

The Optimization, Design and Economics of Industrial NSC Oxidative Pressure Leaching Of Complex Sulfide Concentrates

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ABSTRACT

Nitrogen Species Catalyzed (NSC) pressure leaching of complex sulfide concentrates has been carried out. This entailed performance of bench scale test work on a representative composite sample to ascertain indicative recoveries and identify lead deportment in the residue particularly with regards to avoidance of formation of plumbojarosite and the production of lead sulfide. A major equipment list including materials of construction, equipment size and power requirements was also provided. Detailed block flow diagrams showing each unit process were provided along with basic testing mass balances. Finally, order of magnitude CAPEX and OPEX was ascertained to +/-30%. In summary, industrial NSC pressure leaching was effective in leaching silver, zinc, copper, nickel and cobalt well over 90 % to solution from the complex sulfide concentrates. The NSC treated concentrate composite residue sample was produced as lead oxide and lead sulfide in the DOE testing. In the subsequent locked cycle NSC work, this was optimized to produce only lead sulfide leached residue suitable for conventional smelting.

Date of Submission: 23, October, 2013



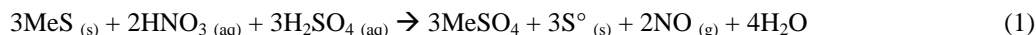
Date of Acceptance: 20, November, 2013

I. INTRODUCTION

The application and optimization of Nitrogen Species Catalyzed (NSC) pressure leach sulfide oxidation of complex sulfide concentrates with production of lead sulfide residue was studied. This entailed lab testing at the scoping and optimization level for partial NSC sulfide oxidation. This focused on optimization of NSC results, locked cycle testing of the optimized flowsheet along with a detailed order of magnitude capital and operating cost assessment for the application of NSC to complex sulfide concentrates.

II. NSC THEORETICAL CONSIDERATIONS

As a first step, the basics of nitrogen species catalyzed (i.e. NSC) hydrometallurgical pressure oxidation will be outlined. The commonly reported leach reaction of a sulfide mineral with nitric acid in conjunction with sulfuric acid is shown below.



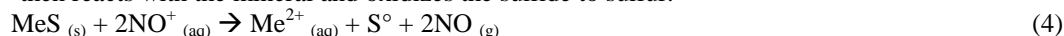
However, it has been postulated and confirmed that the actual reaction species is NO^+ and not NO_3^- (Anderson, 1992, Anderson, 1996, Baldwin, 1996, Gok, 2009). The addition of or presence of NO_2^- instead of NO_3^- accelerates the formation of NO^+ . As shown in Table 1, the NO^+/NO couple is capable of an extremely high redox potential (Peters, 1992). So, NO^+ is readily formed from nitrous rather than nitric acid. For example, a convenient source of nitrous acid can be sodium nitrite (Anderson, 1992, Anderson, 1996). When it is added to an acidic solution, nitrous acid is readily formed.



Nitrous acid further reacts to form NO^+ .



The NO^+ then reacts with the mineral and oxidizes the sulfide to sulfur.



Of course, at higher temperatures and/or nitrogen species concentrations the sulfide can be fully oxidized to sulfate.

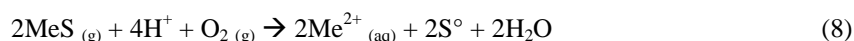
Table 1. Relative Potentials of Hydrometallurgical Oxidizers.

Oxidant	Redox Equation	E° _h (pH = 0, H ₂ ref.)
Fe ³⁺	Fe ³⁺ + e ⁻ → Fe ²⁺	0.770 V
HNO ₃	NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO + 2H ₂ O	0.957 V
HNO ₂	NO ₂ ⁻ + 2H ⁺ + e ⁻ → NO + H ₂ O	1.202 V
O ₂ (g)	O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	1.230 V
Cl ₂ (g)	Cl ₂ (g) + 2e ⁻ → 2Cl ⁻	1.358 V
NO ⁺	NO ⁺ + e ⁻ → NO	1.450 V

As can be seen, nitric oxide gas, NO, is produced from the oxidation of sulfides. As this gas has a limited solubility in aqueous solutions, it tends to transfer out of solution. In the pressure leach system, a closed vessel with an oxygen overpressure is used. The nitric oxide gas emanating from the leach slurry accumulates in the headspace of the reactor where it reacts with the supplied oxygen to form nitrogen dioxide gas. The NO is then regenerated to NO⁺. Overall this can be viewed as:



Since the nitrogen species is continuously regenerated, its role in the overall reaction as the actual oxidizer is not obvious. The net overall reaction has the sulfide mineral reacting with the acid solution and oxygen to solubilize the metal value into the sulfate solution and form some elemental sulfur.



Of course, at higher temperatures and/or nitrous acid concentrations the sulfide would be fully oxidized to sulfate. Overall, the nitrogen intermediates serve as an expedient means to transport oxygen to the surface of the solid particle and allow the resulting reaction to take place at a heightened redox potential. This inherent asset of the unique novel NSC system eliminates the need for the use of high temperatures and high pressures, which lead to higher costs in other pressure leach processes. For example, commonly available stainless steel can be used for the reactor vessel. And, complete oxidation of sulfide to sulfate can be achieved without the excessive conditions found in other pressure leach systems. Thus, the rapid kinetics of the system leads to smaller reactor volumes and higher unit throughputs. Finally, 99.9% of the nitrogen species utilized in the leach system report to the gas phase when the pressure vessel is flashed and they are readily destroyed and contained by commercially available scrubber systems. So, environmental impacts are minimized and the NSC leach plant solutions contain little or no nitrogen species. In summary, NSC was first used industrially from 1984 until 1995 on silver bearing copper concentrates. It has also been found to be applicable to and effective in the treatment of zinc, gold, lead, nickel, cobalt, copper PGM and molybdenum concentrates.

