

# **FGD By-Product Utilization at Ohio Coal Mine Sites: Leaching Studies and Life Cycle Assessment**

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## **ABSTRACT**

The objective of this project was to perform a preliminary environmental evaluation of the utilization of flue gas desulfurization (FGD) gypsum for reclamation at Ohio coal mine sites. The TCLP, SPLP and Kossen framework were used in this study for characterizing the leaching potential of FGD gypsum, and all three tests resulted in concentrations well below regulatory limits. Kossen Tier 1 testing demonstrated that the relative availability of different elements in FGD gypsum varied significantly, but due to low bulk concentrations the total amount leached was low. Tier 2 testing showed the leaching of most elements, including calcium and sulfate, was independent of pH, but the leaching of some elements (Cd, Mg, Mn, Ni, Si, and Zn) increased with decreasing pH. Tier 3 testing showed that the leaching of some elements did vary with leaching time.

A life cycle assessment (LCA) was performed to clarify the overall environmental impacts of using FGD gypsum for mine reclamation, compared to the traditional practice of landfilling. The LCA demonstrated that most of the life cycle emissions associated with mine reclamation with FGD gypsum were a result of truck transportation, power generation and supply, petroleum refineries, and oil and gas extraction. In general, reclamation using FGD gypsum contributes an insignificant amount of emissions and consumes a relatively insignificant amount of energy compared to national resource flows. Utilization of FGD gypsum for reclamation of abandoned highwalls resulted in lower overall CO<sub>2</sub> emissions, CFC-11 equivalents, acidification potential, eutrophication potential and smog potential than managing FGD gypsum in landfills.

## 1. INTRODUCTION

Currently in Ohio, there are over 200,000 acres of abandoned strip mines and over 600,000 acres of abandoned underground mines<sup>1</sup>. These abandoned mine lands (AMLs) present serious threats to human health and environment, which include disrupting the flow of nearby natural streams by waterway sedimentation, discharging highly acidic and metal-enriched water (i.e., acid mine drainages or AMDs) into streams, creating 20-150ft highwalls that are dangerous to outdoor recreation, and establishing hazardous habitats for threatened and endangered animal species. Despite several federal and state rules (e.g., Surface Mining Control and Reclamation Act (SMCRA) implemented by United States Department of Interior in 1977 and Strip Mining coal Act first issued by Ohio government in 1947) have forced coal companies to reclaim active and abandoned strips or underground mines, there remains many acres of unreclaimed mine lands in the United States that were abandoned prior to legislative requirements. The reclamation activities of these AMLs are not supported by federal grants established by the federal or state rules.

To keep AML reclamation a priority despite the lack of funding, collaboration with coal combustion power plants to supply beneficial use materials for reclamation is an appealing cost-saving option. Calcium sulfite flue gas desulfurization (FGD) material has been used in many AML reclamation projects to re-contour the original landscape of AMLs, eliminate dangerous highwalls, abate acid mine drainage (AMD), and reduce sedimentation runoff clogging waterways. However, use of FGD gypsum for AML reclamation has rarely been investigated. The knowledge about potential environmental impacts associated with its beneficial use for AML reclamation has been lacking. In this study, the leaching properties of FGD gypsum, as well as the life cycle analysis (LCA) of utilizing FGD gypsum for abandoned mine reclamation, were investigated.

The motivation for conducting an LCA in this study is to understand the trade-offs and environmental impacts associated with using FGD gypsum for AML reclamation. LCAs have been used in previous studies regarding coal combustion and coal combustion byproducts; however, minimal research targets the actual utilization of coal combustion byproducts for specific beneficial use purposes. In addition, a resource for decision-makers to consider the broader impacts of FGD gypsum application within different scenarios is provided, which will instigate discussion for future detailed investigations.

## 2. MATERIAL AND METHODS

### 2.1 FGD Gypsum

FGD gypsum samples obtained from two power plants (i.e., AC plant in the east of Ohio and FB Plant in the west of Pennsylvania) were tested in this study. The samples were digested with perchloric acid and analyzed for total sulfur content with an Inductively Coupled Plasma Spectrophotometer (ICP) (Teledyne Leeman Labs Prodigy Dual). The mercury concentration was determined by Cold Vapor Atomic Fluorescence Analysis (CETAC M8000). The remaining elemental composition was determined with an ICP.

