Acid generation and heavy metal leachability from waste lignite disposal sites, Oropos basin, North Attica. An assessment on preliminary data.

Kampouroglou E.[1], Kollias K.[2], Arvaniti L.[1], Stouraiti C.[1,*], Papassiopi N.[2]

[1] Department of Geology and Geonvironment, Division of Geochemistry and Economic Geology, National and Kapodistrian University of Athens, Penepistimiopolis Zografou, GR 157 84, Greece
[2] Laboratory of Metallurgy, National Technical University of Athens, GR 157 80, Zografos, Greece

*corresponding author: e-mail: chstouraiti@geol.uoa.gr

Abstract
Lignite mining in the Oropos Neogene basin (North Attica), especially in the areas of Milesi and Markopoulo, operated since last century and ceased in the late 1960's. Piles of complex waste material consisting of lignite tailings and waste rocks are dispersed in the area between the above mentioned mining sites. Environmental characterization of waste piles is performed by applying leaching tests (EN12457, EN15875) as well as bulk geochemical analysis. Mineralogical study revealed that pyrite is the dominant sulfide phase in local wastes. The high sulfur content and low paste pH and Net Neutralization Potential, i.e. values < -20 $CaCO_3$ kg/t in most analyzed samples, all clearly indicate that the waste is prone to acid generation. The analysis of water leachates showed high concentrations in Ni, Zn and Cd, exceeding the EU regulatory limits for the non-hazardous wastes. The preliminary results suggest that the lignite waste pose a potential threat for ground water contamination close to the waste disposal fields due to acid generation and heavy metal mobilization from the lignite matrix or the waste rock.
Keywords: waste lignite, Acid-Base accounting, Nickel, Zinc, Oropos basin

1. Introduction

The Oropos basin was one of the most important lignite-bearing areas in Greece (Voreadis 1952). The existence of lignite in the area has been known since 1830. Initially, lignite was mined in open pits and then exploitation operated in underground galleries until 1966. Today, great amounts of waste from lignite mining activities are left in piles covered by soil, located in the areas of Milesi and Mavrosouvala (Stamatis et al., 2011; Alexakis and Gamvroula 2014).
The geological structure of the study area is dominated by the alpine basement formations and post-alpine lacustrine formations on top (Papanikolaou and Papanikolaou 2007). The lignite deposits in the area of Malakasa – Oropos appear on two characteristic horizons, of which the lower one is in contact or slightly above the pre-Neogene basement and the upper one develops 70 - 80 m higher than the first, within the marls horizons (Mettos, 1992).

Available data from literature indicate that worldwide lignite mine waste are a suspect source for acid mine drainage and heavy metal pollution of the surrounding land however, no systematic geochemical data exist for this type of waste in the study area. This preliminary research aims to determine: a) the bulk chemical and mineralogical composition of the waste, b) the leachability and mobility of heavy metals and the acid generation potential of the waste piles by applying European regulatory tests.

Table 1. Concentrations of potentially toxic elements, total organic carbon-TOC and paste pH of the bulk lignite spoil material (n=8 samples) and water leachate composition according to EN12457-2 standard.

element	Pseudo-total (AR)*	L/S 10:1	Regulatory limits (2003/33/EC) H	Non-H
	(mg/kg)			
As	110 – 190	0.5	25	2
Cr	150 – 4680	4.6	70	10
Cd	3 – 7	1.4	5	1
Co	100 – 1420	121	-	-
Ni	230 – 25575	18	40	10
Zn	70 – 1655	137	200	50
Pb	250 – 1495	0.1	50	10
S (wt%)	3.5 – 10.6			
SO_4 (wt%)	1 – 6.3	3750	50000	20000
TOC (wt%)	13		6	5
paste pH	2.7 – 5.8			6

H: hazardous; Non-H: non-hazardous waste; (AR)*- Aqua Regia digestion, analysis by ICP-MS

2. Results and Discussion

Paste pH of the waste ranges from 2.9 to 5.8 and this parameter correlates with the high total sulfur and the pyrite content of the samples (Table 1). Measurements of total organic carbon (TOC) i.e. 13 wt% mean value, exceeds by far the limit of 6 wt% for hazardous waste disposal, according to 2003/33/EC Decision. This is

expected since the waste material is composed mainly by lignite tailings and lesser amounts of soil/waste rock.

Static tests were performed in an attempt to predict the acid generation from the lignite tailings from the areas. The results of the ABA tests are shown graphically in Figure 1. The interpretation of the ABA test results is based both Net Neutralization Potential - NNP and Neutralization Potential Ratio-NPR (NP/AP ratio). This approach is followed since not a single measurement can be definitive in determination of potentially acid generating material, according to the European static method standard (EN 15875). Net Neutralization Potential values range from -8.5 to -387 kg $CaCO_3$/t and most of the samples show values below -20 kg $CaCO_3$/t, that is the limit value for potential acid generating wastes. The NPR values range from -0.01 to 1.69 and the majority are <1 confirming that the waste is characterized as acid generating.