III. COMPLEX CONCENTRATE ANALYSIS

A complex concentrate comprised of mixed sulphides and precious metals was tested with NSC pressure oxidation. The goal was to dissolve and recover the Ag, Cu, Co, Zn while leaving an insoluble PbS residue suitable for conventional smelting. .

Some general concentrate mineralogy information is as follows:

Copper Chalcopyrite (CuFeS₂) observed visually, chalcocite may also be present, cobalt and nickel are associated with the copper minerals and also occur as fine grained intergrowths of siegenite (CoNi)₄S₃ in the copper minerals.

Lead Primarily as galena (PbS), cobalt nickel and silver are associated with the lead minerals with fine grained intergrowths as siegenite in the galena.

Cobalt Primarily occurring as siegenite, cobalt is intimately associated with nickel and is associated with and intergrown in both copper and lead minerals. It tends to be concentrated in the presence of Mn and diminishes as Zn increases.

Nickel Primarily occurring as siegenite, nickel is intimately associated with cobalt and is associated with and intergrown in both copper and lead minerals.

Silver Primarily associated with lead.

Zinc Present as sphalerite ((Zn,Fe)S), zinc is present in much of the orebody at low levels. Zinc tends to increase as Co content diminishes and increases to the west.

Iron Primarily present as pyrite (FeS₂), the orebody is generally pyrite deficient, particularly where high levels of galena are found. There is little evidence of cobalt associated with pyrite.

Carbon (as kerogen and/or graphite) is found throughout the orebody. It is higher in copper lenses (~6% C) and lower in lead lenses (~2% C). It slimes over particles unselectively during fine grinding and must be depressed during flotation.

Sulfur is primarily associated with copper, lead, iron, cobalt, nickel and zinc.

Two separate complex sulfide concentrates were analyzed and treated with NSC pressure leaching. The first was treated with baseline scoping testing using optimized conditions. The second was treated with Stat Ease DOE based optimization and locked cycle testing. These concentrate analysis were very similar and are summarized as follows in Tables 1 &2 and Figures 1 through 6.

Table 1. Complex Sample #1 Elemental and Size Analyses.

Pb, % Zn, % Co, % Cu, % Ni, % Ag g/T TS, % TC, %
 28.5 2.56 0.47 0.85 0.40 59.1 16.0 7.5

Size (µm)	Ind. Wt. (g)	Ind. Wt. %	Cum. Wt. % Pass
300	0	0.00	100.0
147	0.3	0.17	99.8
106	0.92	0.52	99.3
75	8	4.52	94.8
53	20.91	11.82	83.0
44.6	8.31	4.70	78.3
37.5	10.49	5.93	72.3
31.5	12.40	7.01	65.3
26.5	13.24	7.49	57.8
22.3	13.08	7.40	50.4
18.7	11.94	6.75	43.7
15.8	12.19	6.89	36.8
13.3	11.43	6.46	30.3
11.1	11.51	6.51	23.8
9.4	9.76	5.52	18.3
7.9	10.40	5.88	12.4
6.6	8.57	4.84	7.6
5.6	6.32	3.57	4.0
4.7	5.20	2.94	1.1
3.9	1.87	1.06	0.0

