

# Doornhoek Fluorspar Geochemical Risk Assessment

Waste classification and geochemical modelling

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# **EXECUTIVE SUMMARY**

Existing laboratory data was used to conduct a waste classification of the tailings and overburden material, according to NEMWAA Regulation 635, of the newly proposed Doornhoek fluorspar mine. Numeric geochemical models were used as a tool to evaluate the medium to long term behaviour of the tailings and overburden material and to contextualise and augment the waste classification results. The waste classification and numeric geochemical modelling results were combined to quantify the geochemical risks posed to local environment, i.e. soil, surface water and groundwater resources. Due to the fact that the dolomite aquifer in the region is used by many farmers for their agricultural activities, the aquifer itself is viewed as a sensitive receptor.

## The study showed that:

- 1. The risk for the development of acid mine drainage conditions for all geological mine waste, i.e. tailings and overburden, is insignificant.
- 2. The risk for the contamination of soil, surface water and groundwater resources by metals and metalloids from all geological mine waste, i.e. tailings and overburden, is insignificant.
- 3. The contamination of groundwater by fluoride and sulphate from the tailings material is significant and mitigation measures should be implemented as the dolomite groundwater is a sensitive receptor.
- 4. The tailings classifies as a Type 3, i.e. low risk, waste.
- 5. The overburden classifies as Type 3, i.e. low risk waste. However, the numeric geochemical model, which evaluates the behaviour of the overburden in the medium to long term, has indicated that the material does not pose a significant risk to the local environment.
- 6. If ammonium nitrate based explosive products are to be used in the mining proses, then nitrate needs to be included as a potential groundwater and surface water contamination risk.

# The following recommendations are made following the study:

- 1. Although the tailings and overburden material classifies as Type 3, i.e. low risk, waste and thus according to NEMWAA Regulation 635 and 636 a Type C barrier system, this mitigation measure has been shown in other studies to not be a sustainable option. The recommendation is thus made that the barrier system should only be considered if more sustainable mitigation options cannot be identified and implemented.
- 2. Although the overburden material classifies as Type 3, i.e. low risk, waste, the recommendation is made to downgrade the material to Type 4, i.e. inert, due to insignificant geochemical risks posed to the local environment, including sensitive receptors.
- 3. A monthly monitoring protocol should be implemented and fluoride and sulphate included in the parameters analysed. Any contamination concerns should be flagged and addressed.
- 4. Nitrate should be included in the monthly monitoring protocol if ammonium nitrate based explosives are to be used in the mining process.



- 5. An annual comprehensive analysis should be included in the monitoring protocol and any contamination concerns flagged and addressed.
- 6. If the ore processing methodologies should change, the geochemical models will need to be updated to take these changes into consideration.



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# **LIST OF ABBREVIATIONS**

Abbreviation	Description
DEA	Department of Environmental Affairs
DMR	Department of Mineral Resources
DWS	Department of Water and Sanitation
ENRC	Eurasian Natural Resources Corporation plc
MAE	Mean Annual Evaporation
MAP	Mean Annual Precipitation
MPRDA	Mineral and Petroleum Development Act
NEMA	National Environmental Management Act
NEMLAA	National Environmental Laws Amendment Act
NEMWAA	National Environmental Management Waste Amendment Act
NWA	National Water Act
QEMSCAN	Quantitative Evaluation of Minerals by Scanning Electron Microscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

# **LIST OF UNITS**

Abbreviation	Description					
mg.kg <sup>-1</sup>	milligrams per kilogram					
mg.ℓ <sup>-1</sup>	milligrams per litre					
mm.a <sup>-1</sup>	millimetres per annum					
wt%	weight percent					



# 1 INTRODUCTION

Geodyn Systems (Geodyn) was requested by Exigo Sustainability (Pty) Ltd (Exigo) to conduct a waste classification and geochemical model on the tailings and overburden streams of a newly proposed fluorspar mine, Doornhoek Fluorspar Mine. The waste classification is a legal requirement, while the geochemical modelling is used to evaluate the medium to long terms risks of the material as the legislated waste classification does not take geochemical processes into account.

# 2 PROJECT DESCRIPTION

The following sub-sections serve to outline the project objectives, site locality and environmental factors pertinent to the study.

# 2.1 Project background

A geochemical assessment of mine waste leachate potential, which was aimed at identifying potential geochemical risks associated with the tailings and overburden, was conducted for the Doornhoek Fluorite project by Exigo in 2014. The study included an assessment of acid mine drainage (AMD) by using static acid base accounting (ABA) and net acid generation (NAG) tests. It found that the mine waste posed no risk for the development of AMD conditions, due to the deposit ore and host geology being dominated by carbonate rocks, which have the capacity to neutralise acidity and due to the low sulphide content of the ore and host lithologies.

The study also included an assessment of potential geochemical risks associated with the leaching of potential contaminants from effluent leaching from the waste material. A static distilled water leach test, which also forms part of the current NENMWAA regulations, was used and analysed. The results were compared to the SANS 241-1:2011 drinking water guideline values. This assessment showed that fluoride and sulphate were potential geochemical risks to local groundwater and surface water resources.

A mineralogical analysis was also conducted, which confirmed the abundance of carbonate minerals, especially dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>]. It also showed that the mineral fluorite [CaF<sub>2</sub>] is the most dominant fluoride containing mineral present in the ore and host rocks.

The present study was initiated for the purpose two purposes. The first is for legal compliance with the NEMWAA Regulations. The second is to evaluate the medium to long term behaviour of the mine waste, as the waste classification regulations assessment methodologies do not take dynamic geochemical processes into account. This model allows the quantification of risks taking time into account and allows the waste to be placed in the internationally accepted source-pathway-receptor assessment methodology, which is also preferred by the Department of Environmental Affairs.



# 2.2 Project objectives

The project has the following objectives:

- 1. Conduct a waste classification in terms of NEMWAA<sup>1</sup> Regulation 635.
- 2. Develop a numerical geochemical model to quantify medium to long term environmental risks posed by the tailings and overburden material.

# 2.3 Project locality

The project area is located 220 km northwest of Johannesburg and 18 km south of the town of Zeerust (Figure 3-1).

