needs to be maintained throughout the operation



## \$10.6 million USD

Capital Cost investment required for the project

## **Economic Summary**

#### **Operating Expenses**

Raw Materials Cost (\$/yr)	1,700,000
Total Operating Labor and Maintenance Cost (\$/yr)	910,000
Total Utilities Cost (\$/yr)	280,000
Plant Overhead (\$/yr)	460,000
General and Administrative Costs (\$/yr)	480,000
Total Operating Cost (\$/yr)	3,830,000

#### Sale Streams

Copper Sulphide (\$/yr)	1,200,000
Sulphur Dioxide (\$/yr)	1,100,000
Recycled Cyanide (\$/yr)	1,100,000
Total Products Sales (\$/yr)	3,400,000

## Comparison

- Configuration 1 performs INCO process in Tanks
- Configuration 2 performs INCO in tailing ponds
- Costs in Table do not include
   Operator and Maintenance Costs,
   Plant Overhead, or G/A costs

#### **Our Process vs other Composite Processes [9]**

	Cyanisorb and INCO Process Configuration 1* (2.4 TPD Cyanide)	Cyanisorb and INCO Process Configuration 2* (2.4 TPD Cyanide)	Cyan-ara Process (2.6 TPD Cyanide)
Capital Cost (\$)	14,000,000	12,500,000	10,600,000
Net Cost (\$/yr)	-1,400,000	-1,000,000	+1,400,000

#### \*Prices inflated from 2004 to 2020 prices

### Conclusion



Project is viable and compares well to other



Attractive Economics for leach solutions above 200 mg/L



Future work and challenges More detailed engineering and economic analysis needed to bring costs down

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## Appendix A - PFDs





S-301	E-301	E-302	P-301	F-301	H-301	C-301
Screw Conveyor	Sulphur Melter	Liquid Sulphur	Centrifugal Pump	Oxy-Sulphur	Waste Heat Boiler	Compressor



T-401	R-401	R-402	P-401	P-402	P-403
Water Quench	Cyanide Reactor	Cyanate	Centrifugal Pump	Centrifugal Pump	Centrifugal Pump
Tower		Neutralizer			



## Appendix B - Further Chemistry Details

## **Cyanide Metal Complexes**

- Cyanide is a small and highly basic ligand, so it readily forms coordination complexes with metals.
- Coinage metals (Cu<sup>1+</sup>, Au<sup>1+</sup>, Ag<sup>1+</sup>) form stable dicyanometallates.
- Forms strongly bonded octahedral complexes with many stable metals (Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ti<sup>3+</sup>, Co<sup>3+</sup>)
- Also forms weaker tetrahedral complexes with d<sup>8</sup> metals (Ni<sup>2+</sup>, Pb<sup>2+</sup>). [10]



Strongly Complex Fe(III) Cyanometallate





Prussian Blue: A Cyanometallate Derivative[11]



## Metal Sulphates and Sulphides [12]

- Most transition metals freely form compounds with sulphate and sulphide groups. e.g. CdS,  $Cu_2S$ ,  $FeS_2$ ,  $ZnSO_4$ ,  $PbSO_4$
- All transition metal sulphides are insoluble in water, so sulphidisation is a good option for removing metal ions form solution.
- > Only lead and mercury for insoluble sulphates, so any metal sulphate formed is unrecoverable.
- ➤ Based on electronegativity ionic bond strength goes Zn>Cd>Fe>Co>Cu>Ni.



