

Characterization of Drywall Products for Assessing Impacts Associated with End-of-Life Management



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by

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Gregory Sayles, Director
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Acronyms and Abbreviations

AES	Atomic Emission Spectroscopy
ANS	American Nuclear Society
ASTM	American Society for Testing and Materials, now ASTM International
CDD	Construction and Demolition Debris
CESER	Center for Environmental Solutions and Emergency Response
D _e	Diffusion Coefficient
DI	Deionized (Water)
DOC	Dissolved Organic Carbon
DCP	Dicalcium phosphate
EC	Electrical conductivity
ECD	Electron Capture Detector
EPA	U.S. Environmental Protection Agency
FGD	Flue-gas desulfurization
GC	Gas Chromatography
GFAA	Graphite Furnace Atomic Absorption
H	Hour
HPLC	High-performance liquid chromatography
IC	Ion Chromatography
ICDD	International Centre for Diffraction Data
ICP	Inductively Coupled Plasma
IR	Infrared
L	Liter
LOQ	Limit of Quantification
LSP	Liquid-solid partitioning
L/S	Liquid-to-solid
LX	Leachability Index
MC	Moisture Content
ML	Monolithic Leaching
MDL	Method Detection Limit
MRL	Method Reporting Limit
MS	Mass Spectrometry
NIST	National Institute of Standards and Technology
ORD	Office of Research and Development
OCP	Octocalcium phosphate
PAHs	Polynuclear Aromatic Hydrocarbons
PDF	Powder diffraction file
PCBs	Polychlorinated Biphenyls
QA/QC	Quality Assurance/ Quality Control
RIR	Reference Intensity Ratio
RL	Reporting limit
RPM	Rotation per minute
RPD	Relative percent difference
RSD	Relative Standard deviation
SI	Système International; International System of Units
SIM	Selected ion Monitoring
SVOC	Semivolatile Organic Compound

S/S	Solidification and stabilization
TCP	Tricalcium phosphate
TBT	Tributyltin
U.S.	United States
VOC	Volatile Organic Compound
WLOI	Weight Loss on Ignition

Executive Summary

Drywall, also known as plasterboard, wallboard, sheetrock, and gypsum board, is a panel made of gypsum plaster pressed between two thick sheets of paper. It is one of the major types of construction and demolition debris in modern society. An estimated 3.9×10^9 m² drywall is used per year in North America, representing approximately 50% of the world's use. In recent years, the generation of drywall waste has been on the rise in North America, and most of this waste results from both construction and demolition projects. The disposal of drywall waste in landfills is common, but this can potentially lead to environmental concerns such as hydrogen sulfide gas generation and chemical leaching.

Given the potential concerns associated with drywall disposal in landfills, a scientific study is needed to better understand the chemical composition of drywall products and how chemical constituents may leach from these products upon contact with water. To produce such data, ten drywall samples from the U.S. marketplace (produced by two different manufacturers) were collected, representing a variety of different drywall products (e.g., regular, fire-resistant, and mold-resistant). Drywall product characteristics examined in this study included mineral analysis, moisture content, total sulfur, metal composition, water-soluble sulfur and metal concentrations, trace organic chemical analysis, and two different leaching tests (M1315, and M1316). The results also provide methodological insights related to the evaluation of solid wastes and similar materials with high calcium sulfate content.

The main results of this study were as follows:

1. Moisture content (MC) of the drywall was related to the temperature used for its determination. The average MC of gypsum from drywall measured at 45, 105, 230, 400, and 550 °C was 0.45, 15.4, 20.4, 20.7, and 21.6%, respectively. The average MC of the drywall samples tested at 105 °C was 15.4%. The MC results at 150 °C were unstable because calcium sulfate exists at three levels of hydration. Samples that were air-dried (not oven-dried at high temperatures) were employed in this work, since the mineral phases can change during the high-temperature MC analysis.
2. Drywall, including the gypsum core of the drywall board, contains a small amount of organic carbon. The average total carbon and sulfur content of the gypsum samples using a combustion methodology were 0.87 and 17.6%, respectively (air-dry weight basis). Formaldehyde was detected at a concentration ranging from 500 to 8,500 µg kg⁻¹, with a median and an average of 1,800 and 3,700 µg kg⁻¹, respectively. Tributyltin (TBT) was also detected in some samples, especially in the mold control drywall. Polynuclear aromatic hydrocarbons (PAHs) were also detected in some samples, attributed to the paper fraction of the drywall product.
3. The dominant mineral in the drywall products was gypsum, accompanied by small amounts of hemihydrate and anhydrite. Calcium and magnesium carbonate and silica were also detected.
4. The total acid-extractable sulfur and metal concentrations of the gypsum core of the drywall samples were investigated using different methods. The sulfur and calcium content average in the gypsum samples was 13.7, 17.7, 18.3%, and 18.6, 24.5, 24.0%, using USEPA M3051A, 0.25 M HCl extraction (24 hours (h)) and 10% HNO₃ at 90 °C for 16h methods, respectively. The average strontium content was 140, 175, and 189 mg kg⁻¹, respectively. Re-precipitation is a common occurrence after microwave digestion of materials with high amounts of calcium sulfate minerals, and the re-precipitation was confirmed using digestion experiments followed by dilution at different temperatures. The results suggest that analysts should be cautious of measuring elemental concentrations of gypsum materials using USEPA M3051A; use of this method might significantly underestimate the content of sulfur, calcium, strontium, and other compositions. A new acid extraction procedure (10% HNO₃) at water sub-boiling temperatures (90 °C) for 16h) was developed in this work and is recommended for future work. The results of extractable sulfur in this new procedure were similar to the total sulfur concentration measured

using the combustion technique and significantly higher than that measured using USEPA M3051A. The results for calcium and strontium using the new procedure were also significantly higher than the calcium and strontium measured using USEPA M3051A.

5. Water-extractable sulfate and inorganic element concentrations were studied by repeating a water extraction procedure four times. Very high cumulative water-extractable sulfate and calcium were observed in the gypsum samples tested. The other detectable components of the water extracts were Sr, Ba, Mg, Fe, P, and Si. The average cumulative water-extractable SO_4 , Ca, and Sr concentrations from the gypsum samples were $54.4 \pm 1.5\%$, $22.1 \pm 0.5\%$, and $193 \pm 211 \text{ mg kg}^{-1}$, respectively. Based on the total sulfur content by combustion, 98.2% of the water-extractable sulfur was in the form of sulfate (SO_4). The average water-extractable calcium and strontium content in the gypsum samples was 90%, and 95%, respectively, when the cumulative water extraction concentrations were compared to those measured using the new acid extraction procedure.
6. Kinetics leaching experiments were conducted for periods up to 2 months using five of the drywall products at a fixed liquid-to-solid ratio ($L/S = 20$) and room temperature. The chemical concentrations, pH, and conductivity in the leachates were measured and based on the chemical measurements, and MINTEQA modeling, the kinetics of saturation index (SI) of controlling minerals were assessed. Chemical equilibrium is a dynamic process, and there is no universal time at which chemical equilibrium is reached for all constituents in the leachate. In many cases, a constituent concentration (e.g., calcium) is not controlled by a single mineral phase, and the changes in leachate concentration over time are related to changing mineral phases; however, for most samples, equilibration time of one week was found appropriate.
7. Liquid-solid partitioning of inorganic constituents from the drywall samples was examined on five drywalls using a modified EPA Method 1316 with ten different L/S ratios (from 2.5 to 400). The linear dependence of logarithmic constituent concentration as a function of the logarithmic L/S ratio was observed and found to be dependent on the saturation index (SI) of the minerals controlling constituent equilibrium. When controlling mineral for a leached constituent was at an unsaturated status ($SI < 0$), the linear dependence was found valid for all the studied samples. These relationships were further used to estimate the constituent concentrations in the pore water. The estimated average of pore water concentrations of Sr, B, Ba, Zn, Cu, Mn, Ni, Co, Mo, Cd, and Se were 10, 11.5, 0.29, 5.6, 6.3, 4.1, 0.2, 0.2, 0.23, 0.02, and 0.6 mg L^{-1} , respectively. The linear dependence relationship was noted when the constituent was released from a single mineral phase.
8. Monolithic leaching tests were conducted using USEPA Method 1315 for five different drywall products. A linear relationship was observed between logarithmic cumulative released constituent concentrations, and logarithmic total leaching time with gypsum was the controlling solid phase. The slopes of the linear equation indicated that the leaching process was controlled by dissolution and not diffusion. The dominant species (sulfate, Ca), as well as Sr, leached following a dissolution mechanism. A surface wash-off pattern, a delayed-release pattern, and a depletion pattern were also observed for the other minor elemental constituents depending on the mineral source and composition of the gypsum. The diffusivity of the leached constituents, as well as the leachability index, were further calculated. The average weighted arithmetic means diffusion coefficient (D_e) of S, Ca, Sr, Zn, Mn, Mg, P, Ba, Si, Fe and dissolved organic carbon (DOC) from the samples was 60.2, 55.4, 41.9, 18.1, 6.5, 5.9, 0.45, 0.38, 0.30, 0.21, and $0.02 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively. The more highly leachable constituents were Zn, Sr, SO_4 , and Ca; the moderately leachable constituents were Mg and Mn; and the relatively slow release constituents were P, Fe, Si, Ba, and DOC. The leachability index of most constituents was between 8 and 9.

1. Introduction

Gypsum drywall – also commonly referred to as plasterboard, wallboard, sheetrock, or gypsum board – is a panel comprised of the mineral gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) pressed between two sheets of paper. Drywall is a construction product used for interior walls and ceilings in buildings and serves as a more rapidly installed alternative to the traditional lath and plaster construction method. Approximately 4 billion m^2 of drywall has been estimated to be used annually in North America, representing approximately 50% of the overall amount used in the world (Founie, 2006). The home-building-and-remodeling markets in North America over recent decades have increased demand for building materials, and the gypsum drywall was one of the biggest beneficiaries of increased construction activity as “an average new American home contains more than 7.31 metric tons of gypsum” (Olson, 2001). When discarded, this material represents one of the larger components of construction and demolition debris (CDD) in modern society (USEPA, 1998a; Townsend et al., 2004; USEPA, 2006; Somasundaram et al., 2014; USEPA, 2014a; Jiménez Rivero et al., 2016).

Drywall is manufactured by first calcining source gypsum to remove part of the water (resulting in $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and then rehydrating the gypsum to produce a slurry. The slurry is then spread onto a moving continuous sheet of paper, which is sandwiched between another layer of paper. After initial drying, the drywall becomes hard and ready to cut into panels for a final drying process. The drywall is then trimmed to the dimensions required, bundled, and sent to the market (USEPA, 2015). A variety of gypsum drywall products are manufactured and sold in the U.S. and Canada, including regular whiteboard, and products modified to provide greater fire-resistance, mold-resistance, and soundproofing ability. Examples of drywall currently available on the market include:

- Regular whiteboard comes in thicknesses ranging from $\frac{1}{4}$ -inch to $\frac{3}{4}$ -inch thickness.
- Fire-resistant (“Type X”) drywall comes in different thicknesses and includes additives such as glass fibers to provide necessary properties for improving fire resistance. In some cases, perlite, vermiculite, and boric acid are added to additionally improve fire resistance.
- Green board is a drywall product that contains oil-based additives to provide moisture resistance for applications such as bathrooms; the product is so-named because of the green-colored paper.
- Blue board includes a skim coat of plaster finish to provide additional water and mold resistance.
- Sound dampening drywall incorporates additional materials to limit sound transmission.
- Paperless drywall products do not include the paper coating and backing and are said to pose fewer mildew problems if exposed to water.
- Specialty drywall products as lined with lead (to be used in the walls around radiological equipment) and foil (to serve as a vapor barrier) are also manufactured and marketed.

The primary component of gypsum drywall is the gypsum, a mineral also known as calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Each gypsum molecule is composed of one molecule of calcium sulfate (CaSO_4) and two molecules of water (H_2O). By weight, the compound is 21% water, but by volume, it is nearly 50% water. The source of gypsum used in drywall manufactured includes naturally occurring gypsum deposits (geologically deposited from lakes and seawater). Recycled gypsum is also widely used in drywall manufacture (Pedreno-Rojas et al., 2019; USEPA, 2015). The introduction of the Clean Air Interstate Rule by the U.S. Environmental Protection Agency (EPA) in March 2005 required power plants to “cut sulfur dioxide emissions, which necessitated that coal-fired power plants install scrubbers (industrial pollution control devices) to remove sulfur dioxide present in the output waste gas.

Scrubbers use the technique of flue-gas desulfurization (FGD), which produces synthetic gypsum as a by-product. Though issues such as mercury release during calcining of FGD gypsum have been raised (Heebink and Hassett, 2005), use of FGD gypsum as the gypsum source for drywall manufacture is very common. In addition, post-consumer recycled gypsum (recovered from construction debris) is used as a gypsum source (CDRA, 2015; USEPA, 2015).

The other main component of the drywall board is paper, which is often produced using recycled paper products. Small amounts of other additives may be included in the manufacturing process, including starch, paper pulp, unexpanded vermiculite, and those additional components required for specialty products (see product descriptions above). Starch is added to help the paper adhere to the gypsum core, and paper pulp is added to increase the core's tensile strength (resistance to lengthwise pressure).

Gypsum drywall enters the waste stream from product manufacture, during building construction, and as a result of building demolition. A variety of potential environmental concerns such as generation and emission of hydrogen sulfide and leachate with elevated levels of minerals have been raised regarding the management of the end-of-life of drywall (Venta, 1997; Townsend et al., 2004; USEPA, 2006, 2014a, 2015; Jiménez Rivero et al., 2016), and with the many different types of drywall products historically and currently in use, it is useful to better understand the trace constituents of drywall products. The environmental impacts of drywall disposal in landfill are dependent on its chemical and leaching characteristics. To address this need, ten drywall samples from the US market, representing two different manufacturers and a variety of drywall products, were randomly selected for evaluation in this study. A variety of chemical properties were measured on each of the drywall products, including mineral analysis, moisture content (MC), total sulfur and metal concentration, water-soluble sulfur and metals concentrations, selected organic constituents, and constituent leachability using two different US EPA Leaching Environmental Assessment Framework (M1315 and M1316). The results add to the existing database on gypsum drywall properties that can be used to guide sustainable materials management decision making. Lessons from several issues encountered during drywall analysis will be of value to future researchers examining similar material streams.

2. Materials and Methods

2.1. Sample Collection and Preparation

Ten drywall samples were collected from home improvement and construction product retail stores and represented two different product manufacturers (X and U). The samples collected and analyzed are designated by Sample ID as A, B, C, D, E, F, G, H, I, and L (see Table 2-1).

Table 2-1: Drywall sample identification list

Sample ID	Manufacturer	Type	Thickness	Date of Manufacture
A	X	Lift Lite "TE"	0.5 inch	7/29/2014
B	X	Regular	3/8 inch	7/15/2014
C	X	Mold Defense	0.5 inch	7/24/2014
D	X	Firecheck type X	5/8 inch	7/22/2014
E	U	UL-Regular	0.5 inch	6/2/2015
F	U	UL-MoldTough	0.5 inch	5/28/2015
G	U	UL-Firecheck X	5/8 inch	11/7/2014
H	U	UL-regular	0.5 inch	8/11/2015
I	U	Regular	3/8 inch	7/20/2015
L	U	Mold Tough	0.5 inch	8/12/2015

Upon receipt at the laboratory, gypsum drywall sheets were logged and stored in a storage unit. The paper was removed from the drywall for each sheet, and the paper and gypsum were stored as two separate components (paper and gypsum). The gypsum component was further cut into squares of approximately 6 mm and run through a rock crusher. The processed gypsum was then ground to a fine powder and sieved using a USA Standard Testing Sieve system using an ASTM International (ASTM) #10 sieve (2 mm) to yield the final sized particles. The paper component was cut into 2 to 3 mm squares. The weight of each drywall component (paper and gypsum) was measured to determine their percentage weight.

2.2. Drywall Characterization

2.2.1. Moisture content

The MC of the gypsum drywall samples was measured after the sample size was reduced to less than 2 mm. The samples were placed in an oven, and MC was determined by ASTM C471M-16 (ASTM-International, 2016) and Method D-2216-10 (ASTM-International, 2010). In Method C471M-16, the weight loss on ignition (WLOI) at 45 °C was designated as the “free water” and the WLOI at 230 °C as “combined water.” This manner of describing MC is supported by the infrared spectroscopy and thermal gravimetric analysis results from gypsum, as reported by Reidy et al. (2014). Carbon dioxide (CO₂) has been observed to be released from drywall gypsum at higher temperatures; the WLOI between 230 °C and 550 °C reportedly relates to the decomposition of the organic matter, while the WLOI between 550 °C and 1000 °C relates to the decomposition of carbonate (e.g., calcite or dolomite) (Heiri et al., 2001; Wang et al., 2011; Galan et al., 2013). The MC of the paper samples was measured at 105 °C based on Method D-2216-10 (ASTM-International, 2010).

2.2.2. Total carbon and sulfur content by combustion

The carbon and sulfur content of the gypsum samples was determined by infrared absorption on a Leco CS230 Carbon/Sulfur Analyzer (LECO Corporation, St. Joseph, Michigan, USA) (LECO, 2005). Samples (pre-heated at different temperatures) were added to a crucible along with an accelerator and then placed in an induction furnace combustion chamber. After closing the furnace, oxygen was purged into the combustion chamber, and the induction furnace was started. The oxygen-rich environment, combined with the sample inductive properties and the accelerator, resulted in sample combustion. Carbon dioxide (with some CO) formed as did SO₂. The gases were swept into the carrier stream, and SO₂ was measured in the first infrared cell (IR cell). Any CO present in the carrier stream was converted to CO₂ in the catalytic heater assembly, and the CO₂ was measured in the second IR cell. The concentrations of CO₂ and SO₂ were determined through a reduction in the level of energy at the detector. Sample processing (the pre-heated temperature and time) and MC played a role in the results of the total sulfur content.

2.2.3. Organic compounds in drywall

Concentrations of volatile organic compounds (VOCs) in the gypsum samples were tested using EPA Method 8260B using gas chromatography (GC)/mass spectrometry (MS) (USEPA, 1996b). The samples were purged with inert gas, and the effluent gas passed through a sorbent trap where the volatile organics were trapped. After purging, the sorbent trap was rapidly heated and back-flushed onto the head of a GC column. The GC column was temperature-programmed to separate the volatile compounds, which were subsequently detected and identified using MS. The target VOCs included 48 compounds (e.g., acetone, bromodichloromethane, chloroethane, cyclohexane, dichlorodifluoromethane, ethylbenzene, 2-hexanone, methylene chloride, styrene, trichloroethene, trichlorofluoromethane, and total xylenes). The full list of these compounds and their detection limits and limits of quantification are provided in Table 2-2

Semivolatile organic compound (SVOC) concentrations, including polynuclear aromatic hydrocarbons (PAHs), in the gypsum samples, were determined using USEPA Method 8270C with GC/MS (USEPA, 2014b). Briefly, SVOCs were extracted using acetone and methylene chloride in a microwave (100 °C, 10 min, USEPA Method 3546 (USEPA, 2007d)). The target SVOCs included 65 compounds (e.g., acetophenone, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, benzo(b)fluoranthene, di-*n*-butylphthalate, caprolactam, chrysene, bis(2-ethylhexyl)phthalate, fluoranthene, indeno(1,2,3-cd)pyrene, phenanthrene, phenol, and pyrene). The full compound list and their detection and quantification limits are provided in Table 2-2.

Table 2-2: Target organic compounds and detection limits (µg kg⁻¹)

Compounds	MDL ¹	LOQ ²	Compounds	MDL	LOQ
VOCs			SVOCs		
Acetone	690	2,000	Dibenzofuran	50	99
Benzene	49	490	3,3'-Dichlorobenzidine	300	990
Bromodichloromethane	99	490	2,4-Dichlorophenol	50	99
Bromoform	99	490	Diethyl phthalate	200	500
Bromomethane	200	490	2,4-Dimethylphenol	50	99
2-Butanone	400	990	Dimethyl phthalate	200	500
Carbon Disulfide	99	490	4,6-Dinitro-2-methylphenol	500	1,500
Carbon Tetrachloride	99	490	2,4-Dinitrophenol	890	3,000
Chlorobenzene	99	490	2,4-Dinitrotoluene	200	500
Chloroethane	200	490	2,6-Dinitrotoluene	50	99
Chloroform	99	490	Fluorene	10	51
Chloromethane	200	490	Hexachlorobenzene	10	51

Compounds	MDL ¹	LOQ ²	Compounds	MDL	LOQ
Cyclohexane	99	490	Hexachlorobutadiene	50	99
1,2-Dibromo-3-chloropropane	200	490	Hexachlorocyclopentadiene	500	1,500
Dibromochloromethane	99	490	Hexachloroethane	99	500
1,2-Dibromoethane	99	490	Isophorone	50	99
1,2-Dichlorobenzene	99	490	2-Methylnaphthalene	10	51
1,3-Dichlorobenzene	99	490	2-Methylphenol	50	99
1,4-Dichlorobenzene	99	490	4-Methylphenol	50	99
Dichlorodifluoromethane	200	490	Naphthalene	10	51
1,1-Dichloroethane	99	490	2-Nitroaniline	50	99
1,2-Dichloroethane	99	490	3-Nitroaniline	200	500
1,1-Dichloroethene	99	490	4-Nitroaniline	200	500
cis-1,2-Dichloroethene	99	490	2-Nitrophenol	50	99
trans-1,2-Dichloroethene	99	490	4-Nitrophenol	500	1,500
1,2-Dichloropropane	99	490	N-Nitroso-di- <i>n</i> -propylamine	50	99
cis-1,3-Dichloropropene	99	490	N-Nitrosodiphenylamine	50	99
trans-1,3-Dichloropropene	99	490	Di- <i>n</i> -octyl phthalate	200	500
Ethylbenzene	99	490	Pentachlorophenol	99	510
Freon 113	200	990	2,4,5-Trichlorophenol	50	99
2-Hexanone	300	990	2,4,6-Trichlorophenol	50	99
Isopropylbenzene	99	490	Acetophenone	50	99
Methyl Acetate	200	490	Anthracene	10	51
Methyl Tertiary Butyl Ether	49	490	Benzo(a)anthracene	10	51
4-Methyl-2-pentanone	300	990	Benzo(a)pyrene	10	51
Methylcyclohexane	99	490	Benzo(b)fluoranthene	10	51
Methylene Chloride	200	490	Benzo(g,h,i)perylene	10	51
Styrene	99	490	Benzo(k)fluoranthene	10	51
1,1,2,2-Tetrachloroethane	99	490	Di- <i>n</i> -butyl phthalate	200	500
Tetrachloroethene	99	490	Caprolactam	99	500
Toluene	99	490	Chrysene	10	51
1,2,4-Trichlorobenzene	99	490	bis(2-Ethylhexyl) phthalate	200	510
1,1,1-Trichloroethane	99	490	Fluoranthene	10	51
1,1,2-Trichloroethane	99	490	Indeno(1,2,3-cd)pyrene	10	51
Trichloroethene	99	490	Nitrobenzene	50	99
Trichlorofluoromethane	200	490	Phenanthrene	10	51
Vinyl Chloride	99	490	Phenol	50	99
Xylenes (Total)	99	490	Pyrene	10	51
SVOCs			PCBs		
Acenaphthene	10	51	PCB-1016	3.5	17
Acenaphthylene	10	51	PCB-1221	4.5	17
Atrazine	99	500	PCB-1232	7.9	17
Benzaldehyde	200	500	PCB-1242	3.3	17
1,1'-Biphenyl	50	99	PCB-1248	3.3	17
4-Bromophenyl-phenylether	50	99	PCB-1254	3.3	17
Butylbenzyl phthalate	200	500	PCB-1260	4.8	17
Carbazole	50	99			
4-Chloro-3-methylphenol	50	99			
4-Chloroaniline	99	200			
bis(2-Chloroethoxy)methane	50	99	Formaldehyde	500	1500
bis(2-Chloroethyl)ether	50	99			
2-Chloronaphthalene	20	98			
2-Chlorophenol	50	99			
4-Chlorophenyl-phenylether	50	99			

Compounds	MDL ¹	LOQ ²	Compounds	MDL	LOQ
2,2'-oxybis(1-Chloropropane)	50	99	Tributyltin (TBT)	1.5	3.0
Dibenz(a,h)anthracene	10	51			

¹MDL – method detection limit; ²LOQ – limit of quantification

Polychlorinated biphenyl (PCB) concentrations in the gypsum samples were analyzed using EPA Method 8082 with the GC/electron capture detector (ECD) (USEPA, 2007b). PCBs were extracted using 1:1 acetone and methylene chloride in a microwave (100 °C, 10 mins, EPA Method 3546 (USEPA, 2007d)). Formaldehyde represents a target organic compound related to air quality and building materials; it can be present in the drywall as a constituent of the glues used in drywall manufacture. Formaldehyde concentrations in the gypsum samples were analyzed using EPA Method 8315A via high-performance liquid chromatography (HPLC) (USEPA, 1996a). The sample was extracted using 0.1 M ammonium acetate (pH 4.91- 4.95) for 18 hours (h) at room temperature with a 20:1 liquid-to-solid (L/S) ratio. The concentration of tributyltin (TBT), a biocide used in some anti-fouling paints and reportedly used in the manufacturer of some drywall products, was measured by first extracting with a tropolone and hexane mixture, followed by analysis by GC/MS with selected ion monitoring (SIM) (Krone et al., 1989).

Based on initial test results for the organic chemical constituents only the drywall paper was further tested as the concentration of these constituents in gypsum was negligible.

2.2.4. X-ray diffraction (XRD) Analysis

Crystalline mineral phases in the gypsum samples were investigated from 5 to 110° 2θ on a Philips X'Pert Pro Diffractometer (Philips, Almelo, The Netherlands) using cobalt K_α radiation. The powder diffraction file (PDF) patterns database from the International Centre for Diffraction Data (ICDD) was employed for the search, match, and identification steps. A subset of reference patterns was built for all drywall samples. The semi-quantitative phase analysis was performed by the X'Pert HighScore Plus software (PANalytical BV Alemo, The Netherlands) using the CHUNG Normalized Reference Intensity Ratio Method (RIR) (Chung, 1974). The relative intensity of each phase was given by a scale factor determined by a least-squares fit through all matching reference pattern lines in X'Pert HighScore. The concentration X of phase α was calculated using:

$$X_{\alpha} = \frac{I_{(hkl)\alpha}}{RIR_{\alpha} I_{(hkl)\alpha}^{rel}} \left[\frac{1}{\sum_{j=1}^n \left(I_{(hkl)j} RIR_j I_{(hkl)j}^{rel} \right)} \right]$$

where RIR_{α} = Reference Intensity Ratio (based on the relative net peak height ratio of the strongest line ($I^{rel} = 100\%$) of the phase and of the strongest line of corundum, measured with copper K_α radiation in a mixture of equal weight percentages), and $I_{(hkl)\alpha}$ = Intensity of reflection of hkl in-phase α (hkl are the reflection indices). The normalization used in this method assumed that the sum of all identified phases was 100% and that no unidentified crystalline phases or amorphous phases were present in the sample. Only under these conditions can meaningful semiquantitative results be obtained.

2.2.5. Total metals by EPA Method 3051A and acidic extraction

The drywall samples (<2 mm), including both the paper and gypsum components, were acid-digested using USEPA Method 3051A (USEPA, 2007c). A maximum of 0.25 g of representative solid sample (air-dried) was digested in 10 mL of trace metal grade concentrated nitric acid (HNO₃) using a microwave heating processing with a two-stage program. Initially, the digestion vessel was heated to 175 ± 5 °C within 10 minutes, and then the vessel was maintained at 175 ± 5 °C for an additional 5 minutes. After digestion, samples were cooled to room temperature, and then the digested solution was transferred to a centrifuge tube and brought to a volume of 50 mL with deionized (DI) water. This

solution was centrifuged for 5 minutes at 5000 revolutions per minute (rpm) and filtered using a 0.45- μ m membrane filter to obtain a clear solution for elemental analysis; dilution was performed as necessary. Elemental composition (Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Na, Mg, Mn, Mo, Ni, P, S, Sb, Se, Si, Sr, Ti, V, and Zn) was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Spectra-Tech, Shelton, CT) (EPA Method 6010C (USEPA, 2007a)). Lead and As were further analyzed using Graphite Furnace Atomic Absorption (GFAA) by EPA Method 7010 (USEPA, 1998b). The method detection limits (MDL) for elements in the aqueous phase and the limits of quantification (LOQ) for elements in the solid phase for ICP-AES and GFAA are presented in Table 2-3. Standard reference material 1633C (Coal Fly Ash), blank, spikes, and drywall sample spikes were also digested in every batch for quality control.