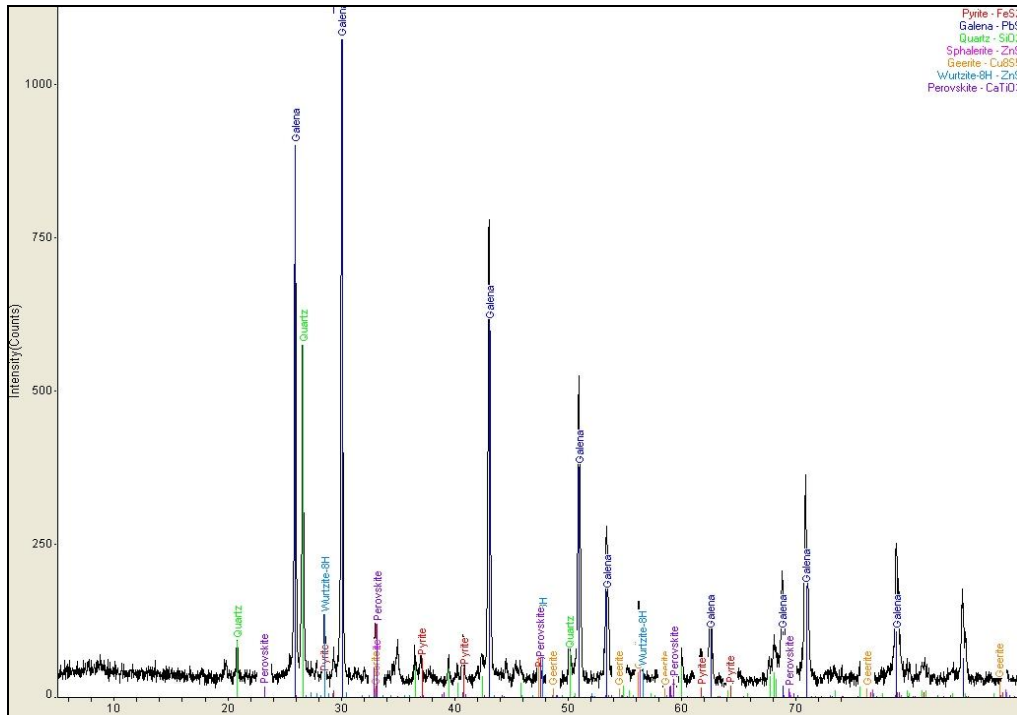


Figure 1. Complex Concentrate #1 XRD Pattern

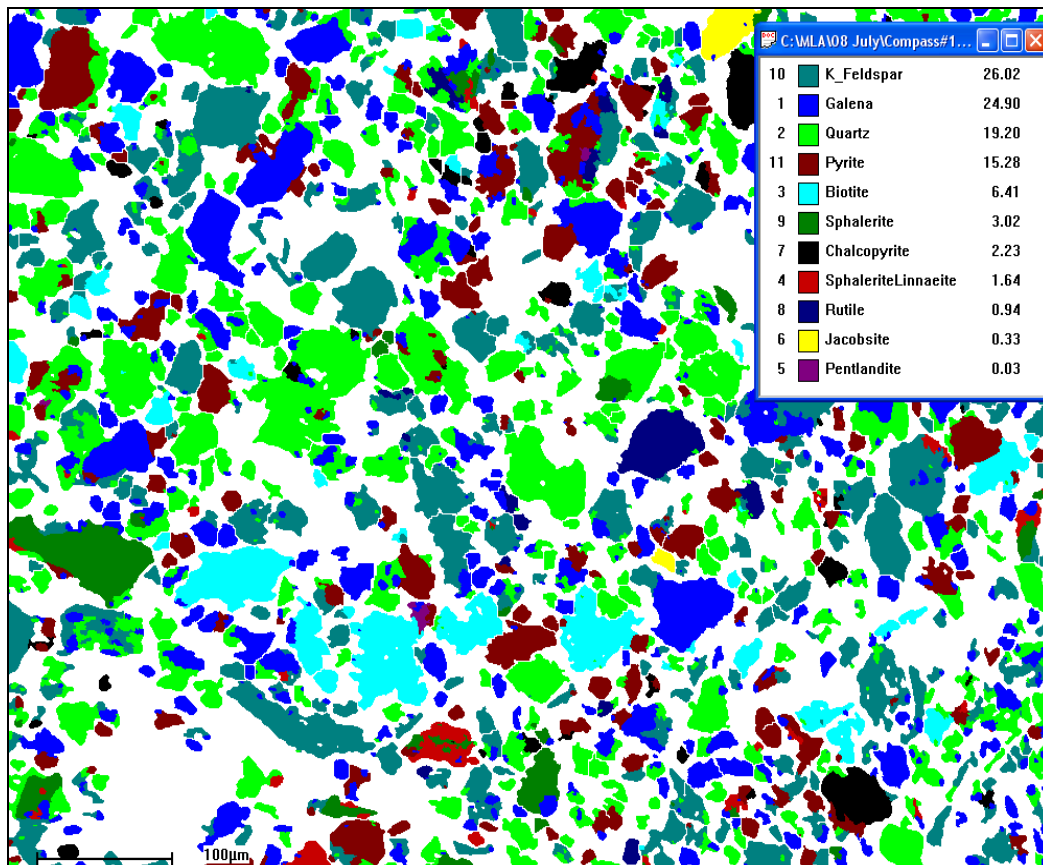


Figure 2. Complex Concentrate #1 MLA Phase Analysis.

Element	wt (%)
Al	2.07
Co	0.48
Cu	0.87
Fe	11.25
H	0.02
K	3.00
Mg	0.30
Mn	0.11
Ni	0.41
O	18.47
Pb	29.14
S	17.74
Si	12.86
Ti	0.66
Zn	2.63
Total	100.00

Figure 3. Complex Concentrate # 1 MLA Elemental Analysis.

Table 2. Complex Sample #2 Elemental and Size Analyses.

Pb, %	Zn, %	Co, %	Cu, %	Ni, %	Ag g/T	TS, %	TC, %
21.6	2.66	0.81	2.02	0.66	53.0	18.9	8.5

Size (μm)	Ind. Wt. (g)	Ind. Wt. %	Cum. Wt. % Pass
300	0	0.00	100.0
147	0.09	0.05	100.0
106	0.08	0.04	99.9
75	1.82	0.95	99.0
53	6.05	3.17	95.8
44.6	3.20	1.68	94.1
37.5	4.21	2.21	91.9
31.5	12.65	6.63	85.3
26.5	15.97	8.37	76.9
22.3	15.36	8.05	68.9
18.7	17.03	8.93	59.9
15.8	18.31	9.60	50.3
13.3	17.88	9.37	40.9
11.1	17.17	9.00	31.9
9.4	16.02	8.40	23.5
7.9	14.05	7.37	16.2
6.6	12.16	6.37	9.8
5.6	9.21	4.83	5.0
4.7	7.02	3.68	1.3
3.9	2.48	1.30	0.0

