Remediation options for wind-remobilised Pb-Zn old tailings: An example from an 80-year Pb-Zn-Ag mine in NW-Argentina

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Abstract

This article describes remediation options for wind-remobilised old tailings at an 81-year Pb-Zn-Ag mine in NW-Argentina. Long-term exposure of the dry surface of the older impoundments to wind led to spread of tailings over 2.5km². Scoping-level geochemical characterisation included grain-size analysis, ICP-MS whole-rock geochemistry, XRD mineralogy, ABA and SPLP tests, and sequential extraction. Results suggested that high Pb-Zn contents are restricted to remobilised waste material and no leaching to the underlying soil occurred. Thus, the thickness was the driving factor to define remediation options. For sectors with up to 0.3m (22%), excavation and mobilisation was suggested. For thicknesses between 0.3 and 0.6m (78%), re-vegetation without impermeabilization was considered the best option. For in-situ old tailings (0.1km²), surface impermeabilization and re-vegetation was strongly suggested.

Keywords: Pb-Zn tailings | wind remobilisation | scoping-level study | remediation options

Introduction

Pb-Zn-Ag mining has an over 80-year history at Mina El Aguilar in Jujuy province, NW-Argentina, where more than 20Mt ore has been processed since 1936. Tailings have been disposed in seven impoundments covering 5km². Most of the exposed surface of the older impoundments has been covered and remediation tasks are ongoing. Long-term exposure of the dry surface of the older impoundments to strong wind has led to remobilisation of tailings with deposition in dunes and layers spread over 2.5km². Only the most recent TSF is lined, in line with current international standards internally adopted by the company and progressively being required by regulators. Progressive closure of the old TSFs started in 2006 by means of geophysics and drilling surveys to determine thickness and material type for remediation purposes. Closure of the two major old TFSs 4 and 5 (≈70% of the TFS area) consisted of a low-permeability cover underlying a layer of soil for revegetation. These closure tasks were concluded in 2014. The same remediation method was planned to be applied for TFS 6 once construction of TFS 7 was complete in 2015/16.

At the starting time for operation at Mina El Aguilar and further decades, virtually no environmental standards were applied and tailings were normally disposed over the natural soil and were not covered after their lifespan. As part of the measures taken by the new owner to upgrade the operation to international environmental standards, a remediation program was undertaken. The challenge was not only to eradicate or minimise health and safety risks, but to optimise the expenditure in terms of environmental conservation and protection.

SRK was commissioned to undertake a scoping-level study for the remediation of the areas covered by remobilized old tailing. The