Table 2-3: Elemental recovery (%) by nitric acid extraction at 90 oC

Name	MDL (mg L ⁻¹)	LOQ (mg kg ⁻¹)	Sample A-G (%)		Sample L-G (%)		Blank (%)	Avg (%)
			Level I	Level II	Level- I	Level-II		
Al	0.25	50	105	105	126	120	105	112
As	0.007	1.5	98	99	101	99	95	98
B	0.044	8.9	99	100	102	100	95	100
Ba	0.005	0.98	93	93	96	95	98	95
Cd	0.001	0.11	95	96	97	96	104	98
Co	0.001	0.27	93	94	95	94	104	96
Cr	0.038	7.63	92	92	94	93	99	94
Cu	0.005	1.07	102	104	103	102	106	103
Fe	0.030	6.00	101	100	101	98	106	101
K	0.568	114	119	119	115	117	98	114
Mg	0.170	34.1	107	117	97	97	108	105
Mn	0.007	1.4	98	98	98	97	105	99
Mo	0.004	0.76	99	99	101	100	104	101
Na	0.097	19.5	107	107	111	110	99	107
Ni	0.002	0.46	95	95	97	96	105	98
P	0.006	1.15	103	105	109	108	103	105
Se	0.015	3.1	101	102	104	103	98	102
Sr	0.005	0.98	99	97	113	106	107	104
Ti	0.020	4.0	99	100	104	103	102	101
V	0.026	5.3	98	98	99	98	105	100
Zn	0.015	2.9	97	97	100	99	96	98

Acid-extractable SO₄ (0.25 M HCl) and metals concentrations were further determined based on Sun and Barlaz (2015). Equilibrium time was 1, 4, 24, 72, 168, 336, and 772 hours at room temperature and S/L ratio of 200. Calcium and sulfate solubility was reported to change depending on acid concentration and environmental temperature (Hulett, 1902; Marshall and Jones, 1966; Freyer and Voigt, 2003; Li and Demopoulos, 2006; Wang et al., 2013). In addition, a new approach to assess sulfate and metal total amounts in the drywall samples was tested by using 10% HNO₃ in a water bath or oven at 90 °C for 16 h. Acid concentration and temperature control calcium sulfate solubility and also can affect the solubility of other elements (Wollmann and Voigt, 2008; Zeng and Wang, 2011; Wang et al., 2015). A liquid-to-solid (L/S) ratio of 250 was used for all extractions, and samples were filtered (0.45 μ m) and analyzed using ICP-AES and ion chromatography (IC). In a manner similar to M3051A, blank spikes and drywall sample spikes were also included in the analysis.

2.2.6. Cumulative water-soluble SO₄ and metals

Water-extractable sulfate and metals cumulative concentrations were tested using the modified method described by Sun and Barlaz (2015). The L/S ratio was 200:1 with an end-over-end rotation at 30±2 rpm, for 60 minutes at ambient temperature with the repeated replacement of DI water. All solutions were filtered (0.45-µm) after extraction, and the residue and used membrane were returned to the container for the next extraction. The same procedure was repeated four times until the conductivity (EC) of the extraction was less than 50 µS/cm.

The content of SO₄ in each extraction after filtering was determined by IC. The metals in each extraction after filtering were acidified (HNO₃) and then analyzed by ICP-AES. The SO₄²⁻ water-extractable (L_{DIW}) results, as mmol kg⁻¹, were calculated from the individual extract concentrations. The concentration of SO₄²⁻ (C_i) in each extraction was measured as a concentration in mmol L⁻¹, and the cumulative mass of SO₄²⁻ (L_{DIW-SO4}) leached from each sampling event was calculated as:

$$L_{DIW-SO4} = \sum V_L \times C_i / M_R$$

where V_L = volume of the extraction fluid and M_R = dry mass of test material in the extractor (in kg).

The total sulfur (S_T) content measured through combustion using the LECO CS230 Carbon/Sulfur Analyzer (LECO Corporation, St. Joseph, Michigan, USA) was converted to units of mmol kg⁻¹, and the percentage of water-extractable SO₄²⁻ (S_{DIW}, %) was determined as:

$$S_{DIW} = \frac{L_{DIW-SO4}}{S_T} \times 100$$

The cumulative water-extractable metals, especially Ca, Mg, and Sr, were calculated similarly to sulfate.

2.3. Drywall Leaching Behavior

The leaching behavior of drywall was investigated using several different approaches. Experiments were performed to examine: 1) drywall leaching kinetics to determine an appropriate equilibrium time for drywall, 2) leaching as a function of liquid-to-solid ratio (USEPA method M1316) (USEPA, 2014c), and 3) leached constituent mass transfer rate using the semidynamic tank leaching procedure (USEPA Method 1315) (USEPA, 2014c).

2.3.1. Leaching processing kinetics

Metal and sulfur release kinetics studies were conducted to determine equilibrium time and conditions. A crushed paper and gypsum mixture at the appropriate weight percentages were used, and DI water was used as an extraction solvent at L/S = 20. Extractions times were: 1 h, 4 h, 24 h, 120 h, 168 h (1 week), two weeks, four weeks, six weeks, and 8 weeks. These experiments were conducted at room temperature (20 °C) using 25 g of the mixture in 500 mL DI water in triplicate. Analytical aliquots of the extracts were filtered (0.45 µm), collected, and preserved as described in the methods to be performed. Target metals (e.g., Ca, As, Pb, Zn, Se, and Sr) and sulfate concentrations were determined by ICP-AES and IC (for anions), respectively. The leachate pH and electrical conductivity (EC) were also measured. VMINTEQ 3.1 was used for chemical speciation, based on the MINTEQA2 (version 4.0) database (Gustafsson, 2016). The ionic strength was given in the model based on the empirical relationship between ionic strength and electrical conductivity (Griffin and Jurinak, 1973).

2.3.2. Liquid-solid partitioning as a function of liquid-to-solid ratio in solid materials – USEPA Method 1316

Liquid-solid partitioning (LSP) of the inorganic constituents from five drywall samples (a mixture of crushed paper and gypsum at appropriate weight percentages) as a function of L/S ratio were determined at a neutral pH. Conditions used approached chemical equilibrium (USEPA Method 1316). This method consists of 10 parallel extractions of samples over a range of L/S ratios from 80 to 200 mL

eluate g⁻¹ material (2.5, 5.0, 7.5, 10, 20, 40, 75, 100, 200 and 400), each with three replications. Also, a blank was carried out through the entire procedure. The samples (both mixed crushed paper and gypsum) were tumbled in an end-over-end fashion for one week, as determined in the previous kinetics studies. After tumbling, the liquid and solid phases were separated via a filter (0.45 µm). Extract pH and electrical conductivity (EC) were measured, and extracts were collected and preserved to meet the requirements of the determinative methods to be performed (anions by IC and metals by ICP, respectively). VMINTEQ 3.1 was also employed for the chemical species. The pore volume of drywall was determined by the following monolithic leaching test (Section 2.3.3).

2.3.3. Mass transfer rates –EPA Method 1315

The long-term leachability of five different drywall products was evaluated using the semidynamic tank leaching procedure (EPA Method 1315). These tests were conducted simultaneously on the monolithic specimens with a fixed surface area (215±5 cm²). The liquid/surface ratio (9 m³ m⁻²) was maintained constant for each leachate renewal. The polyethylene tanks were closed to prevent air penetration and water evaporation during the leaching time. The solution was renewed after 2 h, 24 h, 48 h, 7 d, 14 d, 28 d, 42 d, 49 d, and 63 d. The sample was freely drained, and the weight was recorded to monitor the amount of eluent absorbed into the solid matrix at the end of each leaching interval. The leachate at each period was collected and filtered by membranes of different sizes (5, 0.45, and 0.05 µm) and preserved based on the determinative methods to be performed. The eluate pH and specific conductance were also measured for each time interval. The anion concentration was measured by IC, and metals were determined by ICP.

The interval mass release of each sample was calculated for different leaching intervals as follows:

$$M_{t_i} = \frac{C_i \times V_i}{A}$$

where M_{t_i} = mass release during the current leaching interval, i (mg m⁻²), C_i = concentration of composition i in the eluate for interval (mg L⁻¹), V_i = eluate volume in the interval i (L), and A = specimen external geometric surface exposed to the eluent (m²).

The flux of the composition in an interval was further plotted as a function of the generalized mean of the cumulative leaching time ($\sqrt{t}$). The flux across the exposed surface of the sample was calculated as follows:

$$F_i = \frac{M_i}{t_i - t_{i-1}}$$

where F_i = flux for interval i , (mg m⁻²s⁻¹), M_i = mass released during the current leaching interval i (mg m⁻²), t_i = cumulative time at the end of the current leaching interval i (s), and t_{i-1} = cumulative time at the end of the previous leaching interval $i-1$ (s).

The time used to plot each interval mass was the generalized mean of the square root of the cumulative leaching time using the cumulative time at the end of the i^{th} interval, t_i , and the cumulative time at the end of the previous interval, t_{i-1} .

$$T = \left[\frac{1}{2} \left(t_n^{\frac{1}{2}} + t_{n-1}^{\frac{1}{2}} \right) \right]^2$$

By applying this method, the cumulative fraction of constituents leached from the drywall samples versus time was determined. The cumulative released composition i (or loss composition, $P_{\text{cum-}i}$) was evaluated by the percentage of the total amount of the composition or the leachable amount in the drywall. In this work, the total amount of the composition was assumed to be that measured through

“nitric acid extraction” (10% HNO₃, 90 °C, 16 h).

$$P_{cum-i} = \frac{\sum_{i=1}^n M_i}{\text{Total or leachable amount (composition } i\text{)}}$$

The constituents were assumed to be released primarily through a diffusion-controlled process. Usually, a mathematical diffusion model based on Fick’s second law is used to evaluate the leaching rate with respect to time (Crank, 1975; De Groot, 1993). The American Nuclear Society (ANS) has standardized a Fick’s law-based mathematical diffusion model (ANS, 1986) as follows:

$$\left(\frac{a_n}{A_0}\right) \left(\frac{V}{S}\right) \left(\frac{1}{\Delta t_n}\right) = \left(\frac{D_e}{\pi T}\right)^{0.5}$$

The effective diffusion coefficients were calculated using this model as follows:

$$D_e = \pi T \left[\frac{\left(\frac{a_n}{A_0}\right)}{\left(\frac{1}{\Delta t_n}\right)} \times \frac{V}{S} \right]^2$$

where D_e = effective diffusion coefficient (cm²/s), a_n = contaminant loss (mg) during the particular leaching period with index n , A_0 = initial amount of contaminant present in the specimen (mg), V = volume of the specimen (cm³), S = surface area of the specimen (cm²), Δt_n = duration of the leaching period in seconds, and T = “mean time” for the leaching interval n in seconds, which can be calculated as described above.

D_e values from the above equation shown are termed “effective” because diffusion occurs in the liquid filling the interstitial spaces of a porous body. Therefore, the actual liquid path is longer than the one assumed by the model. The exact solution of the diffusion equation depends on the initial and boundary conditions. The document “Measurements of the Leachability of Solidified Low-Level Radioactive Wastes” by the American Nuclear Society (ANS 16.1) also suggested using the leachability index (LX) to estimate and compare the behavior of different compositions or different wastes (ANS, 1986). The LX is calculated using the diffusion coefficient from the equation shown above and is the average of the negative logarithm of the effective diffusivity terms (expressed in cm²/s). Therefore, the leachability index is defined as follows:

$$LX = \left(\frac{1}{m}\right) \sum_{n=1}^m (-\log(D_e)_n)$$

where n is the number of the particular leaching period, and m is the total number of individual leaching periods. The relative mobility of different contaminants can be evaluated by this index, which varies from 5 ($D_e = 10^{-5}$ cm²/s, very mobile) to 15 ($D_e = 10^{-15}$ cm²/s, immobile) (Dermatas et al., 2004; Moon and Dermatas, 2007).

These equations are valid only when a leachable constituent is leached by diffusion from a uniform regularly shaped solid, and when the leachable constituent is less than 20% of the total amount (ANS, 1986). In these cases, the cumulative mass release can be described by one-dimensional semi-infinite geometry if the composition of concern is not depleted over the time of interest (Crank, 1975; De Groot, 1993). Depletion was assumed to occur when more than 20% of the total leachable content had been released. In Under these conditions, the effective diffusivity can be calculated from a shape-specific solution of the mass transport equations (Anders, 1978; Godbee et al., 1980; Kosson et al., 2002). However, the equations are still not available for the parallelepipeds used in this study. Therefore, the values of D_e or LX in this work were calculated until the total loss composition was more than 20% of the total. The total leaching time for the calculations was not necessarily as long as the real

total experiment time (63 d). The calculated cumulative time was only a partial experimental time. For most constituents in the drywall samples (e.g., Ca and S), the time to reach the leaching equilibrium was approximately one to two weeks. However, extreme situations were observed (24 h (e.g., Mg in one drywall [Drywall B])); and 63 d (e.g., dissolved organic carbon (DOC) in all samples)). The weighted arithmetic mean of the D_e estimates was employed for different drywall or different constituents; the weighting was based on its calculated cumulative time in the model. LX has been used as a performance criterion for the solidification and stabilization (S/S) of wastes in several studies (Canada, 1991; Dermatas et al., 2004; Moon and Dermatas, 2007). If the LX value is greater than 9, then the S/S wastes can be used in “controlled utilization”, provided that the information on the S/S wastes is acceptable for a specific utilization such as quarry rehabilitation, lagoon closure, or road-base material. If the S/S wastes have the LX value higher than 8, they can be disposed of in sanitary landfills. If the S/S wastes have the LX value lower than 8, they are not considered appropriate for disposal.

Based on the diffusion theory model developed by de Groot and van der Sloot (1992), the cumulative maximum release of the component (B_t in mg m^{-2}) is expressed as:

$$\log(B_t) = \frac{1}{2} \log(t) + \log \left(U_{\max} d \sqrt{\left(\frac{D_e}{\pi} \right)} \right)$$

where D_e = effective diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$ for component x , t = contact time in s, $U_{\max}$ = maximum leachable quantity expressed in mg kg^{-1} , and d = bulk density of the product in kg m^{-3} . The three mechanisms potentially controlling composition release (i.e., wash-off, diffusion, and dissolution) can be distinguished by evaluating the slope of the curve in the equation above. Slope values close to 0.5 indicate that the constituent release is slow and controlled by diffusion. Slope values close to 1 indicate that dissolution is the controlling mechanism, whereas the slope values close to 0 would suggest that the constituent release is controlled by wash-off, occurring when a soluble layer exists on the surface of the material.

2.4. Statistical Analysis

Statistical analysis and graphical representation of the data were performed using Microsoft Excel 2013, JMP 9.0, and SigmaPlot 11.0. The statistical analysis technique was chosen based on the properties of parameters. The mean, standard error, minimum and maximum values were used to summarize the content of elements and mineral phases. Box plots with mean diamonds were employed to graphically depict groups of numerical data through their summaries (minimum, lower quartile, median, mean, upper quartile, and maximum). Care must be taken when evaluating the data presented herein due to the exploratory nature of the experiment, the numerous comparisons being made, and the methods being followed, especially when using different methods.

2.5. Quality Metrics

Accuracy checks, precision, calibration of instrumentation, and determination of detection limits were used to ensure quality control and the confidence level of the obtained results. Precise, documented, and valid data are needed for the ultimate decisions to be made. To ensure the quality of the data, all instruments were regularly calibrated. Quality assurance (QA)/quality control (QC) checks, as presented in Table 2-4, were conducted to ensure the precision and accuracy of the data.

Table 2-4: Summary of Experimental QA/QC Checks

Test	Frequency	Measurement	Experimental QC	Acceptance Criteria	Corrective Action
Acid digestion	Once	Total metals	Method blank	Less than 3 times MDL	Vessel Cleaned
			Ref. Std. NIST ⁵ 1633C or 2865C	Recovery 70 - 130 %	Procedure repeated
			Triplicates	% RSD ⁶ < 10%	Procedure repeated
Total Hg	Once	Total Hg	Method blank	Less than 3 times MDL	Vessel Cleaned
			Ref. Std. NIST 2865C	Recovery 85 - 115 %	Procedure repeated
			triplicates	% RSD < 10%	Procedure repeated
Total S and C	Once	Total S and C	Method blank	Less than 3 times MDL	Vessel Cleaned
			Ref. Std. NIST 2865C for S	Recovery 90 - 110 % for S;	Procedure repeated
			Triplicates	% RSD < 10% for S	Procedure repeated
Water-extractable sulfur and metals – Method of Musson et al., 2008	Once	SO ₄ ²⁺ , other anions, and cations K ⁺ , Na ⁺ , Ca ²⁺ , and Mg ²⁺)	Triplicates	% RSD < 10%	Procedure repeated
			Method blank	Less than 3 times MDL	The problem was investigated, analysis repeated if necessary
HCl Extractable sulfur and metals	Once	SO ₄ ²⁺ , other anions, and cations (K ⁺ , Na ⁺ , Ca ²⁺ , and Mg ²⁺)	Triplicates	% RSD < 10%	Procedure repeated
			Method blank	Less than 3 times MDL ¹	The problem was investigated, analysis repeated if necessary
HNO ₃ Extractable sulfur and metals	Once	S and metals	Triplicates	% RSD ² < 10%	Repeat procedure
			Method blank	Less than 3 times MDL	The problem was investigated, analysis repeated if necessary
Formaldehyde	Once	Formaldehyde	Method blank	<RL ³	The problem was investigated, analysis repeated if necessary
			Duplicates	RPD ⁴ <30%	
			Laboratory Control Sample	50-150% Recovery	
			Matrix spike	50-150% Recovery	
PCBs	Once	PCBs	Method blank	<RL	The problem was investigated, analysis repeated if necessary
			Duplicates	RPD<30%	
			Laboratory Control Sample	50-150% Recovery	
			Matrix spike	50-150% Recovery	
VOCs	Once	VOCs	Method blank	<RL	The problem was investigated,
			Duplicates	RPD<30%	

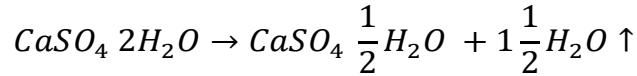
Test	Frequency	Measurement	Experimental QC	Acceptance Criteria	Corrective Action
			Laboratory Control Sample	70-130% Recovery	analysis repeated if necessary
			a matrix spike	70-130% Recovery	
SVOCs	Once	SVOCs	Method blank	<RL	The problem was investigated, analysis repeated if necessary
			Duplicates	RPD<30%	
			Laboratory Control Sample	70-130% Recovery	
			a matrix spike	70-130% Recovery	
Tributyltin	Once	Tributyltin	Method blank	<RL	The problem was investigated, analysis repeated if necessary
			Duplicates	RPD<30%	
			Laboratory Control Sample	50-150% Recovery	
			Matrix spike	50-150% Recovery	
Kinetics leaching test	8 sampling events (0-30 days)	pH, EC Dissolved metals, Inorganic anions, and DOC	Duplicates	% RPD < 10%	Repeat procedure
			Method blank	Less than 3 times IDL	The problem was investigated, analysis repeated if necessary
Method 1316	Once	pH, EC, Total alkalinity, Dissolved Metals, Inorganic anions, and DOC	Triplicates	% RSD < 15%	Occasional data outside acceptance limits were flagged. In case of frequent violation (>20% of the samples), the problem was investigated and the whole experiment was repeated when possible
			Method blank	Less than 3 times MDL	Investigate problem, repeat if necessary
Method 1315	9 time points	pH, EC, Total alkalinity, Dissolved metals, Inorganic anions, and DOC	Triplicates	% RSD < 15%	Occasional data outside acceptance limits were flagged. In case of frequent violation (>20% of the samples), the problem was investigated, and the whole experiment was repeated if possible
			Method blank	Less than 3 times MDL	Investigate problem, repeat if necessary

¹MDL – Method detection limit; ²RSD – Relative standard deviation; ³RL – Reporting limit; ⁴RPD - relative percent difference; ⁵ NIST - National Institute of Standards & Technology; ⁶ RSD -relative standard deviation

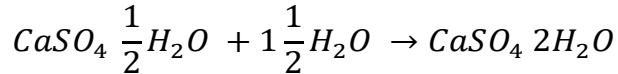
3. Physical and Chemical Properties

3.1. Moisture Content

MC measurements of the drywall samples were made at several different temperatures. Calcium sulfate exists predominantly at three levels of hydration in nature: dihydrate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 0.5(\text{H}_2\text{O})$, α -hemihydrate and β -hemihydrate) and anhydrous state (anhydrite, CaSO_4). When heated, gypsum converts to a partially dehydrated mineral called calcium sulfate hemihydrate, calcined gypsum, or plaster of Paris. This material has the formula $\text{CaSO}_4 \cdot (n\text{H}_2\text{O})$, where $0.5 \leq n \leq 0.8$. Temperatures between 100 °C and 150 °C are required to remove initial water depending on ambient humidity. Temperatures as high as 170 °C are used in industrial calcination, but at these temperatures γ -anhydrite begins to form. At this point, the heat vaporizes the water rather than increasing the mineral temperature. Thus, the temperature rises slowly until the water is gone, and then the temperature increases faster. The equation that describes partial dehydration is:



The endothermic property of this reaction is relevant to the performance of drywall, as it confers fire resistance to the drywall. When calcined gypsum is mixed with water at ambient temperatures, it quickly returns to the preferred dihydrate form, while physically “setting” to form a rigid and relatively strong gypsum crystal lattice.



This reaction is exothermic and is responsible for the ease with which gypsum can be cast into various shapes, including sheets (for drywall), sticks (for blackboard chalk), and molds.

Upon heating to 180 °C, the nearly water-free form, called γ -anhydrite ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ where $n = 0$ to 0.05), is formed. The γ -anhydrite reacts slowly with water to return to the dihydrate state, a property exploited in some commercial desiccants. At temperatures above 250 °C, the completely anhydrous form called β -anhydrite or “natural” anhydrite is formed. Natural anhydrite does not react with water, even over geological timescales, unless very finely ground.

The results of weight loss on ignition (WLOI) measurements of the gypsum samples at different temperatures are presented in Figure 3-1 and Table 3-1. These results demonstrate that MC measurement results at different temperatures depend on the testing procedures used. After reaching 230 °C, gypsum mass was relatively stable, supporting the concept of “combined water” in the ASTM C471M-16 (ASTM-International, 2016). The WLOI measured between 230 to 550 °C can be related to inherent organic matter decomposition in the drywall gypsum core (Heiri et al., 2001; Wang et al., 2011). The MC measured using the “freeze-drying processing” (0.76%) was significantly higher than the MC measured at a temperature of 45 °C (0.35%), but much lower than the MC measured at 105 or 230 °C (13.6 and 19.7%) (Table 3-1).

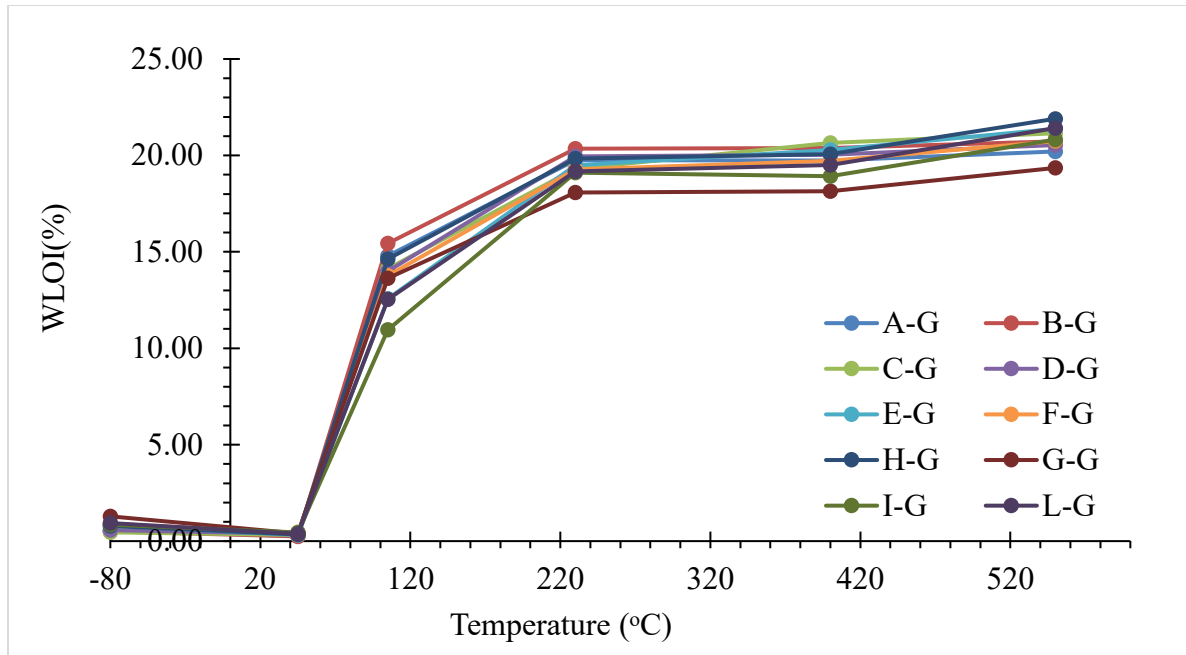


Figure 3-1: WLOI of gypsum of drywall board

Table 3-1: The average of WLOI content of gypsum of drywall (%)

Temp (°C)	Mean	Stdev	Min	Max
-80	0.76	0.25	0.45	1.29
45	0.35	0.07	0.25	0.45
105	13.64	1.31	10.9	15.4
230	19.43	0.62	18.1	20.3
400	19.74	0.74	18.1	20.6
550	20.82	0.71	19.3	21.9

The moisture content at 105 °C presented great variation, even after 100 h (four times the drying time for most soil and rocks as minerals), as mineral phases are still transforming (Table 3-2). However, there was almost no difference in MC among samples dried at 230 °C, as all water should be lost by this point. In addition, MC in gypsum and paper from the same drywall board were quite different, ranging from 12.3-18.3% and 11.2-13.8% (Table 3-3).

Table 3-2: The average of MC of gypsum for drywall after drying procedures (%)

	Average	Stdev	CV
	Free water content @ 45 °C		
A-G	0.26	0.02	8.43
B-G	0.25	0.02	7.34
C-G	0.32	0.03	9.35
D-G	0.38	0.01	1.95
E-G	0.32	0.03	9.98

	Average	Stdev	CV
F-G	0.41	0.04	8.62
G-G	0.40	0.03	6.94
H-G	0.34	0.03	9.07
I-G	0.45	0.03	5.72
L-G	0.38	0.02	5.66
Average of 10	0.35	0.07	18.7
	MC @ 105 °C		
A-G	17.36	0.14	0.82
B-G	18.26	0.50	2.71
C-G	16.46	0.85	5.18
D-G	16.30	2.22	13.6
E-G	14.43	2.79	19.4
F-G	15.97	1.52	9.52
G-G	15.79	0.96	6.09
H-G	17.13	0.41	2.37
I-G	12.34	2.63	21.3
L-G	14.36	2.49	17.4
Average of 10	15.84	1.73	10.9
	The combined water @ 230 °C		
A-G	24.61	0.11	0.46
B-G	25.54	0.12	0.46
C-G	23.91	0.50	2.08
D-G	24.93	0.20	0.82
E-G	24.22	0.97	4.01
F-G	23.88	0.31	1.30
G-G	22.06	0.13	0.57
H-G	24.74	0.15	0.62
I-G	23.63	0.06	0.25
L-G	23.71	0.07	0.29
Average of 10	24.12	0.95	3.93
	MC @ 400 °C		
A-G	24.60	0.04	0.16
B-G	25.60	0.27	1.05
C-G	26.02	0.11	0.41
D-G	25.04	0.05	0.20
E-G	25.44	0.02	0.10
F-G	24.56	0.10	0.42
G-G	22.16	0.10	0.45
H-G	25.11	0.11	0.45
I-G	23.34	0.08	0.36
L-G	24.24	0.08	0.31
Average of 10	24.61	1.15	4.66

Table 3-3: The MC of drywall board at 105°C (%)

	Paper		Gypsum		Drywall board
	Average	Stdev	Average	Stdev	
A	11.97	0.13	17.36	0.14	16.72
B	12.83	1.74	18.26	0.50	17.44
C	13.26	1.47	16.46	0.85	16.09
D	13.80	2.22	16.30	2.22	16.05
E	11.71	1.13	14.43	2.79	14.04
F	11.92	1.21	15.97	1.52	15.37
G	11.60	0.98	15.79	0.96	15.32
H	13.62	1.22	17.13	0.41	16.51
I	11.68	1.10	12.34	2.63	12.21
L	11.24	1.59	14.36	2.49	13.83
Average of 10	12.36	0.93	15.84	1.73	15.36

Dry-weight composition comparison for other chemical constituents is difficult as the temperature used for MC analysis in drywall or other wastes with large amounts of calcium sulfate usually is not described due to change in composition and volatilization lost (Musson et al., 2008; Reidy et al., 2014; Sun and Barlaz, 2015).

3.2. Total Sulfur and Carbon Content

As expected, gypsum total sulfur content increased as drying temperature increased due to weight loss (Table 3-4). The total sulfur content was relatively constant at different temperatures in all samples (e.g., 20 °C, 400 °C and 550 °C); however, differences among different drywall products were observed ($p < 0.01$) (Tables 3-4 and 3-5). In addition, the sulfur content in oven-dried gypsum samples was greater compared to air-dried, indicating rapid rehydration upon air contact. Thus, it is better to compare gypsum chemical compositions in air-dried samples as MC will be unstable in oven drying (105°C). Therefore, all results in this report were expressed on an air-dried basis (referred to as air-dry weight basis), unless otherwise noted. The total sulfur content of pure control gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot (\text{H}_2\text{O})_{0.5}$, α -hemihydrate, and β -hemihydrate) and anhydrite (CaSO_4) was 18.6, 22.0, and 23.5 %, respectively.