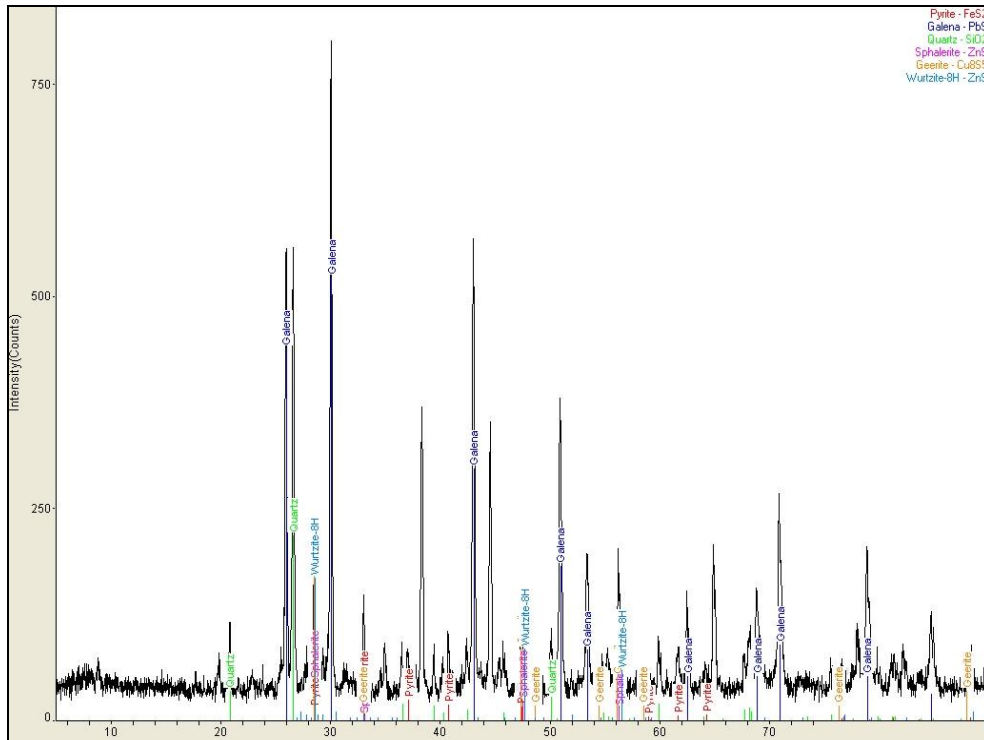


Figure 4. Complex Concentrate #2 XRD Analyses.

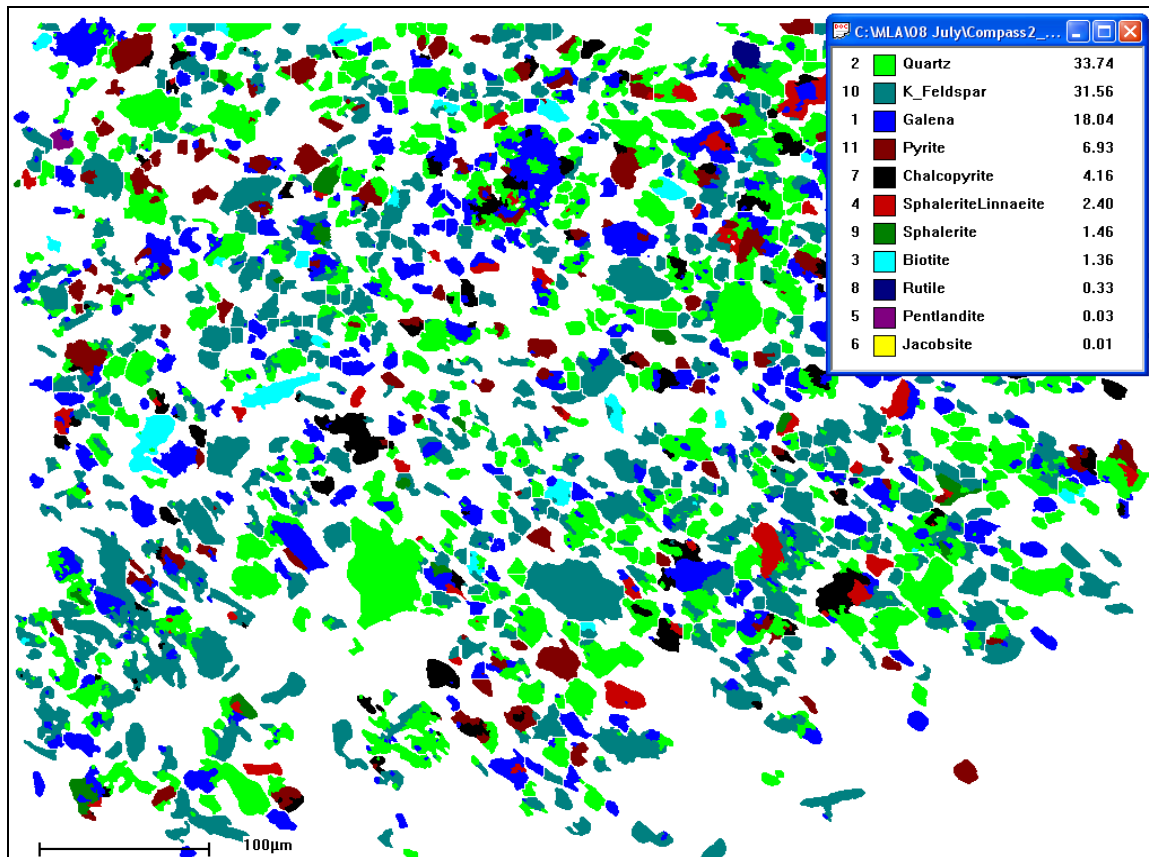


Figure 5. Complex Concentrate #2 MLA Phase Analysis.