# 2.4 Climate and topography

The project area is located in the Northern Transvaal climatic zone and is characterised by wet summers and cool, dry winters. Most (76%) precipitation occurs in the months from November to March, with the driest months being May to September. The mean annual precipitation (MAP) is 573 mm.a<sup>-1</sup>. The mean annual evaporation (MAE) is 1 901 mm.a<sup>-1</sup> (Ages Gauteng, 2013).

# 2.5 Geological context

The geology has been amply described in previous reports (Ages Gauteng, 2013; RPA, 2013; Exigo, 2014). Therefore only geological aspects pertaining specifically to the geochemical environment of the site will be provided in this report.

The project area is located on the rocks of the Chuniespoort Group, belonging to the Transvaal Supergroup. The Chuniespoort Group is largely represented by dolomite, dolomitic limestone, chert and shale. The fluorite-lead-zinc mineralisation is located entirely in the middle zone of the Frisco Formation, which forms part of the Chuniespoort Group. The fluorite ore is therefore entirely hosted by dolomitic lithologies, with the footwall and hanging wall also being dolomitic in nature.

# 3 METHODOLOGY

On the 3<sup>rd</sup> of September 2014 the National Environmental Laws Amendment Act (NEMLAA, Act 25 of 2014), published on 2 June 2014 came into effect. These laws are an attempt by the Department of Environmental Affairs (DEA) in cooperation with other government departments, mainly the Departments of Mineral Resources (DMR) and the Department of Water and Sanitation (DWS), to legislate the waste from mining and industrial activities under one legislative system, termed the *One Environmental System*. This system is subject to certain sections under other acts, such as the Mineral and Petroleum Resources Development Act (MPRDA) and the National Water Act (NWA).

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<sup>&</sup>lt;sup>1</sup> National Environmental Waste Ammendment Act, Act 26 of 2014



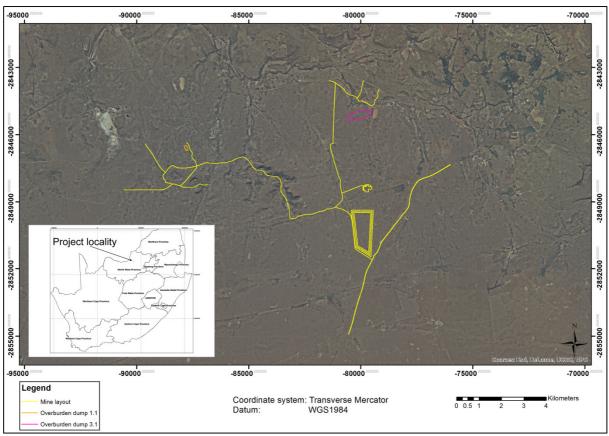


Figure 3-1 Map showing the Doornhoek Fluorspar locality as well as outlines of the resource areas and mine infrastructure

NEMLAA calls for a waste classification to be conducted according to Regulation 635 of NEMWAA, which forms part of the NEMLAA legislation. To conduct the waste classification leach tests and a total analysis needs to be conducted. The leach test entails the leaching of a solid sample of waste with reagent water and the subsequent analysis of the leachate for specific components. The total analysis entails the analysis of the solid material for the total concentration of specific components that are present in the waste sample. The results of these two tests are compared to regulatory criteria and a classification is done based on the results of this comparison.

As part of the waste classification and assessment of the risks from a particular waste, the DEA subscribes to the source-pathway-receptor analysis methodology, which is international best practice. The use of this assessment methodology allows the analysis of the full cycle of a potential contaminant to be evaluated within the proper scientific framework so that risks can be realistically assessed and proper mitigation measures proposed. As opposed to a blanket "one-size-fits-all" approach which often leads to the application of non-sustainable solutions, which have large capital expenditure but no real mitigate value. For the quantification of medium to long term geochemical risks associated with the waste material, i.e. mine tailings and overburden, numeric geochemical modelling is used as a tool. This modelling entails the use of established



thermodynamic and kinetic principles to calculate risks over time. The internationally validated software package PHREEQC is used for this purpose.

Existing data was used to conduct the current study. The following data was made available:

- Distilled water leach test data ICP-MS analysis (Exigo, 2014)
- Total analysis data ICP-MS analysis (Exigo, 2014)
- Mineralogical analysis XRD (Exigo, 2014)
- Mineralogical analysis QEMSCAN (SGS, 2011; Mintek, 2014)
- Total analysis XRF (SGS 2011; Mintek, 2014)

# 4 WASTE CLASSIFICATION

### 4.1 Leachate

The comparison between the leachate results and the regulatory guideline values is shown in Table 4-1. It can be seen that only the lowest fluoride regulatory value (LCT0) is exceeded for the leachate of the tailings and the footwall lithologies, which represents part of the overburden. None of the other parameters are exceeded.

# 4.2 Solids (total concentration in the material)

The comparison between the leachate results and the regulatory guideline values is shown in Table 4-2. It can be seen that only the lowest regulatory value (TCT0) of arsenic, and manganese for all waste samples is exceeded for the solid material. The TCT0 values for cadmium and copper are exceeded for one of the tailings samples and for the footwall rocks. The TCT0 value for zinc is exceeded for one of the tailings samples. The next highest regulatory value, TCT1, is not exceeded by any parameters.

# 4.3 Waste Classification

According to Regulation 635, the results of the comparison of the leach concentration and total concentration need to be used to arrive at a final classification of the waste. The waste falls in the following criteria, which is wastes with any element or chemical substance concentration above the LCTO but below or equal to the LCT1 limits and all TC concentrations below or equal to the TCT1 limits (LCT0 < LC  $\leq$  LCT1 and TC  $\leq$  TCT1) are Type 3 Wastes. According to these criteria, the tailings and overburden classify as Type 3, which according to Regulation 636 requires a Type C barrier system.

Although the waste classifies as Type 3 according to the waste classification regulations, the results need to be contextualised, as the waste classification methodology does not take either geochemical processes or hydrogeochemical baseline conditions into account. The baseline conditions are described in the section below.