Conversely, total carbon measurements in gypsum samples decreased as a result of organic matter heating decomposition (Table 3-6). Total carbon content at 20 °C was much higher (0.87%) than at 400 °C (0.34-0.43%) or 550 °C (0.11-0.14%), respectively ($p < 0.01$) (Tables 3-6 and 3-7). The small amounts of organic carbon in the gypsum samples (0.3-1.9%) likely originated from additives in the manufacturing process.

Based on the weight percentage of paper and gypsum in drywall products, the average total sulfur and carbon content of 10 drywall samples was 16.7 ± 0.77 and $4.47 \pm 0.95\%$, respectively (Tables 3-8 and 3-9).

Table 3-4: The sulfur content (%) of gypsum of drywall (air-dried weight basis)

	20 °C	105 °C	400 °C	550 °C
A-G	17.77	21.88	22.40	22.37
B-G	18.23	22.61	22.67	23.02
C-G	17.93	21.33	22.22	22.74
D-G	18.12	21.97	22.87	23.06
E-G	17.18	20.85	21.80	22.47
F-G	17.29	21.19	21.64	21.40
G-G	16.45	19.86	20.49	21.19
H-G	17.35	21.60	22.33	22.69
I-G	17.88	21.13	22.13	22.60
L-G	17.44	20.63	21.64	22.55
Average of 10	17.56	21.31	22.02	22.41

Table 3-5: The sulfur content (%) of gypsum of drywall (air-dried weight basis)

	20 °C	105 °C	400 °C	550 °C	Average	Stdev	CV (%)
A-G	17.77	18.64	17.98	17.85	18.06	0.40	2.22
B-G	18.23	19.12	18.05	18.25	18.41	0.48	2.63
C-G	17.93	18.32	17.63	17.93	17.95	0.28	1.58
D-G	18.12	18.89	18.29	18.32	18.40	0.34	1.86
E-G	17.18	18.22	17.38	17.67	17.60	0.46	2.63
F-G	17.29	18.27	17.37	16.96	17.47	0.56	3.21
G-G	16.45	17.15	16.77	17.09	16.86	0.34	1.99
H-G	17.35	18.44	17.85	17.72	17.84	0.46	2.58
I-G	17.88	18.81	17.94	17.89	18.13	0.46	2.51
L-G	17.44	18.04	17.42	17.73	17.65	0.29	1.66
Average	17.56	18.39	17.67	17.74	17.84	0.58	3.25

Table 3-6: The carbon content (%) of gypsum of drywall (oven-dried weight basis with no follow-up air drying)

	20 °C	105 °C	400 °C	550 °C
A-G	0.54	0.59	0.24	0.09
B-G	0.30	0.45	0.00	0.02
C-G	1.85	2.18	0.24	0.12
D-G	0.42	0.63	0.09	-0.01
E-G	1.07	1.20	0.58	0.26
F-G	1.06	1.33	0.59	0.36
G-G	0.79	0.99	0.56	0.31
H-G	1.00	1.19	0.55	0.07
I-G	0.67	0.73	0.83	0.07
L-G	1.02	1.11	0.66	0.08
Average of	0.87	1.04	0.43	0.14

Table 3-7: The carbon content (%) of gypsum of drywall (oven-dried weight basis followed by air drying)

	20 °C	105 °C	400 °C	550 °C
A-G	0.54	0.51	0.19	0.07
B-G	0.30	0.38	0.00	0.01
C-G	1.85	1.87	0.19	0.09
D-G	0.42	0.54	0.07	0.00
E-G	1.07	1.05	0.46	0.21
F-G	1.06	1.14	0.47	0.29
G-G	0.79	0.85	0.46	0.25
H-G	1.00	1.02	0.44	0.06
I-G	0.67	0.65	0.67	0.06
L-G	1.02	0.97	0.53	0.06
Average of 10	0.87	0.90	0.35	0.11

Table 3-8: The carbon content (%) of drywall (105 °C dry-weight basis)

	Gypsum part		Paper part		Drywall board	
	Average	Stdev	Average	Stdev	Average	Stdev
A	0.59	0.03	28.08	1.41	3.62	0.06
B	0.45	0.03	25.55	1.42	4.03	0.00
C	2.18	0.06	22.35	1.31	4.16	0.19
D	0.63	0.06	20.85	1.90	2.51	0.23
E	1.20	0.01	28.60	2.06	4.93	0.20
F	1.33	0.03	30.58	1.55	5.35	0.24
G	0.99	0.11	31.83	0.71	4.22	0.30
H	1.19	0.05	27.46	2.06	5.57	0.24
I	0.73	0.05	24.35	1.22	5.21	0.18
L	1.11	0.07	25.94	1.45	5.11	0.39
Average of 10	1.04	0.43	26.56	3.46	4.47	0.95

Table 3-9: The sulfur content (%) of drywall (105 °C dry-weight basis)

	Gypsum part		Paper part		Drywall board	
	Average	Stdev	Average	Stdev	Average	Stdev
A	18.64	0.09	5.22	0.83	17.12	0.18
B	19.12	0.42	6.69	0.91	17.32	0.49
C	18.32	0.28	8.39	0.56	17.21	0.31
D	18.89	0.38	8.80	1.00	17.91	0.44
E	18.22	0.32	5.30	0.87	16.40	0.40
F	18.27	0.54	3.89	0.44	16.21	0.52
G	17.15	0.46	3.12	0.20	15.63	0.43
H	18.44	0.33	5.40	0.50	16.20	0.36
I	18.81	0.57	6.42	0.77	16.42	0.61
L	18.04	0.39	6.53	0.72	16.13	0.45
Average of 10	18.39	0.55	5.97	1.79	16.66	0.70

3.3. Trace Organic Compounds

In all the samples, most SVOC compounds and all VOC and PCB concentrations were below the method detection limits (data not shown). In addition, most PAH concentrations were between the MDL and RL and ranged from 14-622 $\mu\text{g kg}^{-1}$ (Table 3-10). Detected PAHs included carcinogenic compounds such as benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, benzo(b)fluoranthene, di-*n*-butyl phthalate, caprolactam, chrysene, bis(2-ethylhexyl)phthalate, fluoranthene, indeno(1,2,3-cd)pyrene, phenanthrene, phenol, and pyrene (Table 3-10). Drywall sample E presented the highest concentration among those tested. This sample was re-tested, and results showed that PAH concentrations in the paper were almost ten times the PAH concentration of the composite sample, indicating that the PAH source was not from gypsum but from the paper and/or chemical additives or glues used for drywall manufacturing.

Moreover, formaldehyde concentrations in most of the drywall samples ranged from 500 up to 8,500 $\mu\text{g kg}^{-1}$, with a median and average value of 1,800 and 3,700 $\mu\text{g kg}^{-1}$, respectively (Figure 3-2). Tributyltin (TBT) concentrations in two of the three mold-resistant samples exhibited TBT concentrations above detection (19 and 59 $\mu\text{g kg}^{-1}$). However, no difference in TBT concentration in the paper and gypsum fractions was observed in these drywall samples. In addition, these results might differ from the results for old drywall samples as concentrations of formaldehyde and other organics decrease with time.

Table 3-10: The content of PAHs in drywall ($\mu\text{g kg}^{-1}$)

PAH compounds	Drywall											MDL	LOQ
	A	B	C	D	E	F	G	H	I	L	Median		
Acetophenone	ND ¹	ND	ND	ND	ND	91	ND	ND	ND	ND	91	50	99
Di- <i>n</i> -butyl phthalate	ND	ND	ND	ND	280	ND	ND	320	ND	ND	300	200	500
Caprolactam	ND	130	ND	ND	170	ND	ND	ND	ND	ND	150	99	500
bis(2-Ethylhexyl)phthalate	410	220	ND	ND	580	350	330	650	460	380	395	200	510
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	21	ND	ND	ND	ND	ND	21	10	51
Nitrobenzene	ND	ND	ND	ND	ND	61	ND	ND	ND	ND	61	50	99
Phenol	ND	90	63	100	93	120	650	53	ND	ND	93	50	99
Anthracene	ND	ND	ND	ND	19	ND	ND	ND	ND	ND	19	10	51
Benzo(a)anthracene	19	24	47	18	69	17	18	ND	ND	ND	19	10	51
Benzo(a)pyrene	19	19	10	31	67	21	24	11	13	ND	19	10	51
Benzo(b)fluoranthene	22	26	12	41	56	26	23	16	21	15	23	10	51
Benzo(g,h,i)perylene	10	14	ND	14	42	15	15	11	ND	ND	14	10	51
Benzo(k)fluoranthene	16	15	ND	21	38	17	16	11	ND	ND	16	10	51
Chrysene	29	28	22	23	96	23	32	12	14	ND	23	10	51
Fluoranthene	23	23	ND	11	95	ND	33	18	10	ND	23	10	51
Phenanthrene	24	26	ND	12	86	30	34	24	14	11	24	10	51
Pyrene	32	25	ND	22	180	33	39	13	12	ND	29	10	51
Carcinogenic PAHs	194	200	91	193	748	182	234	116	84	26	188	100	510
Total PAHs	604	640	154	293	1892	804	1214	1139	544	406	622	759	2368

¹ND – Not detected

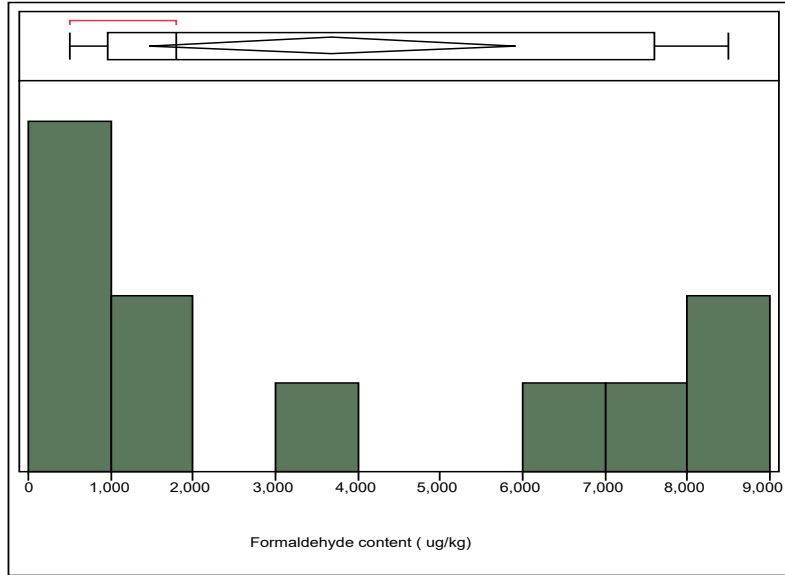


Figure 3-2: Distribution of Formaldehyde content in drywall board

3.4. Crystalline Mineral Phases

Gypsum component mineral phases of the drywall sample were characterized using XRD. A typical gypsum XRD pattern is presented in Figure 3-3. The details of the mineral phases of each sample, including the peak and pattern lists, are presented in Appendix A.

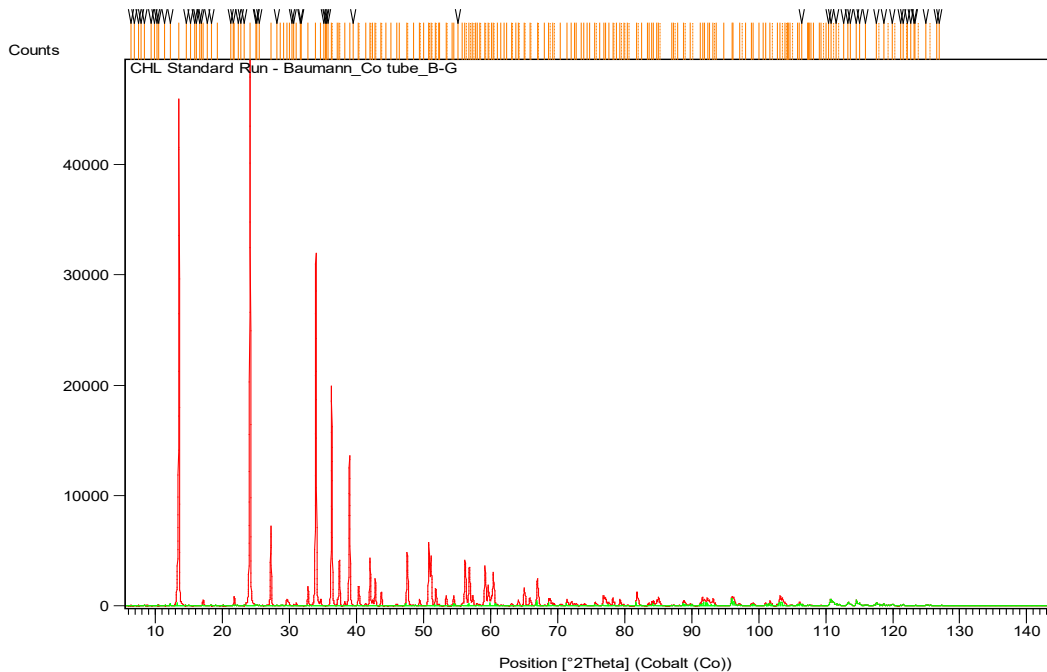


Figure 3-3: Typical XRD pattern of gypsum of drywall board

As expected, the dominant mineral in the samples was gypsum (reference code 01-074-1433, and 00-033-0311), with a small amount of hemihydrate (reference code 01-083-0438) and anhydrite (reference code 01-072-0503) also observed. In addition, Ca and Mg carbonate was detected (reference code 01-072-1652 and 01-086-2236), as was silica (reference code 01-085-0457).

As shown in Table 3-11, the drywall gypsum component (i.e., drywall without paper) was made of 90% gypsum in all samples. The XRD technique is semiquantitative; a built-in assumption is that all phases add to 100%. Based on these semiquantitative results, the average total sulfur content in these samples was 17.9%, which is similar to the total sulfur content detected by the LECO CS230 Carbon/Sulfur Analyzer.

Table 3-11: The Semiquantitative analysis (%) of mineral phases of gypsum from drywall

Compound	Calcium Sulfate				Silicon	Carbonate	
Chemical	$\text{CaSO}_4(\text{H}_2\text{O})_2$		CaSO_4	$\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$	SiO_2	CaC	($\text{Mg}_{.129} \text{Ca}_{.871}$)
Ref. Code	01-074-1433	00-033-0311	01-072-0503	01-083-0438	01-085-0457	01-072-1652	01-086-2336
A-G	52	40	2	2	3	1	1
B-G	53	40	1	2	3	1	1
C-G	51	39	3	2	4	1	1
D-G	53	40	2	2	2		1
E-G	53	38	1	3	2	1	1
F-G	51	39	1	4	2	1	1
G-G	49	38	1	6	3	1	2
H-G	52	40	1	3	2	1	1
I-G	50	40	1	4	2	1	2
L-G	51	39	1	5	2	1	2
Average of 10	52	39	1	3	3	1	1

3.5. Total Acid Extractable Sulfur and Metals

Acid-extractable sulfur content was lower (13.6%) compared to combustion technique sulfur (18.3%, LECO CS230 Carbon/Sulfur Analyzer) (Tables 3-9 and 3-12). The 30% difference might indicate issues during acid digestion using USEPA 3051A. Besides, total acid-extractable calcium average concentration was 18.6%, and the molar ratio of Ca to S was 1.09 (Table 3-12).

Acid-extractable macro- and micro-element results are presented in Figures 3-4 and 3-5. As expected, positive correlations (both Person and Spearman) were observed between elements ($p < 0.01$) (e.g., Ca vs S and Na; Al vs K; Fe vs K, Mn, Ni, Cu, Zn, and Ba; Mg vs Mn, Na, P, and Zn; Na vs Se, Zn, and Hg) (Figure 3-6).

Table 3-12: The sulfur and metal content of gypsum from drywall by USEPA M3051A

	Mean	Std Dev	Lower 95%	Upper 95%	Median	Minimum	Maximum
Ca (%)	18.56	2.82	17.51	19.62	18.7	12.59	23.75
S (%)	13.62	2	12.87	14.36	13.68	9.59	17.37
Mg (mg/kg)	2500	2120	1710	3290	2280	160	7790
K (mg/kg)	340	575	129	560	120	110	2200
Na (mg/kg)	170	63	142	190	150	86	280
Fe (mg/kg)	1030	1230	570	1490	570	250	4780
Al (mg/kg)	550	1000	180	920	240	100	3710
Si (mg/kg)	280	198	200	350	200	120	800
Sr (mg/kg)	140	148	85	196	65	43	472
Ba (mg/kg)	19	30	8.2	30	7.3	4.8	115
Cu (mg/kg)	2.4	3.2	1.22	3.6	1.0	0.97	12.6
Mn (mg/kg)	10	14	5.1	16	5.2	2	55
P (mg/kg)	130	90	92	159	150	9.1	241
Ni (mg/kg)	3.5	7.9	0.5	6.4	0.8	0.39	28.5
Se (mg/kg)	4.1	1.2	3.7	4.6	3.7	3	5.9
Zn (mg/kg)	11	3.4	9.49	12	10.7	4.4	18
As (µg/kg)	125	126	78	170	84	80	530
Pb (µg/kg)	560	270	460	660	440	120	1370
Hg (µg/kg)	165	85	130	200	150	43	360

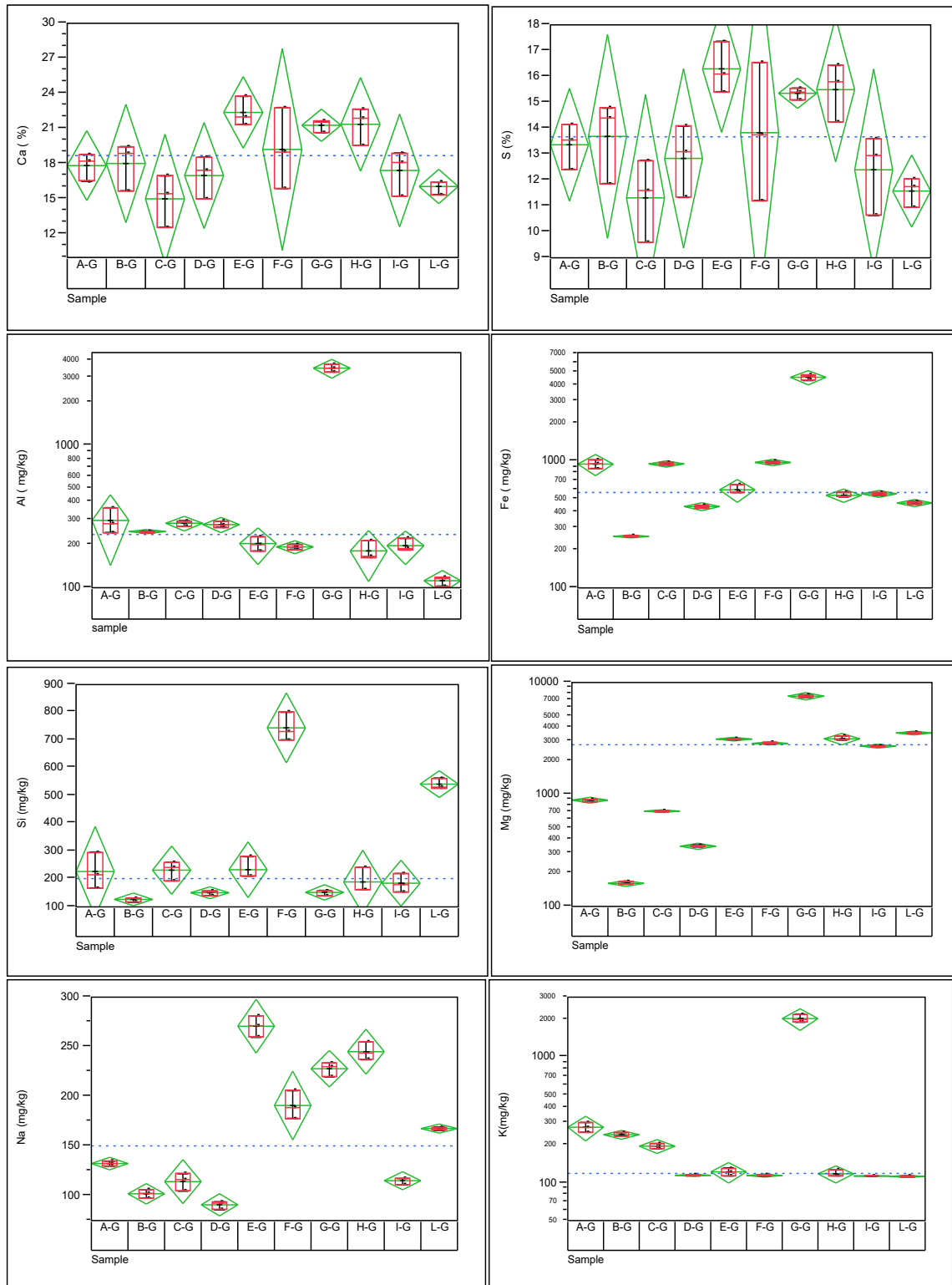


Figure 3-4: Distribution of the macro-elements in the gypsum from drywall. The box-and-whisker plots show the following: the minimum value, the 25th quartile, the

median, the 75th quartile, the maximum value.

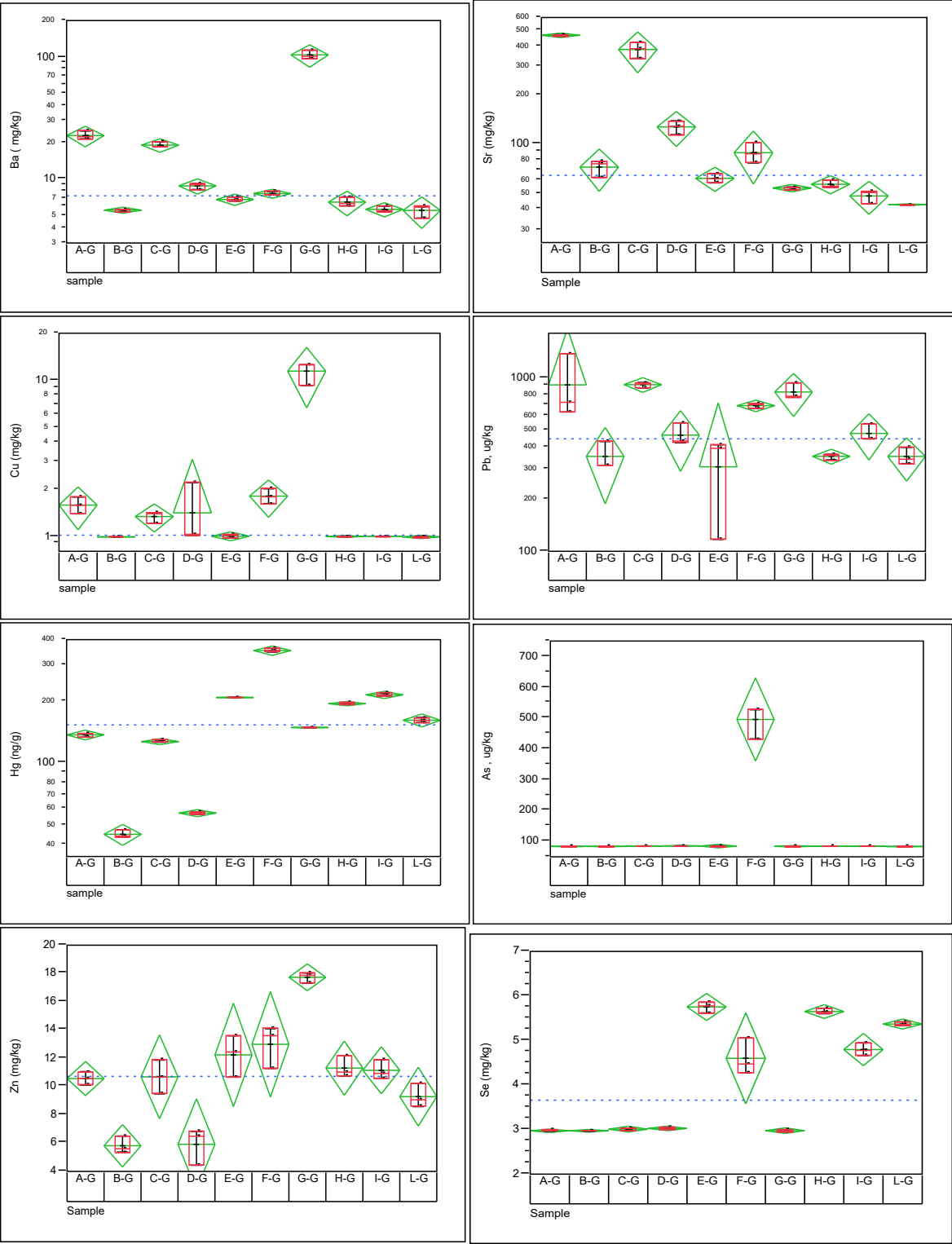


Figure 3-5: Distribution of the micro-elements in the gypsum from drywall. The box-and-whisker plots show the following: the minimum value, the 25th quartile, the

median, the 75th quartile, the maximum value.

All the calcium, sulfate, and other metals from the gypsum samples were assumed to be dissolved in the heating process by microwave. The dilution of samples with DI water before analysis, however, required the temperature to be lowered to room temperature. Upon dilution, the acid concentration in the final digested solution was further decreased ($< 2\text{ M}$), and this is suspected to have resulted in some dissolved calcium and sulfate (and other metals) re-precipitating, in agreement with the transformation and solubility of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) at changing pH and temperature (Freyer and Voigt, 2003; Li and Demopoulos, 2005; Shukla et al., 2008; Wang et al., 2013).