Element	wt (%)
Al	2.43
Co	0.78
Cu	1.81
Fe	6.61
H	0.01
K	3.53
Mg	0.07
Mn	0.00
Ni	0.66
O	26.17
Pb	23.50
S	12.18
Si	20.10
Ti	0.25
Zn	1.89
Total	100.00

Figure 6. Complex Concentrate #2 MLA Elemental Analysis.

NSC DOE OPTIMIZATION TESTING.

For optimization, Stat-Ease Design Expert software was used. The 1/4 testing matrix shown in Table 3. was set up and the NSC tests were run on concentrate #2 according to this table and the conditions shown in Table 4.

Table 3. Stat Ease DOE NSC PARTIAL OXIDATION MATRIX.

	Std	Run	Grind	Time	Initial Acid	Max Temp	Leach Time
	1	1	0	Min	50 g/L	150 C	120 Min
	7	2	0	Min	200 g/L	130 C	60 Min
	5	3	0	Min	50 g/L	150 C	60 Min
	10	4	5	Min	125 g/L	140 C	90 Min
	3	5	0	Min	200 g/L	130 C	120 Min
	4	6	10	Min	200 g/L	150 C	60 Min
	6	7	10	Min	50 g/L	130 C	120 Min
	2	8	10	Min	50 g/L	130 C	60 Min
	8	9	10	Min	200 g/L	150 C	120 Min
	9	10	5	Min	125 g/L	140 C	90 Min

TABLE 4. NSC PARTIAL OXIDATION CONDITIONS

<p>Nitrogen Species Catalyzed <u>Partial Oxidation Leach Conditions.</u></p> <p>Grind Time = Table 3 Initial Free Sulfuric Acid = Table 3 Reactor Working Pressure = 620 kPag Slurry Solids Content = 100 g/L Maximum Temperature = Table 3 Total Time = Table 3 Nitrogen Species Concentration = 2.0 g/L</p>
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TABLE 5. NSC PRESSURE OXIDATION TESTING RESULTS

Std	Run	Grind Time	Initial Acid	Max Temp	Leach Time	Cu%	Co%	Zn%	Ag%	Ni, %
1	1	0 Min	50 g/L	150 C	120 Min	85.1	87.3	85.2	0.0	84.7
7	2	0 Min	200 g/L	130 C	60 Min	92.2	91.3	90.8	93.2	91.7
5	3	0 Min	50 g/L	150 C	60 Min	82.3	81.1	78.2	0.0	83.1
10	4	5 Min	125 g/L	140 C	90 Min	87.2	84.3	81.3	10.7	86.5
3	5	0 Min	200 g/L	130 C	120 Min	92.8	93.2	91.7	94.3	92.1
4	6	10 Min	200 g/L	150 C	60 Min	84.4	82.3	79.2	91.3	85.1
6	7	10 Min	50 g/L	130 C	120 Min	98.2	97.1	98.7	0.0	97.7
2	8	10 Min	50 g/L	130 C	60 Min	97.6	96.9	98.1	0.0	96.6
8	9	10 Min	200 g/L	150 C	120 Min	89.1	89.2	87.9	95.5	89.3
9	10	5 Min	125 g/L	140 C	90 Min	86.9	85.1	81.6	10.9	86.1

These results were then input into the Stat Ease Design Ease software, modeled and optimized. Table 6 illustrates the optimized NSC criteria and results. Table 7 illustrates the results of testing these optimized conditions on Complex concentrate #1 at 200 g/l slurry density. Figures 7 through 10 illustrate various MLA and XRD analysis on a composite sample of the leached NSC residue from the optimization testing.

TABLE 6. STAT EASE DOE MODEL OPTIMIZED NSC PARTIAL OXIDATION CONDITIONS WITH SILVER RECOVERY.

Best Conditions for the Considered Variables and Variable Range			
Factor	Name	Level	
A	Grind Time	10.00	
B	Acid	200.00	
C	Temp	130.00	
D	Leach	60.00	

Response	Prediction	95% CI low	95% CI high
Cu, %	97.3	94.80	99.83
Co, %	96.2	92.60	99.49
Zn, %	97.1	92.63	101.18
Ag, %	92.2	90.80	93.72
Ni, %	97.2	96.18	98.18

TABLE 7. STAT EASE DOE OPTIMIZED CONDITIONS APPLIED TO COMPLEX CONCENTRATE #1.

Nitrogen Species Catalyzed Partial Oxidation Leach Conditions.	
Grind Time	= 10 minutes
Initial Free Sulfuric Acid	= 200 g/L
Reactor Working Pressure	= 620 kPag
Slurry Solids Content	= 200 g/L
Maximum Temperature	= 130 C
Total Time	= 60 minutes
Nitrogen Species Concentration	= 2.0 g/L
Particle Size	= 80% passing 10 micron
Copper Recovery	= 98.5 %
Silver Recovery	= 92.4 %
Cobalt Recovery	= 95.4 %
Zinc Recovery	= 97.2 %
Nickel Recovery	= 96.7 %

