

# Waste Management in the Scope of a Gold Mine Project

Vila, M. C.<sup>1,2,\*</sup>, Fernandes, A.<sup>1</sup>, Dinis, M. L.<sup>1,2</sup>, Futuro, A.<sup>1,2</sup> and Fiúza, A.<sup>1,2</sup>

<sup>1</sup>University of Porto- Faculty of Engineering, Porto, Portugal

<sup>2</sup>CERENA, Department of Mining Engineering, University of Porto, Porto, Portugal

\*corresponding author:

e-mail: mvila@fe.up.pt

## Abstract

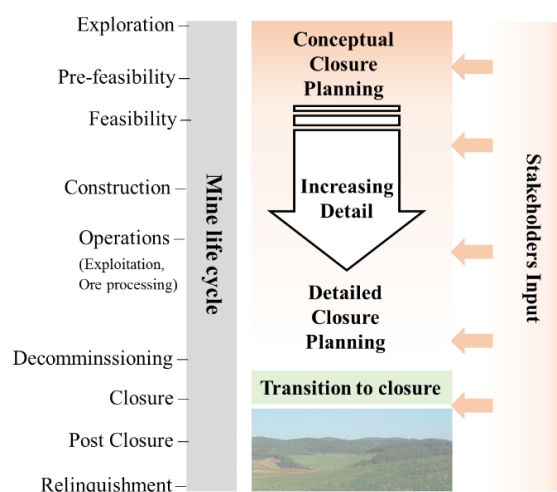
In mining industry, waste management is a key issue since it starts in the conceptual project phase and lasts beyond the mine closure. Tailings and rock wastes have gained such an environmental importance that the *a priori* definition of its management has been caused the unfeasibility of promising mining projects, such as the case of the Castromil gold mine project presented in this work. Located in the NW part of Portugal, the Castromil Au-Ag deposit was intermittently exploited since Phoenician and Roman times until 1940's. In 1990's Castromil area attracted several exploration programs, having in 2000 been rejected due to environmental concerns the last application for an exploitation license. In this study, a strategy is tested in order to avoid or reduce the acid drainage using an acid consuming waste "dregs" from a pulp and paper industry. The residues resulting from laboratory metallurgical tests of technical feasibility, were subjected to several static and dynamic tests of forecast of acidic drainage and evaluate the efficiency of co-disposal of the dregs with the mine tailings such as Net Acid Generation test (NAG), Net Acid Production Potential test (NAPP) and leach column tests.

**Keywords:** Gold mine wastes, tailings, Acid Mine Drainage, Net Acid Generation, Net Acid Production Potential.

## 1. Introduction

The definition of tailings disposal is a key aspect in the environmental impact statement. This becomes more significant in the case of gold mining projects of small capacity, short life and low grade ore where it is more feasible to produce a gold concentrate than to produce metallic bars of gold. Tailings disposal and management are dynamical issues in all mine life cycle since its pre-feasibility stage until mine's post-closure as illustrated in figure 1. This concerns with mine wastes and tailings throughout the mine life cycle justifies the need of research into increasingly accurate tests capable of predicting its long-term effects. One of the prevailing problems caused by mine wastes and tailings is Acid Mine Drainage (AMD). The production of AMD has long been recognized to occur at mine sites from various materials. Mining produces large amounts of waste rock with remaining metal contents too low to economically recover. When sulphides are present in waste rock, AMD can be produced

due to sulphide oxidation, causing the acidification of local hydric resources and consequently the dissolution of heavy metals.



**Figure 1.** The different phases of mine life cycle along which the concerns with tailings are present.

This group of minerals is present, in significant percentages in practically all mines, not only in sulphide ores, but also in the host rock associated with most types of mining activity. One of the most common and studied sulphide mineral is pyrite ( $\text{FeS}_2$ ) that in a resumed balance, each mole of pyrite is capable of producing four protons. The reaction rate is affected by several factors, such as particle size (Erguler, 2015), presence of bacteria, oxygen availability and weather conditions (Nordstrom, 2009). Although not yet standardized mainly due to the intrinsic heterogeneities of mineral wastes, two types of tests to assess AMD are established. The static tests consisting in the quantification of possible generated acidity, while dynamical tests permit a qualitative analysis of the acid formation, simulating the field conditions. The results of these acid generation capacity evaluation should be interpreted by comparing the static NAG tests with the dynamical ones and whenever possible with the real scale observed results in order to accurate the predictions on how harmful to the environment the gold mine project will be. In the search of sustainable solutions, the mixture of alkaline by-products from other industries, such as ash

from coal power plants or dregs from paper pulp industry, with mining tailings becomes an interesting solution, when both acid and alkaline producing wastes are near located. In the present work, dregs from a paper pulp plant were studied envisaging the co-disposal with the Castromil gold mine tailings.