Because of re-precipitation, solid residues were common in the final diluted digestates (EPA 3051A), and thus, centrifugation or filtration was required. In these cases, the extracted analyte concentrations may not reflect the true total concentrations in the sample (USEPA, 2007c); the concentrations of sulfate, calcium, and other constituents assessed through the use of M3051A may be underestimated. This underestimation was further demonstrated by additional testing on one sample (gypsum from Drywall L) diluted at four different temperatures (4, 20, 37, and 80 °C) (five replications at each temperature). The concentrations of calcium, sulfate, strontium, silicate, and titanium in this sample were positively related to the temperature for dilution. The concentrations of iron, aluminum, phosphorus, and magnesium were relatively stable with temperature (Figure 3-7, Table 3-13). These observations are supported by other research on the solubility of calcium sulfate in complex systems (Wollmann and Voigt, 2008; Zeng and Wang, 2011; Wang et al., 2015)

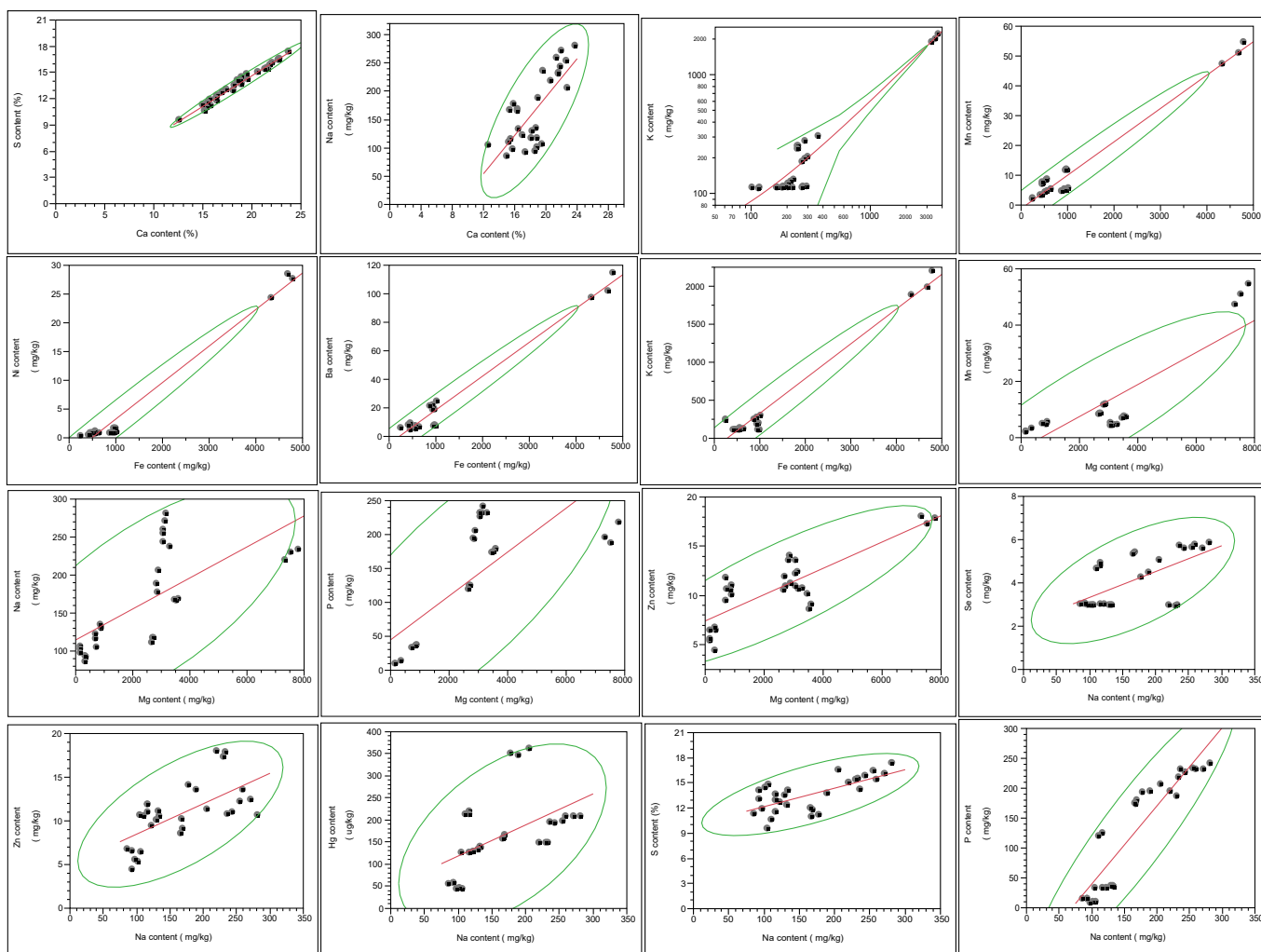


Figure 3-6: Positive correlations among elements in the gypsum from drywall

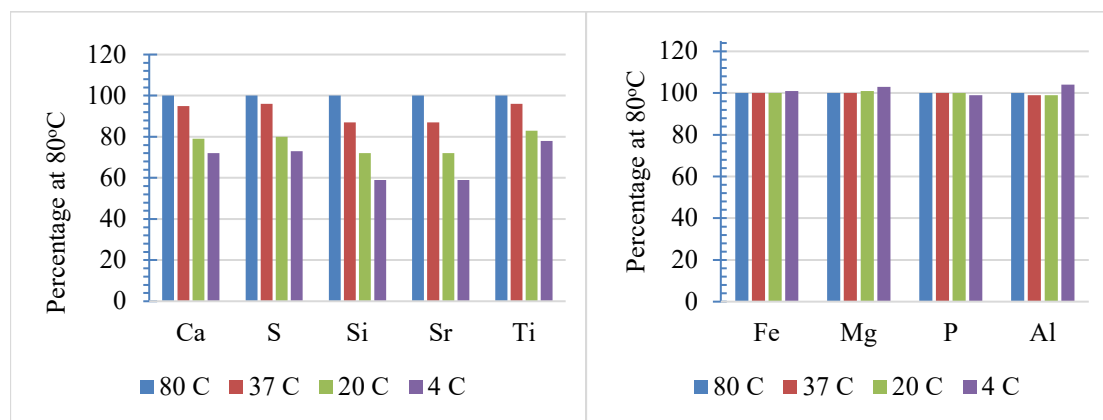


Figure 3-7: Effect of dilution temperature on the relative metal content of gypsum from drywall

Table 3-13: Effect of dilution temperature on the elemental composition of gypsum from Drywall-L

	4 °C			20 °C			37 °C			80 °C		
Ca (%)	15.20	±	1.64	16.52	±	1.09	19.99	±	3.21	20.98	±	0.38
S (%)	10.73	±	1.22	11.81	±	0.76	14.10	±	2.29	14.75	±	0.36
Mg (mg/kg)	3598	±	59	3540	±	43	3502	±	28	3494	±	17
K (mg/kg)	117	±	0.95	118	±	0.79	117	±	1.42	117	±	1.47
Na (mg/kg)	938	±	87.0	1047	±	23.5	893	±	74.3	975	±	72.0
Fe (mg/kg)	479	±	11.0	474	±	12.1	477	±	3.92	476	±	11.4
Al (mg/kg)	108	±	15.3	104	±	7.01	103	±	10.7	104	±	6.74
Si (mg/kg)	421	±	8.15	518	±	43.7	620	±	11.1	717	±	33.9
Ti (mg/kg)	18.9	±	2.25	19.0	±	1.06	22.0	±	2.42	22.1	±	1.12
Sr mg/kg)	47.1	±	2.77	50.1	±	2.11	58.2	±	6.43	60.6	±	0.8
Ba (mg/kg)	5.02	±	0.63	4.90	±	0.34	5.57	±	0.43	5.47	±	0.20
Cu (mg/kg)	1.97	±	0.02	1.98	±	0.01	1.97	±	0.02	1.96	±	0.02
Mn (mg/kg)	7.72	±	0.48	7.30	±	0.19	7.56	±	0.19	8.05	±	0.45
P (mg/kg)	179	±	1.66	182	±	2.29	182	±	1.53	182	±	2.51
Ni (mg/kg)	1.18	±	0.01	1.19	±	0.01	1.18	±	0.01	1.18	±	0.01
Se (mg/kg)	6.50	±	0.22	6.27	±	0.17	6.70	±	0.44	6.39	±	0.32
Zn (mg/kg)	9.07	±	0.07	9.44	±	0.75	9.06	±	0.11	9.23	±	0.35

In a previous study, calcium content average in drywall samples (n = 20) was approximately 10% (9.5±0.5%), or less than half of the theoretical calcium content in the pure gypsum (CaSO₄·2H₂O, 23.3%) (Reidy et al., 2014). However, a study from The Division of Hazard Analysis, U.S. Consumer Product Safety Commission found an average content of calcium of 24.9±7.9% (Garland and Greene, 2009).

Gypsum inorganic trace constituent concentrations compared to previously reported studies are summarized in Table 3-14. The concentration differences may be related to gypsum sources or extraction methods used. Regardless, the evidence suggested that using the EPA 3051A digestion method may be questionable when the method is used for drywall or other materials containing high amounts of calcium sulfate, and thus, a new approach is necessary.

Table 3-14: Elemental composition of gypsum from drywall (mg/kg)

Element	Study	Mean	Std Dev	Media	25%	75%	Range	Max	Min
Mg	2009*	5404	5720	4800	989	7270	18015	18200	185
	2014**	1885	1180	1715	1087	3016	3759	3880	121
	This work	2503	2199	2780	618	3246	7392	7552	161
	All data	5249	5476	3121	1115	8070	19879	20000	121
Al	2009	874	792	726	234	1330	2541	2720	179
	2014	2783	1806	2540	1527	3845	5722	6190	468
	This work	550	1038	226	191	287	3386	3499	113
	All data	1759	1609	1330	281	3255	6077	6190	113
Fe	2009	1413	861	1350	663	1860	2926	3270	344
	2014	1574	959	1080	984	2340	2775	3590	815
	This work	1033	1276	574	463	959	4341	4596	255
	All data	1470	951	1100	710	1910	4341	4596	255
Ba	2009	45.7	60.7	17.5	7.46	80.3	227	229	2.50

Element	Study	Mean	Std Dev	Media	25%	75%	Range	Max	Min
	2014	18.9	16.5	13.2	9.71	27.2	51.0	53.9	2.88
	This work	19.3	30.6	7.2	5.66	20.0	99.0	105	5.58
	All data	43.8	51.3	17.5	7.54	79.0	226.5	229.0	2.50
Sr	2009	1598	1545	776	303	2890	4170	4310	140
	2014	389	115	338	322	464	389	661	272
	This work	140	153	67.2	52.5	191	424	467	42.8
	All data	1054	1164	467	229	1740	4267	4310	42.8
Mn	2009	47.9	35.0	46.0	9.25	78.4	97.1	101	3.92
	2014	24.8	21.6	18.4	11.3	31.5	63.7	68.7	4.99
	This work	10.4	14.5	5.11	4.20	9.30	48.9	51.0	2.05
	All data	40.1	34.1	24.9	8.09	72.0	105.0	107.0	2.05
Pb	2009	2.57	3.84	1.42	1.35	2.02	15.1	16.4	1.29
	2014	1.79	0.96	1.37	1.22	2.15	2.93	4.03	1.10
	This work	0.56	0.25	0.47	0.35	0.85	0.60	0.91	0.31
	All data	1.93	2.48	1.37	1.06	1.96	16.1	16.4	0.31
K	2009	403	319	340	252	586	1279	1320	41
	This work	349	592	147	114	250	1914	2027	112
	All data	382	438	264	116	384	1985	2027	41
Na	2009	247	165	162	114	371	445	553	108
	This work	166	65	150	111	232	180	271	91
	All data	214	138	162	114	264	462	553	91
Cu	2009	2.43	1.64	1.97	1.12	3.22	6.19	6.86	0.67
	This work	2.47	3.19	1.43	1.00	2.02	10.4	11.4	0.99
	All data	2.44	2.32	1.62	1.10	2.75	10.8	11.4	0.67
Zn	2009	3.42	2.18	2.86	1.77	4.43	7.77	8.52	0.75
	This work	10.8	3.44	10.9	8.41	12.4	11.9	17.7	5.81
	All data	6.36	4.55	5.31	2.64	10.6	17.0	17.7	0.75
Ni	2009	1.90	1.37	1.33	0.96	2.19	4.81	5.46	0.65
	This work	3.47	8.22	0.83	0.69	1.2	26.4	26.8	0.40
	All data	2.53	5.20	1.30	0.83	1.85	26.4	26.8	0.40
Hg	2009	0.22	0.30	0.12	0.05	0.26	1.20	1.24	0.04
	This work	0.17	0.09	0.16	0.11	0.21	0.31	0.35	0.04
	All data	0.20	0.24	0.15	0.08	0.21	1.20	1.24	0.04
Se	2009	4.06	3.44	2.20	2.06	4.11	10.18	12.20	2.02
	This work	4.15	1.16	4.09	3.00	5.17	2.78	5.75	2.97
	All data	4.09	2.72	3.40	2.15	5.02	10.2	12.2	2.02
Cr	2009	2.84	4.17	1.87	1.20	2.68	17.02	17.70	0.68
	2014	18.91	9.43	20.15	7.23	28.18	23.86	29.40	5.54
	All data	8.02	9.13	3.07	2.05	11.7	28.7	29.4	0.68
As	2009	2.60	0.91	2.28	2.25	2.37	3.55	5.70	2.15
V	2009	2.80	2.45	2.19	1.98	2.89	10.56	11.20	0.64
Co	2009	1.10	1.38	0.54	0.46	1.06	4.97	5.40	0.43
Cd	2014	0.26	0.03	0.25	0.23	0.28	0.10	0.31	0.22
Cs	2014	0.33	0.17	0.29	0.23	0.37	0.56	0.73	0.17
Ga	2014	0.33	0.19	0.28	0.19	0.40	0.61	0.77	0.16
Rb	2014	3.51	3.22	2.68	1.58	4.11	10.6	11.2	0.57
P	This work	126	93	150	29	208	225	235	9.8
Si	This work	278	201	209	152	310	617	744	127

* Garland and Greene, 2009; ** Reidy et al., 2014

Other acidic extraction methods (e.g., 0.25 M HCl) and different S:L ratio (200:1) were also used for sulfur content extraction in high calcium sulfate wastes at room temperature (Sun and Barlaz, 2015). This method indicated that extractable sulfur was released quickly, but no increase was observed after 24 h up to 1 month (Figure 3-8). The sulfur concentration measured using this approach was close to the results obtained by the combustion methodology ($p>0.05$) (Table 3-15) but greater than that measured using USEPA 3051A ($p<0.01$).

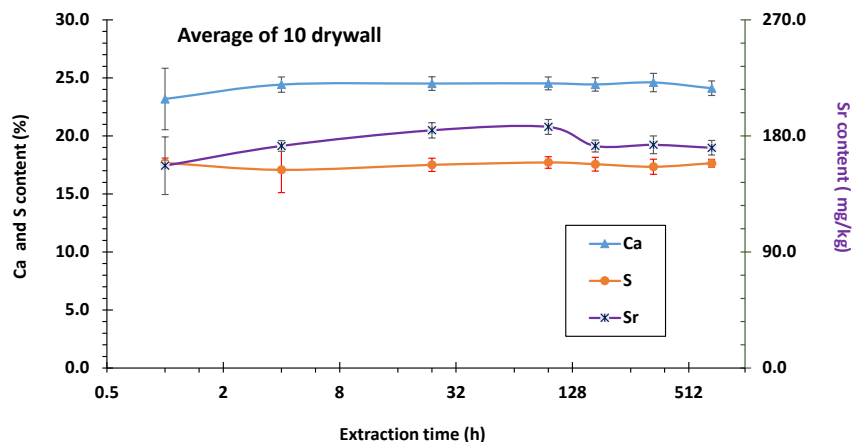


Figure 3-8: Effect of extraction time on the calcium, sulfur and strontium content in gypsum from drywall

The concentrations of other inorganic constituents were also monitored at different extraction times (4 h to 1 month). Similarly, calcium concentrations were stable after 24 h, and they were significantly higher compared to the EPA 3051A method ($p<0.01$) (Table 3-16). Strontium release was stable after 96 h (Figure 3-9 and Table 3-17). However, most of the elements (e.g., Cu, Ni, Fe, Mn, Zn, and Mg) needed a much longer time to reach the maximum release (Figure 3-10). Concentrations measured at these longer extraction times (e.g., 2 weeks) were significantly higher than those measured at the shorter times (4 h and 24 h) ($p<0.01$).

Table 3-15: Sulfur content of gypsum in drywall (%)

	0.25 M HCl (200:1)			USEPA M3051A			Total S by combustion		
	Average	Stdev	CV (%)	Average	Stdev	CV (%)	Average	Stdev	CV (%)
A	17.86	0.13	0.73	13.36	0.88	6.58	17.77	0.57	3.19
B	17.76	0.21	1.16	13.69	1.58	11.57	18.23	0.11	0.60
C	17.04	0.96	5.61	11.32	1.61	14.19	17.93	0.34	1.87
D	17.41	0.05	0.28	12.84	1.40	10.87	18.12	0.25	1.37
E	16.48	0.55	3.33	16.30	0.99	6.09	17.18	0.32	1.88
F	17.51	0.74	4.24	13.84	2.66	19.23	17.29	0.39	2.23
G	16.86	0.10	0.61	15.36	0.23	1.53	16.45	0.13	0.79
H	18.89	0.07	0.37	15.50	1.13	7.26	17.35	0.14	0.81
I	18.60	0.42	2.25	12.40	1.57	12.62	17.88	0.24	1.36
L	18.04	0.14	0.77	11.62	0.46	3.99	17.44	0.28	1.58
Average	17.65	0.75	4.25	13.62	1.67	12.30	17.56	0.53	3.04
Relative %	100			78			100%		

Table 3-16: Calcium content of gypsum in drywall (%)

	0.25 M HCl (200:1)		EPA M3051A		Relative %
	Average	Stdev	Average	Stdev	
A	23.90	0.22	17.84	1.20	133.9
B	23.99	0.08	18.03	2.03	133.1
C	23.82	1.50	15.01	2.22	158.7
D	24.97	0.12	17.00	1.82	146.9
E	24.64	0.30	22.38	1.23	110.1
F	24.43	1.05	19.22	3.47	127.1
G	23.89	0.19	21.29	0.55	112.2
H	24.84	0.14	21.37	1.61	116.2
I	25.39	0.29	17.43	1.94	145.7
L	25.15	0.34	16.16	0.52	155.6
Average	24.50	0.58	18.57	2.43	134.0

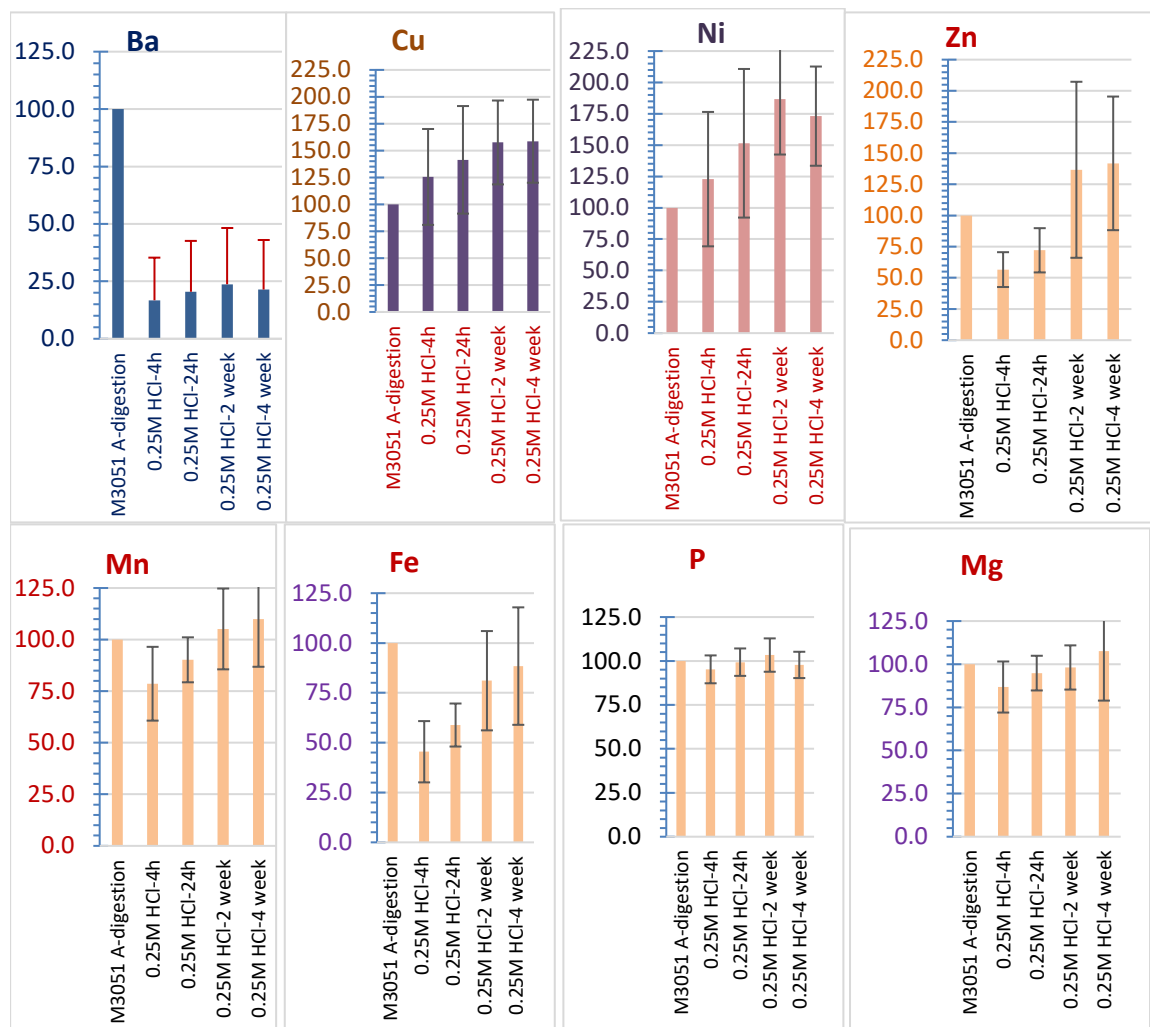
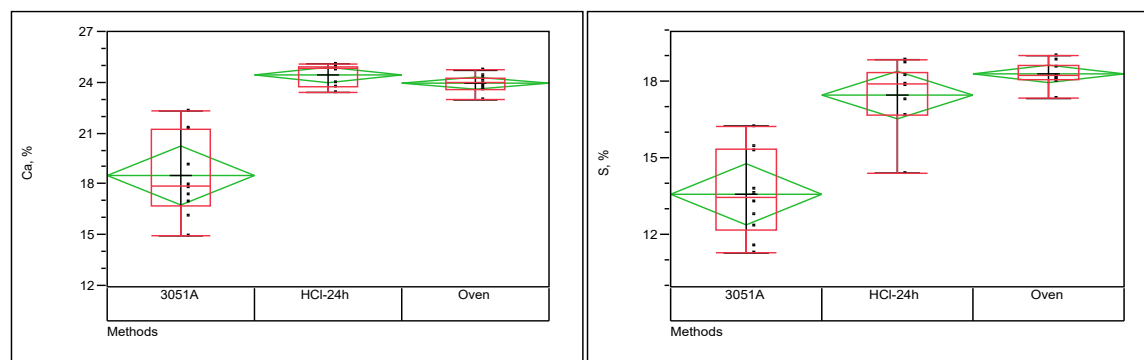


Figure 3-9: Effect of extraction time on the other components in gypsum from drywall

Table 3-17: Strontium content of gypsum in drywall (%)

	0.25 M HCl (200:1)		USEPA M3051A		Relative %
	Average	Stdev	Average	Stdev	
A	608.6	7.86	467.0	5.99	130.3
B	91.2	0.46	72.5	8.48	125.8
C	547.5	32.74	381.7	43.25	143.4
D	167.9	1.76	128.0	12.50	131.2
E	58.9	0.52	61.9	4.21	95.2
F	102.7	4.60	88.9	12.82	115.5
G	63.2	0.28	54.0	1.14	117.1
H	63.5	0.51	57.0	2.92	111.5
I	60.9	0.36	48.3	4.44	126.2
L	59.4	0.59	42.8	0.20	138.9
Average	182.4	211.7	140.2	153.1	123.5

The results for the other constituents extracted by 0.25 M HCl for the ten gypsum samples were compared to the results measured by extracting according to M3051A. In general, the concentrations from the 0.25 M HCl extraction of Cu and Ni were significantly higher ($p < 0.05$), while the concentration of Ba was significantly lower ($p < 0.05$). However, the concentrations of most elements were related to extraction time (Figure 3-10). All these results further suggest low efficiency of the EPA 3051A method for solid wastes containing large concentrations of gypsum (e.g., drywall). Gypsum solubility decreases, and re-precipitation occurs at room temperature in an acidic medium (Van Driessche et al., 2019). Moreover, calcium, sulfur, and strontium results after HCl extraction (0.25 M, L/S=200, room temperature) were stable after 24 h and higher compared to the 3051A method ($p < 0.01$), indicating that HCl extraction is an easy and reliable alternative approach. However, results for other metals (e.g., Cu, Ni, and Zn by HCl) were extremely affected by extraction time. Some longer extractions (e.g., two weeks) exhibited significantly higher concentrations than those conducted over a shorter time (4 h and 24 h).

**Figure 3-10: Calcium and sulfur content in the gypsum from drywall by three methods**

Since temperature plays a key role in controlling the solubility of calcium sulfate and phase transformation in an acidic medium, 10% HNO₃ extraction at 90 °C (sub-boiling, nitric acid extraction, 16 h) was further employed for the gypsum composition of drywall. There were no differences between calcium and sulfur concentration when comparing results using nitric acid extraction and HCl extraction

(24 h) ($p>0.05$). However, concentrations were significantly higher than those measured using from the EPA 3051A method ($p<0.01$) (Table 3-18, Figure 3-11).

Table 3-18: Calcium and sulfate content of gypsum in drywall (%) by three methods

	Calcium			Sulfur		
	3051A	HCl extraction	HNO ₃ extraction	3051A	HCl extraction	HNO ₃
Mean	18.57	24.51	24.03	13.62	17.51	18.34
Std Dev	2.43	0.64	0.50	1.68	1.30	0.48
Lower 95%	16.83	24.05	23.67	12.42	16.58	17.99
Upper 95%	20.31	24.97	24.38	14.82	18.44	18.68
Minimum	15.01	23.48	23.03	11.32	14.46	17.37
Maximum	22.38	25.17	24.78	16.30	18.90	19.05

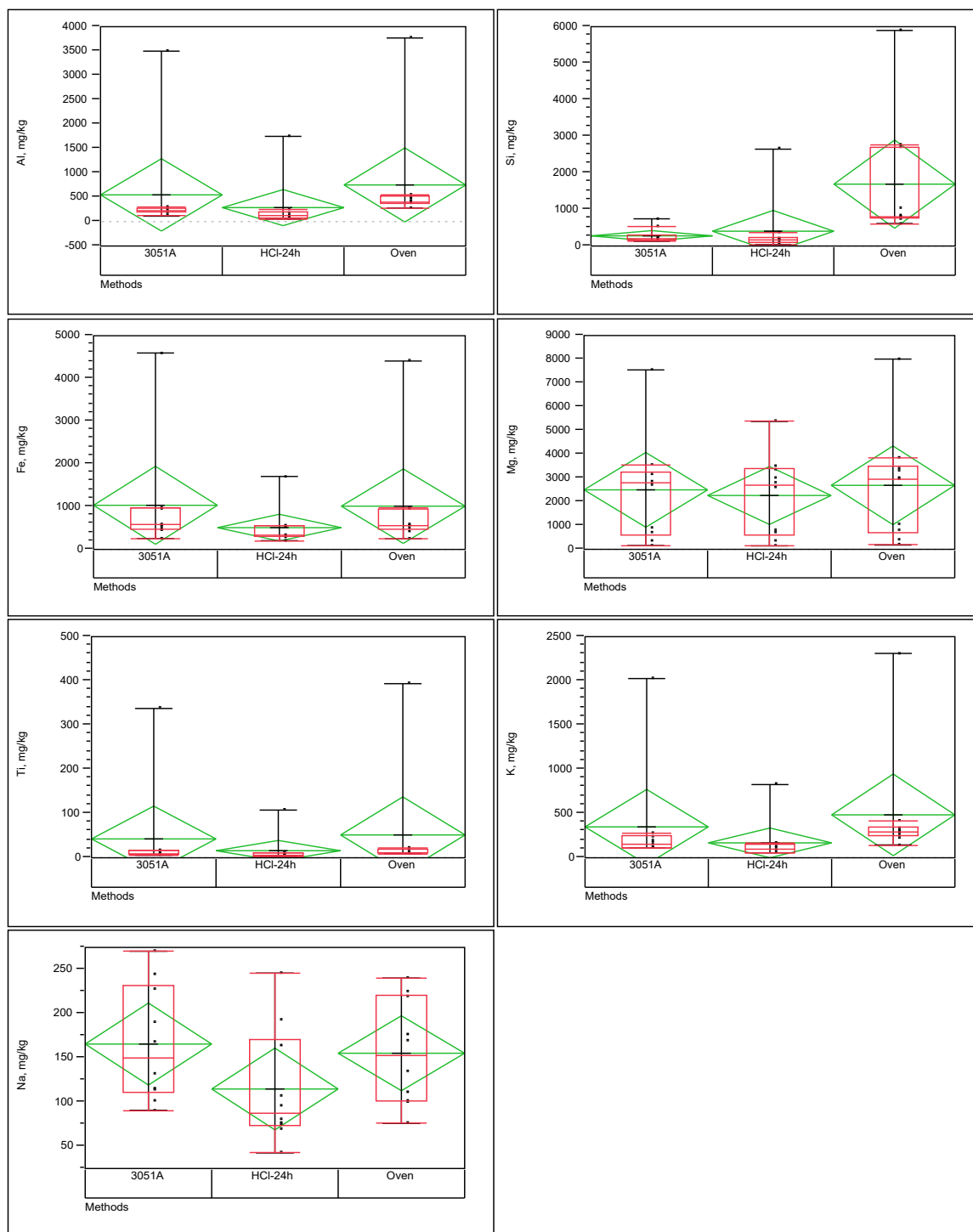


Figure 3-11: Al, Si, Fe, Ti, Mg, K and Na (mg kg⁻¹) content in the gypsum from drywall by three methods

The concentrations of macro- and microelements in the ten gypsum samples using the nitric acid extraction at 90 °C are presented in Tables 3-19 and 3-20 and Figure 3-12. Si, Fe, and Al exhibited the highest concentrations. In addition, Sr, Ba, Mn, and Se presented concentrations higher than those

measured using the other extraction methods (in most cases). However, Cu, Zn, and Ni concentrations were lower compared to the concentrations measured using HCl and long extraction time (Figure 3-10).

Therefore, the extraction method using 10% nitric acid at a sub-boiling temperature presented satisfactory results and recoveries, and it was considered the best approach for measuring inorganic element concentrations in the gypsum samples. Matrix spike recovery for most elements was between 95-105%, except Al, K, and Na (Table 3-19). The composition of drywall paper was also investigated by the nitric acid extraction method (10% HNO₃, 90 °C, 16 h) and EPA 3051A (Table 3-21). Some differences were also noted between these two methods. The concentrations of Mg, Al, Si, K, Na, Sr, and Ba using the nitric acid extraction technique were higher, while the content for Ca, S, and Ni was lower. While the paper was purposefully separated from the drywall products during the initial sample preparation, the paper samples always had some attached gypsum (thus leading to elevated Ca and S).