Cu<sub>2</sub>S Chalcocite-A Very Common Copper Sulphide

## Full Reaction Description For Non Trace Metals [2][4]

Leach Component	Processing	Removal Reaction	Value Added
Copper (Cu⁺)	Recovery	$2Cu(CN)_3^{2-} + HS^- + 5H^+ \rightarrow Cu_2S + 6HCN$	High
Zinc (Zn <sup>2+</sup> )	Recovery	$Zn(CN)_4^{2-} + 2H_2SO_4 \rightarrow ZnSO_4 + 4HCN$	Moderate
Nickel (Ni <sup>2+</sup> )	Recovery	$Ni(CN)_4^{2-} + H_2SO_4 \rightarrow NiSO_4 + 4HCN$	Moderate
Cobalt (Co <sup>2+/3+</sup> )	Recovery	$Co(CN)_4^{2-} + H_2SO_4 \rightarrow CoSO_4 + 4HCN$	Moderate
Cadmium (Cd <sup>2+</sup> )	Recovery	$Cd(CN)_4^{2-} + H_2SO_4 \rightarrow CdSO_4 + 4HCN$	Minimal
Thiocyanate (SCN <sup>-</sup> )	Destruction (10-20%)	$SCN^- + 4SO_2 + 4O_2 + 5H_2O \rightarrow H_2SO_4 + OCN^-$	Very Minimal
Strong Complexed Cyanide (Fe <sup>2+</sup> and Co <sup>3+</sup> )	Destruction	$2Fe(CN)_{6}^{3-} + SO_{2} + 2H_{2}O \rightarrow 2Fe(CN)_{6}^{4-} + 4$ $H_{2}SO_{4}$ $2M^{2+} + 2Fe(CN)_{6}^{4-} \rightarrow M_{2}Fe(CN)_{6 (s)}$	None
Cyanate (OCN <sup>-</sup> )	Destruction	$OCN^- + H^+ + 2H_2O \rightarrow HCO_3^- + NH_4^+$	None

42

#### **General Reaction Schemes**

Leach Component	Processing Agent	Processing Section	Removal Reaction
Metal/Cyanide Complexes	Sulphide	Recovery	$M(CN)_{n}^{(n-m)-} + (m/2)^{*}HS^{-} + (n-m/2)^{*}H^{+} \rightarrow MS_{m/2}^{-} + n^{*}HCN$
Metal/Cyanide Complexes	Sulphuric Acid	Recovery/ Destruction	$M(CN)_{n}^{(n-m)-} + (m/2)*SO_{4}^{2-} + n*H^{+} \rightarrow M(SO_{4})_{m/2} + n*HCN$
Metal/Cyanide Complexes	Sulphur Dioxide/ Cu <sup>2+</sup> Catalyst	Recovery	$\begin{array}{l} M(CN)_{n}^{(n-m)^{-}}+n^{*}SO_{2}+n^{*}O_{2}+n^{*}H_{2}O{\rightarrow}n^{*}OCN^{-}+\\ n^{*}H_{2}SO_{4}+M^{m^{+}} \end{array}$
Thiocyanate (SCN)	Sulphur Dioxide	Destruction (10-20%)	$SCN^- + 4SO_2 + 4O_2 + 5H_2O \rightarrow H_2SO_4 + OCN^-$
Cyanate (OCN)	Sulphuric Acid	Recovery/ Destruction	$OCN^- + H^+ + 2H_2O \rightarrow HCO_3^- + NH_4^+$
Strong Complexed Cyanide (Fe <sup>2+</sup> and Co <sup>3+</sup> )	Sulphur Dioxide	Destruction	$2Fe(CN)_{6}^{3-} + SO_{2} + 2H_{2}O \rightarrow 2Fe(CN)_{6}^{4-} + 4H_{2}SO_{4}$ $2M^{2+} + 2Fe(CN)_{6}^{4-} \rightarrow M_{2}Fe(CN)_{6(s)}$

## Appendix C - Startup and Shutdown

#### Start-up / Shut-down - General Procedure for Plant

#### Start-up Procedure



- Step 1 Fill R-101, TH-101, R-201, TH-201, R-301, R-302 with water and turn on impellers
- Step 2 Turn on P-101/102/201/202/401/403 and continuously circulate water
- Step 3 Start NaOH feed to T-101
- Step 4 Begin feeding utilities: Steam to E-301/302, BFW to H-301. Allow temperature to stabilize.
- Step 5 Feed cold water to T-401 and start P-402, slowly opening the control valve to maintain 1m of liquid in T-401.
- Step 6 Start oxygen feed and pressurize F-301 and H-301 to 10 bar.
- Step 7 Turn on C-301 and begin circulating gas
- Step 8 Pre-heat F-301 to 300 C using built in heater.
- Step 9 Start sulphur feed to E-301 and E-302. Allow E-302 to reach level setpoint.
- Step 10 Start P-301. Ramp P-301 slowly to prevent spikes in furnace temperature.
- Step 11 Start NaHS feed to R-101; catalyst, oxygen, and lime feed to R-401; acid feed to R-402.
- Step 12 Start acid and high Cu leech feed to R-101.