## 2. Materials and Methods

### 2.1. Studied samples

Two mineral samples from Castromil gold deposit with AMD potential were used. Castromil deposit is located within Hercynian granite on the eastern side of Valongo anticline, characterized by the occurrence of reduced and oxidized sulphides and iron oxides, pyrite, chalcopyrite, pyrrhotite, goethite, gold, galena and quartz. Sample A, resulted from lab scale hydrometallurgical experiments while sample B is the raw material before any processing test. Dregs are residues, classified according to the European List of Waste as 03 03 02 “green liquor sludge from recovery of cooking”, and originated in a paper manufacturing company located in Viana do Castelo (less than 80 km away from Castromil). All the samples were submitted to chemical analysis, organic carbon content, and moisture as well as particle size determinations.

### 2.2 Equipment

Chemical analysis were performed in the X-ray Fluorescence (XRF) spectrophotometer Innov-X Alpha 4000 S, using the mode to read light and heavy elements. Carbon concentration of samples was measured using a TOC-VCSH combined with the solid sample module (SSM) from Shimadzu. This equipment measures the concentration of total carbon (TC) and inorganic carbon (IC), allowing to determine the concentration of total organic carbon (TOC) by difference of the measured values. The particle size distribution of the Castromil tailings samples was carried out in two stages: the coarser fraction was analyzed by sieving, the finer fraction was determined using a laser granulometer Malvern Mastersizer 2000, where the particle size distribution of dregs was also analyzed. Castromil samples (A and B) were submitted to static and dynamic acid prediction tests in different dregs addition configurations (0% - 40% Dregs Mixture Ratio - DMR).

### 2.3 Net Acid Generation tests

Net Acid Generation (NAG) tests allow to quantify acidity that a sample can produce through oxidation of the minerals (Weber, 2005-a). In this test 2.5 grams of pulverized sample are placed in a goblet filled with 250 ml of hydrogen peroxide 15%, reacting overnight to oxidize the minerals. After the reaction, the sample is heated for 2 hours or until reaction is complete to remove the remaining H<sub>2</sub>O<sub>2</sub> and to release the neutralizing particles (Stewart, 2006). The solution temperature is lowered to the room temperature then is rinsed with distilled water to achieve the initial volume. The pH of the solution is measured (NAG pH) then it is titrated with NaOH until pH 4.5 then to pH 7. If the final pH is higher than 7 the test is finished, revealing that the sample does not generate acidity. During the titration to pH 4.5 it is neutralized the acidity produced by the free acid and soluble iron and aluminum, while

between 4.5 and 7 are precipitated metallic ions in the form of hydroxides (Smart, 2002). The NAG is calculated in kg H<sub>2</sub>SO<sub>4</sub>/t. Through NAG value it is possible to quantify the balance between acid production and neutralization since both effects are counted during NAG tests, and even the NAG tests only quantify samples that have a positive balance. Only the NAG pH is used to compare to other ARD prediction tests. In certain cases a NAG test it is not enough to oxidize all the minerals present in the sample, originating an underestimation of the produced acidity (Stewart, 2006). To oxidize completely is applied sequential NAG, this tests consists in doing a normal NAG test, titrating only until pH 4.5 to avoid the precipitation of hydroxides. After titration the solid phase is filtrated then it is made a new complete NAG test. This process can be repeated over and over again until the NAG value is zero in the last stage (Stewart, 2006; Chotpantararat, 2011).

