

Online Materials

Table OM1. Chemical analyses of AMD of Pastora mine compared with the results of previous analyses of other representative AMD waters (Tinto and Odiel) and drinking water from that area (Pantones river). Concentrations in mg/l.

	Pastora mine* (Aliseda)	Tinto River** (Niebla)	Odiel River** (Gibraleón)	Pantones River*** (Arroyo de la Luz)
Temperature (°C)	15	19	18	—
pH	3.5	2.8	3.6	8.9
Aluminum	4	77	37	< 0.2
Arsenic	0.007	0.202	0.013	< 0.02
Sulphur	66	224	712	< 10
Calcium	4.8	73	50	< 5.0
Cobalt	0.048	0.558	288	< 0.01
Copper	0.011	19	5.4	< 0.01
Iron	6	157	7.5	< 0.05
Lithium	0.032	0.137	79	—
Magnesium	9.6	76	72	< 5.0
Manganese	1.8	7.8	8.5	< 0.01

Nickel	0.039	0.175	152	< 2.0
Potassium	7.0	3.9	2.8	< 2.5
Sodium	12	38	21	8.5
Silicon	5.2	15	14	—
Zinc	0.063	24	13	< 0.02

* Crespo (2015) **Olías et al., (2010) ***Data (2014.05.28) from Tajo Hydrographic Confederation.

Table OM2. Sulphates identified in Pastora mine. Ammonio sulphates, ammoniojarosite and tschermigite, are highlighted in this table. (*) (Formula proposed by Crespo et al. 2017).

Sulphate mineral	Chemical formulae	Description	Level
Aluminocopiapite	$\text{Al}_{2/3}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$	Yellow masses usually on the floor	L2
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$	White masses	L2
Ammoniojarosite	$(\text{NH}_4)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$	Yellow masses and crust covering walls and ceiling	L1-L2
Apjohnite	$\text{Mn}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	Associated with halotrichite as white globular masses	L1
Copiapite	$\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$	Yellow masses	L2
Dorallcharite	$\text{TiFe}_3^{+3}(\text{SO}_4)_2(\text{OH})_6$	Associated with ammoniojarosite on goethite	L2
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Colorless to white fibrous masses associated with wattervilleite	L1
Ferricopiapite	$\text{Fe}^{3+}_{0.67}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$	Yellow masses usually on the floor	L2

Fibroferrite	$\text{Fe}^{3+}(\text{SO}_4)(\text{OH})\cdot 5\text{H}_2\text{O}$	Pale brown crust on the walls	L2
Gypsum	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	Efflorescences on the walls	L1-L2
Halotrichite	$\text{FeAl}_2(\text{SO}_4)_4\cdot 22\text{H}_2\text{O}$	Associated with pickeringite as white globular masses usually on the floor	L1-L2
Hexahydrite	$\text{MgSO}_4\cdot 6\text{H}_2\text{O}$	White masses on quartzitic walls	L1
Jarosite	$\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$	Yellow crusts on goethite	L1-L2
Kalinite	$\text{KAl}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$	In assemblage with pickeringite and halotrichite	L1-L2
Magnesiocopiapite	$\text{MgFe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2\cdot 20\text{H}_2\text{O}$	Yellow masses usually on the floor	L2
Pickeringite	$\text{MgAl}_2(\text{SO}_4)_4\cdot 22\text{H}_2\text{O}$	Associated with halotrichite as white globular masses	L1-L2
Rozenite	$\text{FeSO}_4\cdot 4\text{H}_2\text{O}$	Associated with copiapite and ammonio sulphates	L2
Slavíkite	$\text{Mg}_4\text{Fe}_{10}(\text{SO}_4)_{15}(\text{OH})_8\cdot 13(\text{H}_2\text{O})^*$	Yellow powder crust on the walls	L2
Tschermigite	$(\text{NH}_4)\text{Al}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$	Colorless efflorescences with vitreous luster usually	L1-L2

		covering ammoniojarosite	
Wattevilleite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}(?)$	Colorless to white fibrous masses associated with epsomite	L1

Table OM3. Association of ammonium minerals identified at level one. Tschermigite (Tmi), ammoniojarosite (Ajrs), kalinite (Kli), slavíkite (Sví), jarosita (Jrs), gypsum (Gp), copiapite group (Cpi), fibroferrite (Ffr), rozenite (Rzn), alunogen (Alg), dorallcharite (Dcr), Other (Oth). Zone: Sheltered zone (SZ), Deep gallery (DG). Numbers are weight percentages of the identified phases determined using XRD with the RIR method (Hubbard and Snyder, 1988; Martín, 2008). All abbreviations are based on the IMA-CNMNC approved mineral symbols (Warr, 2021).

Sample	Form of occurrence	Date of collect	Zone	Tmi	Ajrs	Kli	Sví	Jrs	Gp	Cpi	Ffr	Rzn	Alg	Drc	Oth
PA42	Crusts	2015-04-12	SZ		93.2										6.8
PA133	Crusts	2018-05-02	SZ	76.0	24.0										
PA109	Efflorescences	2017-08-09	DG	85.1	14.9										
PA107	Efflorescences	2017-08-09	DG	70.2	29.8										
PA100	Efflorescences	2016-12-17	DG	33.3	66.7										
PA132	Powder crust	2018-05-02	SZ	76.3				23.7							
PA119	Efflorescences	2017-11-11	DG	32.3						16.2	51.5				
PA108	Efflorescences	2017-08-09	DG	40.8	50.2							8.9			
PA121	Efflorescences	2017-11-11	DG	64.7	14.5				14.5						
PA143	Crust	2020-07-26	SZ	30.9	69.1										
PA144	Efflorescences	2020-07-26	DG	65.0				12.9	22.1						

PA145	Efflorescences	2020-08-01	DG	75.6				24.4							
PA151	Globular masses	2020-10-11	DG	69.2	30.8										
PA152	Globular masses	2020-10-11	DG	47.2				3.5			30.9				18.4