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Environmental assessment and management of Phosphogypsum according to European and United States of America regulations

Francisco Macías[a,1], Rafael Pérez-López[a], Carlos R. Cánovas[a], Sergio Carrero[a], Pablo Cruz-Hernandez[a]

[a]*Geology Department, University of Huelva, Campus "El Carmen", E-21071 Huelva, Spain*

Abstract

Waste derived from fertilizer production has been accumulated worldwide for decades, especially during the last century. This waste is mainly formed by phosphogypsum; a mixture of gypsum along with phosphates, fluorides, and organic matter, which are generated from phosphoric acid production. Phosphogypsum deposits are usually associated with an important load of radionuclides and metals. The present study aims to evaluate and compare the hazard derived from the metals leaching with phosphogypsum deposits located in areas under US and European environmental regulations. Archived samples from Mulberry (USA) and field samples from Huelva (Spain) deposits have been characterized by leaching tests, as outlined in the aforementioned regulations. The obtained results have been collated with EN 12457-2 from the European regulation and TCLP from the US EPA. As a result, Mulberry phosphogypsum was classified as non-hazardous by both regulations. Since the regulations differ on their strictness, only the European regulation classifies the Huelva deposit as hazardous for As and Cd, urging to have monitoring measurements; while the US regulation classifies the deposit as non-hazardous, even though a pre-treatment before depositing is recommended.

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* Corresponding author. Tel.: +34959219834; fax: +34959219810.
E-mail address: francisco.macias@dgeo.uhu.es

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1. Introduction

The phosphate fertilizer industry is basic to maintain the levels of farming production in developed countries, and even more when developing countries reach such production levels. The industrial raw material required for phosphate fertilizer production is phosphoric acid, 90% of which is currently obtained from the manufacturing process of phosphate rock by the "wet acid method"[1]. World phosphate rock production was around 225 Mt in 2014, and is expected to increase up to 258 Mt in 2018. In the same way, world consumption of P_2O_5 contained in fertilizers is projected to increase from 42.2 Mt in 2014 to 45.9 Mt in 2018[2]. The unwanted by-product of such fertilizer manufacturing is referred to as phosphogypsum (PG), which is mainly composed by gypsum and other minor small solid phases (e.g. phosphate, fluoride, feldspar, organic matter).

Most research on phosphogypsum stacks has been focused on radiochemistry impact (e.g.[3, 4]) rather than that caused by metals. In this sense, results of classification and characterization of PGs based on current legislations are not well known. In some cases, the criteria established in environmental regulations among countries can vary widely, which may lead to different waste management strategies at a worldwide scale. For this reason, the main aim of this research is to evaluate the environmental hazards and disposal management strategies of these wastes using leaching tests proposed by European and US environmental regulations. This work includes the results obtained after applying these tests to PGs collected in the stack of Huelva (Spain) and the data of Mostary (2011)[5] from the Mulberry PG stack (USA).

2. Huelva and Mulberry phosphogypsum

Phosphoric acid production in Huelva (Spain) since 1967 has deposited around 120 Mt of phosphogypsum directly on the marshes of the estuary of the Tinto River, less than 1 km from the city of Huelva. The Huelva PG stack is located within the tidal prism of the estuary without any type of isolation. This has caused the occurrence of abundant acidic and metal-rich edge outflows that directly discharge to the estuarine system[6]. This stack acts as an aquifer system, with clearly differentiated unsaturated (0-2 m) and saturated zones (from 2m to the bottom).

Phosphate mining in Florida (US) is one of the largest industries in the state, and produces approximately 40 Mt of PG per year[7], accounting for 14-40% of worldwide PG production. In this US state more than one billion tons of PG are in permanent storage in over 25 giant stacks, some of them up to 60 meters high and covering as many as 2 km^2 surface area each[7]; one of these giant stacks is the Mulberry PG[5].