Table 3-19: Al, Si, Fe, Ti, Mg, K and Na content of gypsum in drywall (%) by three methods

Element	Method	Mean	Std Dev	Lower 95%	Upper 95%	Min	Max
Aluminum mg/kg	3051A	550	1040	0	1290	113	3500
	HCl-24 h	288	517	0	658	53.2	1750
	HNO ₃ , 90 °C	753	1060	0	1510	278	3770
Silicon mg/kg	3051A	278	201	134	421	127	744
	HCl-24 h	406	794	0	970	43.2	2650
	HNO ₃ , 90 °C	1690	1690	486	2900	616	5900
Iron mg/kg	3051A	1030	1280	119	1950	255	4600
	HCl-24 h	509	438	196	823	204	1710
	HNO ₃ , 90 °C	1010	1220	141	1880	248	4410
Titanium mg/kg	3051A	42.6	104	0	117	5.6	338
	HCl-24 h	15.9	32.4	0	39.1	3.18	108
	HNO ₃ , 90 °C	51.6	120	0	138	8.86	394
Magnesium mg/kg	3051A	2500	2200	930	4080	161	7550
	HCl-24 h	2270	1700	1050	3490	144	5380
	HNO ₃ , 90 °C	2690	2320	1040	4350	179	8010
Potassium mg/kg	3051A	349	592	0	773	112.2	2026
	HCl-24 h	168	235	0.35	336	56.6	827
	HNO ₃ , 90 °C	485	645	23.5	946	145.3	2311
Sodium mg/kg	3051A	166	64.8	119	212	90.8	271
	HCl-24 h	115	64.6	68.7	161	42.6	246
	HNO ₃ , 90 °C	155	59.2	113	198	76	240

Table 3-20: Sr, Ba, Mn, Se, P, Cu, Mn, Zn and Ni content of gypsum in drywall by three methods

Element	Method	Mean	Std Dev	Lower 95%	Upper 95%	Min	Max
Sr, mg/kg	3051A	140	153	30.7	250	42.8	467
	HCl-24 h	175	212	23.3	327	58.7	607
	HNO ₃ , 90 °C	189	217.4	33.4	345	62.1	621
Ba, mg/kg	3051A	19.3	30.6	0	41.1	5.58	105
	HCl-24 h	8.65	7.54	3.26	14.2	2.76	27.6
	HNO ₃ , 90 °C	22.9	29.4	1.93	44.3	7.62	104
Mn, mg/kg	3051A	10.4	14.5	0	20.7	2.05	50.9
	HCl-24 h	8.12	8.66	1.92	14.3	1.9	31.5
	HNO ₃ , 90 °C	11.5	17.4	0	23.9	2.18	60.4
	3051A	4.15	1.16	3.32	4.97	2.97	5.75
Se, mg/kg	HCl-24 h	2.98	1.13	2.17	3.79	1.74	4.77
	HNO ₃ , 90 °C	4.21	1.37	3.23	5.18	2.40	5.86
	3051A	126	93.3	58.9	193	9.83	235
P, mg/kg	HCl-24 h	128	96.8	59.0	198	8.09	260
	HNO ₃ , 90 °C	126	92.7	59.4	192	10.8	236
Cu, mg/kg	3051A	2.47	3.19	0.18	4.75	0.99	11.4
	HCl-24 h	2.47	1.33	1.51	3.42	1.71	6.12
	HNO ₃ , 90 °C	2.51	2.64	0.62	4.39	1.34	9.93
Zn, mg/kg	3051A	10.8	3.44	8.30	13.2	5.81	17.7
	HCl-24 h	7.30	2.48	5.53	9.07	4.48	11.9
	HNO ₃ , 90 °C	8.53	3.06	6.34	10.7	5.84	16.2
Ni, mg/kg	3051A	3.47	8.22	0	9.34	0.4	26.8
	HCl-24 h	2.59	4.11	0	5.53	0.94	14.2
	HNO ₃ , 90 °C	3.52	7.66	0	9.00	0.69	25.3

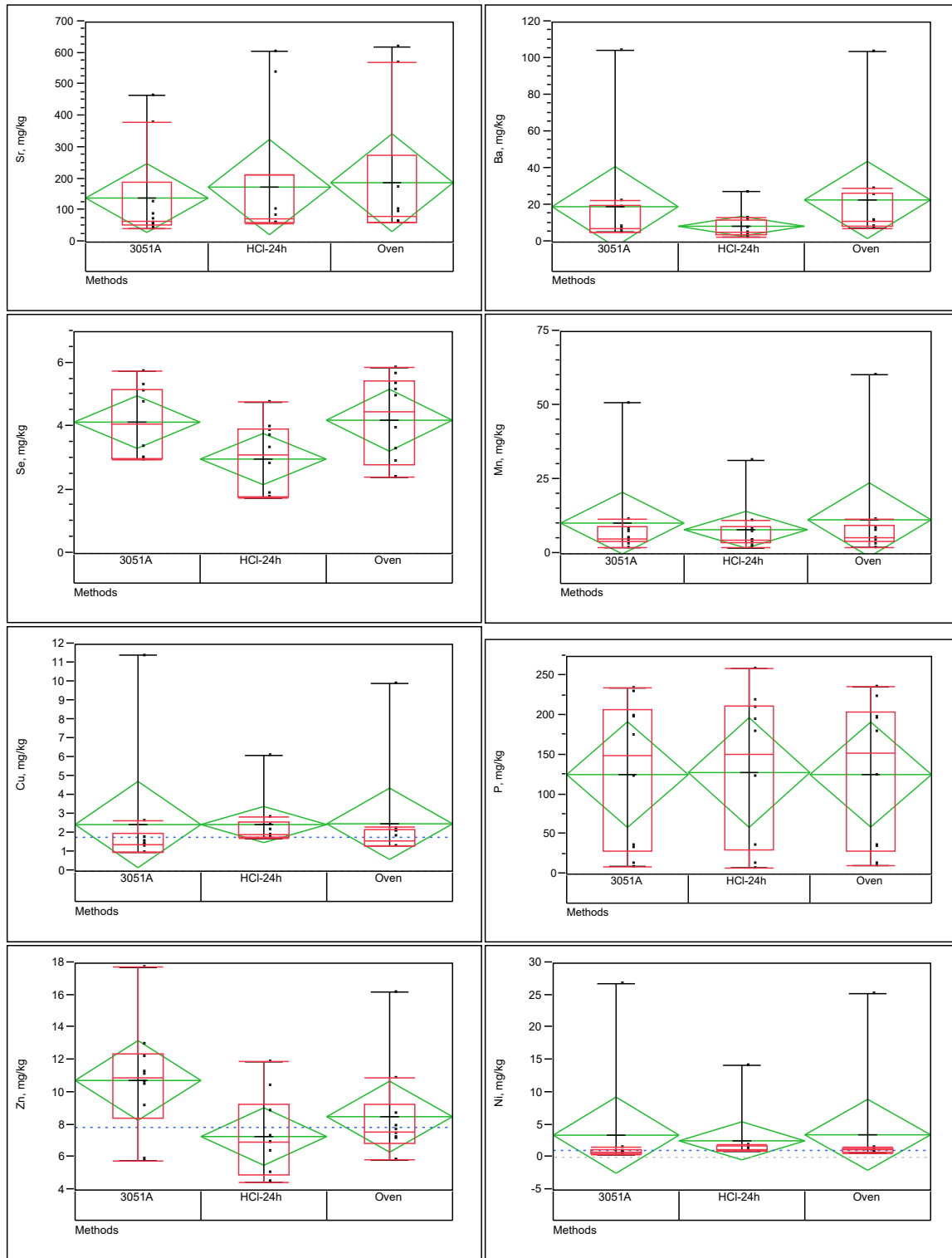


Figure 3-12: Sr, Ba, Mn, Cu, Zn, Ni, Se and P (mg kg⁻¹) content in the gypsum from drywall by three methods

Table 3-21: Elemental recovery (%) by nitric acid extraction at 90 °C *

Element	Standard composition mg/L	Sample A-G		Sample L-G		Blank	Average
		Level I	Level II	Level I	Level II		
Al	1000	105	105	126	120	105	112
As	500	98	99	101	99	95	98
B	100	99	100	102	100	95	100
Ba	500	93	93	96	95	98	95
Cd	200	95	96	97	96	104	98
Co	1000	93	94	95	94	104	96
Cr	500	92	92	94	93	99	94
Cu	500	102	104	103	102	106	103
Fe	1000	101	100	101	98	106	101
K	1000	119	119	115	117	98	114
Mg	1000	107	117	97	97	108	105
Mn	200	98	98	98	97	105	99
Mo	200	99	99	101	100	104	101
Na	1000	107	107	111	110	99	107
Ni	500	95	95	97	96	105	98
P	200	103	105	109	108	103	105
Pb	500	90	92	93	93	99	94
Se	500	101	102	104	103	98	102
Sr	200	99	97	113	106	107	104
Ti	200	99	100	104	103	102	101
V	500	98	98	99	98	105	100
Zn	200	97	97	100	99	96	98

* Level I: added 2 mL standard solution in 50 mL extractions; Level II: added 3 mL standard solution in 50 mL extractions

Based on the percentage of paper and gypsum in the drywall board, the composition of the drywall board is presented in Tables 3-22 to 3-24.

Table 3-22: The sulfur and metal content of the 10-drywall paper samples by “Nitric acid extraction” and EPA M3051A

	Nitric acid extraction					M3051A				
	Mean	STDev	Median	Min	Max	Mean	STDev	Median	Min	Max
S (%)	6.44	1.28	6.9	4.33	8.34	12.51	1.43	12.5	10.33	14.73
Ca (%)	9.02	1.57	9.44	6.15	11.22	17.19	2.06	16.78	14.51	20.4
Mg	1180	428	1180	683	1860	2350	1990	2580	253	6950
K (mg/kg)	588	588	242	202	1750	373	524	153	115	1830
Na	1440	276	1420	1020	1820	315	94	312	170	459
Fe	424	113	382	263	638	970	1140	558	265	4160
Al	1010	228	976	811	1580	605	939	325	201	3270
Si (mg/kg)	1190	592	881	711	2360	279	195	211	136	732
Sr	91.1	87.7	46.2	37	263	133	146	63.1	40.5	439
Ba	16.5	4.4	15.1	11.3	24.5	18.9	27.4	8.0	6.3	95.3
Cu	6.28	1.01	6.03	46.4	8.05	3.54	2.92	2.44	2.02	11.6
Mn	27	4.78	26.6	20.2	36.7	13.1	12.9	8.15	5.56	48.8
Ni	1.34	0.84	1.07	0.82	3.68	3.25	7.38	0.89	0.46	24.2
Zn(mg/kg)	83.1	134	22.7	16.5	411	23.0	21.6	14.2	7.81	76.5

	Nitric acid extraction					M3051A				
Se	2.75	0.66	2.45	2.17	4.00	4.10	1.06	4.03	3.04	5.56
P (mg/kg)	302	267	215	45.8	692	156	118	175	16	323

Table 3-23: The sulfur and metal content of the 10 drywall boards by EPA M3051A

	Mean	Std Dev	Lower 95%	Upper 95%	Median	Minimum	Maximum
Ca (%)	17.19	2.06	15.72	18.67	16.78	14.51	20.40
S (%)	12.51	1.43	11.48	13.54	12.50	10.33	14.73
Mg (mg/kg)	2350	1990	928	3780	2580	253	6950
K (mg/kg)	373	524	0	748	153	115	1830
Na (mg/kg)	315	94	248	382	312	170	459
Fe (mg/kg)	970	1140	148	1790	558	265	4160
Al (mg/kg)	605	939	0	1280	325	201	3270
Si (mg/kg)	279	195	140	418	211	136	732
Sr (mg/kg)	133	146	29	237	63.1	40.5	439
Ba (mg/kg)	18.9	27.4	0	38.6	8.0	6.3	95.3
Cu (mg/kg)	3.54	2.92	1.45	5.63	2.44	2.02	11.6
Mn (mg/kg)	13.1	12.9	3.88	22.4	8.15	5.56	48.8
P (mg/kg)	156	118	71.8	240	175	16	323
Ni (mg/kg)	3.25	7.38	0	8.53	0.89	0.46	24.2
Se (mg/kg)	4.10	1.06	3.34	4.86	4.03	3.04	5.56
Zn (mg/kg)	23.0	21.6	7.53	38.5	14.2	7.81	76.5

Table 3-24: The sulfur and metal content of the 10-drywall boards by “Nitric-acid extraction”

	Mean	Std Dev	Lower	Upper	Median	Minimum	Maximum
Ca (%)	21.6	1.05	20.8	22.3	21.8	19.4	23
S (%)	16.4	0.91	15.7	17.1	16.6	14.7	17.9
Mg	2373	1923	998	3749	2582	252	6709
K (mg/kg)	513	602	82	602	291	155	2191
Na (mg/kg)	353	117	270	437	365	167	522
Fe (mg/kg)	933	1074	164	1701	540	251	3924
Al (mg/kg)	828	1036	87	1568	520	356	3768
Si (mg/kg)	1639	1552	528	2749	815	630	5459
Sr (mg/kg)	179	202	34.6	324	79.75	59	578
Ba (mg/kg)	22.9	27.7	3.1	27.7	12.1	8.2	99
Cu (mg/kg)	3.05	2.35	1.37	4.73	2.35	2	9.7
Mn	13.39	14.52	3	23.78	8.2	5.2	53.8
P (mg/kg)	152	115	69	234	171.8	16.1	305
Ni (mg/kg)	3.27	6.9	0	8.21	1.15	0.7	22.9
Se (mg/kg)	3.98	1.21	3.11	4.85	4.15	2.4	5.4
Zn(mg/kg)	19.6	19.8	5.42	33.8	10.35	6.9	65.6
Ti (mg/kg)	47.5	110	0	126	11.65	8.4	361.2
V (mg/kg)	4.75	2.76	2.77	6.73	3.85	3.7	12.6
B (mg/kg)	12.5	9.5	5.75	19.3	9.9	6.1	38

	Mean	Std Dev	Lower	Upper	Median	Minimum	Maximum
Co (mg/kg)	0.79	1.1	0.003	1.58	0.4	0.3	3.8

3.6. Water-Extractable Sulfur and Metals

As expected, sulfate in the drywall products gypsum component was highly water-soluble and present as sulfate (SO_4)⁻² (Figure 3-13). The average water-extractable sulfate content by IC (cumulative, four times, L_{DIW}) in the gypsum samples was $54.4 \pm 1.5\%$, which indicated that almost all sulfur (S_{DIW} , $98.2 \pm 1.7\%$) is in the water-extractable (SO_4)⁻² form (Figure 3-13). The cumulative water-extractable S (as SO_4) was significantly higher than the determination of the total S concentration measured using the M3051A digestion procedure ($p < 0.001$).

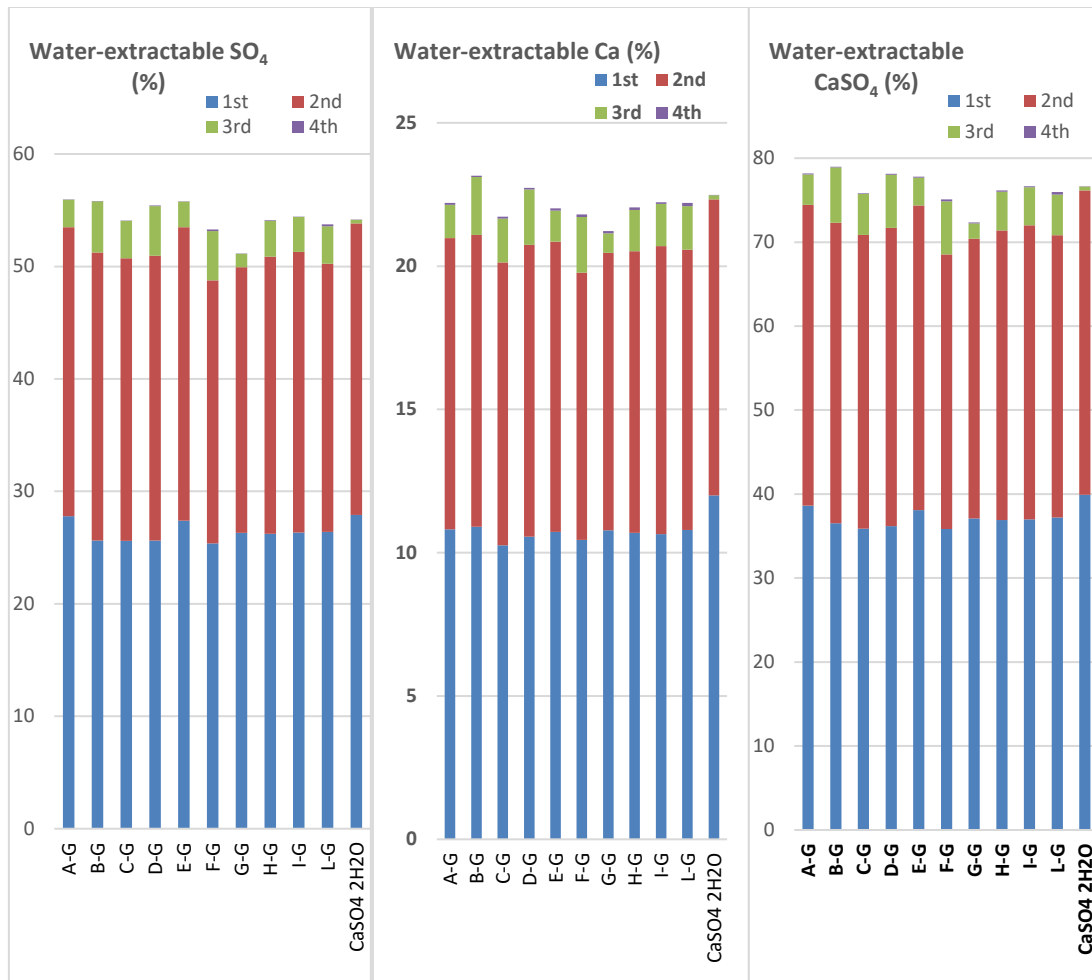


Figure 3-13: Water-extractable sulfate, calcium, and CaSO₄ in the gypsum from drywall

Like sulfate, water-extractable calcium was also rapidly released from the gypsum samples (Figure 3-13). The average cumulative water-extractable Ca concentration was $22.1 \pm 0.5\%$, which was higher compared to the EPA 3051A method ($p < 0.01$). Compared to the 0.25 M HCl extractable Ca

($24.5 \pm 0.64\%$) and the nitric acid-extractable Ca ($24.0 \pm 0.50\%$), at least 90% of the Ca was dissolved by water ($> \text{Ca}_{\text{DIW}}$, 90%).

The average content of the cumulative water-extractable CaSO_4 from the gypsum samples was $76.1 \pm 1.9\%$ (Figure 3-13). When accounting for the combined water content ($19.4 \pm 0.6\%$) based on WLOI determination at 230°C , the average content of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the water extraction was $95.6 \pm 2.5\%$. The overall molar ratio of Ca to SO_4 in the water extraction was close to 1 (0.98 ± 0.02). The ratio at the initial extractions (1st and 2nd) for all gypsum from drywall was close to 1.0 (< 1.0), whereas one in the last extraction (4th) was much higher ($>> 1.0$) (Figure 3-14), indicating that the initial extractions had high concentrations of SO_4 and Ca (saturated from gypsum), whereas the last extraction had low concentrations of SO_4 and Ca (some other calcium mineral, likely calcium carbonate (calcite) controlled the equilibrium in the last extraction) (Figure 3-15), as supported by the high pH in the last extraction (Figure 3-16), as well as the chemical species analysis by VMINTEQ.

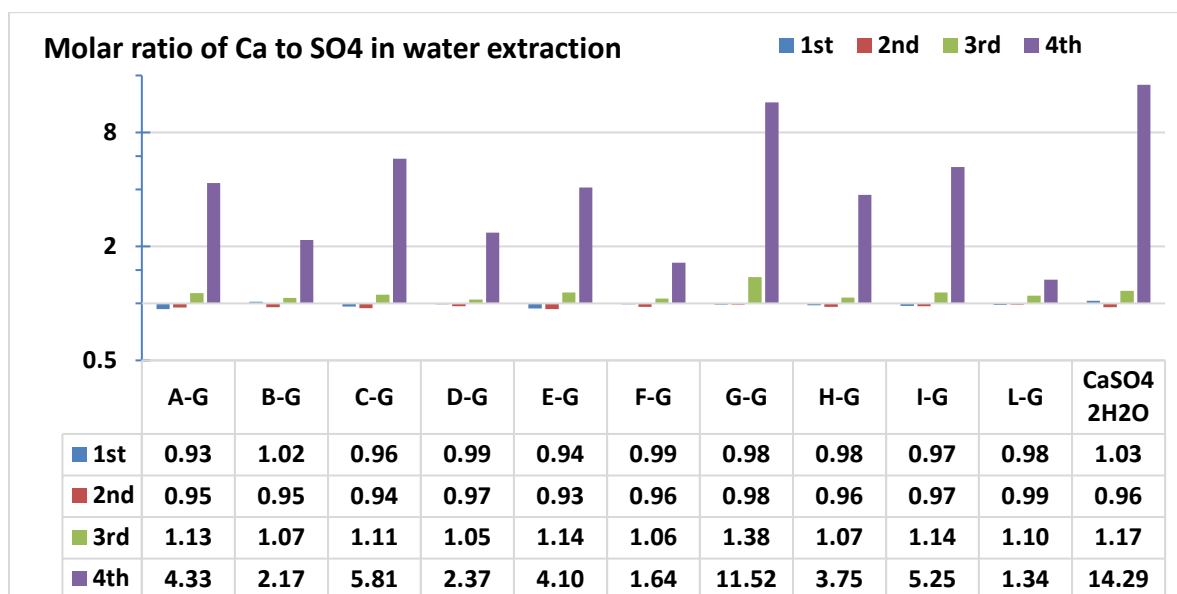


Figure 3-14: The molar ratio of Ca/S in the water extraction in the gypsum from drywall

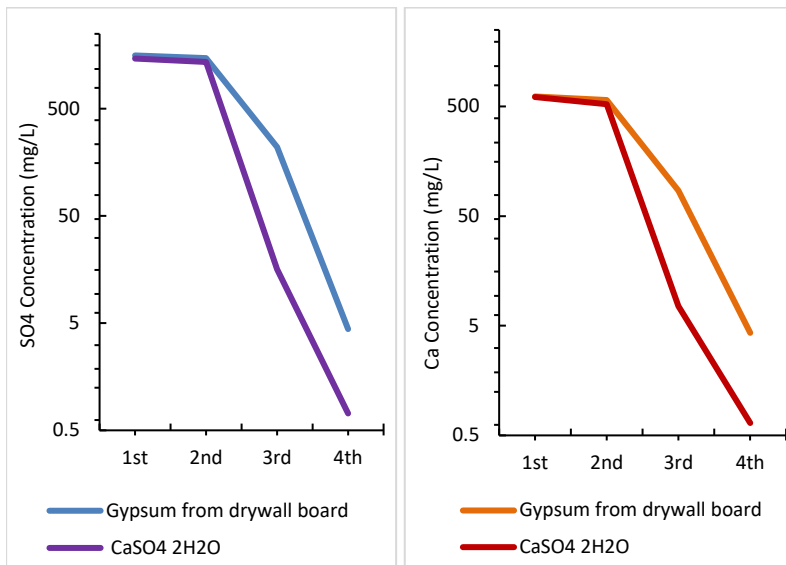


Figure 3-15: Effect of gypsum sources on the concentration of Ca and SO₄ in the water extraction

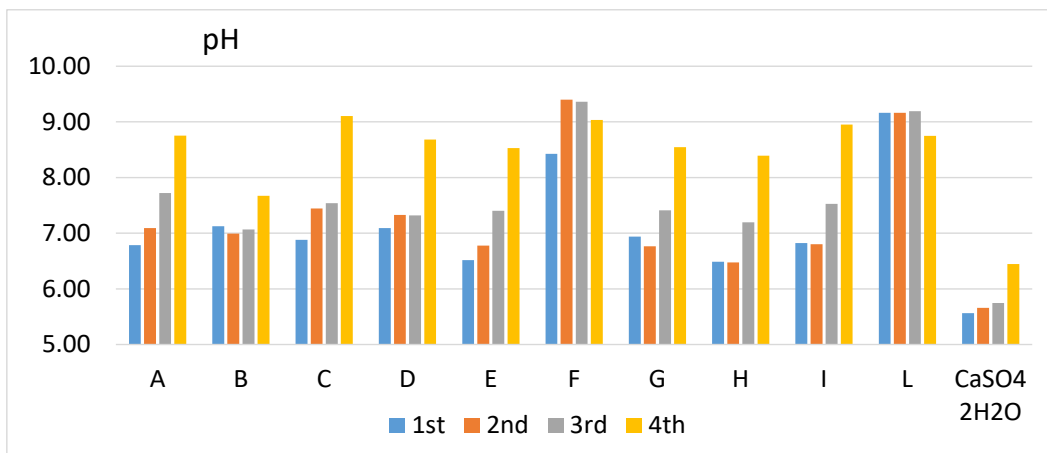


Figure 3-16: pH of the extraction in the gypsum from drywall

The water-extractable concentrations of other elements (in addition to Ca and S) in the gypsum samples were less than 0.2% of the total. The primary elements measured in these water extractions were Si, P, Mg, and Sr (Figure 3-17, Table 3-25). Gypsum from drywall samples F and L exhibited higher concentrations of water-soluble silicate and iron. Gypsum from drywall samples E, G, H, and I exhibited relatively high concentrations of phosphate and sodium, while drywall samples A, B, C, and D exhibited a larger concentration of strontium.

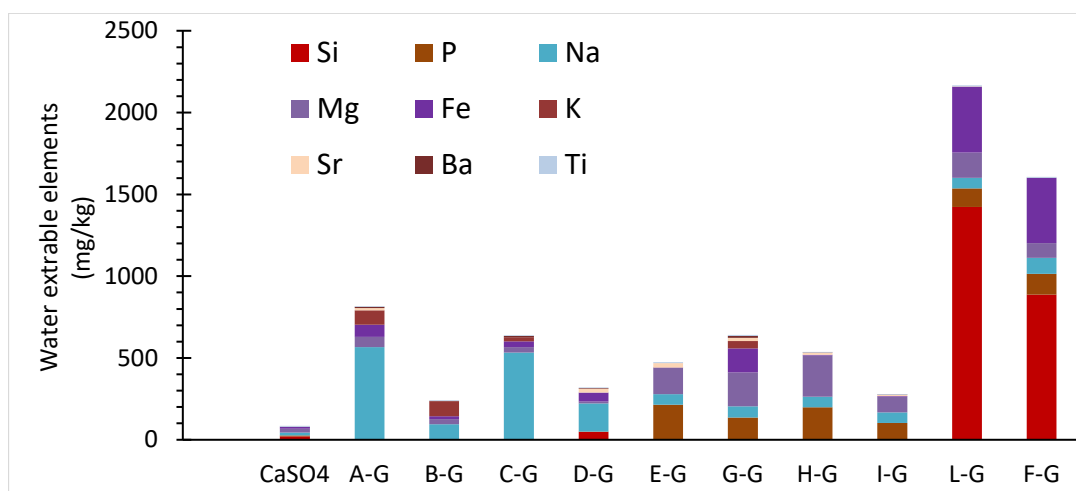


Figure 3-17: Water-extractable elements (other than Ca) in the gypsum from drywall

Table 3-25: The water cumulative extractable sulfate and metal content of gypsum from drywall

	Mean	Stdev	Lower 95%	Upper 95%	Minimum	Maximum
SO ₄ %	54.4	2.0	53.6	55.1	50.5	59.7
Ca %	22.1	0.6	21.9	22.3	21.1	23.5
Ba, mg/kg	4.0	5.2	2.0	5.9	BDL*	16.5
Sr, mg/kg	193	211	115	272	65	631
Mg, mg/kg	139	196	65	212	BDL	546
Fe, mg/kg	20	35	7	33	BDL	149
P, mg/kg	103	89	70	137	BDL	228
Si, mg/kg	310	612	82	539	BDL	1675

*BDL, below detection limit

Among the microelements, strontium had the largest water-extractable concentration (up to 1.8 mg/L) and with a cumulative amount of 193±211 mg/kg (predominantly from the first two extractions). The cumulative water-extractable strontium was close to the value for the 0.25 M HCl (24 h) or 10% HNO₃ (90 °C) extractions, but higher compared to M3051A ($p<0.01$) (Figure 3-18), possibly indicating that most strontium in the drywall was in the form of strontium sulfate (SrSO₄).