### 2.4 Net Acid Production Potential

Net Acid Production Potential (NAPP) is obtain by the difference of the following experiments: Maximum Potential Acidity (MPA) expressing only the acidity that a sample can produce in kg H<sub>2</sub>SO<sub>4</sub>/t, and Acid Neutralizing Capacity (ANC), that expresses total acid neutralization inherent to a sample in the same units. In contrast to NAG tests, NAPP tests allow to quantify the acid base-accounting (ABA) even for non-acid samples since the determination of each is made in separated tests. The MPA is determined by assuming that all the sulphur contained in a sample is acid forming. The ANC can be determined by several methods (Weber, 2005-b; Weber, 2004), for this study it was applied the Lawrence (Mills, 2017) and Modified Sobek variants (Smart, 2002). In the ANC Lawrence 2 grams of sample are placed in a flask and emerged with 90 ml of distilled water and 2 drops of 25% HCl, then is agitated for 2 hours where it is added more acid according to table 1. After 22 hours of agitation if the pH it is above 2.5 it should be added more acid, then agitated for more 2 hours. If the pH is below 2 the test should be repeated using less acid. After the digestion the solution is rinsed with distilled water until a total volume of 125 ml, then is titrated with NaOH until pH 8.3, the quantities of added acid and base are used to calculate the ANC according to equation (1).

$$ANC = \frac{(N_{HCl}V_{HCl} - N_{NaOH}V_{NaOH})}{W} \cdot 49 \quad (1)$$

Where N is the normality (mol/l), V the volume (ml) and W the weight of the sample in grams. In the determination of ANC modified Sobek the quantity of added acid is determined by the same way of Lawrence, however the quantities are distinct (Table 1). In this test 2 grams of sample are submerged in 20 ml of distilled water and HCl according to the fizz rating, then is heated for 1 to 2 hours with intermittent agitation. After the solution reaches room temperature it is added distilled water until a total volume of 125 ml, then the solution is titrated with NaOH until pH 5, at this point it is added 2 drops of H<sub>2</sub>O<sub>2</sub> (30%) to oxidize siderite completely (Skousen, 1997), then the titration is made until pH 7, allowing to calculate the ANC through equation (1).

**Table 1.** ANC Lawrence and Modified Sobek fizza rating

Lawrence		Mofidied Sobek			
Reaction	Volume of 1.0N HCl (mL)		Reaction	N (mol/L)	V (mL)
	At time =0 h	At time =2 h	No Reaction	0.5	4
None	1.0	1.0	Slight Reaction	0.5	8
Slight	2.0	1.0	Moderate Reaction	0.5	20
Slight	2.0	2.0	Strong Reaction	0.5	40
Strong	3.0	2.0	Very strong reaction	1	40

**2.5 Column tests**

In column tests the sample is percolated by distilled water for 5 successive days. The resulting leachate is analyzed. For this study the pH and total carbon were considered the most important parameters. Since the distilled water pH in the installations varied between 6 and 7 the leachates of the percolate indicate AMD if it's pH is below the range. The concentration of carbon was measured particularly for the columns with sample B mixed with dregs to track if part of the dregs dissolved into the leachate. In column tests 200 grams of sample were placed in a column with an internal diameter of 4.3 cm and a height of 43 cm. Each day it was added 200 ml of distilled water that percolated the sample during one hour, using a peristaltic pump to control the percolation velocity. After the percolation which can be called as a humidity cycle it was made a dryness cycle, by injecting compressed air from the top then through the bottom of the column in order to dry the sample and promote the contact of oxygen to oxidize the sample forcing the AMD.

**3. Results**

**3.1. Samples properties**

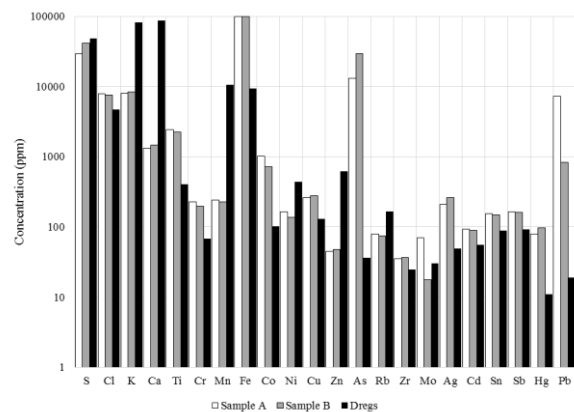
Due to the nature of dregs the concentration of carbon is high, since cellulose's main element is carbon, justifying the high concentration of organic carbon, the inorganic carbon is mainly in the form of carbonates (Table 2). Castromil samples (A and B) showed a low concentration of inorganic carbon which is explicable due to their mineral nature.