## 2.2 Leaching Test

The leaching behavior of these samples were characterized using Toxicity Leaching Characteristic Procedure (TCLP) (i.e., EPA Method 1311) and Synthetic Precipitation Leaching Procedure (SPLP) (i.e., EPA Method 1312). An Integrated Framework established by Kosson et al.<sup>2</sup> was carried out for the FGD sample collected from AC Plant. The TCLP was implemented to determine the mobility of inorganic constituents within the synthetic calcium sulfate at an initial pH of  $4.93 \pm 0.05$  with the use of acetic acid. The SPLP was implemented to determine the mobility of inorganic constituents exposed to synthetic rainwater at a pH of  $4.90 \pm 0.05$  with the use of a sulfuric acid and nitric acid mixture. The Tier 1 of the integrated Kosson leaching framework, which is in accordance with the Netherland's Environmental Agency Standard NEN 7371 (2004), was used to evaluate the total availability of each constituent present in FGD gypsum. The release of each constituent in FGD gypsum as a function of pH was measured in the Tier 2 of the leaching framework. In Tier 3, the leaching kinetic of the FGD gypsum was investigated. To carry out the Tier 3 test, a monolithic sample was prepared by compacting the AC Plant FGD sample into a 10-cm diameter cylindrical concrete test-mold to a height of 10 cm.

All leachate samples were filtered through either  $0.7 \mu\text{m}$  (for TCLP and SPLP) or  $0.45 \mu\text{m}$  (for Kosson leaching framework) polypropylene membrane and preserved with 2.5% nitric acid for analysis. Each leachate sample was analyzed for Al, As, B, Ba, Be, Ca, Bd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, S, Sb, Se, Si, Sr, Tl, V, and Zn with ICP. Sulfate was measured with an Ion chromatograph (Dionex DX 120). Mercury concentration was measured by a cold vapor atomic fluorescence spectroscopy.

## 2.3 Life Cycle Analysis

A conventional LCA database aggregated by the North American Industry Classification System (NAICS), which classifies all industrial processes into sectors according to their activities, was used to model different AML reclamation scenarios. An Economic Input-Output LCA (EIO-LCA)<sup>3</sup> was used to determine the flows of emissions and energy through various sectors that support AML reclamation. An Ecological LCA (Eco-LCA) database<sup>4</sup>, which accounts for natural capital, goods and services provided by natural, carbon sequestration, land and water usage, and energy made available through sector activities, was used to categorize overall environmental impacts of AML reclamation, such as global warming potential and ozone depletion potential.

The LCA carried out in this study is specified to represent FGD gypsum application for AML reclamation in the Eastern Ohio. Six different scenarios were modeled based on AML site characteristics within a defined radius of the AC Plant and the reclamation processes common across all AML reclamation activities. The system of interest includes all processes such as the produced FGD gypsum and all materials, equipment, energy, labor, etc. Four major categories, raw material acquisition, manufacturing, use, and waste management, was considered in the life cycle of AML reclamation with FGD gypsum. By designating FGD gypsum as the primary raw material, all activities involved

in storing, handling, and transporting FGD gypsum are included in the raw materials acquisition process. The manufacturing process simply involves the stabilization of FGD gypsum with fly ash and lime, if necessary. The use process involves all equipment, tools, ancillary materials, labor, and energy needed for the reclamation. Finally, all equipment, labor, and transportation needed for required monitoring activities is included in the waste management process.

The Life Cycle Inventory (LCI) of the AML reclamation was then performed by first developing a flow diagram to consider all relevant input-output streams and processes as discussed above. It includes all energy and material inputs, energy and material consumptions, output emissions to the atmosphere, water, and soil, and other waste streams. Next, details regarding AMLR activities were used from ODNR records and represent common practices, loads, and prices. Process-level emissions data was queried through USEPA's NONROAD2008 model, which represents equipment-specific data. All aggregated life cycle emissions and energy were taken from the Eco-LCA and EIO-LCA models.

Next, a life cycle impact assessment (LCIA) is performed to evaluate the potential human and environmental health effects associated with the LCI data. Five impact categories, i.e., global warming, stratospheric ozone depletion, acidification, eutrophication, and photochemical smog, were studied. The impact of the selected six AML reclamation scenarios in each category was compared to the overall sectors in the United States.