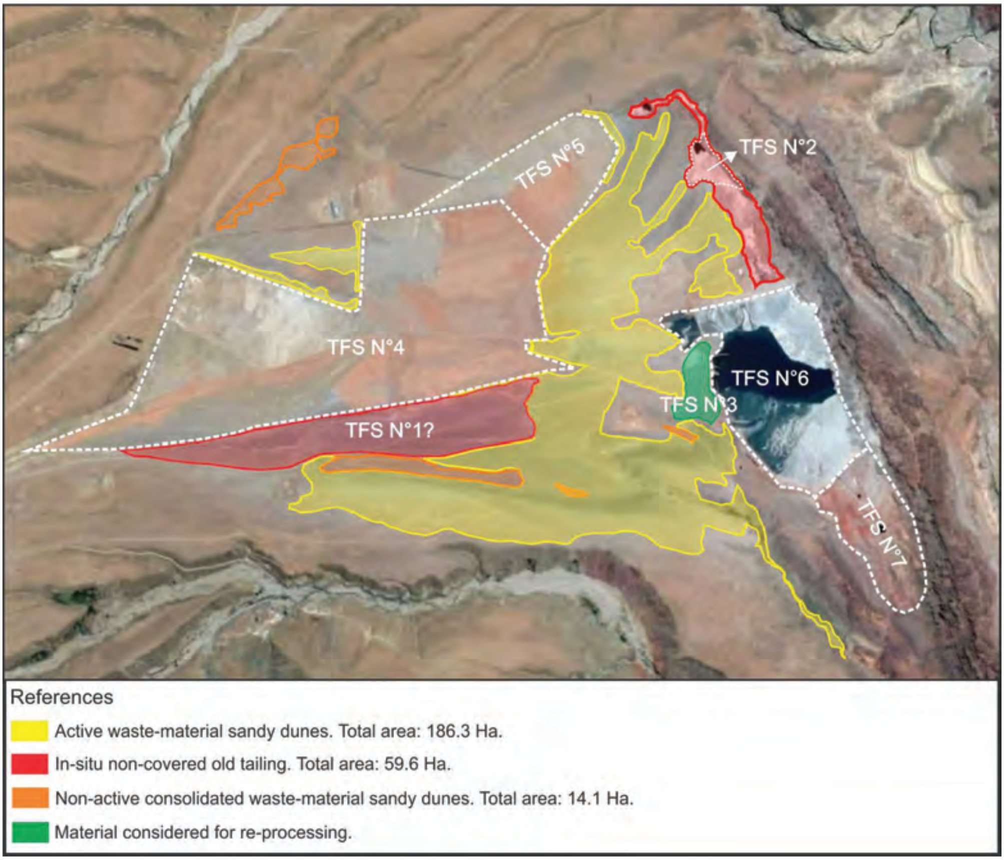

Figure 1 *Main lithotypes for wind-remobilized tailings.*

study included an initial geochemical characterization of the waste material, estimation of the volume of each waste-material category and recommendations for conceptual remediation options.

Project background

The region of Mina El Aguilar is characterized by arid climate, scarce rainfall, (<300mm a year) and strong wind most part of the year. The TFSs and wind-remobilized tailings area is composed of fossil alluvial fans where virtually no drainage network is present. These alluvial deposits end against an outcrop called "Espinazo del Diablo", mainly composed of Cretaceous/Tertiary sandstones and shales. Average alluvial sediments thickness in the study area is between 30 and 50m and they are mainly composed of conglomerates with a red-coloured matrix formed by silt/clay and minor sand.

Five groundwater monitoring wells were installed in the TFSs area and surroundings until 2013 (Ausenco-Vector, 2013), three of which are located in the study area itself. The water level measured during the drilling campaign at these two wells was 33 and 50m below surface. Hydraulic testing at these wells yielded hydraulic conductivity values between 10^{-7} and 10^{-9} m/s for the hosting sedimentary aquifers, suggesting low permeability. Physic-chemical analyses were performed on water samples collected in three wells. Groundwater is neutral to slightly alkaline (pH 7-8) and electrical conductivity suggests fresh water in the periphery (EC 850-1,500 µS/cm) and brackish (EC up to 4,000 µS/cm) in the central area. However, further hydrogeological studies are required to distinguish different aquifers. Metals such as Pb, Zn, Cd, Fe, Mn and Cu are below maximum limits for drinking water (DR N° 5980/06, Government of Jujuy Province, Argentina) and frequently below detection limits (LODs). This suggests

***Figure 2** (a) Active waste-material sandy dunes; (b) Non-active waste-material sandy dunes; (c) In-situ old tailings.*

that metals possibly leached from overlying TFSs and remobilized tailings might be retained in the waste material itself and/or the pre-mining sediments. However, further sampling and static/kinetic geochemical testing together with further data from hydrochemical monitoring is necessary to assess chemical leaching from sediments to groundwater.

SRK distinguished three main types of remobilized waste material (Figure 1).

