TECHNICAL COMMUNICATION



A Comparison Between Kinetic Test Results and Natural Weathering: The Abandoned Kettara Mine Tailings Pond

K. El Amari¹ · M. Hibti¹

Received: 10 July 2019 / Accepted: 30 October 2019 / Published online: 6 December 2019 © Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

More than three million tons of sulfide tailings were discarded without any protection for more than 36 years at the since-abandoned Kettara mine. The impact of these tailings as well as the coarse wastes disorderly dumped on the surface site is highlighted by the elevated sulfate levels in the wells downstream of the wastes. Kinetic tests carried out on these sulfide tailings over 10 years ago, showed similar trends in metal dissolution despite large difference in test duration (21 and 53 weeks for the weathering and humidity cell tests, respectively). 40% of the sulfate release occurred in the first 3 weeks of the humidity test. However, in this study, the elevated sulfate levels in the groundwater was shown not be linked to the tailings, where the original sulfide material is still present under an oxidized layer of 10 cm–1.2 m. Thus, kinetic test results should not be extrapolated to field scale without accounting for site-specific factors, especially particle size and climate.

Keywords Acid mine drainage · Prediction · Simulation · Extrapolation

Introduction

Methods to predict the potential of acid generation are well known and largely described (Bouzahzah 2013; Chotpantarat 2011; Coastech Research Inc. 1991; Lapakko 2002; Price 2009; Sherlock 1995; U.S. EPA 1994). Static tests, which are short term and relatively inexpensive, give information on the theoretical balance between acid producing/neutralizing components of a waste sample and the mobility of potential contaminants. Kinetic tests, such as humidity cells, are also commonly used, and are complementary to static tests. They simulate natural and accelerated weathering of mine tailings under controlled conditions. They are used when static tests do not clearly identify the tailings as acid generating or not and provide information on the long term rate of acid generation, contaminant release, leachate quality, and depending on the test conditions, secondary minerals precipitation phenomena. Tests can take weeks to years and the choice of when to terminate the test is relatively arbitrary (Bowell

Humidity cell tests (HCT) operating conditions differ from field conditions (Sapsford and Williams 2005). The potential for a mine to generate AMD depends on site-specific factors as water, oxygen, bacteria, mineralogy, particle size, permeability, physical weathering characteristics, and hydrology (Pat-Espadas et al. 2018). HCTs do not directly simulate field conditions (Barnes et al. 2015) and the challenge is how to use their data in predictive geochemical models (Sunkavalli 2014).

At the Kettara mine in Morocco, the exploited ore was mainly pyrrhotite. The sulfide ore ($\approx 20\%$ S) was extracted to produce sulfuric acid, which was used in Moroccan phosphate ore leaching. The ore was crushed to 0–15 mm, and processed by gravimetric separation (jig) to produce a concentrate of 32% S with an efficiency of 65% by weight and 85% sulfur recovery (Panorama de l'Industrie Minière 1990). Mining ceased in 1982, leaving about three million tons of pyrrhotite-bearing sulfide tailings (El Amari et al.



et al. 2006): tests are typically stopped when the average release stabilizes. ASTM D5744-96, reapproved in 2001, recommends a minimum of 20 weeks. Some authors refer to conflicting results obtained from the same sample, depending on the type of kinetic test (e.g. Bouzahzah 2013). Kinetic tests are more affected by sulfide and secondary mineralogy, grain size, and length of exposure to aeration than static tests (Bowell et al. 2006).

Georesources Laboratory-CNRST (URAC42), Department of Earth Sciences, Faculty of Science and Technology Guéliz, Cadi Ayyad University, Abdelkarim ElKhattabi Avenue, Guéliz, P.O. Box 549, 4000 Marrakech, Morocco

2014) exposed. The structure of the tailings pond has been interpreted by geophysical methods, which showed a depth variation of 2–8 m (Lghoul et al. 2012).

The Kettara mine tailings are a real example of field-scale sulfide weathering. Static and humidity cell tests were conducted on the tailings and compared to weathering results, as was done by Hornberger and Brady (1998). The study showed that kinetic tests have to be amended to account for the climatology of the mine site and the final solid waste that will be discarded, especially the grain size, as mentioned by Lappako (2002).