**Table 2.** Concentration of organic and inorganic carbon for samples A, B and dregs

	Organic Carbon (ppm)	Inorganic Carbon (ppm)
Sample A	8394	171
Sample B	1180	182
Dregs	336037	32998

Sample A and B present a similar chemical composition (Figure 2), having both an iron concentration higher than 10% and a great arsenic concentration since arsenopyrite is

one of the major minerals, responsible for the local contaminations (Silva, 2004).



**Figure 2.** Chemical composition of Samples A, B and dregs.

Sulphur is one of the major elements in all the samples, resulting in their capacity to generate acidity. Besides dregs have a higher concentration of sulphur part of it is in the form of sulphate, so only 11% of the total sulphur in dregs is capable to generate acidity. The concentration of calcium is high due to the characteristic concentration of carbonates in dregs. The results of the particle size analysis (Table 3) showed the sample A to be coarser, followed by sample B and finally composed of very fine particles are the dregs.

**Table 3.** Particle size characterization for samples A, B and dregs

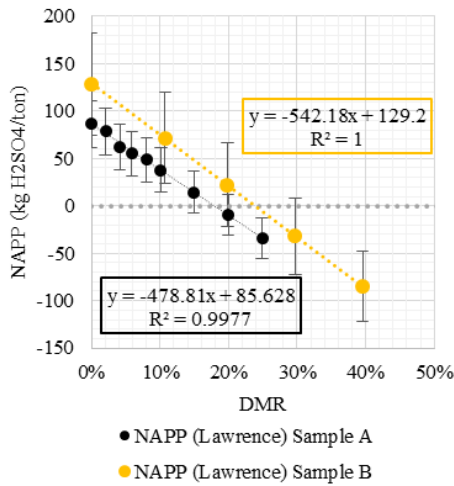
	d <sub>10</sub> (µm)	d <sub>50</sub> (µm)	d <sub>90</sub> (µm)
Sample A	76.2	453.0	833.7
Sample B	17.5	267.9	796.9
Dregs	25.5	134.6	487.2

**3.2. Acid generation prediction tests**

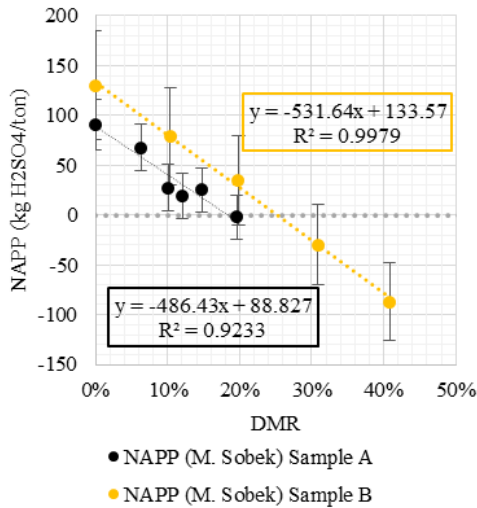
According to the NAG tests, a DMR of 4.6% and 12.3% it is enough to neutralize samples A and B acidity, respectively, considering a pH 4.5. NAG pH is higher as the DMR increases, but near pH 10 the changes are not significant. Unexpectedly the NAG value did not varied linearly with the variation of the DMR, in contrast to the NAPP results. Since it was suspected that in single NAG tests the oxidation of the mixtures was not complete. Besides sequential NAG tests are only applied to samples that reveal strong acidity in the first stage, this test was applied for the mixtures that did not indicated acid generation to verify if the mine wastes would release acidity in a second stage (Table 4). The NAPP calculation resulted in a linear variation with the DMR (Figures 3 and 4). The error bars have high values, due to the XRF poor precision, the maximum imprecision for the ANC tests was below 0.1% while for MPA it was higher since the sulphur concentration error was 30% for XRF measurements.