3. Methods

Samples from the Huelva PG were collected from a bore-hole at different depths (0.48, 1.6, 2.9, 3.5, 4.15, 5.15, 6 and 7.1 m.), including the unsaturated and saturated zones (Table 1). The deepest sample (7.1 m) corresponds to the PG basement, directly in contact with the estuarine salt-marsh. Data from Mulberry PG were obtained from Mostari (2011)[5]; the samples were collected from four locations on the walls of the stack at different depths in the first 0.6 m. Samples collected from different depths for each location were thoroughly mixed to get a homogenous sample for that location, obtaining finally a total of 8 samples. This study includes the mean values obtained from these samples.

For the characterization of Huelva and Mulberry PGs, leaching tests proposed by the current European and US environmental regulations (i.e. EN 12457-2[8] and TCLP[9], respectively) have been applied to both wastes. These tests are used to: (1) classify the hazardousness of the waste based on the concentrations of various metals in the leachate, (2) identify whether a treatment prior landfill disposal is required (TCLP), and (3) discern the type of landfill that best meet the requirements for a safe disposal of the waste (EN 12457-2). The EN 12457-2 test was conducted by mixing waste with deionized water at a liquid-solid ratio of 10:1, followed by agitation of the mixture for 24 hours, filtration of the supernatant and determination of dissolved elements by ICP-AES and ICP-MS. The concentrations observed in the test were compared with the limit threshold values established by the European Council[10]. In the TCLP test the PGs were extracted with CH_3COOH (pH = 4.93) for 18 h by agitation on a shaker with a liquid-solid ratio of 20:1, following EPA method 1311[11]. After centrifugation, the supernatant was filtered, acidified with HNO_3 and kept refrigerated until analysis by ICP-AES and ICP-MS. Metal concentrations observed in the TCLP leachates

were compared with those established by the US Land Disposal Restrictions[12] which determines if a specific waste needs to be submitted to a universal treatment standard (UTS) for a safe disposal.

4. Results

Table 1 shows the upper threshold levels for waste acceptance at different landfill disposal sites (inert, non-hazardous and hazardous) according to European rules, and the results of the EN 12457-2 leaching test applied to the Huelva PG profile and the data consulted from Mulberry PG.

Table 1. Upper threshold levels for waste acceptance at landfills (council decision 2003/33/EC), and leached metals concentrations of Huelva and Mulberry PGs after EN 12457-2 test. Data in mg/kg.

Landfills for:	**As**	**Ba**	**Cd**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**	**SO_4**
Inert	0.5	20	0.04	0.5	2	0.5	0.4	0.5	0.06	0.1	4	6000
Non-hazardous	2	100	1	10	50	10	10	10	0.7	0.5	50	20000
Hazardous	25	300	5	70	100	30	40	50	5	7	200	50000
Huelva PG												
Depth(m)												
0.48 (No sat)	0.03	0.19	0.12	d.l.	0.03	0.04	0.09	d.l.	d.l.	0.06	0.31	13758.63
1.6 (No sat)	0.09	0.20	0.11	d.l.	0.04	0.05	0.10	0.02	d.l.	0.07	0.32	14067.45
2.9 (Sat)	4.24	0.29	0.35	0.22	0.78	0.02	0.43	0.13	0.03	0.02	2.63	15045.97
3.5 (Sat)	3.72	0.29	0.34	0.33	0.74	0.02	0.41	0.14	0.04	0.02	2.57	14799.06
4.15 (Sat)	3.47	0.35	0.38	0.39	1.52	0.02	0.48	0.17	0.05	0.02	2.57	16168.68
5.15 (Sat)	3.22	0.28	0.35	0.34	1.26	0.03	0.38	0.11	0.06	0.03	6.73	18082.20
6 (Sat)	6.71	0.30	0.42	0.26	0.70	0.02	0.46	0.10	0.04	0.03	9.16	16739.63
7.1 (Bottom)	6.76	0.23	1.78	0.03	1.78	0.18	1.06	0.01	0.05	0.10	24.71	18028.75
Mulberry PG												
mean value (n=8)	d.l.	0.80	d.l.	d.l.	2.40	1.00	0.40	d.l.	d.l.	d.l.	3.60	n.a.