Methodology

To our knowledge, no AMD prediction tests were done on the Kettara tailings pond prior to or during mining. However, in 2008, two kinetic test methods (humidity and weathering cells) were carried out with the goal of rehabilitating the mine site. In this study, we took advantage of the existence of these full-scale mining wastes to assess the effectiveness of those kinetic tests. The current tailings pond of the Kettara mine (photo a) can be considered as a reference "kinetic field test" that has been going on for more than 36 years, allowing field observations to be compared to the predictive



Fig. 1 The land surface variably coloured by secondary minerals

Table 1 Results of X-ray diffraction analysis of collected samples from the Kettara mine site

Sample	Identified minerals
Primary sulfides	Pyrrhotite, pyrite, chalcopyrite
Sulfide tailings	Quartz, clinochlore, pyrrhotite, talc
Secondary minerals	Goethite, hematite, heulandite, natrojarosite, halotrichite, melanterite, copiapite, jarosite, rozenite, hydroniumjarosite, gypsum, talc, muscovite



test results (Hakkou et al. 2008a, b). This paper focuses on the production or release of sulfate ions.

Results

The current state of the abandoned mine's solid wastes, variously colored and covering about 37 ha, is evidence of the oxidation of the initially black-gray sulfides (Fig. 1). Furthermore the stagnant acid water (pH of 2.8) on the site contains metals: Cu; 16.8 mg/L, Zn; 7 mg/L, Fe; 27.4 mg/L, and Cr; 7.7 mg/L. Pyrrhotite and pyrite are the main sulfides in the material (El Amari et al. 2014; Hakkou et al. 2008a). The various secondary minerals (Table 1) coming from sulfide dissolution are the source of the colored surface wastes (El Amari et al. 2014). Thanks to the arid climate, they trap sulfate ions as well as the other chemical elements, reducing the potential of groundwater pollution.

The potential acid generation of the Kettara sulfide tailings was confirmed by static tests carried out on samples of 0.8-13.6% sulfur and d_{80} of 13-95 µm with an acid potential (AP) of 91–453 kg CaCO₃/t (Hakkou et al. 2008a). Weathering and humidity cell tests were also used to predict their potential for AMD and to estimate the mineral reaction rates and depletion (Hakkou et al. 2008b). These tests were carried out for 21 and 53 weeks, respectively, in accordance with ASTM D5744-96 (1998), Morin and Hutt (1997), and SRK (1989). The general trend of metal dissolution was essentially similar for both methods and the authors suggested that these tailings would continue to release acidity and sulfate for a long time. The sulfate production rate obtained by the humidity cell tests were very high (2000–8000 mg SO₄/kg/ week) during the first weeks and then dropped to 78-600 mg SO₄/kg/week after 9 weeks (Hakkou et al. 2008b). After three cycles, 40% of the original amount of sulfur had been released. However, sulfate depletion rates were higher for the weathering cell tests. Hakkou et al. (2008b) interpreted the drop in the sulfate release rate to coating of the sulfide surfaces by secondary mineral precipitation.

A rehabilitation project (Hakkou et al. 2008a) was undertaken, initially based on these results and from tests carried out on coarse tailing piles on the site surface. Environmental impact studies on soils and groundwater demonstrated the contamination of waters downstream of the mining wastes,

especially by sulfate ions. But they linked the pollution to the site lithology, wastewaters of the village of Kettara, located upstream of the more sulfate polluted wells and which contain up to 1739 mg/L (El Amari et al. 2014; Moyé et al. 2017; Toughzaoui et al. 2015; Zouhri et al. 2019), and the coarse waste piles disorderly dumped on the surface site, but not the tailings. The tailings, in their current state, cannot be considered a groundwater pollution source because if one compares the field observations to the kinetic test results, one can see that:

 40% of sulfate release obtained after three cycles of humidity cell test does not agree with reality. Indeed, tailings exposed to atmospheric conditions since 1982 show a thin layer of oxidized material (typically 10 to 20 cm thick, though it can be up to 1.2 m), based on 10