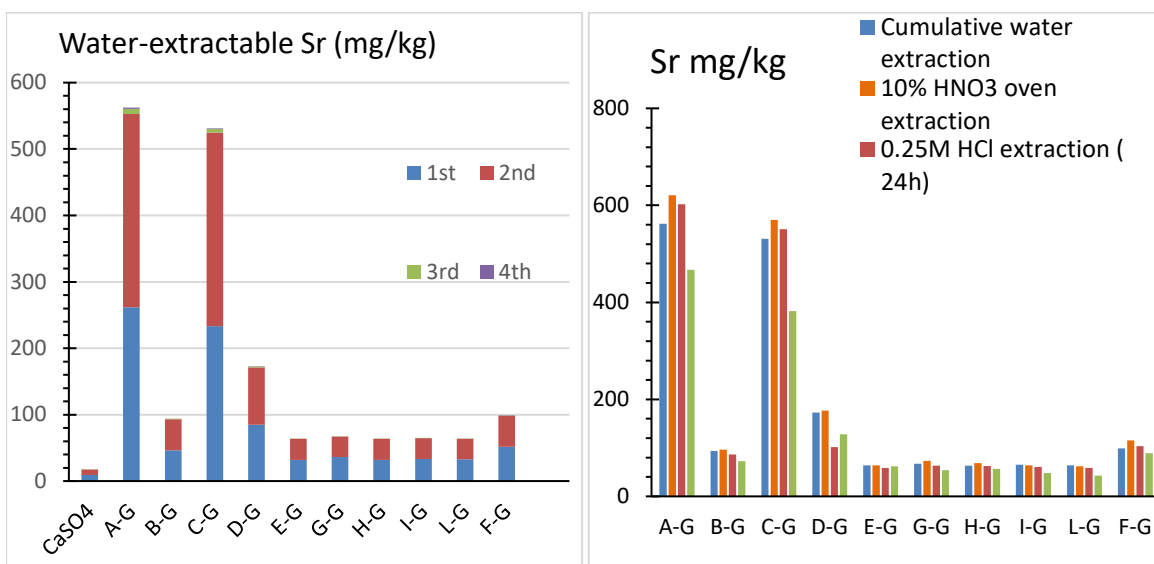


Figure 3-18: Water-extractable Sr in the gypsum from drywall

Conversely, Ba was detected in only half of the studied samples in the water extractions ($>0.005 \text{ mg L}^{-1}$). The cumulative water-extractable Ba concentration was much lower than the value from the three acidic extractions, probably due to barite (BaSO_4) formation (Figure 3-19) (Alhajri et al., 2020). The average of the cumulative water-extractable Ba concentrations of the ten gypsum samples was $3.3 \pm 4.3 \text{ mg kg}^{-1}$, whereas the amounts measured using 10% HNO_3 , the 0.25 M HCl extraction, and the M3051A digestion, were 23 ± 29 , 8.7 ± 7.5 , and $19 \pm 31 \text{ mg}^{-1}$, respectively.

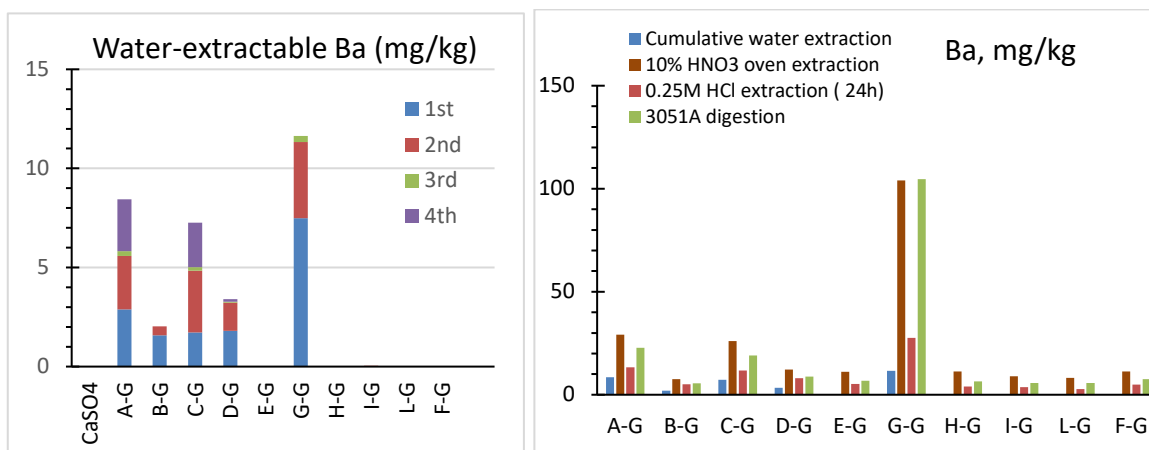


Figure 3-19: Water-extractable Ba in the gypsum from drywall

Like Ba, the cumulative water-extractable Mg concentration was only a small portion of the acidic extractable Mg concentration, from 0.02% up to 20% (Figure 3-20). The average of cumulative water-extractable Mg concentrations from the ten drywall samples was $139 \pm 203 \text{ mg kg}^{-1}$, whereas the amounts measured using the 10% HNO_3 , 0.25 M HCl, and M3051A techniques were $2,570 \pm 2,130$, $2,270 \pm 1,700$, and $2,500 \pm 2,200 \text{ mg kg}^{-1}$, respectively. The patterns of water-extractable Mg also differed from the patterns of Sr or Ba; some samples only exhibited high concentrations of Mg from the initial

extraction (e.g., G-G, and F-G), while other samples were only detectable at the third or fourth extraction (e.g., H-G, I-G). This observation might be related to their mineral phases and pH in the water extraction. In addition, $\text{Mg}(\text{OH})_2$ and MgCO_3 can be formed at pH above 7 (da Silva et al., 2018).

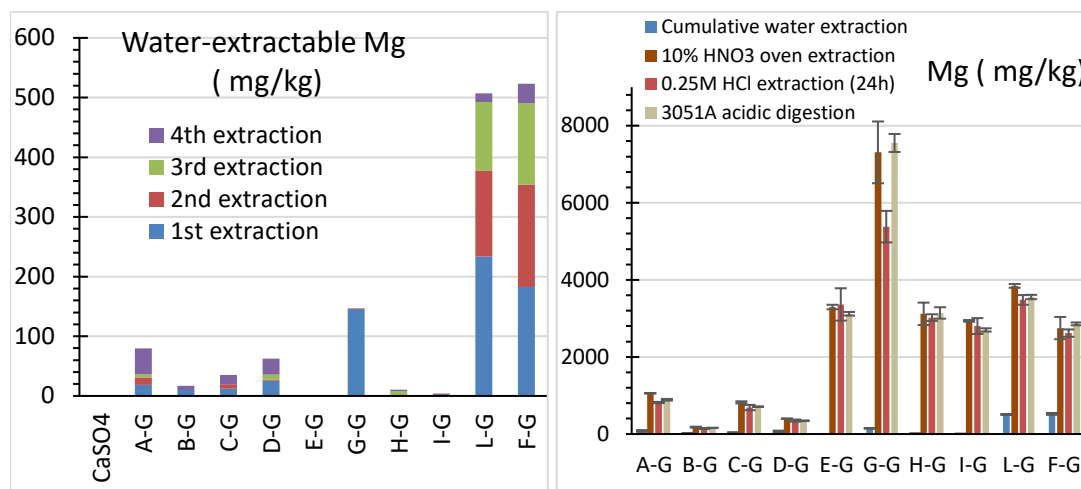


Figure 3-20: Water-extractable Mg in the gypsum from drywall

Water-extractable P had very low concentrations ($<10 \text{ mg kg}^{-1}$) in almost half of the samples, whereas the other half of the samples were higher ($170 \pm 42 \text{ mg kg}^{-1}$) (Figure 3-21). The cumulative water extraction concentrations from these six samples were very close, even higher than their corresponding acidic extractions (although either HCl or HNO_3 extraction was not designed for total P). Brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) has a higher water solubility than P and can coexist with gypsum in nature.

Like water-extractable P, water-soluble Si exhibited very low concentrations, being undetected in most of the samples (7) ($<5 \text{ mg kg}^{-1}$). However, two samples (F and G) had a considerable amount ($>1000 \text{ mg kg}^{-1}$) of water-soluble Si, though the Si took a long time to be released (Figure 3-22). This behavior was similar to the behavior observed in the HCl extractions. The amount of Si in the extraction after two weeks was significantly higher than the amount of Si in 24 h ($p < 0.01$). All three acidic extraction methods (HNO_3 , HCl, or M3051A) were not designed for determination of total Si (only partial Si was extracted by these acids). The behavior of water-extractable Si was also related to the silicon minerals in the drywall.

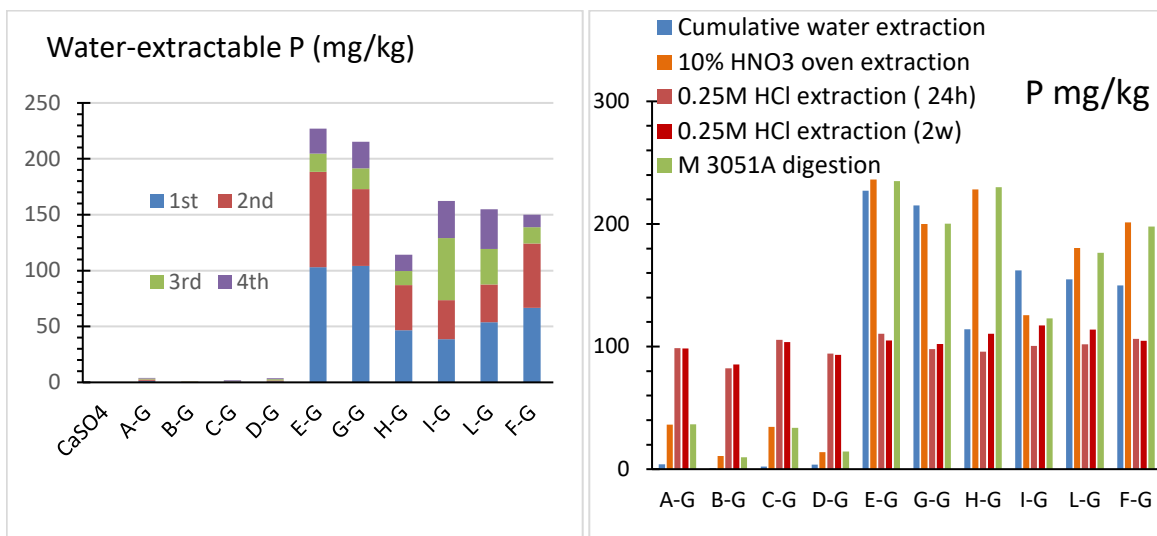


Figure 3-21: Water-extractable P in the gypsum from drywall

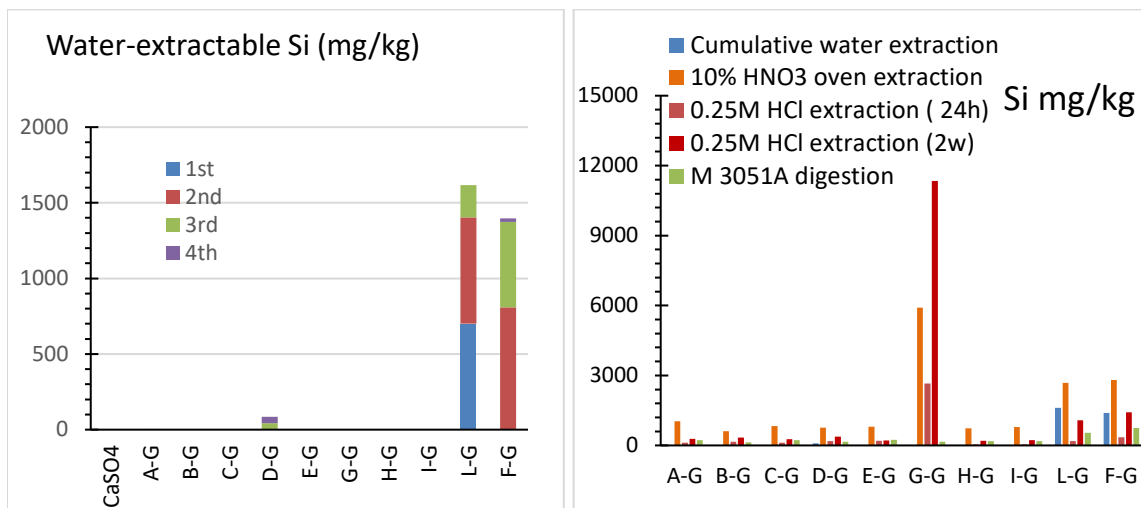


Figure 3-22: Water-extractable Si in the gypsum from drywall

4. Leaching Behavior of Drywall

4.1. Kinetics of Leaching Processing

As described earlier, the dominant component (by mass) of gypsum drywall is calcium sulfate, which can exist at three levels of hydration in the drywall board: dihydrate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$, α -hemihydrate and β -hemihydrate) and the anhydrous state (anhydrite, CaSO_4). In the kinetic leaching experiments, sulfate and calcium solution concentrations from each of the five samples tested did not change significantly ($p < 0.05$) under the experimental conditions ($L/S = 20$), although some variations were noted during the 2-month testing period (Figure 4-1). Based on the chemical species model VMINTEQ (Gustafsson, 2016), all solutions were near saturation states for gypsum ($\text{SI}_{\text{gypsum}}$ approximately 0) and undersaturation for the anhydrite ($\text{SI}_{\text{anhydrite}} < 0$), and both saturation indexes (SIs) of gypsum and anhydrite did not change significantly from 1 h up to 2 months (Figure 4-2), except for sample L.

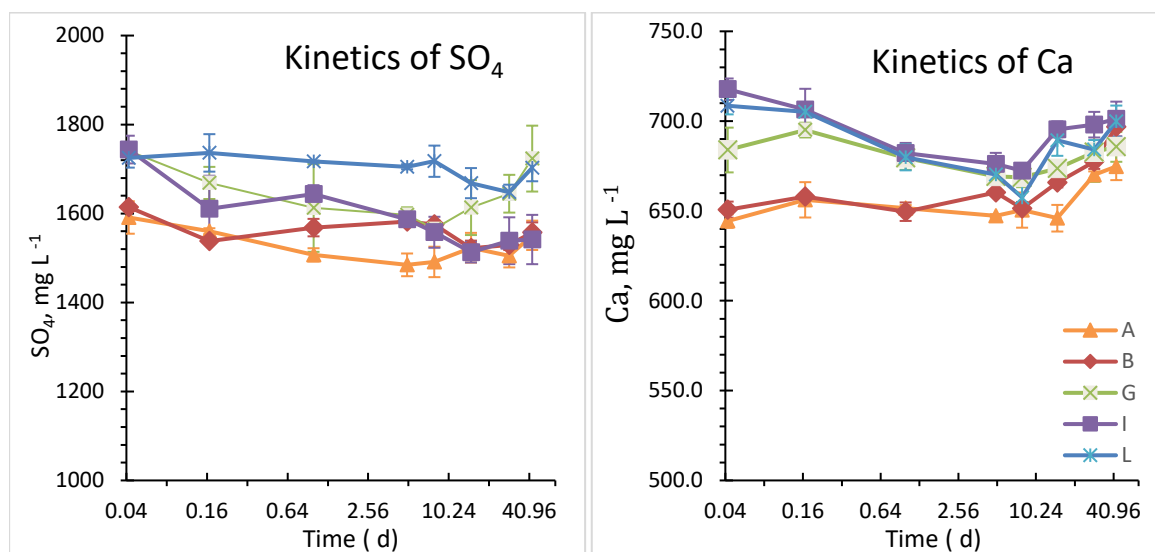


Figure 4-1: Kinetics of SO₄ and Ca of different drywalls

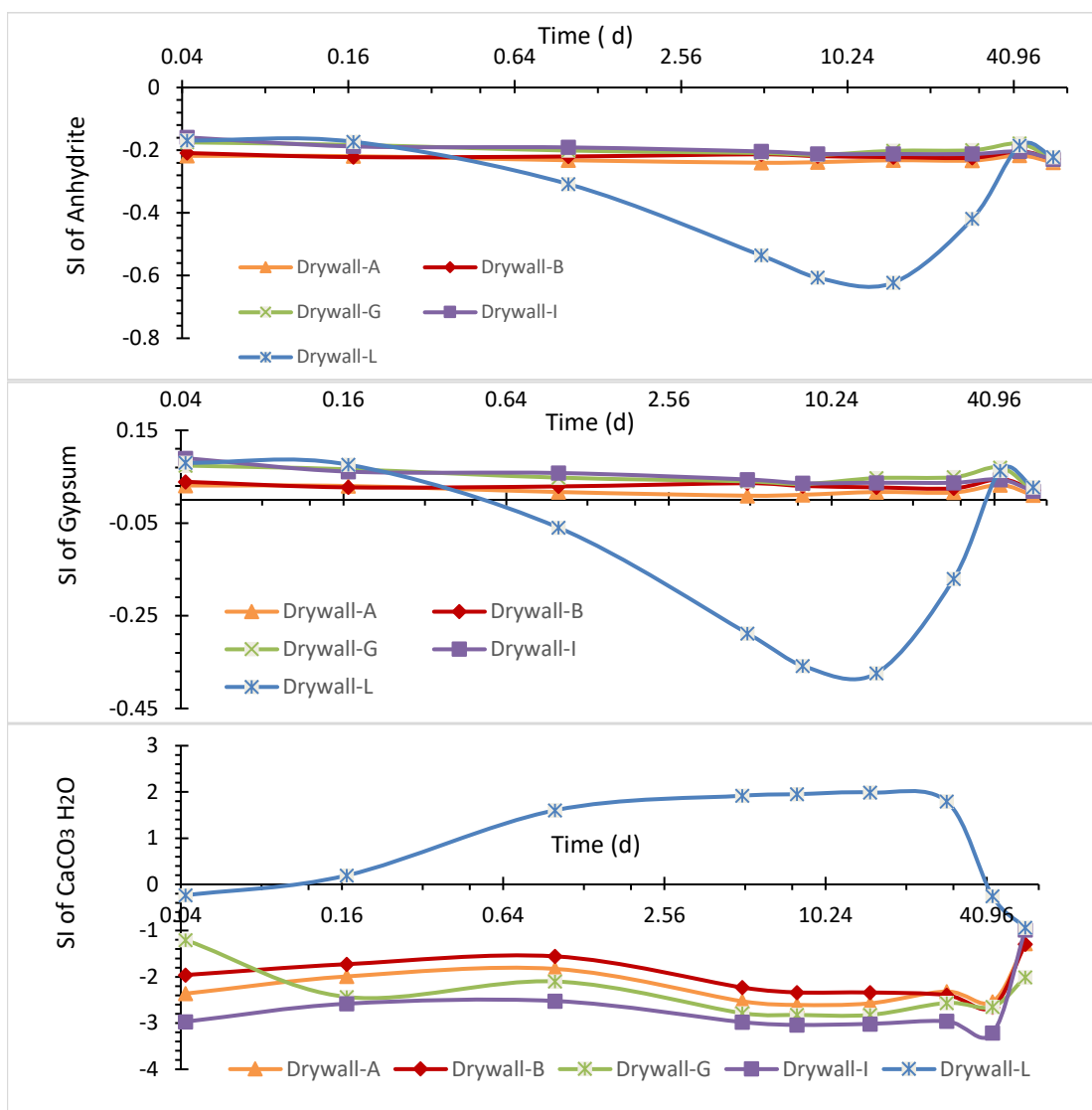


Figure 4-2: Kinetics of saturation index (SI) of anhydrite, gypsum and $\text{CaCO}_3 \cdot \text{H}_2\text{O}$

All five samples displayed similar patterns for EC (Figure 4-3), but the patterns of pH behavior did vary among samples (Figure 4-4) and can be differentiated between two groups. For Group I (samples A, B, G, and I), solution pH was initially approximately neutral (pH 7) followed by an increase over time. For Group II (sample L), solution pH was initially higher (up to 9) and then decreased to more neutral conditions (pH 7) after one month. The different patterns may have been related to the mineral composition of the individual drywall products (Table 3.4-1), further supported by the SI of $\text{CaCO}_3 \cdot \text{H}_2\text{O}$. The SI of $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ in sample L changed from initially being negative, then becoming positive, followed by a return to being negative (Figure 4-2). The SI in the other four samples was always negative. The concentration of calcium in solution was not only related to the calcium sulfate mineral phases present, but also to other calcium minerals (e.g., $\text{CaCO}_3 \cdot \text{H}_2\text{O}$) in the system.

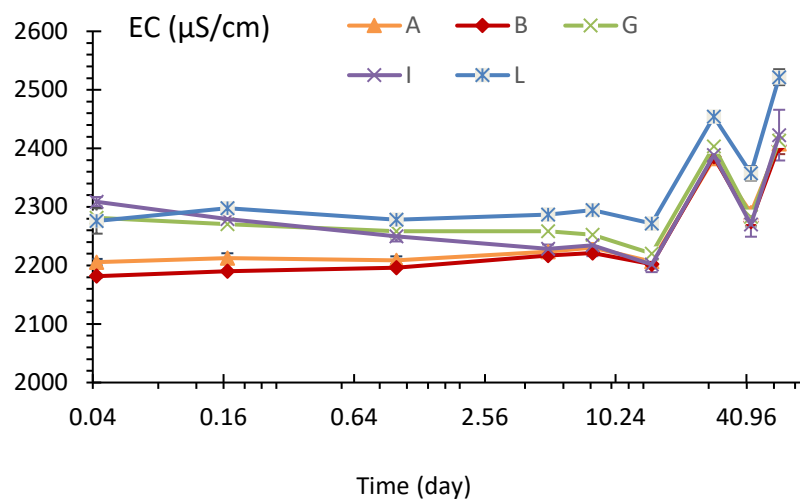


Figure 4-3: Kinetics of conductivity of different drywall

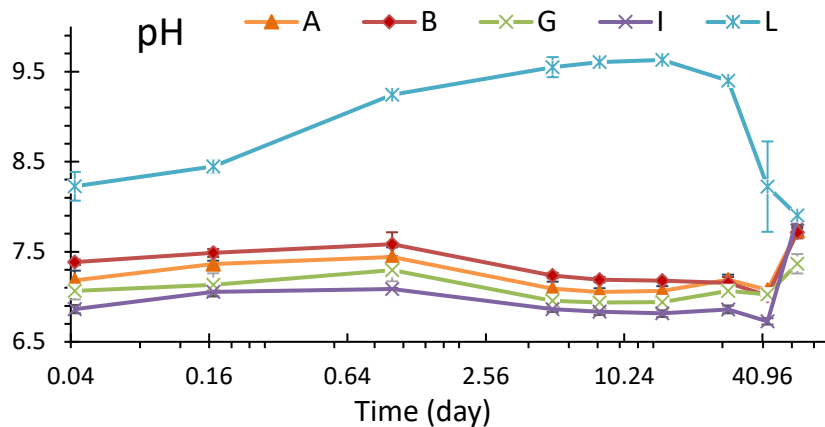


Figure 4-4: Kinetics of pH of different drywalls

Unlike the relatively consistent calcium and sulfate concentrations observed in the leachates from the kinetic experiments, the concentrations of most minor ions changed with time. For example, measured Sr concentrations increased with time, as did the saturation index for celestite (SrSO_4), which was always below zero (under saturation), and increased with time up to 1 month (Figure 4-5).

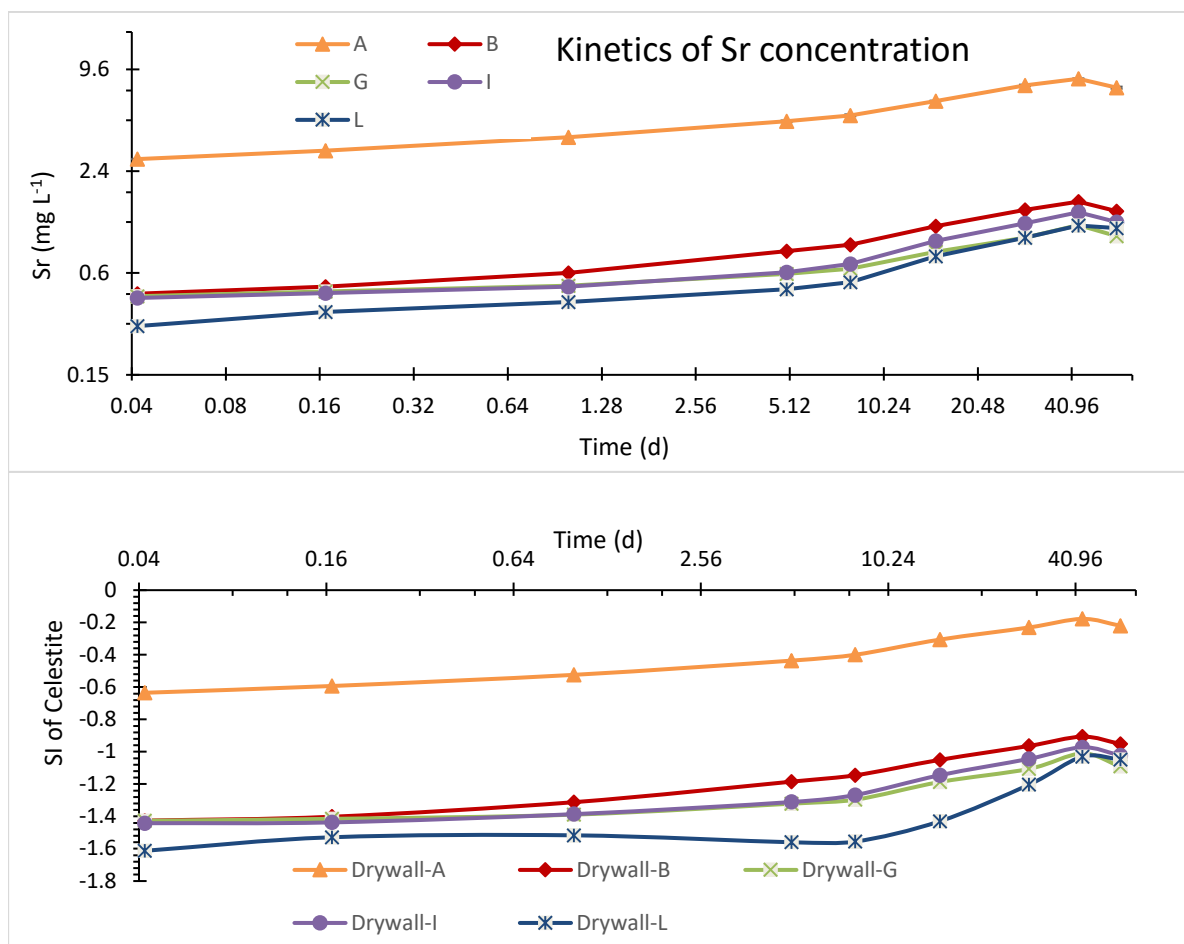


Figure 4-5: Kinetics of Sr concentration and saturation index (SI) of celestite (SrSO_4) in the solution

The same trend was also observed for Si. For the Group I samples, the concentration of Si increased initially and then reached equilibrium (Figure 4-6); the SI of SiO_2 (am, gel) was always negative. For the Group II sample (Drywall L), the SI was initially negative and then became positive after two weeks. The time needed for dissolved constituents to reach equilibrium for the samples tested related to the specific mineral composition of the different samples. There was no single time required for all samples to reach equilibrium in the kinetic leaching experiment.

Element concentrations in the leachate solutions may not be controlled by a single mineral but rather may be influenced by several related minerals in the system (Gorski et al., 2017). For calcium in the drywall-water system, the minerals involved included gypsum, anhydrite, and different calcium carbonates. For Ba, the kinetics that dictate Ba concentrations relate to both barite (BaSO_4) and witherite (BaCO_3) (Figure 4-7). In most cases, barite was over-saturated ($\text{SI} > 0$) in solution, whereas the witherite ($\text{SI} < 0$) was unsaturated. As a result, the concentrations of Ba in the leachate were increased.