No sat (unsaturated zone), Sat (saturated zone), d.l. (under detection limit), n.a. (no analyzed)

According to the European standards, the Huelva PG must be deposited in an hazardous waste landfill due to high leaching of As in the deepest samples of the profile (from 2.9 m deep to the bottom), and Cd in the deepest sample (7.1 m), which exceeded the limits for landfilling of non-hazardous waste. On the other hand, under the European standard guidelines, the Mulberry PG could be deposited in a non-hazardous waste landfill due to the moderate leaching of Cu, Mo and Ni that exceed the limits for inert landfill but are below the limits that would require more stringent restrictions.

However, based on US EPA regulations, the Huelva PG can be considered as a non-hazardous waste (Table 2), since no limit value is exceeded for any metal in the profile. Although, considering the UTS limits the Huelva PG should be treated before its disposal due to the high Cd release in the deepest sample (7.1 m; Table 2). Mulberry PG is considered non-hazardous waste and no further actions must be taken before disposal, because TCLP and UTS limits are not exceeded (Table 2).

Table 2. Upper threshold limits for hazardous waste classification (TCLP limits) and landfill disposal restrictions (UTS limits) according to US EPA regulations, and leached metals concentrations of Huelva and Mulberry PGs after TCLP test. Data in mg/L.

	As	**Ba**	**Cd**	**Cr**	**Ni**	**Pb**	**V**	**Zn**	**Se**	**Sb**
Hazardousness	5	100	1	5	n.r.l.	5	n.r.l.	n.r.l.	1	n.r.l.
Disposalrestrictions	5	21	0.11	0.6	11	0.75	1.6	4.3	5.7	1.15
Huelva PG										
(depth, m)										
0.48 (No sat)	0.002	0.027	0.010	d.l.	0.011	0.002	d.l.	0.026	d.l.	d.l.
1.6 (No sat)	0.006	0.026	0.008	d.l.	0.012	0.005	d.l.	0.021	0.004	d.l.
2.9 (Sat)	0.213	0.036	0.019	0.005	0.026	0.008	0.015	0.124	d.l.	0.002
3.5 (Sat)	0.185	0.034	0.020	0.008	0.027	0.009	0.033	0.126	d.l.	0.003
4.15 (Sat)	0.177	0.041	0.022	0.005	0.029	0.004	0.028	0.121	d.l.	0.003
5.15 (Sat)	0.345	0.032	0.024	0.005	0.027	0.001	0.019	0.419	d.l.	0.002
6 (Sat)	0.156	0.028	0.020	0.007	0.024	0.001	0.018	0.304	d.l.	0.002
7.1 (Bottom)	0.400	0.030	0.127	0.008	0.068	0.008	0.075	1.591	0.004	0.004
Mulberry PG										
mean value (n=8)	d.l.	0.110	d.l.	0.030	0.030	d.l.	d.l.	0.140	d.l.	d.l.

No sat (unsaturated zone), Sat (saturated zone), d.l. (under detection limit), n.r.l. (not regulated imit)

5. Discussion and conclusions

US regulation classifies both Huelva and Mulberry PGs as non-hazardous wastes, although Huelva PG should be treated before its disposal, which indicates a higher environmental risk for the Huelva PG. However, compared to the European regulation there is a complete disagreement between classifications of both wastes and therefore on the required waste management. Mulberry PG is considered a non-hazardous waste (as for the US regulation) while Huelva PG is considered as a hazardous waste, which demonstrates that US EPA regulations are less restrictive for these wastes.

The results of leaching tests applied to both PGs reveal a higher environmental risk for the Huelva PG, with a potential release of As, Cd, Cr, Pb, Sb and Se several orders of magnitude higher than Mulberry PG (Table 2). This fact implies the urgent adoption of suitable measures for a safe disposal of these wastes. However, more research is needed to elucidate the anomalous metal release from Huelva PG compared to Mulberry.

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