#### **Shut-down Procedure**



- Step 1
   Stop acid and high Cu leech feeds to R-101 and replace with clean water feed.

   Allow 1 hour to treat and purge residual leech solution.
- Step 2 Stop NaHS feed to R-101; catalyst, oxygen, and lime feed to R-401; acid feed to R-402.
- Step 3 Close valves between T-401 to R-401, diverting all SO, to storage.
- Step 4 Ramp down P-301 and sulfur feed to E-301/302. Reduce sulfur to furnace slowly to prevent drops in furnace temperature.
- Step 5 Shutdown C-301.
- Step 6 Stop oxygen feed.
- Step 7 Shutdown P-402.
- Step 8 Stop utilities: Steam to E-301/302, BFW to H-301, CW to T-401.
- Step 9 Shutdown P-101/102/201/202/401/403.
- Step 10 Drain water from vessels to leeching ponds
- Step 11 Stop NaOH feed to T-101

#### Start-up / Shut-down - Detailed Procedure for P&ID

#### Start-up Procedure



#### Start-up

- Step 1 Start natural gas and air flow to preheat oxygen line.
- Step 2
   Start Oxygen flow to the furnace by closing valve PV-302 and opening valves FV-302 and FV-303. Allow F-301 and H-301 to pressure up to 10 bar. Use valve PV-302 to maintain a pressure of 10 bar in the system.

Maintain preheat sequence. Read temperature from TT-301. If the temperature of the furnace is below 300 °C, open PV-302 and FV-302. When the temperature setpoint is reached close FV-302 and PV-302. Continue sequence until system is ready to operate.

- Step 3 Start steam flow to E-301/E-302 by opening valves FV-304 and FV-305. Ensure valve PV-304 is closed and STM-315 is unblocked. Allow the steam system to pressurize to setpoint.
- Step 4 Open valve LV-302 to allow boiler feed water to flow into H-301. Ensure valve PV-301 is closed to build up pressure on the steam side.
- Step 5 Start M-301 to action S-301. When level in E-301 reaches 40%, start agitator.
- Step 6 Allow Sulphur to overflow from E-301 into E-302. When level in E-302 reaches 40%, start agitator.
- Step 7 Start M-302 to action C-301 and slowly open valves PV-302, FV-302, and FV-303. Ensure 10 bar is maintained in the system.
- Step 8
   Start P-301 and slowly open valve FV-301 while choking fuel flow to preheat exchanger. Switch

   FFIC-302 and TIC-301 to automatic and allow steady-state operation to take place.
- Step 9 Set PIC-304 to automatic and block-in STM-315. Ensure all controllers are in AUTO.

#### **Shut-down Procedure**



#### Shutdown

Step 1

- Set valves FV-301, FV-302, and FV-303 to manual.
- Step 2
   Reduce feed to F-301 by incrementally closing FV-301. Monitor TT-301 ensuring the temperature does not drop by more than 200 °C / 15 minutes.
- Step 3 Once TT-301 reads 400 °C, shutdown S-301 by stopping M-301.
- Step 4 Allow E-301 and E-302 to reach LL Level and trip P-301.
- Step 5 Close valve FV-301.
- Step 6 Once TT-301 reads 250 C, close LV-302 to stop utilities.
- Step 7 Open PV-301, FV-303 to flush all steam to steam header.
- Step 8 Allow F-301 to cool below 60 °C.
- Step 9 Shutdown C-301 by stopping M-302.
- Step 10 Close valves FV-302 and FV-303.
- Step 11 Allow the system to slowly depressurize by manipulating PV-302
- Step 12 Drain boiler water to water header.
- Step 13 If required for maintenance, drain E-301 and E-302 by using a Vacuum Truck.

