Sulphate Mineral Speciation by Sequential Extraction

for the proposed Veladero Mine, Argentina

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Veladero gold/silver project in Argentina with predominant mineralogy of waste rock:

- alunite ($KAl_3(SO_4)_2(OH)_6$)
- jarosite ($KFe_3(SO_4)_2(OH)_6$) and
- quartz
- only small quantities of pyrite.

Equations for jarosite & alunite acidity release are (D.Langmuir, 1995):

$KFe_3(SO_4)_2(OH)_6 + 3H_2O = K+ + 3Fe(OH)_3$ (ppt) $+ 2SO_4^{2-} + 3H^+$ equilibrium pH = 3.8

$KAl_3(SO_4)_2(OH)_6 = 3H_2O = K+ + 3Al(OH)_3$(ppt) $+ 2SO_4^{2-} + 3H^+$ equilibrium pH = 6.8

The objective of the study was to determine whether it would be possible to:

- Distinguish between alunite, jarosite and pyrite.
- Account for most of the total sulphate as to minimise sulphur reporting as insoluble sulphate.

There are two basic methods for determining sulphate-sulphur in waste rock material:

- Alkaline leaching consisting of either sodium carbonate or sodium hydroxide.
- Acid leaching using hydrochloric acid.

Sequential Extractions Investigated

Extraction 1:

- 20 mL of HCl
- boil

Extraction 2:

- sodium carbonate
- boil or prolonged heating

Extraction 3:

- 1:7 HNO_3
- room temperature overnight

Three variables were investigated to improve the recovery of sulphate by:

- Increasing the concentration of HCl from 25% to concentrated,
- Increasing the concentration of sodium carbonate from 2 g/L to 5 g/L, and
- Increasing the reaction time of the sodium carbonate from a 1 h boil to 16 h @ 70°C.

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Test Samples

- Two wasterock samples, 1701 and 1705, tested in duplicate.
- The extracts from each of the sequential extractions for metals by ICP-OES.
- Sample 1701 mineralogy by the Rietveld XRD method at UBC.
- Three relatively pure specimens grade mineralogical samples of alunite, jarosite and pyrite.
- The alunite and jarosite specimen were subjected to the sequential leach testing.
- The pyrite sample was leached sequentially with 25% HCl followed by 1:7 HNO_3 at room temperature.

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Table 1a: Sulphur Recoveries by Sequential Extraction

	Sample 1701							
	A	B	C	D	E	F	G	H
	25% HCl		Conc. HCl		Conc. HCl		Conc. HCl	
Sulphate-S (%)	0.30	0.27	0.65	0.73	0.82	0.79	0.83	0.75
	2 g/L, Na_2CO_3 1 h boil		5 g/L, Na_2CO_3 1 h boil		2 g/L Na_2CO_3 16 h @ 70C		5 g/L Na_2CO_3 16 h @ 70C	
Sulphate-S (%)	0.83	0.83	0.59	0.51	0.54	0.63	#N/A	0.75
	1:7 HNO_3 for 16 h @ RT		1:7 HNO_3 for 16 h @ RT		1:7 HNO_3 for 16 h @ RT		1:7 HNO_3 for 16 h @ RT	
Sulphide-S (%)	0.02	0.01	-0.01	0.01	-0.01	-0.01	0.01	0.01
Total S in Extracts	1.15	1.11	1.23	1.26	1.35	1.42	#N/A	1.52
Total S by Leco	2.20	2.20	2.20	2.20	2.20	2.20	2.20	2.20
Insoluble S (%)	1.05	1.09	0.97	0.94	0.85	0.78		0.68
% S accounted for in extracts	52%	51%	56%	57%	61%	64%	#N/A	69%
	Sample 1705							
	25% HCl		Conc. HCl		Conc. HCl		Conc. HCl	
Sulphate-S (%)	0.25	0.22	0.53	0.84	0.53	0.68	0.77	0.83
	2 g/L, Na_2CO_3 1 h boil		5 g/L, Na_2CO_3 1 h boil		2 g/L Na_2CO_3 16 h @ 70C		5 g/L Na_2CO_3 16 h @ 70C	
Sulphate-S (%)	0.91	1.20	1.09	1.11	1.11	1.19	1.55	1.43
	1:7 HNO_3 for 16 h @ RT		1:7 HNO_3 for 16 h @ RT		1:7 HNO_3 for 16 h @ RT		1:7 HNO_3 for 16 h @ RT	
Sulphide-S (%)	0.01	0.02	0.02	0.03	0.01	0.01	0.01	0.01
Total S in Extracts	1.17	1.44	1.64	1.98	1.65	1.88	2.32	2.27
Total S by Leco	4.52	4.52	4.52	4.52	4.52	4.52	4.52	4.52
Insoluble S	3.35	3.08	2.88	2.54	2.87	2.64	2.20	2.25
% S accounted for in extracts	26%	32%	36%	44%	37%	41%	51%	50%