**Table 4.** Sequential NAG results (\* units are kg of H<sub>2</sub>SO<sub>4</sub>/t)

DMR %	Stage 1		Stage 2		
	NAG pH	NAG pH 4.5 *	NAG pH	NAG pH 4.5 *	NAG pH 7 *
16.4	8.61	0	2.23	28.12	35.51
18.0	9.10	0	2.36	23.79	30.36



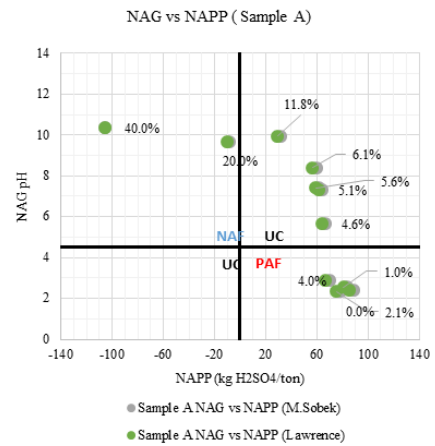
**Figure 3.** Lawrence NAPP results.



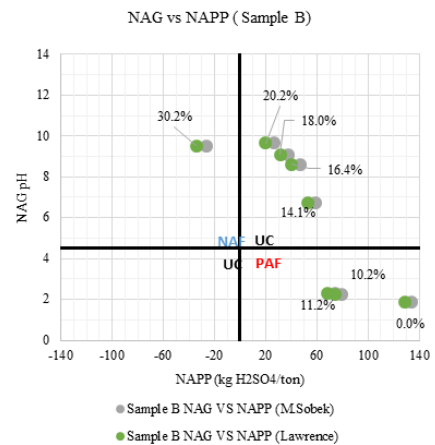
**Figure 4.** Sobek NAPP results.

Compared to NAG, NAPP results indicate that a higher concentration of dregs is necessary to neutralize the samples acidity. In the ANC tests the mixtures reacted completely, resulting in the expected linear variation, except for sample A through the Modified Sobek method. The two variants of the ANC test resulted in similar values, although the Modified Sobek variant indicates a lower ANC since the application of hydrogen peroxide oxidizes sulphides that were counted in the MPA, resulting in a

higher NAPP. For sample A the DMR that neutralizes the formed acidity it is 17.9% and 18.3% through Lawrence and Modified Sobek variants respectively, while for sample B is 23.8% and 25.1%. Since NAG tests do not quantify non-acid generative samples it is common to use NAG pH values to compare with NAPP (Stewart, 2006). This comparison allows to classify the data points as Non Acid Forming (NAF), Potentially Acid Forming (PAF) and Uncertain (UC) (Smart, 2002). Samples with a NAG pH below 4.5 and a positive NAPP are classified as PAF since both tests reveal acid generation, contrarily a pH above 4.5 and a negative NAPP are classified as PAF. If both test results are controversial they are classified as UC. Samples located in the lower left quadrant normally have a high concentration of organic carbon, leading to a NAG overestimation, while samples located in the upper right quadrant have a possible underestimation of the non-sulphide sulphur. For some DMR used in the NAG tests it was calculated the NAPP, according to the calculated linear variations (Figures 5 and 6). It can be stated that for sample A, a DMR between 4.6% and 11.8% conducts to an uncertain acid production, while for sample B the uncertain acid production domain leads to a DMR between 14.1% and 20.2%.



**Figure 5.** NAG vs NAPP for sample A with different dregs mixture ratios (DMR in %).



**Figure 6.** NAG vs NAPP for sample B with different dregs mixture ratios (DMR in %).

### 3.3. Column percolation tests

The percolation in column tests indicated that sample A does not generate acidity, since the pH was high, besides the static tests revealed that the sample is acid. Sample B revealed acidity in the percolation in column tests, so the column tests with sample B mixed with dregs could reveal which is the DMR that would lead to a pH between 6 and 7 (Figure 7). Comparing the results obtained in the acid generation prediction tests with that obtained in column tests, it is verified there is lack of uniformity in these tests. It is not possible to infer the results of one from the results of the other.

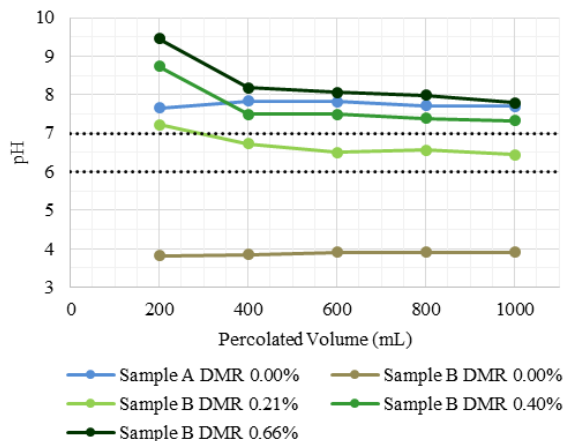


Figure 7. Leachates pH obtained in column tests.