### 3. RESULTS AND DISCUSSION

#### 3.1 TCLP and SPLP

Results obtained from TCLP and SPLP are displayed in Table 1. In general, both TCLP and SPLP yielded concentration levels of arsenic, barium, cadmium, chromium, copper, mercury, lead, and selenium well below Ohio non-toxic criteria for both FGD samples, which provide justification for classifying FGD gypsum as a non-hazardous material. In fact, except for mercury, the concentration levels of these elements were all lower than the EPA drinking water standard. When comparing to the Ohio Secondary Maximum Contaminant Level Standards, which represent the maximum concentrations that can leave a public water system intended for public consumption and use, the concentration of sulfate surpasses the secondary criteria. The TCLP results also show that concentration of Fe from the AC Plant gypsum sample surpasses the limit. The Ohio Secondary Maximum Contaminant Level Standards does not necessarily place any restriction on utilizing FGD gypsum for AML reclamation.

#### 3.2 Kosson Leaching Framework

The availability of each constituent relative to the concentrations within the solid FGD gypsum sample was determined and displayed as a percentage in Table 2. The leachable concentration of mercury was approximately 0.0002% of the total

concentration, a seemingly insignificant quantity. Contrarily, almost all the boron present in the solid sample leached in solution (94.7%). Since boron is very soluble in water, this high leachable concentration is important to consider when applying FGD gypsum to AML reclamation projects.

Table 1 TCLP and SPLP Results Compared to Beneficial Use and Drinking Water Criteria.

Element	AC Plant Gypsum		BM Plant Gypsum		Limits		
	SPLP	TCLP	SPLP	TCLP	Ohio Non-Toxic Criteria	Ohio Secondary Levels	EPA MCL
Al	µg/mL <0.034	<0.034	<0.034	<0.034		0.2	
As	µg/mL <0.006	<0.006	<0.006	0.008 ± 0.002	0.3		0.01
B	µg/mL 0.130 ± 0.001	0.137 ± 0.004	0.030 ± 0.003	0.026 ± 0.001			
Ba	µg/mL 0.101 ± 0.007	0.37 ± 0.02	0.098 ± 0.008	0.270 ± 0.007	60		2
Be	µg/mL <0.0005	<0.0005	<0.0005	<0.0005			
Ca	µg/mL 520 ± 6	848 ± 3	460 ± 20	668 ± 10			
Cd	µg/mL 0.002 ± 0.002	0.0017 ± 0.0000	0.0005 ± 0.0000	0.0006 ± 0.0000	0.15		0.005
Co	µg/mL <0.0007	0.0015 ± 0.0000	<0.0007	<0.0007			
Cr	µg/mL 0.0044 ± 0.0000	0.0059 ± 0.0000	0.0048 ± 0.0000	0.006 ± 0.001	3		0.1
Cu	µg/mL <0.001	<0.001	<0.001	<0.001			1.3
Fe	µg/mL <0.0009	0.34 ± 0.03	0.015 ± 0.015	0.022 ± 0.002		0.3	
Hg	ng/mL 0.0036 ± 5E-04	0.018 ± 0.010	0.0027 ± 0.0011	0.0026 ± 0.000	0.06		0.002
K	µg/mL <0.4	2.01 ± 0.13	<0.4	1.76 ± 0.05			
Li	µg/mL 0.077 ± 0.012	0.13 ± 0.02	0.070 ± 0.006	0.084 ± 0.004			
Mg	µg/mL 1.290 ± 0.007	14.7 ± 0.9	0.26 ± 0.03	0.236 ± 0.002			
Mn	µg/mL 0.068 ± 0.005	0.15 ± 0.002	0.0014 ± 0.0000	<0.0003		0.05	
Mo	µg/mL 0.00275 ± 0.0000	0.0021 ± 0.0000	0.0031 ± 0.001	0.004 ± 0.002			
Ni	µg/mL 0.00185 ± 0.0000	0.008 ± 0.001	0.0016 ± 0.0000	<0.0009			
P	µg/mL <0.004	0.017 ± 0.004	0.033 ± 0.005	0.029 ± 0.007			
Pb	µg/mL <0.003	<0.003	<0.003	<0.003	1.5		0.015
S	µg/mL 422 ± 18	570 ± 15	485 ± 18	690 ± 20			
Sb	µg/mL 0.026 ± 0.001	0.023 ± 0.001	0.030 ± 0.003	0.024 ± 0.002			
Se	µg/mL <0.011	0.012 ± 0.003	<0.011	<0.011	1		0.05
Si	µg/mL 0.13 ± 0.02	0.432 ± 0.010	0.18 ± 0.03	0.195 ± 0.004			
SO <sub>4</sub> <sup>-2</sup> as S	µg/mL 482 ± 7	615 ± 2	484 ± 3	729 ± 2		250	
Sr	µg/mL 0.616 ± 0.017	1.130 ± 0.004	0.45 ± 0.03	0.693 ± 0.009			
Tl	µg/mL <0.007	0.008 ± 0.003	<0.007	<0.007			
V	µg/mL 0.014 ± 0.0010	<0.001	<0.001	0.002 ± 0.001			
Zn	µg/mL 0.046 ± 0.008	0.170 ± 0.004	0.080 ± 0.005	0.056 ± 0.010		5	