Active sandy dunes (ASD) are the most widespread waste material cover an area of 1.86 km^2 and are composed of fine and medium-grained grey-coloured sand with no cementation. Non-active sandy dunes (NASD) are present in relatively small patches which cover 0.14 km^2 all together. This material is characterized by fine and medium-grained dark grey sand slightly cemented and more stabilized against wind. In-situ old tailings (IOT) possibly corresponding to the oldest TFSs were identified immediately southwards from TFS 4 and to the northwest of the study area, covering a total area of 0.6 km^2. This material is composed of strongly cemented layered fine sediments partially covered by aeolian sand. TFS 3 was found to host economic Ag, Pb and Zn contents and is being considered for reprocessing. Examples for the mentioned lithologies are shown in Figure 2.

Methods

The owner carried out the first sampling campaign in 2012 which consisted of 90 samples from 30 sampling soil pits, where sediments were collected each 0.3m for whole rock chemical analyses. Results showed that the highest Pb, Zn and Cd total contents occur in the upper sediments, although no relationship between chemistry and lithology was assessed. For this reason, SRK carried out a complementary sampling at a scoping level.

18 new soil pits were excavated to sample the identified lithologies in surface and up to about 1.5 m. Material types were first distinguished and 3 to 5 samples were collected from each pit according to the described lithotypes. Special care was taken to avoid sample contamination of pre-mining sediments from the overlying waste material. 63 new samples were collected to perform the following static geochemical tests:

- Whole-rock chemistry: 63 analyses by the ICP-MA-39 method. Maximum LODs were 10,000 ppm for Pb, Zn and As and 2,000 for Cd.
- X-Ray diffractometry: 23 samples without previous heavy mineral separation.
- Acid-Base Accounting (ABA): 12 samples to assess overall acid rock drainage (ARD) potential from disulfides, including pH-paste tests. The modified ABA test (Lawrence and Wang, 1997) was preferred.
- Synthetic Precipitation Leaching Procedure (SPLP): 13 samples to assess short-term metal mobility.
- Sequential extraction: 9 samples to assess metal speciation. The method designed by Renella et al. (2004) was used to assess Cd speciation, which consists of a preliminary step of sample exposure to ammonium nitrate to optimize separation of Cd-bearing soluble species.

Additionally, thickness of the waste-material was measured in 229 points to assess volume estimation of each lithotype for engineering purposes.

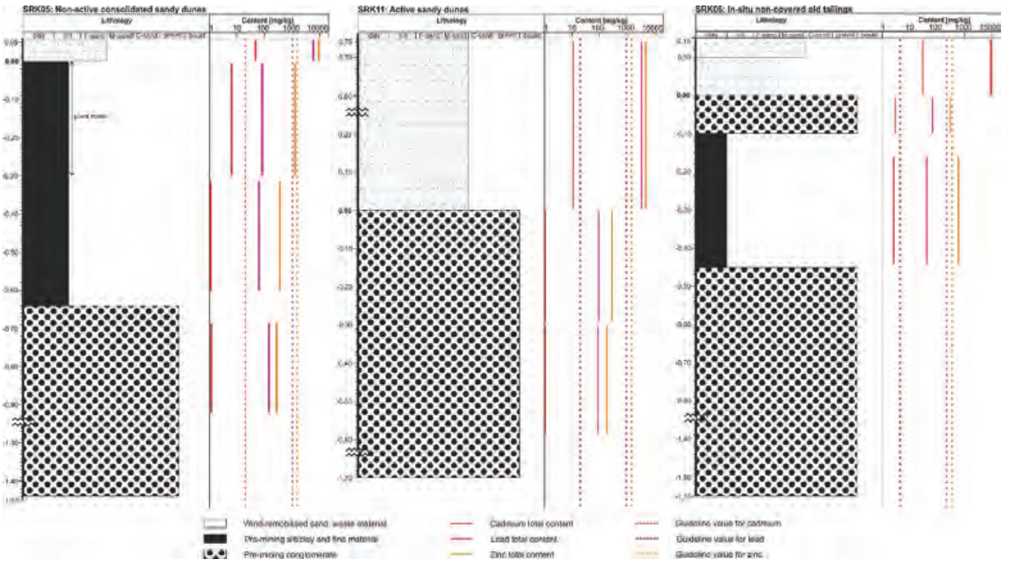

Figure 3 *Chosen examples to represent NASD, ASD and IOT-type waste material sites.*