- recent deep trenches, under which the material is pasty, suggesting that it keeps its original moisture (Fig. 2).
- The altered layer is thinnest where the tailings are also thinnest due to an impermeable hardpan, which creates rainwater puddles, pending evaporation. The layer is thickest where secondary mineralization (efflorescence) causes swelling of the old tailings pond surface. This limits the alteration to less than 1.2 m (Fig. 2). This variation in the thickness of the oxidized layer could be linked to grain size distribution, which affects oxygen access to the sulfide minerals.
- The limited oxidation layer on the top of the tailings pond is evidence that the AMD does not percolate. Superficial AMD generation is subjected to dissolution—re-precipitation of secondary minerals, paced by rainfall episodes. This observation does not comply with the depletion of

Fig. 2 a Tailings pond with the locations of the trenches shown; b, c unoxidized sulfide tailings under 10 and 20 cm of impermeable hardpan; d unoxidized sulfide tailings under swollen surface; e the tailings pond surface (hardpan and swollen)





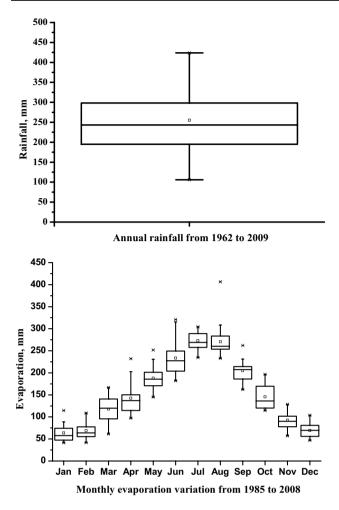


Fig. 3 Annual rainfall and evaporation near Kettara (recorded at the LallaTakerkoust meteorological station)

- reactive minerals and/or their passivation by the secondary phase coating observed in the humidity cell tests.
- The kinetic tests results did not simulate the natural world because grain size distribution of the material was not considered. The kinetics of solid leaching depends on the grain size and this dependence is more accentuated in the real world, where permeability can limit oxygen diffusion and leaching solution percolation. The material permeability in the kinetic tests was modified by adding sandy silica (Hakkou et al. 2008b).

The climate of the mining site is also a parameter to be considered: the mean annual rainfall of 250 mm and annual potential evaporation exceeding 2500 mm (Fig. 3) differ considerably from the conditions in which kinetic tests are carried out, where the climate cannot ensure a regular supply of water.

The supply of oxygen and water seem to be the two most important factors in humidity-cell testing protocol (Lapakko

2003). This is why scaling up the 2008 HCT data to field level by weight correction is not appropriate.

Conclusion

The three million tons of tailings of the Kettara mine that were disposed of in a tailings pond and abandoned without any protection for more than 36 years was an opportunity for researchers to compare humidity cell test results with reality. Kinetic tests, which have to be interpreted according to their operating conditions, can give information on the tailings reaction, release rates and depletion of sulfates and contaminants, and secondary mineral precipitation. They can provide valuable information on how to control AMD during and after the exploitation period. However, this study has demonstrated how it can be unrealistic to extrapolate kinetic test results to real world conditions without considering the processing method (grain size distribution, chemical and mineralogical compositions, etc.). Site climatology should also be considered.

Failing a good extrapolation and in view of the fact that the duration of kinetic tests is relatively arbitrary, extending them is not justified once one has the desired information.

References

ASTM (1998) Norm D 5744-96, Standard test method for accelerated weathering of solid materials using modified humidity cell. Ann Book ASTM Stand 11.04:259–271, ASTM International

Barnes A, Bowell R, Warrender R, Sapsford D, Sexsmith K, Charles J, Declercq J, Santonastaso M, Dey B (2015) Comparison between long-term humidity cell testing and static net acid generation (NAG) tests: potential for NAG use in preliminary mine site water quality predictions. Proc, 10th International Conf on Acid Rock Drainage (ICARD) & IMWA Annual Conf, pp 1–10

Bouzahzah (2013) Modification et amélioration des tests statistiques et cinétiques pour une prédiction fiable du drainage minier acide. Thesis, Univ du Québec en Abitibi-Témiscamingue [in French]

Bowell RJ, Sapsford DJ, Dey M, Williams KP (2006) Protocols affecting the reactivity of mine waste during laboratory—based kinetic tests. Proc, 7th ICARD, pp 247–270