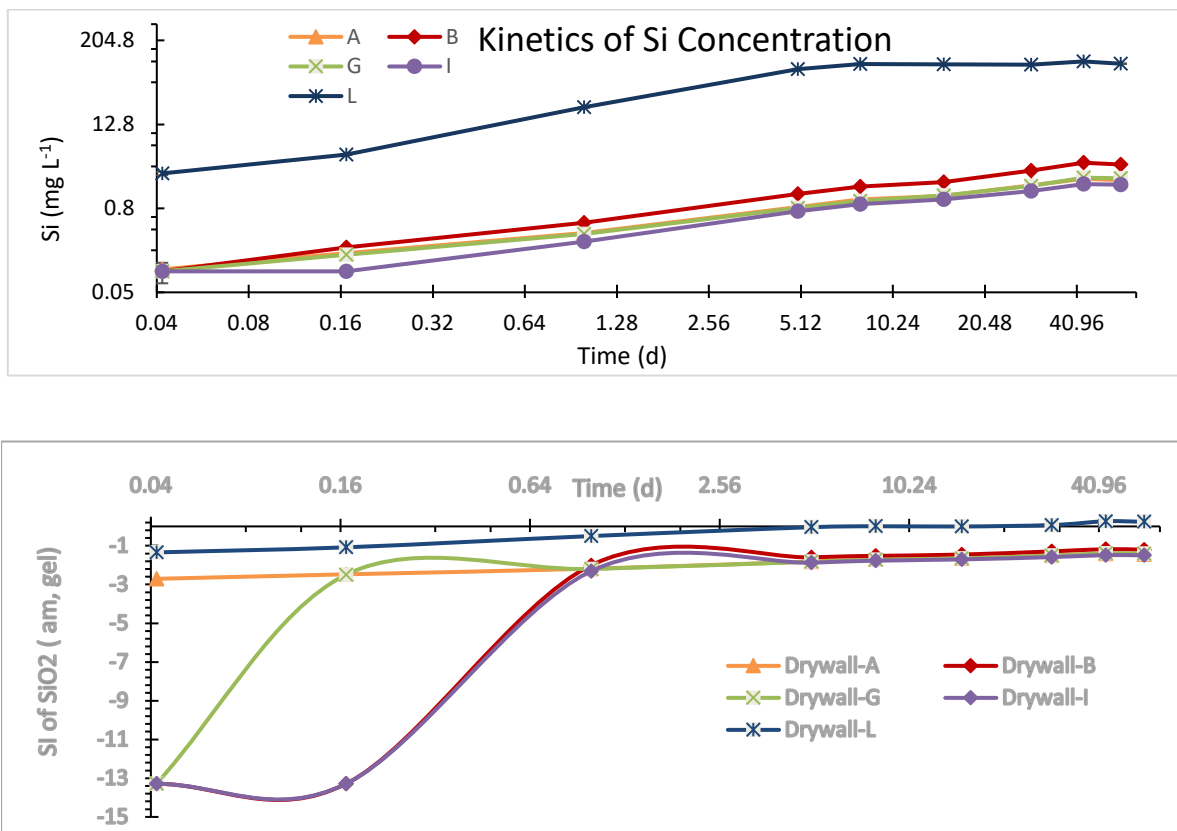


Figure 4-6: Kinetics of Si concentration and saturation index (SI) of SiO₂ (am, gel) in the solution

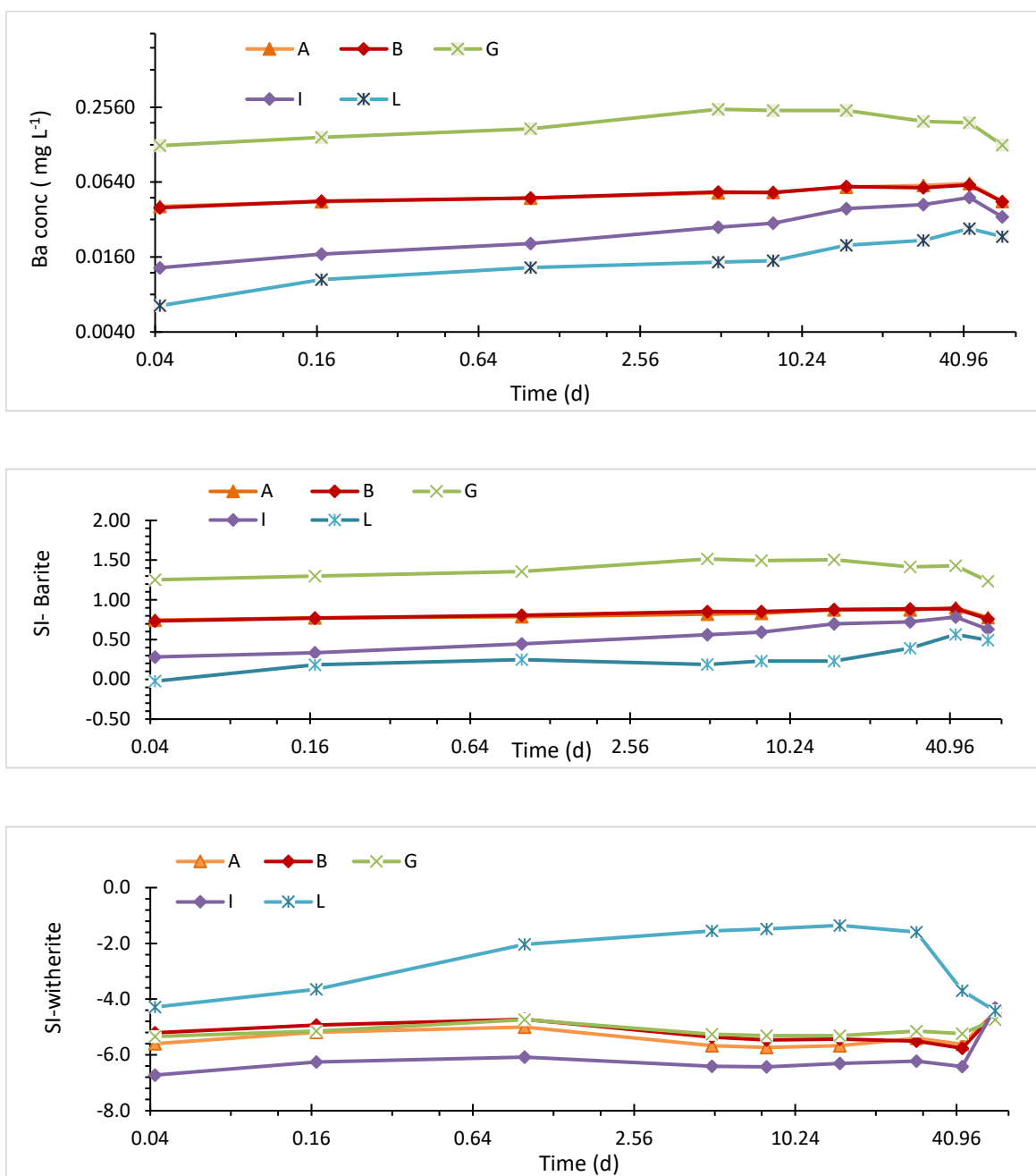


Figure 4-7: Kinetics of Ba concentration and SI of barite (BaSO_4) and witherite (BaCO_3) in the solution

For phosphorus in the drywall-water system, the minerals primarily involved are the different calcium phosphates, including brushite (dicalcium phosphate, DCP), tricalcium phosphate (TCP), and octocalcium phosphate (OCP). The calcium-phosphate double-function plot indicated that the control mineral was related to the particular sample (Figure 4-8). TCP and OCP controlled the phosphate release for samples A and B with lower concentrations of phosphate in solution. OCP and DCP controlled phosphate release in samples G and I, while DCP controlled for Drywall L. The controlling mineral shifted during the kinetics experiment (e.g., from the initial OCP to the final DCP for samples G and I).

The dissolution of OCD from samples G and I may contribute to high phosphate concentration (Figure 4-8).

In general, the results demonstrate that both calcium and sulfate in the leachates from the samples tested can reach equilibrium in a relatively short time (less 24 h), whereas the other constituents (e.g., Si, Sr, Ba or P) in the leachates require a much longer time (Figure 4-8). This observation also relates to the minerals found in the samples that control their equilibrium concentrations. The ambiguity in the definition and measurement of equilibration times has been acknowledged as a major problem in past kinetic studies (Boulding, 1996; Sparks, 2013).

Under the assumption that the concentration at 7 d represents 100%, the kinetic patterns of all constituents are presented in Figures 4-9 and 4-10. Some constituents in Figure 4-9 and 4-10 A (e.g., Ca, and S) may reach (or approach) relative equilibrium within a week, but others that are shown in Figure 4-9 and 4-10 B (e.g., Sr, P, Se) still change noticeably with additional time. EPA has suggested that the equilibration time should be the minimum amount of time needed to establish a rate of change of the solute concentration in solution equal to or less than 5% per 24-h interval (Rey et al., 1992). Therefore, a one-week equilibrium time was employed in this work for further study

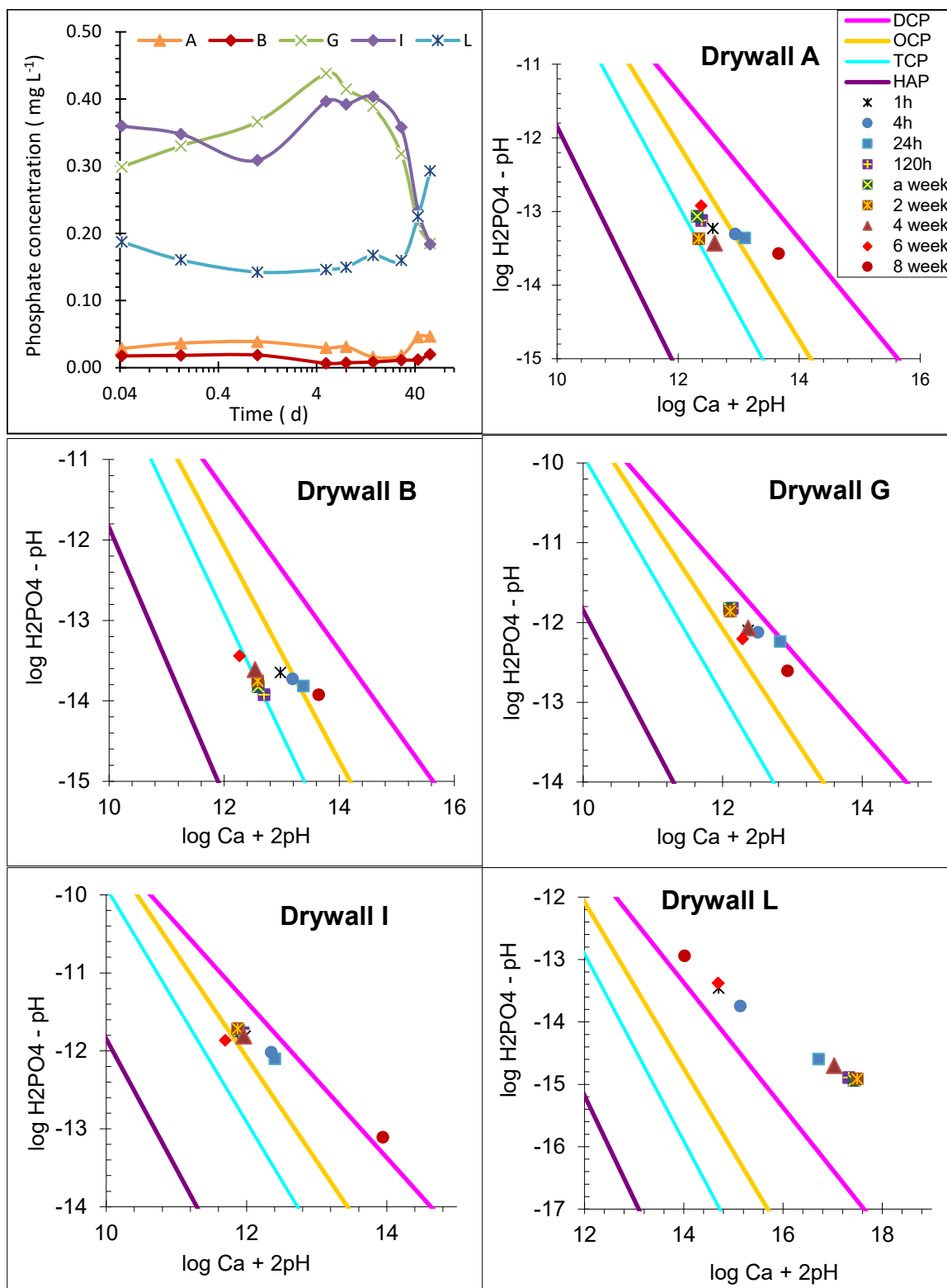


Figure 4-8: Kinetics of P concentration and calcium phosphate double function plot

of the solubility for different drywalls

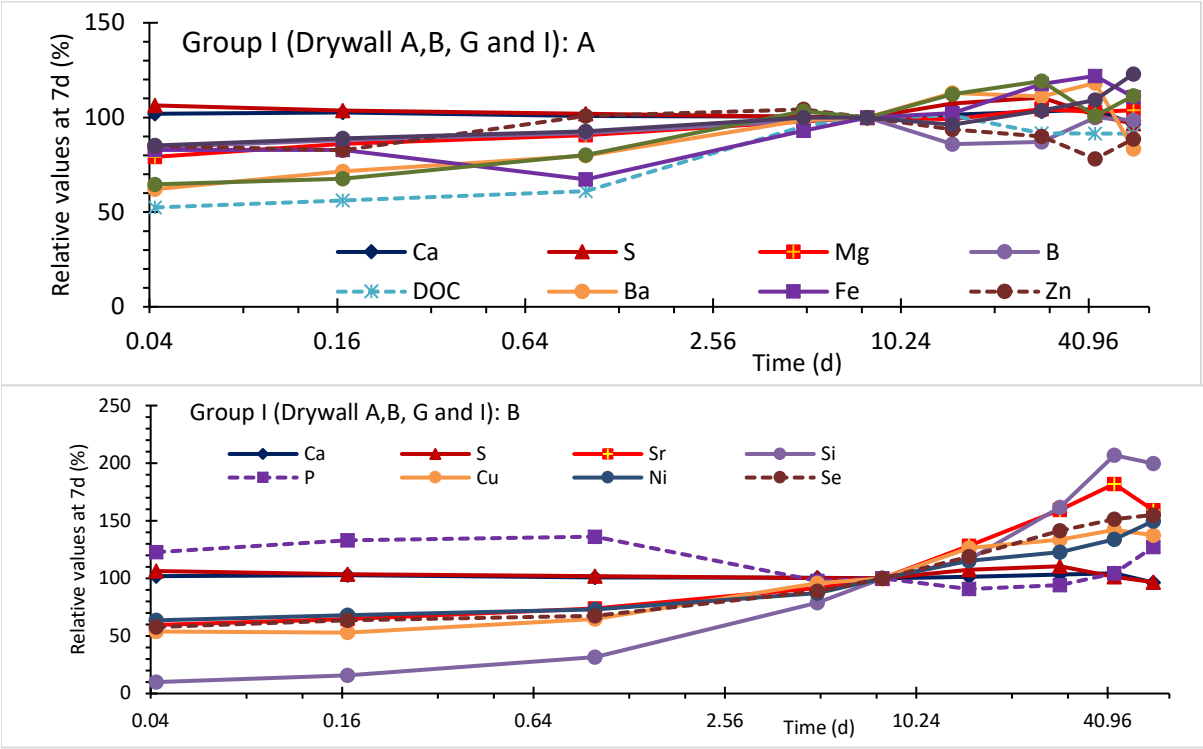


Figure 4-9: Equilibrium time and composition changes in drywall (group I, average of A, B, G and I)

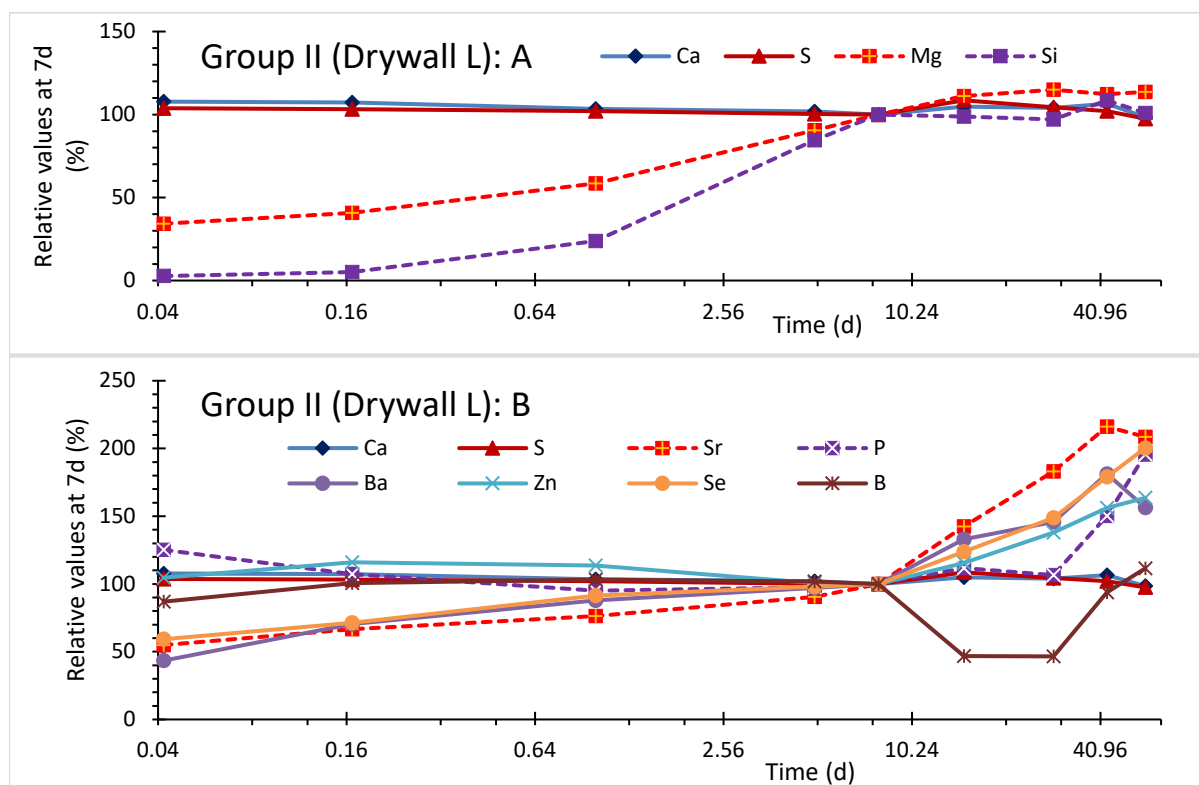


Figure 4-10: Equilibrium time and composition changes in drywall (group II, Drywall-L)

4.2. Liquid-Solid Partitioning Tests

The purpose of this leaching experiment was to assess the concentrations of the constituents leached from the samples at steady-state conditions. The plotting of pH according to the L/S ratio as well as the plotting of constituent concentrations and/or release amount provides useful information on the available quantities and solubility of different constituents. Figure 4-11 displays the pH levels of the five samples tested. In general, pH decreased as the L/S ratio increased; also, the pH of Drywall L was significantly higher than the pH values of the other four (Group I).

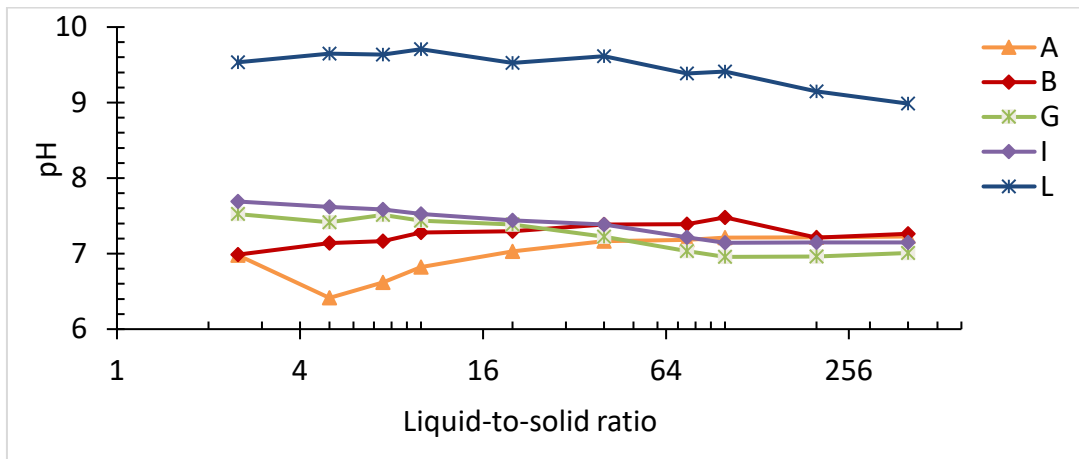


Figure 4-11: Effect of L/S ratio on the pH of drywall leachate

Figure 4-12 shows constituent concentrations in leachates from sample A as a function of L/S ratio. As expected, the leached concentration of most constituents decreased dramatically when the L/S ratio decreased, except for the Ca and S concentration (slight decrease). The most dramatically changed constituents can be described by linear dependence (logarithmic concentration *vs* the logarithmic L/S ratio) (Figure 4-12). Gypsum is the key mineral to control both calcium and sulfate concentration in the leachates at different L/S ratios. Gypsum at the studied conditions (L/S from 2.5 to 200) for all drywalls (except drywall L) was confirmed to be over-saturated or close to saturation ($SI_{\text{gypsum}} < 0$ or ~ 0). Moreover, calcium carbonates were also over-saturated ($SI_{\text{CaCO}_3} > 0$) in many cases, which indicated that calcium carbonate was the controlling mineral phase for the calcium concentration under high pH leaching conditions (e.g., Drywall L) (Table 4-1).

Table 4-1: Saturation index of minerals related to calcium in leachates

Drywall	Anhydrite	Gypsum	CaCO ₃ xH ₂ O(s)	Aragonite	Calcite
	L/S =2.5				
A	-0.232	0.017	-2.209	-1.017	-0.873
B	-0.227	0.021	-2.219	-1.026	-0.883
G	-0.207	0.041	-1.66	-0.467	-0.324
I	-0.216	0.033	-1.318	-0.125	0.019
L	-0.599	-0.35	1.941	3.133	3.277
	L/S =5				
A	-0.220	0.029	-2.192	-1.000	-0.856
B	-0.221	0.028	-2.251	-1.059	-0.915
G	-0.211	0.038	-1.880	-0.688	-0.544
I	-0.222	0.027	-1.467	-0.274	-0.131
L	-0.760	-0.511	2.017	3.209	3.353
	L/S =20				
A	-0.248	0.001	-2.364	-1.172	-1.028
B	-0.228	0.021	-2.37	-1.177	-1.034
G	-0.242	0.007	-1.93	-0.737	-0.594
I	-0.229	0.02	-1.829	-0.636	-0.493
L	-0.751	-0.502	2.006	3.198	3.342
	L/S =100				
A	-0.220	0.029	-3.457	-2.121	-2.121
B	-0.236	0.012	-3.464	-2.128	-2.128
G	-0.231	0.018	-2.783	-1.447	-1.447
I	-0.222	0.027	-2.451	-1.115	-1.115
L	-0.674	-0.425	1.911	3.247	3.247
	L/S =200				
A	-0.218	0.031	-3.88	-2.688	-2.544
B	-0.23	0.019	-3.895	-2.703	-2.559
G	-0.244	0.005	-2.789	-1.597	-1.453
I	-0.216	0.033	-2.412	-1.219	-1.076
L	-0.58	-0.331	1.783	2.975	3.119
	L/S =400				
A	-0.321	-0.072	-2.786	-1.594	-1.45
B	-0.312	-0.063	-2.8	-1.608	-1.464
G	-0.355	-0.106	-2.751	-1.558	-1.415
I	-0.342	-0.093	-2.477	-1.285	-1.142
L	-0.533	-0.284	1.627	2.819	2.963

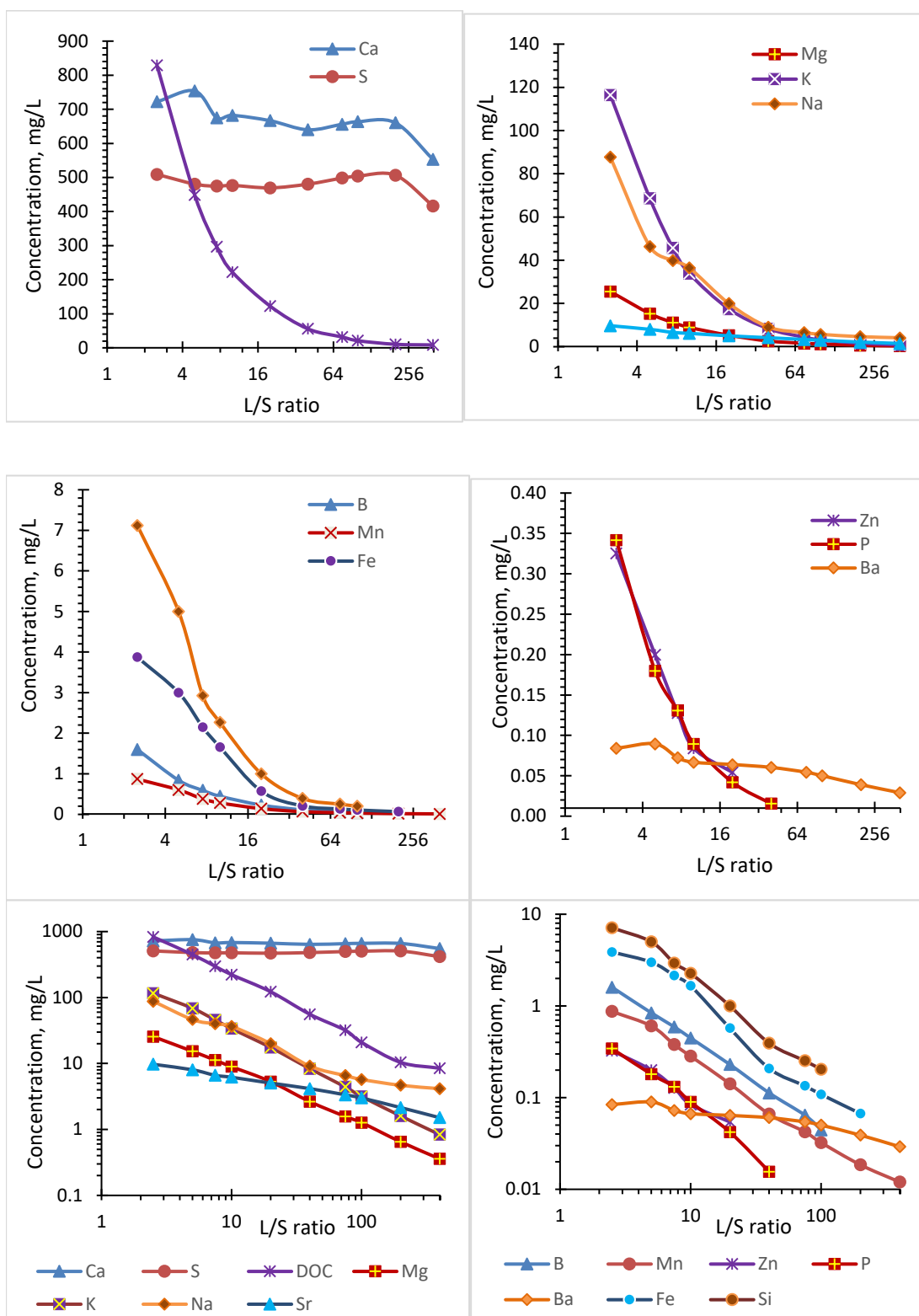


Figure 4-12: Effect of L/S ratio on the concentrations of different constituents in the Drywall-A leachates

These linearly dependent patterns were not limited to a specific drywall sample and can be observed in all the samples. For example, the results for Sr from all five samples are presented in Figure 4-13. The linear correlations were valid ($p < 0.01$). Assuming the drywall water-holding capacity as the pore volume (L/S) (which might represent the real situation for drywall in a landfill), concentrations of Sr as high as 5 to 17 mg L⁻¹ (with an average of 10 mg L⁻¹) are predicted. In these cases, the mineral celestite (SrSO₄), which controls the Sr concentration in the leachate, was at unsaturation status, and the corresponding SI_{Celestite} in all leachates was negative (Table 4.-2). The saturation index of another related mineral, strontianite (SrCO₃), is also presented.

Table 4-2: Saturation index of minerals related to Sr in leachates

L/S ratio	Mineral	Drywall				
		A	B	G	I	L
2.5	Celestite	-0.165	-0.728	-0.699	-0.762	-0.942
	Strontianite	-2.276	-2.853	-1.328	-1.997	1.464
5	Celestite	-0.254	-0.832	-0.961	-0.892	-1.209
	Strontianite	-2.359	-2.996	-1.776	-2.271	1.433
10	Celestite	-0.344	-0.945	-0.973	-1.048	-1.444
	Strontianite	-2.552	-3.19	-2.026	-2.634	1.264
20	Celestite	-0.34	-1.137	-1.262	-1.268	-1.639
	Strontianite	-2.589	-3.413	-2.414	-3.002	0.984
40	Celestite	-0.492	-1.454	-1.474	-1.252	-1.629
	Strontianite	-3.024	-3.999	-3.038	-3.128	0.995
100	Celestite	-0.628	-1.68	-1.643	-1.668	-1.955
	Strontianite	-3.998	-5.042	-13.254	-4.031	0.496
200	Celestite	-0.757	-1.757	-1.842	-12.152	-1.917
	Strontianite	-3.998	-5.042	-13.254	-4.031	0.496
400	Celestite	-0.952	-1.825	-1.979	-12.18	-2.01
	Strontianite	-3.55	-4.446	-13.118	-14.449	0.016

The same patterns were observed for Mg and B in all the leached samples. The concentration of Mg and B in the leachate increased significantly as the L/S ratio decreased, also exhibited linear dependence (Figure 4-13). Based on these linear equations, the concentrations of B in pore water would range from 5.5 to 18 mg L⁻¹ with an average of 11 mg L⁻¹. The concentration of Mg in pore water would be as high as 2,000 mg L⁻¹ with an average of 580 mg L⁻¹. This pattern was also observed for the total dissolved organic matter (DOC) in the leachates (Figure 4-13), with average concentrations of DOC in pore water expected to be approximately 3600 mg L⁻¹ (2500 to 4900 mg L⁻¹).