Table 3: Sulphur Speciation by Sequential Leaching of Specimen Grade Samples

Sample	Total S Leco (%)	Sequential Leach	Extracted S (%)	Recovery (%)
Pyrite	51.84	25% HCl	0.02	0%
		1:7 HNO3 @ RT	35.67	69%
				Total = 69%
Alunite	14.5	Conc. HCl	0.01	0%
		5 g Na2CO3 16h	0.57	4%
				Total = 4%
Jarosite	11.23	Conc. HCl	10.63	95%
		5 g Na2CO3 16h	2.56	23%

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Mass Balance Calculations

- very little barite, pyrite or feldspar type minerals.
- jarosite and alunite minerals were known to be mainly potassium based.
- from metal and sulphate analysis it should be possible to calculate the jarosite and alunite concentrations assuming that all of these minerals could be dissolved.
- should be a good correlation between the moles of dissolved potassium and moles of iron and aluminum.

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Table 1b: Calculations to Determine Alunite and Jarosite Content

Conditions	Extract	Al (ppm)	Fe (ppm)	K (ppm)	SO_4-S (ppm)	K assoc. with SO_4-S (ppm)	K accounted for in Jarosite + Alunite (%)	SO_4-S assoc. with Fe (ppm)	Jarosite based on Fe (%)	SO_4-S remaining after accounting for jarosite (ppm)	SO_4-S assoc. with Al (ppm)	Alunite based Al (%)	SO_4-S remaining after accounting for alunite & jarosite (ppm)	(%)
Sample 1701														
25% HCl	B HCL	690	7095	1660	2666	1629	98%	2,710	2.12	(44)	545	0.28	-589	
2g/100 mL 1h boil	B Na_2CO_3	7200	32	5860	8325	5086	87%	12	0.01	8,313	5,689	2.91	2624	
1:7 HNO3	B HNO3	680	4732	340	133	81	24%	1,808	1.41	(1,674)	537	0.27	-2212	
Totals		**8570**	**11859**	**7860**	**11125**				**3.54**			**3.46**	**-177**	**-2%**
Conc. HCl	D HCL	3870	11171	3670	7299	4459	122%	4,267	3.34	3,032	3,058	1.56	-26	
2g/100 mL1h boil	D Na_2CO_3	5840	10	4000	5128	3133	78%	4	0.00	5,124	4,614	2.36	510	
1:7 HNO3	D HNO3	460	48	280	133	81	29%	18	0.01	115	363	0.19	-249	
Totals		**10170**	**11229**	**7950**	**12561**				**3.36**			**4.11**	**236**	**2%**
Conc. HCl	F HCL	3840	12022	3800	7899	4826	127%	4,592	3.59	3,307	3,034	1.55	273	
2g/100 mL 16h @ 70(	F Na_2CO_3	6540	32	4520	6327	3865	86%	12	0.01	6,315	5,167	2.64	1147	
1:7 HNO3	F HNO3	420	70	140	-67	-41	-29%	27	0.02	(93)	332	0.17	-425	
Totals		**10800**	**12124**	**8460**	**14160**				**3.62**			**4.36**	**995**	**7%**
Conc. HCl	H HCL	3480	12154	3780	7533	4602	122%	4,643	3.63	2,890	2,750	1.41	140	
5g/100 mL 16h @ 70(	H Na_2CO_3	8100	22	7540	7526	4598	61%	8	0.01	7,517	6,400	3.27	1117	
1:7 HNO3	H HNO3	340	80	120	133	81	68%	31	0.02	103	269	0.14	-166	
Totals		**11920**	**12256**	**11440**	**15192**				**3.66**			**4.81**	**1092**	**7%**
Sample 1705					0									
25% HCl	B HCL	2750	1448	1220	2200	1344	110%	553	0.43	1,647	2,173	1.11	-526	
2g/100 mL 1h boil	B Na2CO3	11700	12	7200	11988	7324	102%	5	0.00	11,983	9,244	4.73	2739	
1:7 HNO3	B HNO3	580	72	220	200	122	55%	28	0.02	172	458	0.23	-286	
Totals		**15030**	**1532**	**8640**	**14388**				**0.46**			**6.07**	**1927**	**13%**
Conc. HCl	D HCL	9660	1601	3950	8432	5152	130%	612	0.48	7,821	7,633	3.90	188	
2g/100 mL 1h boil	D Na2CO3	12520	6	7580	11056	6754	89%	2	0.00	11,053	9,892	5.06	1161	
1:7 HNO3	D HNO3	900	20	360	333	203	57%	8	0.01	325	711	0.36	-386	
Totals		**23080**	**1627**	**11890**	**19821**				**0.49**			**9.32**	**964**	**5%**
Conc. HCl	F HCL	9700	1613	3870	6766	4134	107%	616	0.48	6,150	7,664	3.92	-1514	
2g/100 mL 16h @ 75(	F Na2CO3	13160	20	8500	11855	7243	85%	8	0.01	11,847	10,398	5.32	1449	
1:7 HNO3	F HNO3	320	30	100	133	81	81%	11	0.01	122	253	0.13	-131	
Totals		**23180**	**1663**	**12470**	**18754**				**0.50**			**9.36**	**-196**	**-1%**
Conc. HCl	H HCL	10000	1640	4140	8266	5050	122%	626	0.49	7,639	7,901	4.04	-262	
5g/100 mL 16h @ 75(	H Na2CO3	17900	20	13940	14319	8748	63%	8	0.01	14,311	14,143	7.23	168	
1:7 HNO3	H HNO3	500	26	80	133	81	102%	10	0.01	123	395	0.20	-272	
Totals		**28400**	**1686**	**18160**	**22718**			**0.50**	**0.50**			**11.47**	**-365**	**-2%**