Table 4-1 Results of the comparison between the leach concentration threshold (LCT) values of Regulation 635 and the mine waste material

		R635 Leach Concentration Threshold Values			Doornhoek Fluorspar Waste Leachate Concentrations					
Inorganic Waste	Al-land dation	LCT0	LCT1	LCT2	LCT3	Old tailings	New tailings	Hangingwall	Footwall	
constituents	Abbreviation	mg.ℓ⁻¹	mg. <b>ℓ</b> ⁻¹	mg. <b>ℓ</b> ⁻¹	mg. <b>ℓ</b> ⁻¹	$mg.ℓ^{-1}$	mg.ℓ-1	$mg.ℓ^{-1}$	$mg. \pmb{\ell}^{-1}$	
	Metal Ions									
Arsenic	As	0.01	0.5	1	4	<0.001	<0.001	<0.001	<0.001	
Cadmium	Cd	0.003	0.15	0.3	1.2	0.001	0.0001	<0.0001	<0.0001	
Cobalt	Co	0.5	25	50	200	< 0.001	<0.001	<0.001	< 0.001	
<b>Chromium (Total)</b>	Cr(Total)	0.1	5	10	40	< 0.001	<0.001	<0.001	< 0.001	
Chromium (VI)	Cr(VI)	0.05	2.5	5	20	< 0.010	<0.010	< 0.010	< 0.010	
Copper	Cu	2.0	100	200	800	< 0.001	<0.001	0.001	< 0.001	
Manganese	Mn	0.5	25	50	200	< 0.001	0.040	<0.001	<0.001	
Molybdenum	Мо	0.07	3.5	7	28	< 0.001	< 0.001	<0.001	0.001	
Nickel	Ni	0.07	3.5	7	28	< 0.001	0.001	0.002	0.001	
Lead	Pb	0.01	0.5	1	4	< 0.001	< 0.001	<0.001	<0.001	
Selenium	Se	0.01	0.5	1	4	0.001	0.002	<0.001	0.001	
Vanadium	V	0.2	10	20	80	< 0.001	< 0.001	<0.001	< 0.001	
Zinc	Zn	5.0	250	500	2 000	0.004	0.002	<0.001	0.002	
				Inc	rganic Anions	S				
Total Dissolved Solids	TDS	1 000	12 500	25 000	100 000	278	340	42	50	
Chloride	Cl	300	15 000	30 000	120 000	7	<5	6	<5	
Sulphate	SO <sub>4</sub>	250	12 500	25 000	100 000	174	209	<5	<5	
Nitrate as Nitrogen	NO <sub>3</sub> -N	11	550	1 100	4 400	<0.2	<0.2	<0.2	<0.2	
Fluoride	F	1.5	75	150	600	3.4	2.5	1.2	2.0	



Table 4-2 Results of the comparison between the total concentration threshold (LCT) values of Regulation 635 and the mine waste material

			otal Concen reshold Valu		Doornhoek Fluorspar Waste Leachate Concentrat			trations
		тсто	TCT1	TCT2	Old tailings	New tailings	Hangingwall	Footwall
Waste constituents	Abbreviation	mg.kg <sup>-1</sup>	mg.kg <sup>-1</sup>	mg.kg <sup>-1</sup>	mg.kg <sup>-1</sup>	$mg.$ ℓ $^{^1}$	$mg.oldsymbol{\ell}^{ extstyle 1}$	$mg.$ ℓ $^{-1}$
				Meta	I lons			
Arsenic	As	5.8	500	2 000	40.8	18.8	21.6	24.8
Cadmium	Cd	7.5	260	1 040	23.4	<0.4	<0.4	<0.4
Cobalt	Co	50	5 000	20 000	3.6	2	2.4	4
Chromium (Total)	Cr(Total)	46 000	800 000	n.a	8.4	4.8	<0.4	<0.4
Chromium (VI)	Cr(VI)	6.5	500	2 000	<0.05	<0.05	<0.05	<0.05
Copper	Cu	16.0	19 500	78 000	19.2	8.8	12.4	18.8
Manganese	Mn	1 000	25 000	100 000	8 400	7 600	8 000	7 600
Molybdenum	Мо	40	1 000	4 000	0.4	0.8	0.4	0.8
Nickel	Ni	91	10 600	42 400	16.4	23.2	8	16.4
Lead	Pb	20	1 900	7 600	11.2	8.4	32	12.4
Selenium	Se	10	50	200	0.8	<0.4	<0.4	<0.4
Vanadium	v	150	2 680	10 720	<0.4	<0.4	<0.4	<0.4
Zinc	Zn	240.0	160 000	640 000	1 864	96	16	20
				Inorgani	ic Anions			
Fluoride	F	100	10 000	40 000	7 680	7 680	7 680	7 680

The equation also indicates that the dissolution of the sulphides pyrite and pyrrhotite introduces sulphate and acidity, as  $H^+$ , into the tailings pore water solution.

# 5 ANALYSIS OF HYDROGEOCHEMICAL BASELINE CONDITIONS

The 2016 Exigo hydrocensus data was used to calculate a baseline using the 95<sup>th</sup> percentile. This data, together with the 2014 Exigo baseline data was compared to the SANS drinking water guideline values to assess hydrogeochemical baseline conditions specifically for the groundwater.

The data shows that the salinity is dominated by bicarbonate, calcium, magnesium and sulphate. The elevated calcium, magnesium and bicarbonate concentrations are from the dolomite minerals, while sulphate is most probably from the natural oxidation of sulphides. Fluoride and manganese concentrations are naturally elevated above the SANS drinking water guideline values, while ammonia exceeds the guideline values in the 2016 hydrocensus data. The elevated fluoride values are most probably due to the natural weathering of the mineral fluorite, which occurs in the dolomite aquifer matrix. This indicates that the aquifer water in the region contains naturally elevated fluoride and manganese concentrations. With the exception of manganese and lead in the 2014 data, all other metals and metalloids are below detection and with the exception of manganese, all metals and metalloid concentrations, are below the SANS drinking water guideline values.