Chotpantarat S (2011) A review of static tests and recent studies. Am J Appl Sci 8(4):400–406

Coastech Research (1991) Acid Rock Drainage Prediction Manual. MEND Report, Project 1.16.1b, Natural Resources Canada

El Amari K, Valera P, Hibti M, Pretti S, Marcello A, Essarraj S (2014) Impact of Kettara mine tailings on surrounding soils and ground water. J Afr Earth Sci 100:437–449

Hakkou R, Benzaazoua M, Bussière B (2008a) Acid mine drainage at the abandoned Kettara Mine (Morocco): 1. Environmental characterization. Mine Water Environ 27:145–159

Hakkou R, Benzaazoua M, Bussière B (2008b) Acid mine drainage at the abandoned Kettara Mine (Morocco): 2. Mine waste geochemical behavior. Mine Water Environ 27:160–170

Hornberger RJ, Brady KBC (1998) Kinetic (leaching) tests for the prediction of mine drainage quality. In: Brady KBC, Smith MW, Schueck J (eds) Coal mine drainage prediction and pollution



- prevention in Pennsylvania. Dept of Environmental Protection, Harrisburg, PA
- Lapakko KA (2002) Metal Mine Rock and Waste Characterization Tools: An Overview. Mining, Minerals and Sustainable Development. N 67. Report, Mining, Mineral and Sustainable Development (MMSD)
- Lapakko K, A (2003) Development in humidity-cell tests and their application. In: Jambor JL, Blowes AIM DW, Ritchie (Eds), Environmental aspects of mine wastes, mineralogical assoc of Canada short course, vol 31, Ch 7
- Lghoul M, Teixidó T, Pena JA, Hakkou R, Kchikach A, Guérin R, Jaffal M, Zouhri L (2012) Electrical and seismic tomography used to image the structure of a tailings pond at the abandoned Kettara Mine, Morocco. Mine Water Environ 31:53–61
- Morin KA, Hutt NM (1997) Environmental geochemistry of mine site drainage: practical theory and case studies. MDAG Publ, Vancouver
- Moyé J, Picard-Lesteven T, Zouhri L, El Amari K, Hibti M, Benkaddour A (2017) Groundwater assessment and environmental impact in the abandoned mine of Kettara (Morocco). Environ Pollut 231:899–907
- Panorama de l'Industrie Minière (1990) Kettara Mine. Royaume du Maroc, Ministère de l'énergie et des Mines, Tome 2, pp 135–140 [in French]
- Pat-Espadas AM, Portales RL, Amabilis-Sosa LE, Gómez G, Vidal G (2018) Review of constructed wetlands for acid mine drainage treatment. Water 10:1685. https://doi.org/10.3390/w10111685

- Price WA (2009). Prediction manual for drainage chemistry from sulphidic geological materials. MEND Report, Natural Ressources Canada. 1.20.1
- Sapsford DJ, Williams KP (2005) Predominant chemical kinetics in laboratory prediction of ARD. Proc, 9th International Mine Water Association Congress, pp 57–65
- Sherlock EJ (1995) Evaluation of static and kinetic prediction test data and comparison with field monitoring data. Thesis, Univ of British Columbia
- Steffen, Robertson and Kristen (1989) Guide technique préliminaire sur le drainage rocheux acide, BC AMD Task Force, Centre de Recherches Minérales, Ouébec, vol 1 [in French]
- Sunkavalli SP (2014) Gap between humidity cell testing data and geochemical modeling of acid rock drainage. Hydrol Curr Res 5:1. https://doi.org/10.4172/2157-7587.1000e115
- Toughzaoui S, El Amari K, Benkaddour A, HibtiM Essarraj S (2015) Hydrogeochemical and isotopic studies of Kettara mine watershed, Morocco. Mine Water Environ 34(3):308–319. https://doi.org/10.1007/s10230-015-0326-8
- U.S. Environmental Protection Agency (1994) Acid Mine Drainage Prediction. Technical document. EPA 530-R-94-036, NTIS PB94-201829
- Zouhri L, El Amari K, Marier D, Benkeddour A, Hibti M (2019) Bacteriological and geochemical features of the groundwater resources: Kettara abandoned mine (Morocco). Environ Pollut 252:1698–1708