In order to predict water quality drained from the waste piles the EN12457-2 test method was applied and the composition of the water leachates are presented in Table 1, together with the regulatory limits of this test. Water leachates show high concentrations in Ni, Zn and Cd which exceed the European regulatory limits for the non-hazardous wastes but still below the limits for hazardous wastes.

Statistical analysis of bulk waste compositions (XRF analysis) shows a strong positive correlation for Co-Ni, Ni-Zn-Cu and As-Sr. These correlations provide further indication for the mineralogical control of the element distribution: Co and Ni in the lignite can be attributed to the contribution of ultramafic rock masses surrounding the basin. The elements As and Sr can be attributed to the sedimentary (marly) formation of the local bedrock which host the lignite beds. The Ni- and -Cu correlation in lignite wastes can be associated to detrital minerals including oxides and serpentine-group minerals as well as mixed-layer clays (Iordanidis et al. 2001).

The ABA results showed that lignite-rich waste samples have high risks of producing acid upon oxidation. The low pH values of the samples indicate that the abandoned waste piles may pose potential threat for groundwater contamination around the lignite waste disposal fields due to localized increased metal mobility.

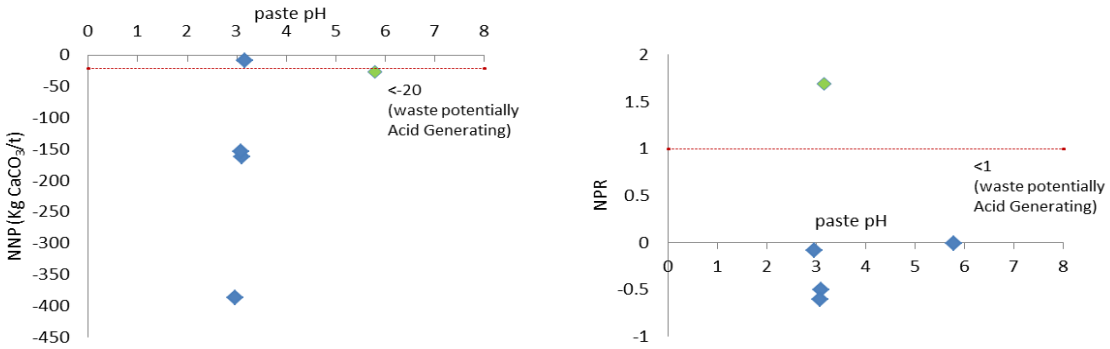

Figure 1. Paste pH *versus* NNP (left) and NPR values (right) of representative samples from the lignite waste piles, Oropos basin.

References

Alexakis D., Gamvroula D. (2014), Arsenic, Chromium, and Other Potentially Toxic Elements in the Rocks and Sediments of Oropos-Kalamos Basin, Attica, Greece. Applied and Environmental Soil Science Volume 2014, doi.org/10.1155/2014/718534.

Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC (L11/27)

EN 12457-2 (2002), "Characterization of waste – Leaching – Compliance test for leaching of granular waste material and sludge – Part 2. European Committee for Standardization.

EN 15875 (2011), Characterization of waste - Static test for determination of acid potential and neutralisation potential of sulfidic waste.

Iordanidis A., Georgakopoulos A., Filippidis A., Kassoli-Fournaraki A. (2001), A Correlation Study of Trace Elements in Lignite and Fly Ash Generated in a Power Station. International Journal of Environmental Analytical Chemistry 79, 2, 133-141, DOI: 10.1080/03067310108035905

Mettos, A. (1992), Geological and paleogeographical study of the continental Neogene and Quaternary formations of NE Attica and SE Boeotia. PhD thesis, National and Kapodistrian University of Athens, Greece, (in Greek).

Papanikolaou D., Papanikolaou I. (2007), Geological, geomorphological and tectonic structure of the NE Attica and seismic hazard implications for the northern edge of the Athens plain. Bulletin of the Geological Society of Greece 40, 425–438.

Stamatis G., Alexakis D., Gamvroula D, Migiros, G. (2011), Groundwater quality assessment in Oropos–Kalamos basin, Attica, Greece. Environ. Earth Sci., 64, 973–988. DOI 10.1007/s12665-011-0914-2

Voreadis G. (1952). The Tertiary lignite-bearing basin of Malakasa-Oropos. *Geol. Geophy. Research*, IGEY, **2**,141-180.