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The results of Rietveld XRD analysis of 1701:

- 86% quartz
- 3% jarosite
- 11% alunite
- Trace pyrite and trace rutile

Comparison with sequential leach:

- jarosite 3% vs. 3.66%
- alunite 11% vs. 4.81%
- suggests difference, 6.2% alunite (11% - 4.8), was insoluble and accounts for 0.96% insoluble sulphate (64/414.1 X 6.2%).
- Wet chemistry data showed 0.68% insoluble sulphur equivalent to (0.68% X 414.1/64 = 4.4% alunite
- Adding this quantity to the amount found by sequential extraction (4.8 + 4.4 = 9.2%) the comparison is 11% vs. 9.2% by sequential extraction.

Method for calculating jarosite and alunite:

1. Calculating the quantity of alunite, dissolved in the HCl extract, from the concentration of aluminum.

2. The equivalent sulphate associated with the HCl dissolved alunite was then calculated and subtracted from the total HCl sulphate-sulphur. The remaining sulphate was then assumed to be associated with jarosite only and calculated accordingly.

3. The insoluble sulphate was assumed to be associated with alunite only and was added to the aluminum based alunite calculated in Step 1 above.

Table 4: Comparison of Mineral Analysis by Reitveld XRD and Sequential Extraction

Mineral	Sample 7407	Sample 7829	Sample 7384	Sample 7999	Sample 1701
Quartz (%)	71.4	97.9	83.3	99.7	86
Alunite					
Reitveld (%)	27.1	1.4	ND	ND	11
Seq. Leach (%)	28.17	2.51	0.27	0.51	9.2
% Deviation	-3.8%	-83.5%	NA	NA	16.4%
Jarosite					
Reitveld (%)	0.8	0.1	16.1	ND	3
Seq. Leach (%)	0.23	<0.08	17.15	<0.08	3.5
% Deviation	71.0%	NA	-6.3%	NA	-16.7%
Pyrite					
Reitveld (%)	0.1	0.2	0.2	0.3	NA
Seq. Leach (%)	0.04*	0.02*	0.09*	0.19*	NA

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CONCLUSIONS

- Concentrated HCl dissolved all of the jarosite and a portion of the alunite.
- Sodium carbonate at 5 g/100 ml over an extended reaction time of 16 h at ~70°C dissolved only a portion of the alunite.
- The sum of the aluminum in the HCl extract and acid insoluble sulphur, upon conversion to equivalent alunite, showed good correlation with alunite measured by the Rietveld Method.
- When samples contained <0.15% sulphate-sulphur, equivalent to 1 and 1.2% alunite and jarosite, respectively, poor correlation between the potassium and sulphate was observed. These values probably represent limits of detection for these two minerals by this sequential extraction procedure.
- The procedure developed provided a cost effective method for speciating both alunite and jarosite for this project.