Table 5-1 2016 hydrocensus data and 2014 Exigo baseline data compared to SANS drinking water guideline values

Parameter	Abbreviation	Units	SANS drinking water	2014 Exigo Baseline	2016 Hydrocensus
рН	рН	pH units	5 - 9.7	8	8.48
Total Dissolved Solids	TDS	mg.ℓ <sup>-1</sup>	1 200	759	501
Bicarbonate	HCO <sub>3</sub>	mg CaCO₃.ℓ⁻¹	n.g.v	413	483
Chloride	CI	mg.ℓ <sup>-1</sup>	300	91	25
Sulphate	SO <sub>4</sub>	mg.ℓ <sup>-1</sup>	250	130	95
Nitrate	NO <sub>3</sub>	mg.ℓ <sup>-1</sup>	50	7	6
Nitrite	NO <sub>2</sub>	mg.ℓ⁻¹	3.0	n.a	1.1
Ammonia	NH <sub>4</sub>	mg.ℓ⁻¹	1.9	0.3	1.9
Phosphate	PO <sub>4</sub>	mg.ℓ⁻¹	n.g.v	0.07	0.08
Fluoride	F	mg.ℓ <sup>-1</sup>	1.5	2.2	1.8
Aluminium	Al	mg.ℓ⁻¹	0.3	b.d	b.d.
Arsenic	As	mg.ℓ <sup>-1</sup>	0.01	b.d	b.d.
Calcium	Ca	mg.ℓ <sup>-1</sup>	n.g.v	116	86
Cadmium	Cd	mg.ℓ <sup>-1</sup>	0.003	b.d	b.d.
Cobalt	Со	mg.ℓ <sup>-1</sup>	0.5	0.01	b.d.
Total Chromium	Cr (Total)	mg.ℓ <sup>-1</sup>	0.05	b.d	b.d.
Hexavalent Chromium	Cr (VI)	mg.ℓ <sup>-1</sup>	n.g.v	b.d	n.a
Copper	Cu	mg.ℓ⁻¹	2	b.d	b.d.
Iron	Fe	mg.ℓ⁻¹	0.3	b.d	b.d.
Potassium	K	mg.ℓ⁻¹	n.g.v	4.5	7.0
Magnesium	Mg	mg.ℓ <sup>-1</sup>	n.g.v	67.0	54.1
Manganese	Mn	mg.ℓ⁻¹	0.1	1.0	1.3
Molybdenum	Мо	mg.ℓ <sup>-1</sup>	0.07	n.a	b.d.
Sodium	Na	mg.ℓ <sup>-1</sup>	n.g.v	42.2	10.1
Nickel	Ni	mg.ℓ <sup>-1</sup>	0.07	0.01	b.d.
Lead	Pb	mg.ℓ <sup>-1</sup>	0.01	b.d	b.d.
Selenium	Se	mg.ℓ <sup>-1</sup>	0.01	b.d	b.d.
Uranium	U	mg.ℓ <sup>-1</sup>	0.015	b.d	n.a
Vanadium	V	mg.ℓ <sup>-1</sup>	0.2	0.0	n.a
Zinc	Zn	mg.ℓ <sup>-1</sup>	5	n.a	b.d.

# 6 QUANTIFICATION OF GEOCHEMICAL RISKS RELATED TO GEOLOGICAL WASTE

The modelling of geochemical processes is used as a tool to quantify the medium to long term geochemical risks associated with the waste material. This quantification is based on a conceptual understanding, built on the foundations of the data collected and on sound scientific principles, which is used to build a numeric geochemical model, which considers the geochemical processes over time.

# 6.1 Conceptual understanding of the waste geochemical system

# 6.1.1 Tailings

The tailings as a geochemical system can be visualised using Figure 6-1. As water is the transport medium of dissolved potential contaminants in the tailings facility, the most important water flow paths are shown in Figure 6-1. The water flow paths then correspond to the contaminant flow paths, excluding the atmospheric pathway, which is the transport medium for windblown dust and is outside the scope of this study.

The mineralogical analyses have shown that the most important fluoride bearing mineral phase is fluorite [CaF<sub>2</sub>]. The Mintek (2014) metallurgical study has shown that 6% of the fluoride contained in the ore remains as a residual phase and thus ultimately lands up in the tailings facility. In the tailings facility, fluorite can dissolve slowly to introduce  $Ca^{2+}$  and  $F^{-}$  ions to the tailings pore water solutions according to:

$$CaF_{2(s)} \leftrightarrow Ca^{2+} + F^{-}$$
 Equation 1

The reaction in Equation 1 above is indicated as reversible, as the amount of Ca and F added to the tailings pore water solution will depend on the solubility product of fluorite in the specific tailings system. Fluoride can thus be expected to reach a maximum concentration in the tailings pore water.

The mineralogical data of Mintek (2014) and SGS (2011) indicated that the ore material contains ~1 wt% pyrite [FeS<sub>2</sub>] and pyrrhotite [Fe<sub>1- $\chi$ </sub>S]. Both of these minerals are unstable in the presence of atmospheric oxygen and react according to the following reaction, using pyrite, which is the dominant sulphide mineral phase, as an example:



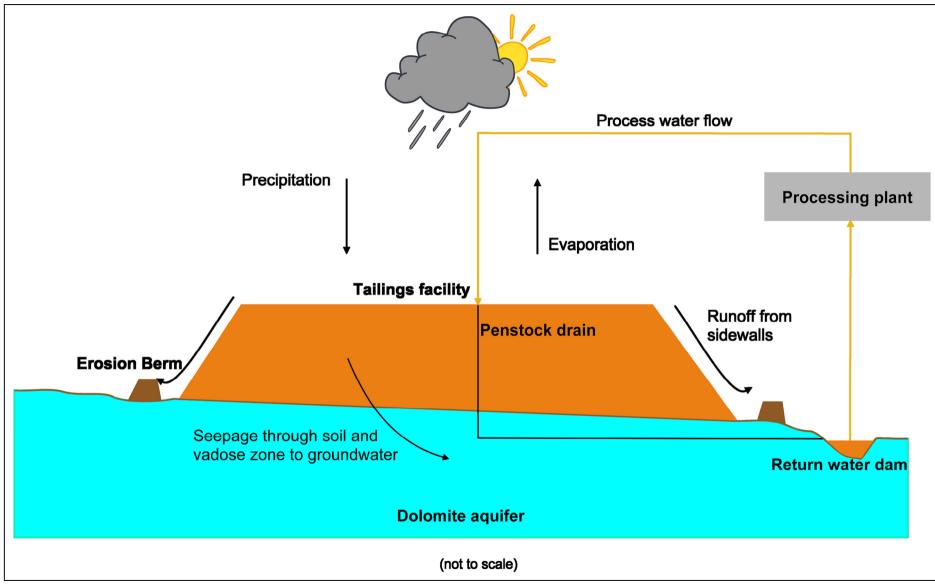


Figure 6-1 Conceptual model of the tailings as a geochemical system showing the most important water flow paths



$$\text{FeS}_{2(s)} + \frac{7}{2}O_{2(aq)} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$
 Equation 2