Tier 2 of the Kosson leaching framework was performed to assess the leaching potential of each constituent as a function of pH. Resulting data is displayed in Table 3. As shown, Al, As, Co, Cu, K, P, Pb, Se, and V concentrations were below detection limits at each pH value. B concentrations remained stable at approximately 0.22 µg/mL, and only slight fluctuations were seen in Li, Mo, and Sb. Concentrations of Ba, Mg, Mn, and Ni decreased as pH increased, likely because species containing these elements complexed and/or approached saturation as pH increased. Hg concentrations remained relatively stable, but spiked at pH 6 and 9, which is likely due to the inherent variation of mercury in the FGD gypsum sample.

The leaching kinetics of a monolithic sample of the FGD gypsum collected from AC plant over defined time intervals was tested in the Tier 3 of Kosson leaching framework. Table 4 lists the results. As shown in the table, the concentrations of As, Cd, Cu, Pb, and Se were below detection limits. Generally, K, Mg, Mn, Mo, Ni, and B, and Sr concentrations tended to increase with time. If AML reclamation conditions remain within a pH range of 6.5-9.5, the solubility of gypsum will not likely be altered<sup>5</sup> and leachable Ca, S, and SO<sub>4</sub> concentrations will remain stable over time. Maximum leaching of Hg occurred after one day, then decreased over the remaining seven days, suggesting that long-term leaching of Hg at AMLR sites is not necessarily a concern likely due to adsorption onto Al and Fe particles.

### 3.3 Life Cycle Analysis

Six different reclamation scenarios were modeled based on AML site characteristics within a defined radius of the AC Plant. They are highwall pit within a 5-mile radius of plant (HWP, 5), highwall pit within a 10-mile radius of plant (HWP, 10), highwall within a 5-mile radius of plant (HW, 5), underground mine seal and highwall within a 5-mile radius of plant (UM), abandoned gob pile (GP), and subtitle D landfill within a 1-mile radius of plant (LF).

Figure 1 (a)-(e) illustrates how each scenario contributes to each impact category relative to the total impacts by all U.S. sectors. As shown in the figures, the normalized values are relatively insignificant compared to total U.S. flows, which implies that reclamation activities do not negatively impact the environment on a national scale when comparing to other sectors. The only impact category that might be a subject of interest is the global warming potential. Although relative to other sectors reclamation activities do not contribute much to global warming, reclamation does require the use of heavy trucks and off-road machinery that emit carbon monoxide, carbon dioxide, and methane – key contributors to total greenhouse gas emissions. It is worth noting that the data in this LCA do not account for the positive impacts AMLR has on local environments (e.g., AMD abatement). Thus, it is possible that AMLR may contribute more positive impacts than negative impacts at a local scale.

Table 2 Results from Tier 1 Kosson Leaching Framework for the Gypsum Sample from the AC Plant