Results

Figure 3 shows one typical example representing each waste-material type and the total Zn, Pb, Cd contents sampled in depth and related to lithology. As no baseline control limits are available, maximum reference limits based on the guidelines (DR N° 5980/06, Government of Jujuy Province, Argentina) for industrial use of soil for Zn (15,000 ppm), Pb (10,000 ppm) and Cd (30ppm) are also plotted in Figure 3. Whole-rock chemistry showed that high total contents of Zn, Pb and Cd are restricted to the waste material in the ASD (pit SRK11), suggesting poor to virtually absent leaching to the underlying PMS. In the typical example of NASD (pit SRK05), high contents in the mentioned metals exceeding the reference values are also restricted to the waste material. However still high Zn concentrations were measured up to 30cm depth, suggesting leaching of this metal at shallow depths. The example representing the IOT sites (pit SRK06) shows high contents in Zn, Pb and Cd in the tailing material although Zn is virtually exceeding its reference value until 0.5 m depth, suggesting relatively strong leaching of this metal to the underlying PMS.

A summary of results for each lithotype is shown in Table 1, which includes Zn, Pb and Cd total contents, total vs sulphide S and neutralization vs acid potential (NP/AP) from ABA testing. Pre-mining underlying sediments and paleo-soils (PMS) are added to Table 1 for comparison with the waste material. Overall, Zn, Pb and Cd total contents in the waste material are much higher than those in the PMS. The PMS are richer in Zn, Pb and Cd only in the close vicinity of

Table 1 *Summary of results for total contents, ratios and ABA testing.*

Lithotype	St	S2-/St	Zn	Pb	Cd	NP/AP	pH-paste
ASD	2.02 to 2.91	0.71 to 0.91	3,341 to >10,000	2,031 to >10,000	13 to 55	0.01 to 0.70	7.0 to 7.8
NASD	2.33	0.68	9,164 to >10,000	4,166 to 6,561	27 to 44	1.04	7.2
IOT	1.98 to 6.67	0.55 to 0.70	4,337 to >10,000	3,398 to >10,000	163 to 361	0.01 to 1.27	7.2 to 7.8
PMS	N/A	N/A	40 to 2,546	17 to 299	<1 to 13	N/A	6.0 to 7.8

the IOT, specially that one possibly related to an ancient TFS (TFS 1?). Among the waste-material lithotypes, the IOT are the highest in total S although it generally in the oxidized form as the total-S/sulphide-S tend to be relatively low. The neutralization potential ratio (NP/AP) is very low in the waste material (0.01 to 1.27), which combined with the sulphide S contents (>1%) would classify this material as potentially acid producing. However, this result show inconsistency with high paste-pH values (7.0 to 7.8), suggesting that either sulphide S is somehow encapsulated or speciated in monosulfides that do not produce ARD when oxydized (e.g. galena, sphalerite). Unfortunately, NAG testing was not performed to assess directly acid producing by disulphide rapid oxidation due to tight budget and schedule. NAG testing is strongly recommended for a forthcoming PFS level of remediation engineering.

The most abundant minerals identified by X-Ray diffractometry were quartz, muscovite, plagioclase, K-feldspar and gypsum. Chlorite is frequent in the NASD whereas dickite and muscovite are more frequent in the ASD. The most frequent sulphide is sphalerite and galena was not detected in this sample batch, which possibly requires a previous separation from light minerals. A Pb-carbonate was identified as shannonite in the ASD, which forms in strongly oxidized environments from further oxidation of cerussite. However, further mineralogical studies should be performed to identify Pb and Zn carbonates and sulphates that might be present in the waste material.