Equation 2 is shown as irreversible, because in the major part of the tailings facility, pyrite can be expected to be unstable due to the presence of dissolved oxygen.

The mineralogical analyses indicated that the carbonate minerals calcite [CaCO<sub>3</sub>] and dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>], with dolomite being the most abundant carbonate phase, occur in the tailings material. These minerals have the capacity to neutralise acid formed from the dissolution of the sulphide minerals according to the following equations:

$$CaCO_{3(s)} + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$$
 Equation 3

$$CaMg(CO_3)_{3(s)} + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$$
 Equation 4

Equations 3 and 4 above are shown as reversible. This is due to the overabundance of carbonate minerals relative to the sulphides indicating that the buffer capacity of the tailings material far outstrips the acidity produced by the oxidation of sulphides. The laboratory data has shown that the tailings material contains > 50 times as much neutralising as acid producing capacity. Therefore the amount of Ca, Mg and bicarbonate ions added to the tailings pore water solution will depend on the solubility of these minerals in the specific tailings system.

The dissolution of the sulphide minerals adds ferrous iron (Fe<sup>2+</sup>) to the tailings pore water solution. In the presence of oxygen, ferrous iron is oxidised to ferric iron according to the following equation:

$$Fe^{2+} + \frac{1}{4}O_{2(aq)} + H^{+} \rightarrow Fe^{3+} + H_{2}O$$
 Equation 5

Ferric iron is not soluble above pH values of ~3. Therefore ferric iron will precipitate as ferrihydrite, of which ferric hydroxide [Fe(OH<sub>3</sub>)] is a proxy, according to:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$$
 Equation 6

Equation 6 above is shown as irreversible, as the buffering capacity of the carbonate minerals precludes the pH values of < 3. Iron oxides and hydroxides were identified in the mineralogical analyses, which indicate that this process is already taking place in the natural environment of the in situ ore body.

Iron hydroxides have the capacity to adsorb<sup>2</sup> potential contaminants from solution. This is shown generically in the following equation for cations<sup>3</sup> and anions<sup>4</sup>:

$$> OH + Me^{2+} \leftrightarrow > Me + H^{+}$$
 Equation 7

$$>OH + L^{2+} + H^+ \leftrightarrow > L^- + H_2O$$
 Equation 8

 $<sup>^2</sup>$  Adsorption is the removal of a solute from solution to a contiguous solid phase and refers to the 2 dimensional accumulation of the solute on the mineral surface.

<sup>&</sup>lt;sup>3</sup> Cation is a positively charged ion.

<sup>&</sup>lt;sup>4</sup> Anion is a negatively charged ion.



In equations 7 and 8 above, >OH is the mineral surface with associated hydroxyl group, Me is the metal or metalloid and L is the anionic ligand, of which sulphate would be an example. The equations are also written as reversible, as adsorption is a completely reversible process, depending on the local physicochemical conditions.

Due to sulphate produced from the oxidation of sulphides as well as calcium introduced due to the dissolution of carbonate minerals, it is likely that the mineral gypsum [CaSO<sub>4</sub>.2H<sub>2</sub>O] is likely to form in the tailings facility according to:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4. 2H_2O_{(s)}$$
 Equation 9

The formation of gypsum will de[pend on the solubility product of the mineral under the specific conditions within the tailings facility and it is unlikely that enough will precipitate to completely buffer the tailings pore water sulphate concentrations.

Tailings facilities containing sulphide minerals can be subdivided vertically into three geochemical zones, analogous to the layers of a half-onion. These are from top, i.e. in contact with the atmosphere, to the bottom: Oxidation zone (OZ), the Transition Zone (TZ) and the Reduction Zone (RZ). Three numeric geochemical models are developed for each and coupled into a tailings facility model.

### 6.1.2 Overburden

A conceptual model of the overburden showing the most important water flow and thus also mass flow paths is depicted in Figure 6-2. The overburden facility as a geochemical system is analogous to that of the tailings facility. Major differences are the lower concentration of fluorite in the overburden and the fact that the overburden, unlike the tailings, is not connected to the processing plant reticulation system. This implies that salt build-up in the process water reticulation system due to the overburden facility is highly unlikely. Another important difference is the grain size distribution in the overburden, which is expected to be much coarser than in the tailings, which has hydrological implications.

# 6.1.3 Dolomite aquifer

The dolomite aquifer is for the purposes of this study considered from a hydrogeochemical perspective to aid in the quantification of geochemical risks to the environment. From this perspective the aquifer should be considered a sensitive receptor as well as an important potential transport pathway for potential contaminants.

From a hydrogeochemical perspective the most important processes in the dolomite aquifer are expected to be mixing, dilution and precipitation, mostly of gypsum, but potentially also of carbonate minerals and fluorite, when tailings effluent is allowed access to the aquifer water. The precipitation of gypsum and fluorite will depend on the concentrations of calcium, sulphate and fluoride in the tailings seepage as well as in the dolomite aquifer water. Adsorption is not deemed to be a likely, as the iron content in the dolomite aquifer water is expected to be low and thus



also the amount of iron oxides and hydroxides, which could act as mineral substrates for dissolved constituents.