Element	Leachate Concentration ( $\mu\text{g/mL}$ )	Concentration in AD FGD Gypsum ( $\mu\text{g/g}$ )	Relative Availability (%)
Al	<0.034	307	<1.11
As	<0.006	<1.3	ND
B	0.0405	4.31	94.7
Ba	0.161	65.5	24.7
Be	<0.0005	<0.09	ND
Ca	582	20700	28.3
Cd	0.0017	<0.05	ND
Co	<0.0008	<0.15	ND
Cr	0.0076	<0.19	ND
Cu	0.0059	<0.4	ND
Fe	0.66	750	8.9
Hg	6.03E-06	0.355	0.00017
K	<0.4	<80	ND
Li	0.0367	28.5	13
Mg	12.9	1460	89
Mn	0.057	<0.06	ND
Mo	0.004	<0.2	ND
Na	0.070	<13	ND
Ni	0.035	<0.18	ND
P	<0.004	<1.0	ND
Pb	<0.003	<0.8	ND
S	388	13600	28.8
Sb	0.020	6.12	32.5
Se	<0.01	<2	ND
Si	0.201	389	5.2
Sr	0.668	187	36
Tl	<0.007	<0.19	ND
V	0.003	<0.3	ND
Zn	0.075	1.55	ND

Table 3. Results from Tier 2 Kosson Leaching Framework for the Gypsum Sample from the AC Plant

Element (µg/ml)	pH 11	pH 9	pH 7	pH 6	pH 5	pH 4	pH 3	pH 2
Al	<0.034	<0.034	<0.034	<0.034	<0.034	<0.034	<0.034	<0.034
As	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
B	0.0077	0.217	0.227	0.222	0.222	0.220	0.220	0.224
Ba	0.0755	0.142	0.168	0.164	0.179	0.187	0.184	0.136
Be	<0.00046	<0.00046	<0.00046	<0.00046	<0.00046	<0.00046	<0.00046	0.0005
Ca	295	451	527	486	558	582	564	404
Cd	<0.00024	<0.00024	<0.00024	<0.00024	0.0003	0.0004	0.0007	0.0015
Co	<0.00073	<0.00073	<0.00073	<0.00073	<0.00073	<0.00073	<0.00073	<0.00073
Cr	0.0047	0.0019	0.0043	0.0051	0.0047	0.0032	0.0037	0.0056
Cu	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Fe	0.0022	<0.00085	<0.00085	0.205	0.0051	<0.00085	0.0011	<0.00085
Hg	6.92E-06	7.90E-05	9.55E-06	2.16E-05	8.11E-06	8.18E-06	7.32E-06	8.25E-06
K	0.6460	<0.373	<0.373	<0.373	<0.373	<0.373	<0.373	<0.373
Li	<0.017	0.0270	0.0377	0.0420	0.0379	0.0413	0.0278	0.0313
Mg	0.0649	1.63	2.25	2.46	2.81	6.36	10.7	18.9
Mn	0.0058	0.0022	0.109	0.143	0.149	0.182	0.213	0.315
Mo	0.0016	0.0083	0.0049	0.0062	0.0050	0.0053	0.0096	0.0076
Na	0.0684	6.20	0.428	0.388	0.429	0.456	0.506	0.312
Ni	0.0012	<0.00091	0.0013	0.0017	0.0032	0.0038	0.0064	0.0165
P	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Pb	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
S	238	397	414	406	391	382	374	376
Sb	0.0135	0.0283	0.0299	0.0295	0.0266	0.0263	0.0370	0.0244
Se	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011
Si	<0.011	0.275	0.210	0.309	0.250	0.350	0.485	1.07
SO4-S	322	495	499	493	487	472	455	422
Sr	0.339	0.593	0.698	0.644	0.745	0.782	0.771	0.578
Tl	<0.007	<0.001	0.0077	0.0018	0.0051	<0.001	0.0022	0.0049
V	<0.001	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
Zn	0.0095	<0.002	<0.002	0.0077	0.0071	0.0166	0.0356	0.0345