## 4. Conclusions

The application of NAG procedures for the tested mixtures showed that single NAG it is not the most indicated since the dregs effect overcome the potential acid production of the mine wastes. While NAPP results showed a linear variation and close results which is preferable than NAG. For ANC Modified Sobek the tracking of released sulphur with the addition of hydrogen peroxide would be a useful technique to detect the released acidity from oxidized sulphides. Compared to the NAPP results, the percolation in column showed a lower DMR to neutralize the mine waste, since NAPP results show the effect of complete reaction, while percolation in column shows possible produced leachates in a short period of time, remaining most part of the acid potential in the sample.

## Acknowledgments

This work was a part of the project supported by the Portuguese National Funding Agency for Science, Research and Technology (FCT), "Tools for sustainable gold mining in EU (SUSMIN)", <http://projects.gtk.fi/susmin>, Reference ERA-MIN/0002/2013 Network on the Industrial Handling of Raw Materials for European Industries (ERA-MIN). The authors are grateful to the Europac Group for the supply of wastes from the pulp paper industry.

## References

- Chotpantararat, S. (2011), A Review of Static Tests and Recent Studies, *American Journal of Applied Sciences*, 8 (4), 400–406.
- Erguler, Z. A. and Erguler, G. K. (2015), The effect of particle size on acid mine drainage generation: Kinetic column tests, *Miner. Eng.*, **76**, 154–167.
- Mills, C., Acid Base Accounting (ABA) Procedures, <http://technology.infomine.com/enviromine/ard/acid-base%20accounting/acidbase.htm#Lawrence%20Sobek>, accessed in March, 2017.
- Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L., and Ziemkiewicz, P. (1997), Neutralization potential of over burden samples containing siderite, *J. Environ. Qual.*, **26**, 673–681.
- Silva, E. F., Zhang, C., Serrano Pinto, L., Patinha, C., and Reis, P. (2004), Hazard assessment on arsenic and lead in soils of Castromil gold mining area, Portugal, *Appl. Geochemistry*, **19** (6), 887–898.
- Smart, R., Skinner, B., Levay, G., Gerson, A., Thomas, J., Sobobieraj, H., Schumann, R., Weisener, C., Weber, P., Miller, S. and Stewart, W. (2002), ARD test handbook: Project P387A prediction and kinetic control of acid mine drainage, *Proj. P387A, Predict. Kinet. Control acid mine Drain*, **May**, 42–42.
- Stewart, W., Miller, S., Smart, R., Gerson, A., Thomas, J., Skinner, W., Levay, G. and Schumann, R. (2003), Evaluation of the Net Acid Generation ( NAG ) Test for Assessing the Acid Generating Capacity of Sulfide Minerals, Sixth International Conference on Acid Rock Drainage (ICARD), **July**, 12–18.
- Stewart, W. A., Miller, S. D. and Smart, R. (2006), Advances in Acid Rock Drainage (ARD) Characterisation of Mine Wastes, 7th Int. Conf. Acid Rock Drain. 2006, ICARD, **3**, 2098–2119.
- Weber, P. A., Stewart, W.A., Skinner, W. M., Weisener, C. G., Thomas, J. E. and Smart, R. S. C. (2004) Geochemical effects of oxidation products and frambooidal pyrite oxidation in acid mine drainage prediction techniques, *Appl. Geochemistry*, **19** (12), 1953–1974.
- Weber, P. A., Thomas, J. E., Skinner, W. M. and Smart, R. S. C. (2005-a) Calculated acid-base balance for H<sub>2</sub>O<sub>2</sub> oxidation of carbonate-poor pyritic mine-rock, *Can. Mineral.*, **43** (4), 1193–1203.
- Weber, P. A., Thomas, J. E., Skinner, W. M. and Smart, R. S. C. (2005-b) A methodology to determine the acid-neutralization capacity of rock samples, *Can. Mineral.*, **43**, (4), 1183–1192.