Results from SPLP testing showed concentrations below the maximum limits of the method for the majority of the analysed material. Waste material collected from the NASD resulted in 1.098 mg/L for Cd and 5.141 mg/L for Zn in the leachates, strongly exceeding the respective limits of 0.03 and 0.084 mg/L. The sample representing the IOT showed even stronger exceedances in the produced leachate, containing 4.108 mg/L of Cd and 6.251 mg/L of Zn.

The total accumulated concentration of metals released in the four stages of the chosen sequential extraction methodology (Renella et al., 2004) is difficult to check against total contents for QC purposes, as the maximum LOD of ICP-MA-39 is 10,000 mg/L for Zn and Pb. Overall, 40-65% of the Pb content is released in the first stage of soluble exchangeable cations. Contrastingly, very high Pb contents are released in the second stage when Fe-Mn oxi-hydroxides are attacked. An even higher proportion (around 75%) is released in the third stage when sulphides and sulfosalts are attacked, suggesting that Pb is speciated in these reduced minerals and might be released in oxidizing conditions. Geochemical kinetic tests simultaneous with mineralogical studies should be performed to assess metals speciation and release into solution. Very high Zn contents were released in the first step of soluble cation exchange. Cd was not extracted during the previous exposure to ammonium nitrate at pH 3 and 7, suggesting that it is not speciated in calcium carbonate. The sample representing the IOT released about 80% of Cd during the third stage (secondary sulphides) although this metal also shows positive correlation with Zn.

Discussion

Results from static geochemical studies and mineralogical assessment were conclusive enough to perform a preliminary classification of the wind-remobilized waste material. These results together with detailed lithological mapping and thickness measurement allowed for a scoping-level assessment on remediation options based on geochemical characterization and volume estimation of each lithotype. The three waste-material types shown Zn, Pb and Cd contents much higher than the underlying pre-mining sediments. However, the IOT released these metals in exceedance during the short-term leaching tests, suggesting that important metal release is highly possible during long-term leaching in natural conditions, despite of the dry climate at the study area. Indeed, the underlying pre-mining sediments were affected by release of metals (mainly Zn) from the overlying IOT until at least 0.5 depth. Thus, characteristics and volumes for the studied waste materials can be summarized as follows:

- Active sandy dunes: 619,797 m^3 distributed in 1.86 km^2. Metal leaching potential is considered to be low. About 30-50 samples to complete static geochemical characterization at a PFS level. 3 to 5 samples necessary for kinetic testing.

- Non-active sandy dunes: 15, 129 m^3 distributed on 0.14 km^2. Metal leaching potential is low to medium, the latter especially in the vicinity of in-situ old tailings. About 20-30 samples to complete static geochemistry al PFS level. 3 to 5 samples to perform kinetic testing.
- In-situ old tailings: 264,506 m^3 distributed in 0.60 km^2. Metal leaching potential is considered to be high and short-term with enough rainfall. About 25-40 samples to complete static geochemistry at a PFS level. 8-10 samples for kinetic testing.

Conclusion

At a conceptual level, only economic factors were considered for the ASD as they are not geochemically reactive. Given their small area and volume, as well as their low to medium leaching potential the NASD were incorporated to the ASD until further studied are performed. Thus, the thickness was the driving factor to define conceptual remediation options for the both mentioned units. For sectors with up to 0.3m (22%), excavation and mobilisation was suggested. For thicknesses between 0.3 and 0.6m (78%), re-vegetation without impermeabilization was considered the best option. For in-situ old tailings (0.60km^2), surface impermeabilization and re-vegetation was strongly suggested, regardless the thickness of these deposits. To upgrade the level of this study to PFS or higher, further geochemical assessment consisting of volumetrically representative sampling for static tests to complete waste-material characterization and kinetic testing running at least 40 weeks to assess chemical reactivity are recommended.

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