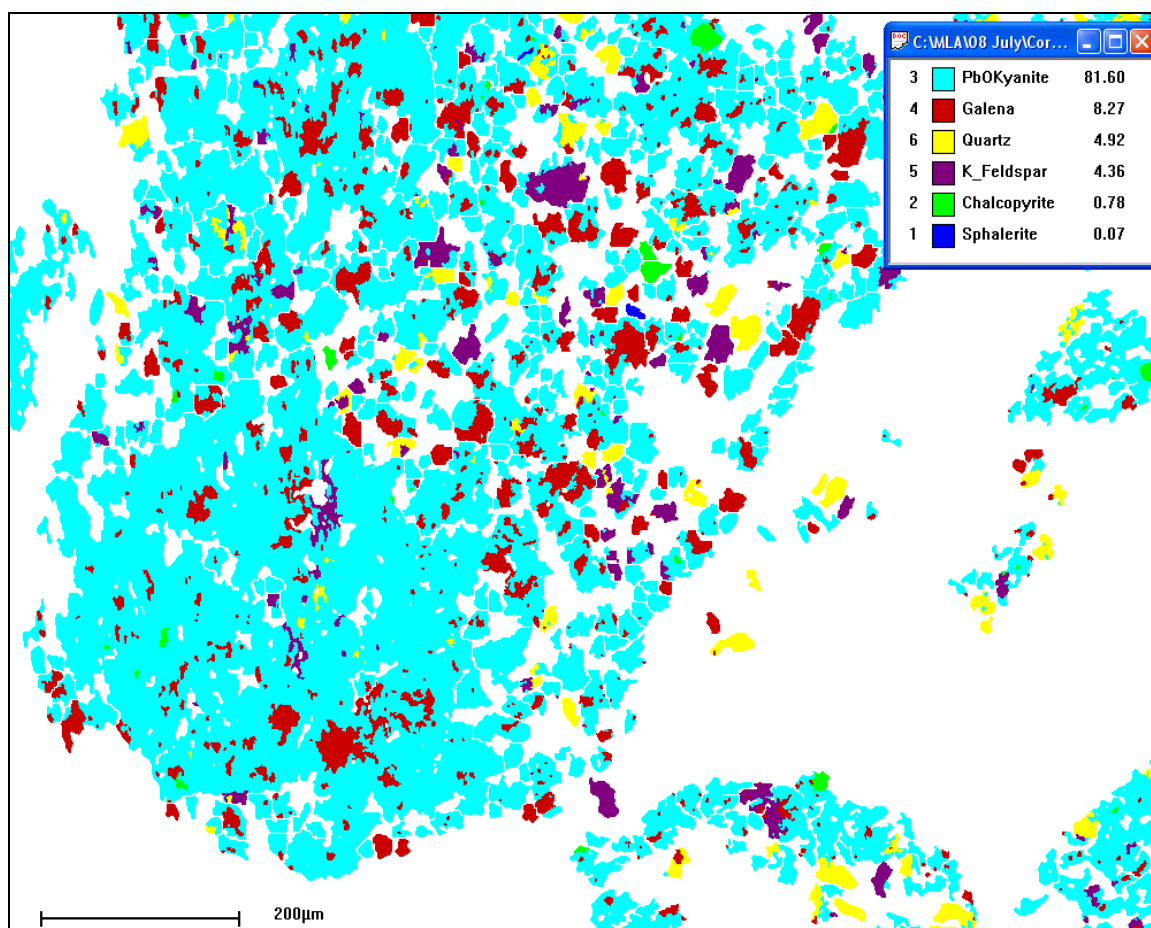


Figure 7. MLA Phase Analysis of NSC DOE Leach Testing Treated Residue Composite Sample.

Element	wt (%)
Al	17.29
Cu	0.27
Fe	0.24
K	0.38
O	24.78
Pb	34.76
S	2.23
Si	20.00
Zn	0.04
Total	100.00

Figure 8. MLA Elemental Analysis of NSC DOE Leach Testing Treated Residue Composite Sample.