# 6.2 Quantification of the medium to long term behaviour of mine waste

Numeric geochemical modelling is used as a tool to quantify the medium to long term behaviour of the mine waste material and thus also the risks to the local environment, including soil and groundwater. Models were developed for the operational and post-operational phases of the mining project.

Only a synopsis of the model and its results are presented in the main body of the report. For the detail of the model setup and determination of uncertainty and sensitivities, the reader is referred to the Appendix.

### 6.2.1 Model results

# 6.2.1.1 Operational Phase

### 6.2.1.1.1 Tailings

The results for the three geochemical zones in the tailings facility are shown below in Table 6-1. The values in Table 6-1 should be viewed as a quantitative guide to risk assessment rather than an absolute prediction of tailings pore water concentrations. The climate alone can cause fluctuations in water chemistry within a tailings facility implying that one single predicted value cannot be provided for the tailings water quality. The model thus provides an indication of the probability that a potential contaminant could be expected to occur in the tailings pore water, which could impact on sensitive receptors.

The model results show that sulphate values in the tailings pore water exceed regulatory as well as groundwater baseline values. This is due to the oxidation of sulphide minerals in predominantly the oxidation zone of the facility.

Fluoride values are also shown to exceed regulatory values, but are similar to the baseline values. It is interesting to note that the model fluoride concentrations increase with depth in the tailings facility from the OZ to the RZ. The dissolution of fluorite is not dependent on the pH or the oxygen content of the system, as is the case with the sulphides. Therefore as water percolates vertically through the tailings facility, new fluoride is added to the tailings pore water. The fluoride concentrations in the tailings can thus be seen to range from 0.9 mg. $\ell^{-1}$  to 2.7 mg. $\ell^{-1}$ , with the latter value a maximum.

Potential metal and metalloid contaminants, i.e. arsenic, manganese, copper and cadmium were also evaluated. The model results indicates that due to the circum neutral pH values and adsorption capacity provided by the presence of iron oxides and hydroxides, these potential contaminants pose a negligible risk to the local environment.



#### 6.2.1.1.2 Overburden

The results for the overburden facility leachate are shown below in Table 6-2. The values in Table 6-2, as with the tailings results, should be viewed as a quantitative guide to risk assessment rather than an absolute prediction of tailings pore water concentrations.

The overburden leachate does not contain any sulphate, as the XRD as well as the ABA analyses indicated that sulphide mineral content is below detection and is thus not a significant contributor to the overburden geochemical system. The overburden does contain fluorite, which weathers to introduce fluoride into the leachate at a model concentration of 1.7 mg. $\ell^{-1}$ .

As with the tailings material pore water, the overburden leachate does not contain any metal or metalloid contaminants.

### 6.2.1.2 Post-operational phase

### 6.2.1.2.1 Tailings

The main conceptual difference between the operational and post-operational phases for the tailings facility specifically is the decrease in phreatic water level upon cessation of pumping of slurry to the tailings facility. This decrease causes the exposure of larger parts of the facility material to atmospheric oxygen. These two aspects, the decrease in the amount of water in the facility as well as an increase in oxygen is taken into account in the post-operational scenario.

The results are similar to those of the operational phase, including circum neutral pH values, with two important differences. The first is the increase in sulphate concentration in the post-operational phase to 1 470 mg.l<sup>-1</sup>. This can be ascribed to the lower water content as well as the increase in amount of oxygen into the system, thus exposing more pyrite to oxidation. The second important difference is the lower fluoride concentration in the tailings pore water compared to the operational phase. This is due to the increase amounts of fluoride that are added to the tailings pore water, thus causing the supersaturation of the mineral fluorite, which then precipitates and buffers the pore water fluoride concentration to 1.1 mg.l<sup>-1</sup>. Fluoride is undersaturated in the operational phase, hence the elevated fluoride concentrations.

# 6.2.1.2.2 Overburden

The operational and post-operational scenarios for the overburden facility are similar. The main reason for this is the similar water content between the two scenarios. Unlike tailings facilities, which receive material in the form of slurry, overburden is generally deposited as is, in the dry state. Therefore from a geochemical point of view, the operational and post-operational scenarios can be viewed as equivalent.

# 6.2.2 Environmental geochemical risks

Although the hydrogeological aspects are outside the scope of this study, a few comments are made to contextualise the geochemical results. The groundwater aquifer contained in the



dolomites is not only a potential transport medium for potential pollution, but should also be viewed as a sensitive receptor from a groundwater use perspective. Dolomite aquifers generally have uncontaminated water due to the buffering capacity provided by the carbonate minerals, chiefly dolomite and calcite, which compose the host rocks of the aquifer. Therefore every precaution should be taken to ensure the sustainability of this resource.

From this perspective sulphate and fluoride should be considered as likely contaminants from specifically the tailings facility in the operational and post-operational phases. Even though fluoride concentrations are shown to be comparable to the upper values of the baseline distribution, only two values in the 2016 hydrocensus exceeded SANS drinking water standards. The fluoride concentrations in the post-operational phase in the tailings pore water is buffered by the precipitation of fluorite and is therefore not considered a post-closure concern. Both of these occur in the project area, indicating that these values are most likely associated with the fluorspar ore body. The tailings facility has thus the potential of extending these elevated values to areas beyond the ore body due to hydrostatic pressure.

The geochemical modelling indicated that the risk of the development of acid mine drainage conditions and the contamination of local soil and water sources with metals and metalloids is insignificant.

The model does not take nitrate content into account, which results from blasting with ammonium nitrate based explosives. If this type of explosive is to be used in the mining process, nitrate should be included as a potential contaminant.