## Appendix D - Further Economic Analysis

#### **Project After Tax Cash Flow**



### **Sources of Capital**

- ★ Average cyanide concentration treated - 500 mg/L
- ★ Our Operating cost \$3.8 million / yr

Cyanide Concentration (mg/L)	Gold Leached (kg)	Profit (\$50/g of gold)
500	3650	\$182,500,000
600	4380	\$219,000,000
700	5110	\$255,500,000

### Area Equipment Cost Breakdown

Area	Function	Total Direct Cost (\$ USD)
100	Copper Sulphide Recovery	827,500.00
200	Cyanide Recovery	738,600.00
300	Sulphur Dioxide Production	984,300.00
400	Cyanide Destruction	855,500.00

## Area-100 Equipment Costs

Equipment Tag	Equipment Type	Total Direct Cost (\$ USD)
TH-101	Thickener	157,000.00
R-101	Agitated Tank, Enclosed	367,900.00
P-103	Centrifugal Pump	52,200.00
P-102	Centrifugal Pump	54,400.00
P-101	Centrifugal Pump	31,300.00
FL-101	Rotary Drum Filter	164,700.00

## **Area-200 Equipment Costs**

Equipment Tag	Equipment Type	Total Direct Cost (\$ USD)
TH-201	Thickener	157,000.00
P-201	Centrifugal Pump	27,900.00
FL-201	Rotary Drum Filter	164,700.00
P-202	Centrifugal Pump	47,700.00
R-201	Agitated Tank, Enclosed	341,300.00

## Area-300 Equipment Costs

Equipment Tag	Equipment Type	Total Direct Cost (\$ USD)
H-301	Waste Heat Boiler	360,200.00
E-301	Agitated Reactor, Jacketed	328,900.00
P-301	Centrifugal Pump	87,000.00
F-301	Refractory Lined Pressure Vessel	208,200.00
R-201	Agitated Tank, Enclosed	341,300.00

## Area-400 Equipment Costs

Equipment Tag	Equipment Type	Total Direct Cost (\$ USD)
R-402	Agitated Reactor, Enclosed	342,800.00
R-401	Agitated Reactor, Enclosed	193,700.00
T-401	Quench Tower	220,400.00
P-401	Centrifugal Pump	27,200.00
P-402	Centrifugal Pump	35,700.00
P-403	Centrifugal Pump	35,700.00

## Comparison

 ★ Average cyanide concentration treated - 500 mg/L

 ★ Our Operating cost - \$3.8 million / yr

#### Effect of CN concentration on operating costs

	Cyanide Concentration (mg/L)			
	100	150	200	400
Process	\$MM/year*			
INCO	1.5	2.25	2.74	5.48
Cyanisorb	1.3	0.85	0.41	1.37
Combined	2.8	3.1	3.15	6.85

Economic Analysis Parameters

\_\_\_\_\_

Number of Weeks per Period	Weeks/period	52
Number of Periods for Analysis	Period	14
Duration of EPC Phase	Period	0.67
Duration of EPC Phase and Startup	Period	1.06
Working Capital Percentage	Percent/period	5
Operating Charges	Percent/period	25
Plant Overhead	Percent/period	50
Desired Rate of Return/Interest Rate	Percent/period	6.5
ROR Annuity Factor		15.38
Tax Rate	Percent/period	40
ROR Interest Factor		1.06
Economic Life of Project	Period	14
Salvage Value (Percent of Initial Capital Cost)	Percent	20
Depreciation Method		Straight Line
Project Capital Escalation	Percent/period	5
Products Escalation	Percent/period	5
Raw Material Escalation	Percent/period	3.5
Operating and Maintenance Labor Escalation	Percent/period	3
Utilities Escalation	Percent/period	3
Desired Return on Project for Sales Forecasting	Percent/Period	10.5
General and Administrative Evnenses		0
General and Administrative Expenses	Percent/Period	ŏ

## Appendix E - Project and Technology Development

## **Technology Development**

#### **Gold Cyanidation**

- Many easy access deposits were quickly depleted
- Extraction from trace gold ores required
- Cyanide complexation developed in late 1800s

#### **Destruction and Recovery**

- Cyanide recovery creates a value added recycle stream
- Dependent on local mineralogy (ex. Not viable for iron rich areas)
- Destruction process guarantees cyanide removal

#### Pure SO<sub>2</sub> Reagent

- Downstream destruction of cyanide is a needed
- Many possible reagents: SO<sub>2</sub>, Caro's Acid,  $H_2O_2$ .
- SO<sub>2</sub> has lowest reagent cost.
- Pure SO<sub>2</sub> reduces capital and operating costs

#### **Gold Mining Decision Flowchart**