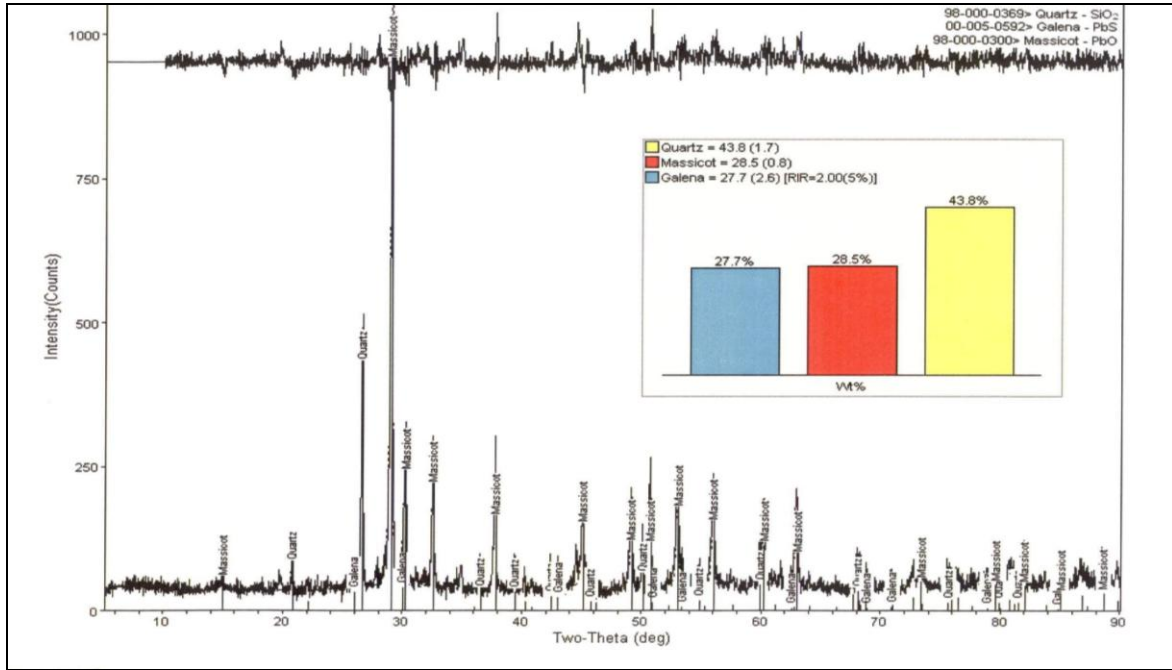


Figure 9. Semi Quantitative XRD Analysis of DOE NSC Leaching Treated Composite Sample.

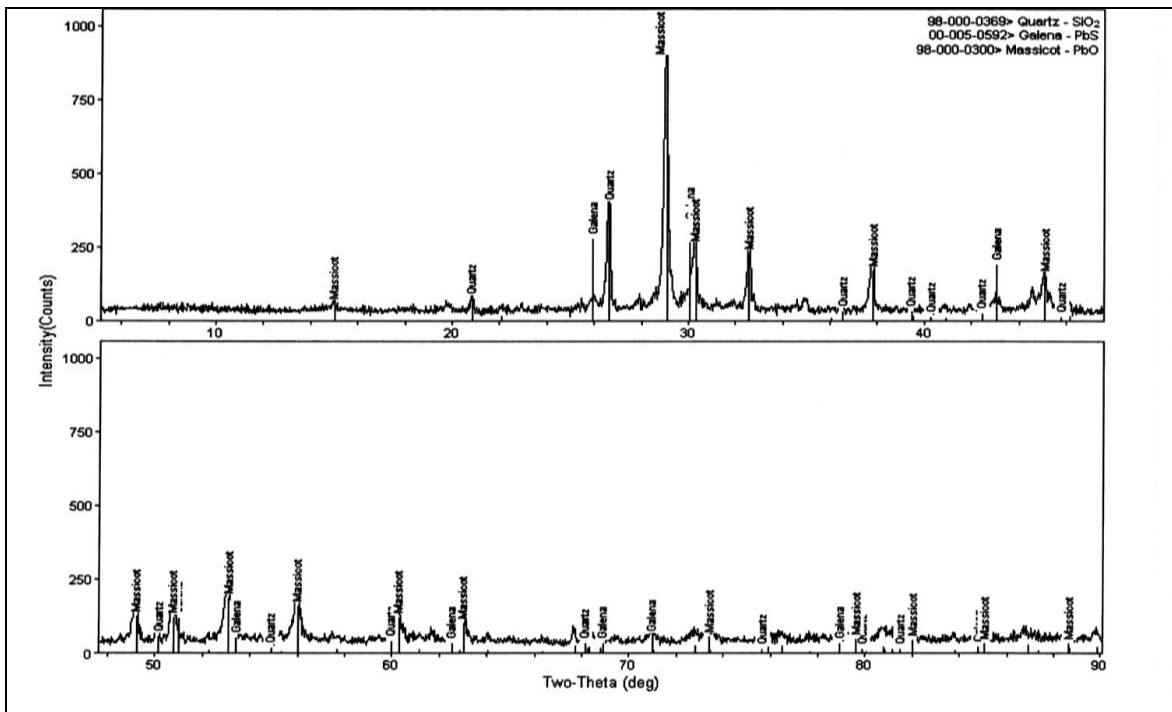


Figure 10. XRD Qualitative Phase Analysis of DOE NSC Leaching Treated Composite Sample.

**TABLE 8. STAT EASE OPTIMIZED LOCKED CYCLE
NSC PARTIAL OXIDATION FINAL RESULTS**

Nitrogen Species Catalyzed <u>Partial Oxidation Leach Conditions.</u>	
Locked Cycles =	7
Recycle Percentage =	25 %
Grind Time =	10 minutes
Initial Free Sulfuric Acid =	200 g/L
Reactor Working Pressure =	620 kPag
Slurry Solids Content =	100 g/L
Maximum Temperature =	130 C
Total Time =	60 minutes
Nitrogen Species Concentration =	2.0 g/L
Copper Average Recovery =	95.1 %
Silver Average Recovery =	96.2 %
Cobalt Average Recovery =	97.3 %
Zinc Average Recovery =	98.4 %
Nickel Average Recovery =	96.8 %

From the locked cycle testing and the NSC plant operating experience of personnel a general flowsheet was generated. The NSC process battery limits were concentrate regrind through to the flash system. This is illustrated in Figure 11..