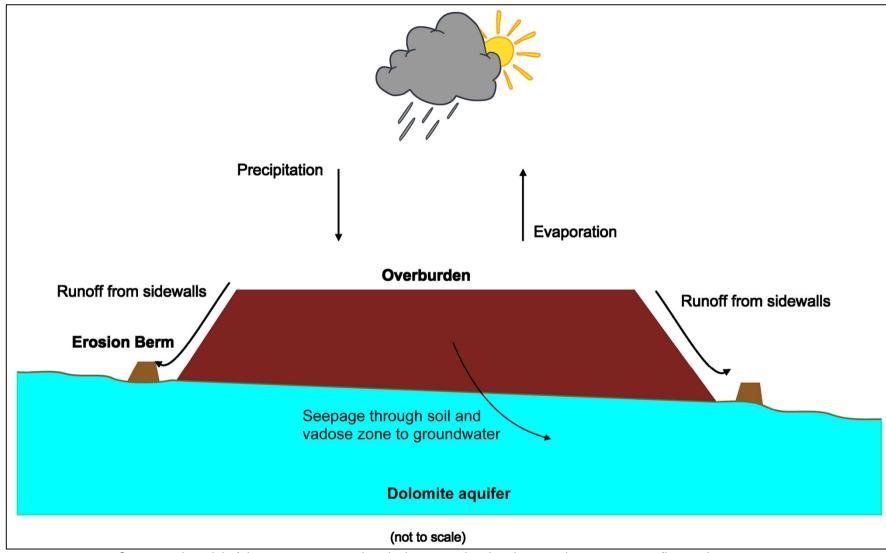


Figure 6-2 Conceptual model of the waste as a geochemical system showing the most important water flow paths



Table 6-1 Model results for the three geochemical zones in the tailings facility in relation to the waste classification LCT0 values as well as historic and calculated 95% confidence level value for the operational phase

Parameter	Abbreviation	Units	Waste classification LCT0	Previous Baseline Estimate (Exigo 2014)	2016 Hydrosensus Baseline	Oxidation Zone	Transition Zone	Reduction Zone
			Value	Value	Value	Value	Value	Value
pН	рH	pH units	n.r.v. <sup>5</sup>	8	8.5	6.38	6.38	6.38
Total Dissolved Solids	TDS	mg.l <sup>-1</sup>	1 000	759	501	2 161	2 165	2 166
Alkalinity	Alkalinity	mg CaCO₃.「¹	n.r.v.	504	396	640	640	640
Calcium	Ca	$mg.ℓ^{-1}$	n.r.v.	116	86	477	480	480
Magnesium	Mg	mg.ℓ <sup>-1</sup>	n.r.v.	67	54	22	22	22
Bicarbonate	HCO <sub>3</sub>	mg.ℓ <sup>-1</sup>	n.r.v.	413	483	781	781	781
Sulphate	SO <sub>4</sub>	mg.ℓ <sup>-1</sup>	250	130	95	880	880	880
Fluoride	F	mg.ℓ <sup>-1</sup>	2.0	2.2	1.8	0.9	1.8	2.7
Arsenic	As	μg.ℓ <sup>-1</sup>	10	b.d. <sup>6</sup>	b.d.	< 1	< 1	< 1
Manganese	Mn	μg.ℓ <sup>-1</sup>	500	997	1 277	< 1	< 1	< 1
Cadmium	Cd	μg.ℓ <sup>-1</sup>	3	b.d.	b.d.	< 1	< 1	< 1
Copper	Cu	μg.ℓ <sup>-1</sup>	2 000	b.d.	b.d.	< 1	< 1	< 1

<sup>&</sup>lt;sup>5</sup> n.r.v. is "no regulatory value".

<sup>&</sup>lt;sup>6</sup> b.d. is "below detection".



Table 6-2 Model results for the overburden leachate facility in relation to the waste classification LCT0 values as well as historic and calculated 95% confidence level value of the operational and post-operational phases

Parameter	Abbreviation	Units	Waste classification LCT0	Previous Baseline Estimate (Exigo 2014) Value	2016 Hydrosensus Baseline Value	Overburden Value
pH	рH	pH units	n.r.v.	8	8.5	6.5
Total Dissolved Solids	TDS	pri units mg.ℓ⁻¹	1 000	759	501	994
Alkalinity	Alkalinity	mg CaCO₃.ℓ⁻¹	n.r.v.	504	396	494
Calcium	Ca	$mg.ℓ^{-1}$	n.r.v.	116	86	375
Magnesium	Mg	mg.ℓ <sup>-1</sup>	n.r.v.	67	54	14
Bicarbonate	HCO <sub>3</sub>	mg.ℓ <sup>-1</sup>	n.r.v.	413	483	603
Sulphate	SO <sub>4</sub>	mg.ℓ <sup>-1</sup>	250	130	95	< 1
Fluoride	F	mg.ℓ <sup>-1</sup>	2	2.2	1.8	1.7
Arsenic	As	μg.ℓ <sup>-1</sup>	10	b.d.	b.d.	< 1
Manganese	Mn	μg.ℓ <sup>-1</sup>	500	997	1 277	< 1
Cadmium	Cd	μg.ℓ <sup>-1</sup>	3	b.d.	b.d.	< 1
Copper	Cu	μg.ℓ <sup>-1</sup>	2 000	b.d.	b.d.	< 1



Table 6-3 Model results for the three geochemical zones in the tailings facility in relation to the waste classification LCT0 values as well as historic and calculated 95% confidence level value for the operational phase

	Post-operational Phase											
Parameter	Abbreviation	Units	Waste classification LCT0	Previous Baseline Estimate	2016 Hydrosensus Baseline	Oxidation Zone	Transition Zone	Reduction Zone				
			Value	Value	Value	Value	Value	Value				
pH	рН	pH units	n.r.v.	8	8.5	6.11	6.113	6.113				
<b>Total Dissolved Solids</b>	TDS	mg. ℓ <sup>-1</sup>	1 000	759	501	3 756	3 756	3 757				
Alkalinity	Alkalinity	mg CaCO3.I-1	n.r.v.	504	396	1 216	1 216	1 216				
Calcium	Ca	mg. ℓ <sup>-1</sup>	n.r.v.	116	86	763	764	765				
Magnesium	Mg	mg. ℓ <sup>-1</sup>	n.r.v.	67	54	38	38	38				
Bicarbonate	НСО₃	mg. ℓ <sup>-1</sup>	n.r.v.	413	483	1 484	1 483	1 483				
Sulphate	SO <sub>4</sub>	mg. ℓ <sup>-1</sup>	250	130	95	1 470	1 470	1 470				
Fluoride	F	mg. ℓ <sup>-1</sup>	2.0	2.2	1.8	1.1	1.1	1.1				
Arsenic	As	μg. ℓ <sup>-1</sup>	10	b.d.	b.d.	< 1	< 1	< 1				
Manganese	Mn	μg. ℓ <sup>-1</sup>	500	997	1 277	< 1	< 1	< 1				
Cadmium	Cd	μg. ℓ <sup>-1</sup>	3	b.d.	b.d.	< 1	< 1	< 1				
Copper	Cu	μg.ℓ <sup>-1</sup>	2 000	b.d.	b.d.	< 1	< 1	< 1				