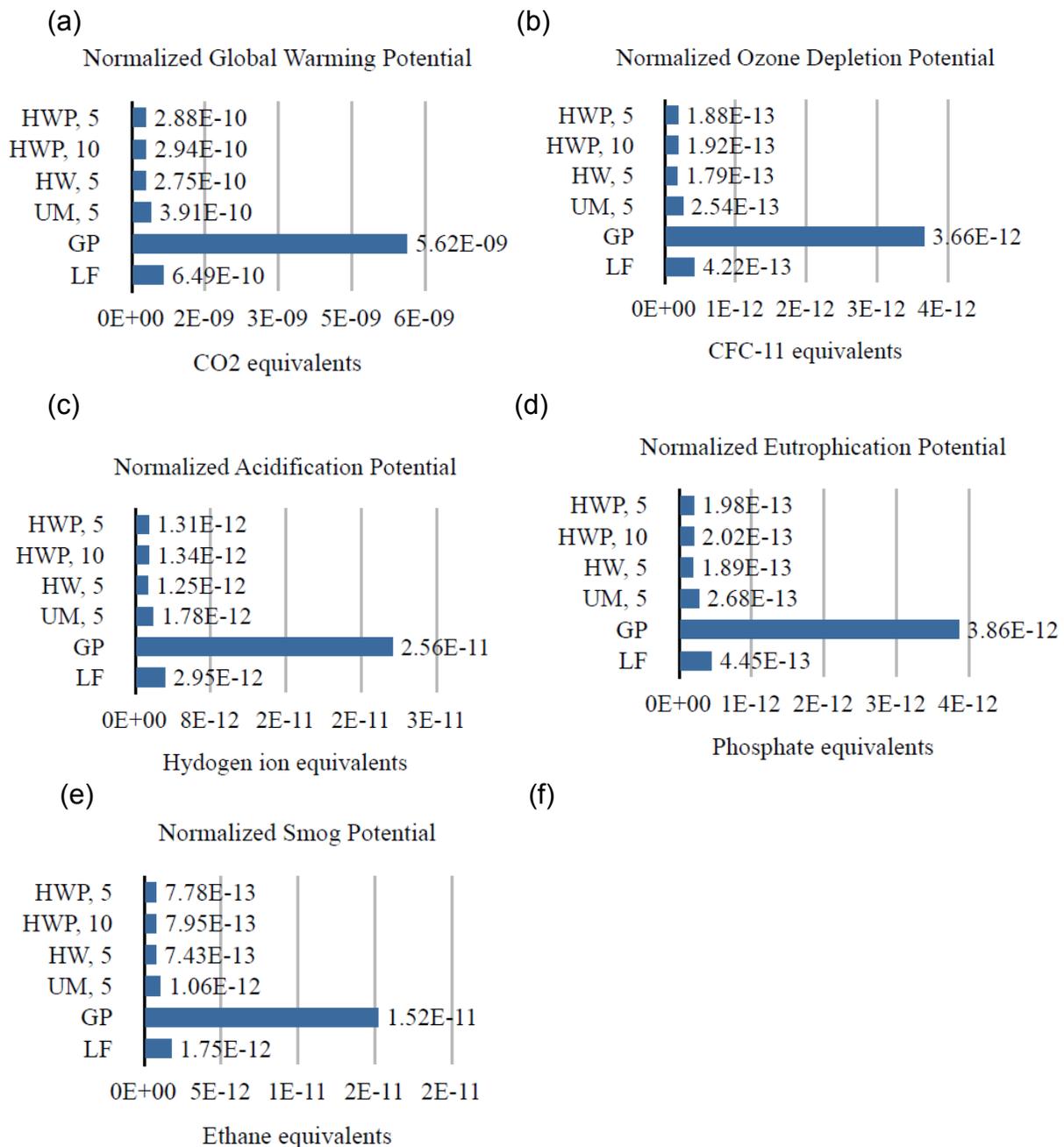


Figure 1. Impact categories normalized against US flow.

#### 4. CONCLUSION

The TCLP, SPLP, and Kossen et al. framework were useful for characterizing the leaching potential of hazardous constituents from FGD gypsum, and all three tests resulted in concentrations well below regulatory limits. Most of the leaching activity occurred within one hour, suggesting that long-term leaching of hazardous elements is not a concern for AMLR application.

The LCA provided valuable insight into the flow of hazardous pollutants throughout the AMLR process, both directly and indirectly. In addition, it showed how AMRL contributes to the national flow of pollutants and energy through economic activity. The process-level emissions and energy consumption are primarily a result of the heavy-duty equipment used for clearing/grubbing, channeling, earthwork, and hauling. Most of the life cycle emissions were a result of truck transportation, power generation and supply, petroleum refineries, and oil and gas extraction. In general, AMLR contributes an insignificant amount of emissions and consumes a relatively insignificant amount of energy compared to nation resource flows.

Overall, FGD gypsum is a favorable material for AMLR because of its neutral or moderately alkaline pH that is compatible with natural soil ecologies, abundant calcium and sulfur concentrations that are essential for vegetation growth, low leaching availability of mercury and other environmentally hazardous constituents, relatively inexpensive transportation and earthwork unit costs, and reliable production by coal

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