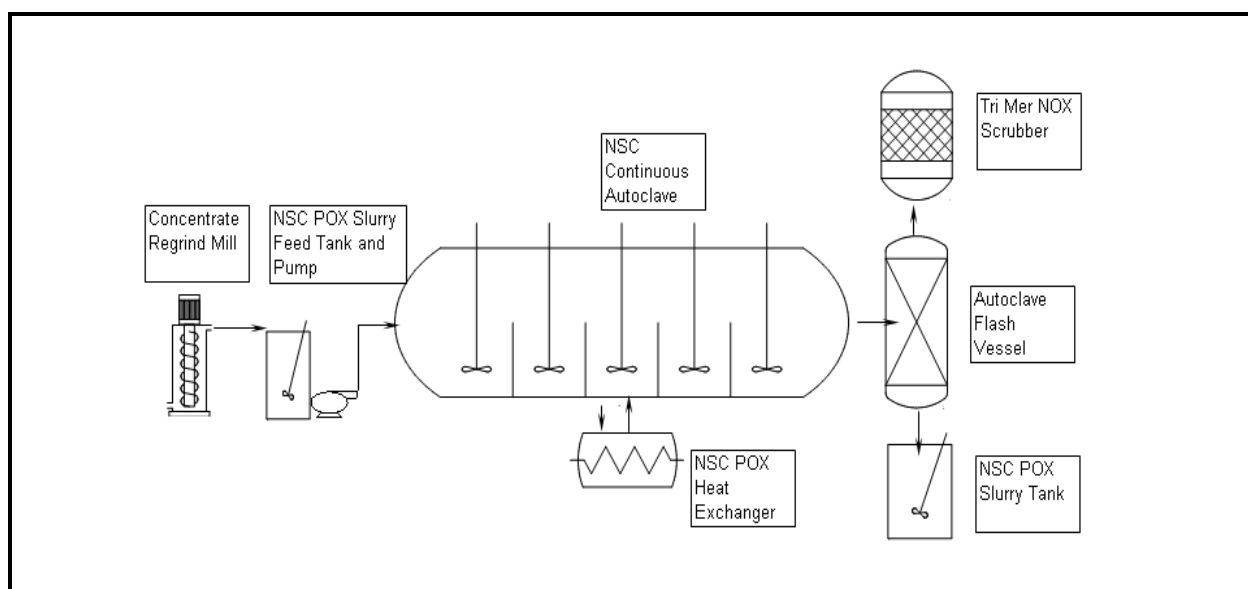


Figure 11. Proposed NSC POX Flowsheet.

ORDER OF MAGNITUDE CAPEX AND OPEX.

Based on the testing data and the NSC plant operating experience of personnel, CAPEX and OPEX estimates were generated. Again, the NSC process battery limits were concentrate regrind through to flash. Table 9 illustrates the concentrate annual tonnages and quality. Tables 10 and 11 illustrate the order of magnitude capital and operating cost estimates with silver recovery.

TABLE 9. COMPLEX CONCENTRATE ANNUAL PROJECTED QUANTITY AND QUALITY.

Tonnes Per Annum		841,000	
Assay	Pb	25.00	%
	Cu	2.8	%
	Co	0.74	%
	Ni	0.44	%
	Zn	1.41	%
	Ag	43.29	g/T
	Fe	6.71	%
	TS	12.83	%

TABLE 10. ORDER OF MAGNITUDE CAPITAL COST ESTIMATE.

Equipment Costs		\$5,250,000
Installation	43%	\$2,257,500
Piping & Instruments	20%	\$1,501,500
Engineering	25%	\$2,252,250
Sub Total		\$11,261,250
Contingency	30%	\$3,378,375
TOTAL CAPITAL COSTS USD:		\$14,639,625

TABLE 11. ORDER OF MAGNITUDE OPERATING COST ESTIMATE.

Regrinding of Feed		
	15 kWh/t	15
	\$ 0.1351/kWhr All In	\$ 0.12
	Annual Cost	\$ 1,705,438.00
Agitation and Pumping		
	400 kWh/tS	400
	0.1351/kWh	\$ 0.10
	Annual Cost	\$ 5,830,932.21
Oxygen		
	160 Kg/T	160
	O2 \$ 150.00/t	\$ 140.00
	Annual Cost	\$ 20,197,632.00
Maintenance		
	5 \$/t S	\$ 5.00
	Annual Cost	\$ 539,501.50
Labor		
	8 Operators	
	Annual Cost	\$ 800,000.00
Supplies		
	\$ 1.00 per T Con	\$ 1.00
	Annual Cost	\$ 841,000.00
Sulfuric Acid with Silver Recovery		
	100 Kg/tonne	100
	\$ 132/tonne	400
	Annual Cost	\$ 11,108,698.00

Nitrogen Species	
10 Kg/Tonne	10
\$ 1,050/T	\$ 1,050.00
Annual Cost	\$ 8,830,500.00
NOX Scrubbing	
\$ 0.50/tonne	\$ 0.50
Annual Cost	\$ 420,500.00
TOTAL ANNUAL COST USD	\$ 69,739,713.50
COST PER TONNE USD	\$ 82.92

IV. SUMMARY

NSC pressure leaching of complex sulfide concentrates was carried out. This entailed performance of bench scale test work on representative composite samples to ascertain indicative recoveries and identify lead deportment in the residue particularly with regards to the formation of plumbojarosite. A major equipment list including materials of construction, equipment size and power requirements was also included. Detailed block flow diagrams showing each unit process were provided along with basic testing mass balances. Finally, order of magnitude CAPEX and OPEX was ascertained to +/-30%. In summary, NSC pressure leaching was effective in leaching silver, zinc, copper, nickel and cobalt well over 90 % to solution from the complex sulfide concentrates. This was confirmed in optimized testing of another complex concentrate previously received. The NSC treated concentrate composite residue sample was produced as lead oxide and lead sulfide in the DOE testing. In the subsequent locked cycle NSC work, this was optimized to produce only the desired lead sulphide leached residue.

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