# 7 CONLCUSIONS

The following conclusion can be made:

- The risk for the development of acid mine drainage conditions for all geological mine waste, i.e. tailings and overburden, is insignificant. The laboratory data has shown that the tailings and overburden contains > 50 times as much acid neutralising capacity as acid producing capacity.
- The risk for the contamination of soil, surface water and groundwater resources by metals and metalloids from all geological mine waste, i.e. tailings and overburden, is insignificant.
- 3. The contamination of groundwater by fluoride and sulphate from the tailings material in the operational phase is significant and mitigation measures should be implemented as the dolomite groundwater is a sensitive receptor.
- 4. The contamination of groundwater by sulphate from the tailings material in the post-operational phase is significant and mitigation measures should be implemented as the dolomite groundwater is a sensitive receptor.
- 5. The contamination of groundwater by fluoride from the tailings material in the postoperational phase is insignificant and fluoride contamination in the post-operational phase is not considered a risk to groundwater resources.
- 6. The tailings classifies as a Type 3, i.e. low risk, waste.
- 7. The overburden classifies as a Type 3, i.e. low risk waste. However, the numeric geochemical model, which evaluates the behaviour of the overburden in the medium to long term in the operational and post-operational phases, has indicated that the material does not pose a significant risk to the local environment.
- 8. If ammonium nitrate based explosive products are to be used in the mining prosess, then nitrate needs to be included as a potential groundwater and surface water contamination risk.

# 8 RECOMMENDATIONS

The following recommendations are made:

1. Although the tailings and overburden material classifies as Type 3, i.e. low risk, waste and thus according to NEMWAA Regulation 635 and 636 a Type C barrier system, this mitigation measure has been shown in other studies to not be a sustainable option. The recommendation is thus made that the barrier system should only be considered if more sustainable mitigation options cannot be identified and implemented. Some options are the capturing of the plume by the open pit (this option will need to be evaluated in the hydrogeological specialist study) or bioremediation through specific tree species or capping of the tailings post-closure to ensure minimal influx of oxygen to specifically the oxidation zone of the tailings.



- Although the overburden material classifies as Type 3, i.e. low risk, waste, the
  recommendation is made to downgrade the material to Type 4, i.e. inert, due to
  insignificant geochemical risks posed to the local environment, including sensitive
  receptors.
- A monthly monitoring protocol should be implemented and fluoride and sulphate included in the parameters analysed. Any contamination concerns should be flagged and addressed.
- 4. Nitrate should be included in the monthly monitoring protocol if ammonium nitrate based explosives are to be used in the mining process.
- 5. An annual comprehensive analysis should be included in the monitoring protocol and any contamination concerns flagged and addressed.
- 6. If the ore processing methodologies should change, the geochemical models will need to be updated to take these changes into consideration.



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# 10 APPENDIX - MODEL SETUP AND EVALUATION

# 10.1 Model parametrisation

The existing laboratory data was used as input values for the numeric geochemical models, including the mineral concentrations as well as the concentrations of the potential contaminants. Distilled water was used as the initial water flux to the tailings and overburden systems. The maximum oxygen content was fixed at a fugacity of 0.21, which is the atmospheric value.

# 10.2 Assumptions

The precautionary principle, enshrined in NEMA was used as a guiding principle where any assumptions needed to be made. The following assumptions are made for the modelling purposes:

- The maximum oxygen fugacity was assumed to be 0.21, which is the atmospheric value.
   This assumption is deemed reasonable, as there is no reason to assume that the concentration will be higher as both the tailings and overburden facilities are open to the atmosphere.
- The tailings facility is assumed to be composed of three geochemical zones. This
  assumption is deemed reasonable, as many peer reviewed literature studies, e.g. Dold
  and Fontboté, 2001; Hansen, 2015, indicate that this is the case for sulphide-bearing
  tailings facilities.
- 3. Pyrite oxidation by oxygen was assumed to be the dominant reaction mechanism. This is due to the pH buffering effect of the overly abundant carbonate minerals, which preclude the solubility of ferric iron in solution.
- 4. The water-rock ratio was assumed to be 1:1. This is due to the fact that during the operational phase the tailings facility particles will be coated with a layer of water for the bulk of the tailings facility. This scenario is expected to change in the post-operational phase.

# 10.3 Sensitivity analysis

A sensitivity analysis is the process of determining how changes in model input values and assumptions (including boundaries and model functional form) affect the model outputs. The model was found to be sensitive to the following parameters:

- Pyrite reaction rate. The reaction rate law of Williamson and Rimstidt (1994) was used to
  model the pyrite oxidation reaction. It has been established that laboratory reaction rates
  are up to three orders of magnitude faster than natural rates. Therefore although the
  model is shown to be sensitive to the pyrite oxidation rate, the rate law used renders the
  reaction rate conservative.
- 2. Fluorite reaction rate. The fluorite reaction rate was calibrated using the maximum fluoride values from the historic baseline data and the recent (2016) hydrocensus. This is



deemed reasonable, as the dissolution of calcium fluorite is not dependent on the oxygen content. Some sensitivity of the fluorite reaction rate to pH fluctuations have been demonstrated in laboratory studies, however, the pH is buffered in the Doornhoek tailings and overburden systems.

# 10.4 Model limitations

The geochemical models were developed for the Doornhoek geological mine waste systems and should therefore not be applied to other fluorspar ore deposits and associated geological mine waste. Each ore deposit is unique from a geological and therefore also from an environmental geochemical perspective.

The models were developed for the current ore processing methods. If this should change, the geochemical models will need to be updated to take these changes into consideration.