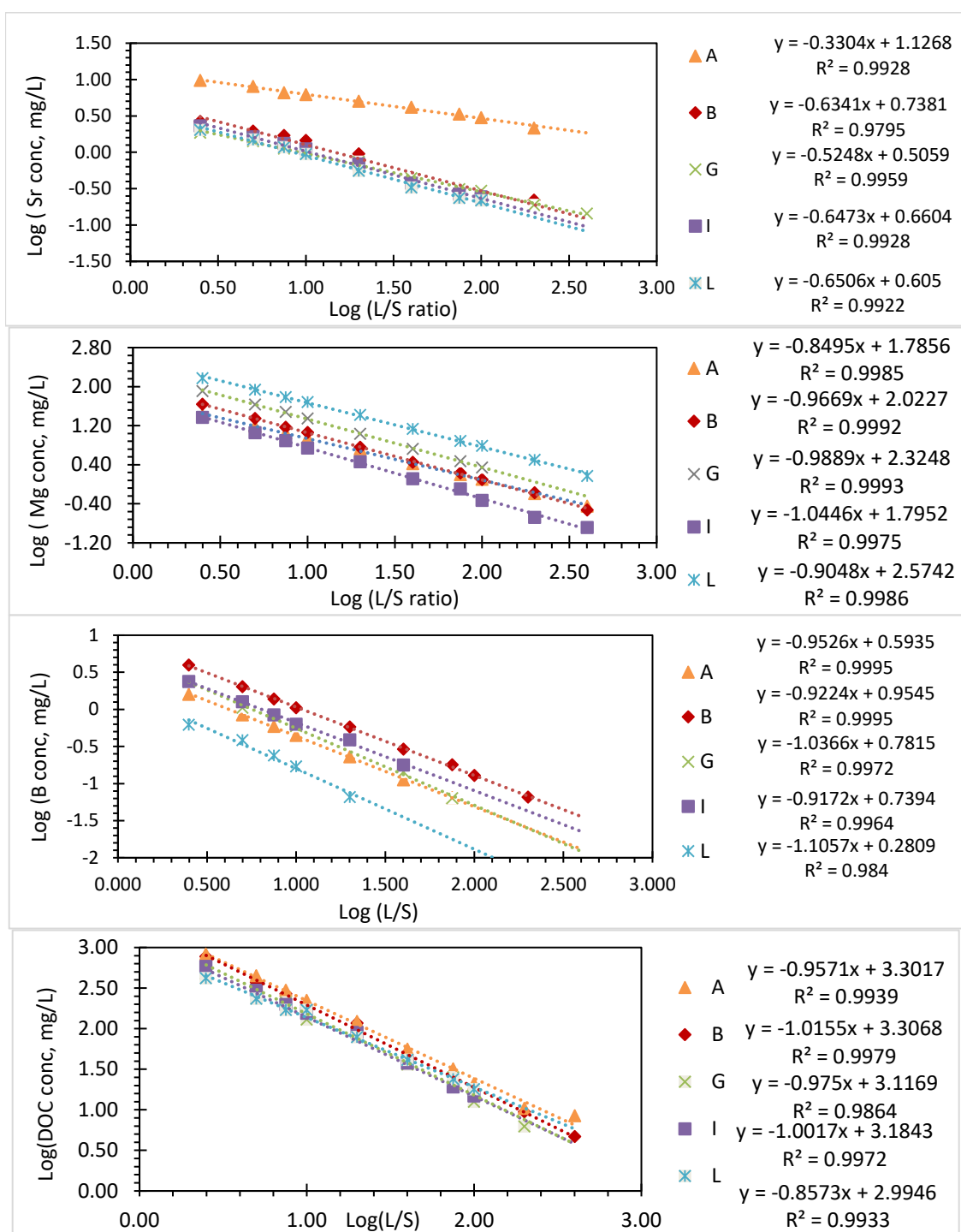


Figure 4-13: Effect of L/S ratio on the concentrations of Sr, Mg, B, and DOC in five drywall leachates

The behavior of Si in the leachate was sample-specific (Figure 4-14 and Table 4-3). The linearly dependent logarithmic Si concentration on the logarithmic L/S ratio patterns was only valid for the Group I samples (A, B, G, and I), not the Group II sample (Drywall L with the low L/S ratio). As described earlier, the SI of SiO_2 (am, ppt) was always negative for Group I, whereas the value became positive for the Drywall L (Group II) at the low L/S ratio ($\text{L/S} < 10$).

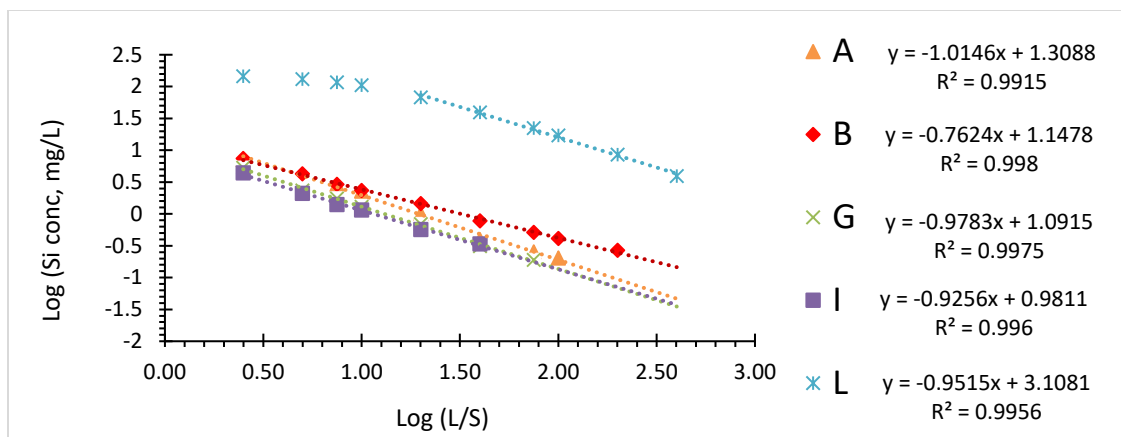


Figure 4-14: Effect of L/S ratio on the concentrations of Si in five drywall leachates (the linear correlation for Drywall L was from the ratio 40 to 400)

Table 4-3: Saturation index of minerals related to Si in the leachate

L/S ratio	Mineral	Drywall				
		A	B	G	I	L
2.5	SiO ₂ (am,gel)	-0.882	-0.866	-1.961	-1.096	0.186
	SiO ₂ (am,ppt)	-0.852	-0.836	-1.931	-1.066	0.216
	Cristobalite	-0.242	-0.226	-1.321	-0.456	0.826
	Quartz	0.408	0.424	-0.671	0.194	1.476
5	SiO ₂ (am,gel)	-0.864	-1.108	-1.363	-1.414	0.094
	SiO ₂ (am,ppt)	-0.834	-1.078	-1.333	-1.384	0.124
	Cristobalite	-0.224	-0.468	-0.723	-0.774	0.734
	Quartz	0.426	0.182	-0.073	-0.124	1.384
10	SiO ₂ (am,gel)	-1.379	-1.368	-1.625	-1.676	-0.016
	SiO ₂ (am,ppt)	-1.349	-1.338	-1.595	-1.646	0.014
	Cristobalite	-0.739	-0.728	-0.985	-1.036	0.624
	Quartz	-0.089	-0.078	-0.335	-0.386	1.274
20	SiO ₂ (am,gel)	-1.731	-1.571	-1.89	-1.983	-0.175
	SiO ₂ (am,ppt)	-1.701	-1.541	-1.86	-1.953	-0.145
	Cristobalite	-1.091	-0.931	-1.25	-1.343	0.465
	Quartz	-0.441	-0.281	-0.6	-0.693	1.115
40	SiO ₂ (am,gel)	-2.141	-1.84	-2.246	-2.209	-0.422
	SiO ₂ (am,ppt)	-2.111	-1.81	-2.216	-2.179	-0.392
	Cristobalite	-1.501	-1.2	-1.606	-1.569	0.218
	Quartz	-0.851	-0.55	-0.956	-0.919	0.868
100	SiO ₂ (am,gel)	-2.43	-2.111	-13.287	-2.475	-0.738
	SiO ₂ (am,ppt)	-2.4	-2.081	-13.257	-2.445	-0.708
	Cristobalite	-1.79	-1.471	-12.647	-1.835	-0.098
	Quartz	-1.14	-0.821	-11.997	-1.185	0.552
200	SiO ₂ (am,gel)	-2.43	-2.304	-13.287	-13.288	-0.992
	SiO ₂ (am,ppt)	-2.4	-2.274	-13.257	-13.258	-0.962
	Cristobalite	-1.79	-1.664	-12.647	-12.648	-0.352
	Quartz	-1.14	-1.014	-11.997	-11.998	0.298
400	SiO ₂ (am,gel)	-13.288	-2.369	-13.288	-13.288	-1.277
	SiO ₂ (am,ppt)	-13.258	-2.339	-13.258	-13.258	-1.247
	Cristobalite	-12.648	-1.729	-12.648	-12.648	-0.637
	Quartz	-11.998	-1.079	-11.998	-11.998	0.013

The relationship of phosphate was also sample-dependent with the phosphate minerals present (Table 4-1 and Figure 4-15). Phosphate concentrations in the leachates from sample G were significantly higher than all the others and might be controlled by the $\text{Ca}_3(\text{PO}_4)_2$ (beta); the low level of phosphates in the other leachates might be controlled by $\text{Ca}_3(\text{PO}_4)_2$ (am) or other Ca-P minerals. The oversaturated $\text{Ca}_3(\text{PO}_4)_2$ (beta) was confirmed in sample G, whereas the $\text{Ca}_3(\text{PO}_4)_2$ (am) values were at undersaturated status for all samples (Table 4-4).

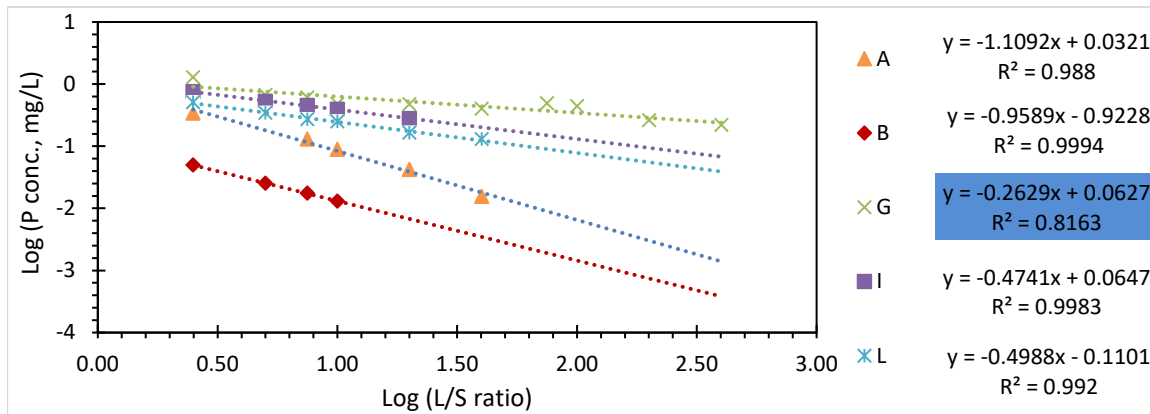


Figure 4-15: Effect of L/S ratio on the concentrations of P in five drywall leachates

L/S	Mineral	Drywall-A	Drywall-B	Drywall-G	Drywall-I	Drywall-L
2.5	$\text{Ca}_3(\text{PO}_4)_2$ (am1)	-3.058	-4.775	-1.466	-1.400	-0.312
	$\text{Ca}_3(\text{PO}_4)_2$ (am2)	-0.308	-2.025	1.284	1.350	2.438
	$\text{Ca}_3(\text{PO}_4)_2$ (beta)	0.362	-1.355	1.954	2.020	3.108
	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}(\text{s})$	-0.997	-3.568	1.116	1.044	1.047
	$\text{CaHPO}_4(\text{s})$	-1.112	-1.966	-0.591	-0.729	-1.814
	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$	-1.394	-2.247	-0.873	-1.011	-2.095
	Hydroxyapatite	7.604	5.024	10.267	10.537	13.798
5	$\text{Ca}_3(\text{PO}_4)_2$ (am1)	-3.254	-5.388	-2.119	-1.852	-0.805
	$\text{Ca}_3(\text{PO}_4)_2$ (am2)	-0.504	-2.638	0.631	0.898	1.945
	$\text{Ca}_3(\text{PO}_4)_2$ (beta)	0.166	-1.968	1.301	1.568	2.615
	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}(\text{s})$	-1.300	-4.472	0.247	0.440	0.270
	$\text{CaHPO}_4(\text{s})$	-1.219	-2.257	-0.807	-0.881	-2.099
	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$	-1.500	-2.538	-1.089	-1.162	-2.380
	Hydroxyapatite	7.318	4.087	9.177	9.783	13.096
10	$\text{Ca}_3(\text{PO}_4)_2$ (am1)	-4.276	-6.032	-2.349	-2.285	-1.086
	$\text{Ca}_3(\text{PO}_4)_2$ (am2)	-1.526	-3.282	0.401	0.465	1.664
	$\text{Ca}_3(\text{PO}_4)_2$ (beta)	-0.856	-2.612	1.071	1.135	2.334
	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}(\text{s})$	-2.770	-5.395	-0.129	-0.110	-0.164
	$\text{CaHPO}_4(\text{s})$	-1.668	-2.536	-0.953	-0.998	-2.251
	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$	-1.949	-2.817	-1.234	-1.279	-2.533
	Hydroxyapatite	5.723	3.078	8.863	9.037	12.686

L/S	Mineral	Drywall-A	Drywall-B	Drywall-G	Drywall-I	Drywall-L
20	Ca ₃ (PO ₄) ₂ (am1)	-4.992	-25.300	-2.535	-2.778	-1.348
	Ca ₃ (PO ₄) ₂ (am2)	-2.242	-22.550	0.215	-0.028	1.402
	Ca ₃ (PO ₄) ₂ (beta)	-1.572	-21.880	0.885	0.642	2.072
	Ca ₄ H(PO ₄) ₃ ·3H ₂ O(s)	-3.820	-34.279	-0.353	-0.768	-0.540
	CaHPO ₄ (s)	-2.002	-12.153	-0.991	-1.163	-2.365
	CaHPO ₄ ·2H ₂ O(s)	-2.283	-12.434	-1.272	-1.444	-2.646
	Hydroxyapatite	4.626	-25.839	8.528	8.214	12.276
40	Ca ₃ (PO ₄) ₂ (am1)	-6.252	-25.644	-2.942	-2.909	-1.649
	Ca ₃ (PO ₄) ₂ (am2)	-3.502	-22.894	-0.192	-0.159	1.101
	Ca ₃ (PO ₄) ₂ (beta)	-2.832	-22.224	0.478	0.511	1.771
	Ca ₄ H(PO ₄) ₃ ·3H ₂ O(s)	-5.569	-34.660	-0.799	-0.904	-0.971
	CaHPO ₄ (s)	-2.490	-12.189	-1.030	-1.168	-2.495
	CaHPO ₄ ·2H ₂ O(s)	-2.771	-12.470	-1.312	-1.449	-2.776
	Hydroxyapatite	2.594	-26.491	7.755	7.957	11.804
100	Ca ₃ (PO ₄) ₂ (am1)	-26.778	-26.801	-3.512	-25.428	-22.737
	Ca ₃ (PO ₄) ₂ (am2)	-24.028	-24.051	-0.762	-22.678	-19.987
	Ca ₃ (PO ₄) ₂ (beta)	-23.358	-23.381	-0.092	-22.008	-19.317
	Ca ₄ H(PO ₄) ₃ ·3H ₂ O(s)	-35.953	-35.984	-1.392	-34.431	-32.575
	CaHPO ₄ (s)	-12.348	-12.356	-1.053	-12.176	-13.012
	CaHPO ₄ ·2H ₂ O(s)	-12.629	-12.637	-1.334	-12.457	-13.293
	Hydroxyapatite	-28.600	-28.639	6.636	-26.072	-19.854
200	Ca ₃ (PO ₄) ₂ (am1)	-27.451	-27.494	-3.981	-25.359	-22.641
	Ca ₃ (PO ₄) ₂ (am2)	-24.701	-24.744	-1.231	-22.609	-19.891
	Ca ₃ (PO ₄) ₂ (beta)	-24.031	-24.074	-0.561	-21.939	-19.221
	Ca ₄ H(PO ₄) ₃ ·3H ₂ O(s)	-36.751	-36.808	-2.092	-34.347	-32.368
	CaHPO ₄ (s)	-12.473	-12.487	-1.284	-12.161	-12.900
	CaHPO ₄ ·2H ₂ O(s)	-12.754	-12.768	-1.565	-12.443	-13.181
	Hydroxyapatite	-29.821	-29.893	5.929	-25.949	-19.775
400	Ca ₃ (PO ₄) ₂ (am1)	-25.848	-25.888	-4.126	-25.484	-22.466
	Ca ₃ (PO ₄) ₂ (am2)	-23.098	-23.138	-1.376	-22.734	-19.716
	Ca ₃ (PO ₄) ₂ (beta)	-22.428	-22.468	-0.706	-22.064	-19.046
	Ca ₄ H(PO ₄) ₃ ·3H ₂ O(s)	-34.893	-34.947	-2.328	-34.502	-32.027
	CaHPO ₄ (s)	-12.219	-12.232	-1.376	-12.191	-12.734
	CaHPO ₄ ·2H ₂ O(s)	-12.500	-12.513	-1.657	-12.472	-13.015
	Hydroxyapatite	-26.869	-26.937	5.731	-26.170	-19.590

A poor linear relationship for Ba in the leachates was observed in some samples (Figure 4-16). The saturation index of barite (BaSO₄) in these leachates was positive, especially at the low liquid-to-solid ratio, though the witherite (BaCO₃) was negative in many cases (Table 4-5), suggesting that the linear relationships were related to the minerals that control dissolution. If a mineral were oversaturated,

the linear equations would not be valid for this composition. Witherite might be the controller of Ba samples L and I, whereas barite may control the concentration of Ba in samples A, B, and G.

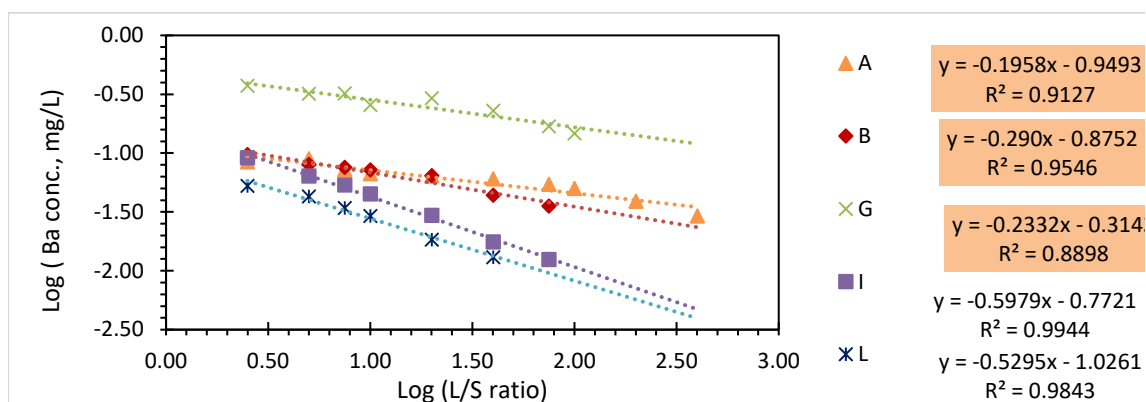


Figure 4-16: Effect of L/S ratio on the concentrations of Ba in five drywall leachates

The same patterns were observed for Fe in the leachates (Figure 4-17). The oversaturated status of iron oxides (e.g., ferrihydrite, goethite, magnetite, and hematite) was confirmed by the chemical species model (Table 4-5 and 4-6) for all leachates at the low ratio ($L/S < 40$), exhibiting a poor linear dependence, as expected.

Table 4-4: Saturation index of minerals related to Ba in leachate

L/S ratio	Drywall A		Drywall B		Drywall G		Drywall I		Drywall L	
	Barite	Witherite	Barite	Witherite	Barite	Witherite	Barite	Witherite	Barite	Witherite
2.5	0.986	-5.185	1.044	-5.141	1.66	-3.986	1.043	-4.253	0.726	-0.928
5	0.088	-6.078	0.989	-5.235	-0.161	-6.024	0.936	-4.503	0.492	-0.926
10	0.909	-5.36	0.997	-5.308	-0.174	-5.952	0.946	-4.7	0.27	-1.082
20	0.913	-5.396	0.901	-5.435	-0.184	-6.065	0.94	-4.853	0.006	-1.431
40	0.878	-5.714	0.743	-5.862	-0.167	-6.388	0.958	-4.978	0.017	-1.418
100	0.852	-6.579	0.579	-6.843	1.268	-5.478	0.111	-6.312	-0.127	-1.736
200	0.731	-7.124	0.364	-7.495	0.078	-6.661	-0.044	-6.433	-0.225	-2.056
400	0.551	-6.108	0.135	-6.546	-0.089	-6.679	-0.171	-6.5	-8.836	-10.87

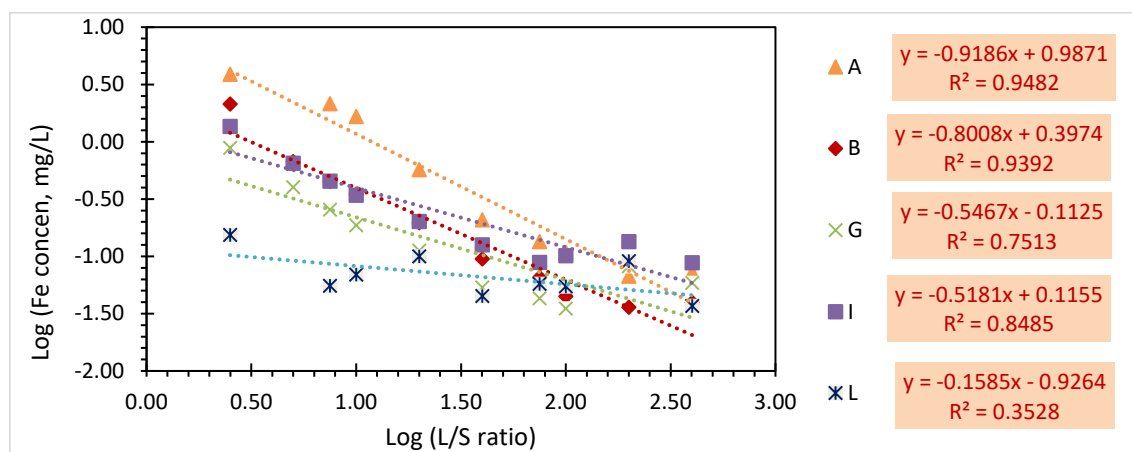


Figure 4-17: Effect of L/S ratio on the concentrations of Fe in five drywall leachates

Table 4-5: Saturation index of minerals related to iron in leachate

L/S ratio	Drywall	Ferrihydrite	Ferrihydrite (aged)	Goethite	Hematite	Maghemite
2.5	Drywall A	5.536	6.046	8.246	18.892	11.088
	Drywall B	5.268	5.778	7.977	18.356	10.552
	Drywall G	5.175	5.685	7.885	18.171	10.367
	Drywall I	5.69	6.2	8.4	19.2	11.396
	Drywall L	4.233	4.743	6.943	16.286	8.482
5	Drywall A	5.384	5.894	8.094	18.588	10.784
	Drywall B	4.762	5.272	7.472	17.344	9.54
	Drywall G	4.726	5.236	7.436	17.272	9.468
	Drywall I	5.151	5.661	7.861	18.122	10.318
	Drywall L	3.723	4.233	6.433	15.266	7.462
10	Drywall A	5.125	5.635	7.834	18.069	10.265
	Drywall B	4.441	4.951	7.15	16.702	8.898
	Drywall G	4.424	4.934	7.133	16.667	8.863
	Drywall I	4.763	5.273	7.473	17.346	9.542
	Drywall L	3.751	4.261	6.46	15.321	7.517
20	Drywall A	4.629	5.139	7.339	17.078	9.274
	Drywall B	4.171	4.681	6.881	16.162	8.358
	Drywall G	4.144	4.654	6.853	16.107	8.303
	Drywall I	4.458	4.968	7.168	16.736	8.932
	Drywall L	3.971	4.481	6.681	15.763	7.959
40	Drywall A	4.07	4.58	6.779	15.959	8.155
	Drywall B	3.729	4.239	6.439	15.278	7.474
	Drywall G	3.686	4.196	6.396	15.192	7.388
	Drywall I	4.206	4.716	6.915	16.231	8.427
	Drywall L	3.6	4.11	6.31	15.02	7.216
100	Drywall A	3.394	3.904	6.103	14.607	6.803
	Drywall B	2.994	3.504	5.703	13.807	6.003
	Drywall G	-6.571	-6.061	-3.861	-5.322	-13.126
	Drywall I	-6.382	-5.872	-3.672	-4.944	-12.748
	Drywall L	3.796	4.306	6.505	15.411	7.607
200	Drywall A	2.962	3.472	5.672	13.744	5.94
	Drywall B	-7.119	-6.609	-4.41	-6.419	-14.223
	Drywall G	-6.571	-6.061	-3.861	-5.322	-13.126
	Drywall I	-6.392	-5.882	-3.683	-4.964	-12.768
	Drywall L	4.126	4.636	6.835	16.071	8.267
400	Drywall A	-6.543	-6.033	-3.834	-5.267	-13.071
	Drywall B	-6.546	-6.036	-3.837	-5.273	-13.077
	Drywall G	-6.515	-6.005	-3.806	-5.211	-13.015
	Drywall I	-6.376	-5.866	-3.667	-4.933	-12.737
	Drywall L	3.926	4.436	6.636	15.672	7.868

Linear patterns have been observed and reported by other researchers (Tiruta-Barna et al., 2004; Van Praagh and Persson, 2008). Table 4-7 provides a summary of all equations that described constituent concentration as a function of the L/S ratio. The dominant mineral in drywall is gypsum

(>95%); hence, the leachate composition was relatively simple compared to the other solid wastes, especially when compared to actual landfill leachates.

Table 4-6: Summary of the linear dependence logarithmic concentration on the logarithmic L/S ratio in drywall leachates

Concentration (mg/L)	Drywall	Equations	R ²
Sr	A	$\log(\text{Sr}) = -0.3304 \log(\text{L/S}) + 1.1268$	0.9978
	B	$\log(\text{Sr}) = -0.6341 \log(\text{L/S}) + 0.7381$	0.9795
	G	$\log(\text{Sr}) = -0.5248 \log(\text{L/S}) + 0.5059$	0.9959
	I	$\log(\text{Sr}) = -0.6473 \log(\text{L/S}) + 0.6604$	0.9928
	L	$\log(\text{Sr}) = -0.6506 \log(\text{L/S}) + 0.605$	0.9922
B	A	$\log(\text{B}) = -0.9526 \log(\text{L/S}) + 0.5935$	0.9995
	B	$\log(\text{B}) = -0.9224 \log(\text{L/S}) + 0.9545$	0.9995
	G	$\log(\text{B}) = -1.0379 \log(\text{L/S}) + 0.8339$	0.9718
	I	$\log(\text{B}) = -0.9172 \log(\text{L/S}) + 0.7394$	0.9964
	L	$\log(\text{B}) = -0.9054 \log(\text{L/S}) + 0.1561$	0.9465
Mn	A	$\log(\text{Mn}) = -0.8943 \log(\text{L/S}) + 0.3308$	0.9943
	B	$\log(\text{Mn}) = -0.8295 \log(\text{L/S}) + 0.1524$	0.998
	G	$\log(\text{Mn}) = -0.8995 \log(\text{L/S}) + 0.4808$	0.9988
	I	$\log(\text{Mn}) = -0.939 \log(\text{L/S}) + 0.5049$	0.9993
	L	$\log(\text{Mn}) = -1.2917 \log(\text{L/S}) - 0.7258$	0.9901
Zn	A	$\log(\text{Zn}) = -0.8785 \log(\text{L/S}) - 0.1453$	0.9887
	B	$\log(\text{Zn}) = -0.7228 \log(\text{L/S}) - 0.2072$	0.9559
	G	$\log(\text{Zn}) = -0.9948 \log(\text{L/S}) + 0.0885$	0.9961
	I	$\log(\text{Zn}) = -0.8795 \log(\text{L/S}) + 0.1392$	0.9861
	L	$\log(\text{Zn}) = -0.8743 \log(\text{L/S}) + 0.6153$	0.9918
Ni	A	$\log(\text{Ni}) = -1.0207 \log(\text{L/S}) - 1.095$	0.9993
	B	$\log(\text{Ni}) = -0.9957 \log(\text{L/S}) - 1.2524$	0.9947
	G	$\log(\text{Ni}) = -0.9856 \log(\text{L/S}) - 0.5726$	0.9997
	I	$\log(\text{Ni}) = -1.0475 \log(\text{L/S}) - 0.6979$	0.999
	L	$\log(\text{Ni}) = -0.8414 \log(\text{L/S}) - 1.152$	0.9962
Co	A	$\log(\text{Co}) = -0.9623 \log(\text{L/S}) - 1.6158$	0.9841
	B	$\log(\text{Co}) = -0.9506 \log(\text{L/S}) - 1.3921$	0.9927
	G	$\log(\text{Co}) = -1.1052 \log(\text{L/S}) - 0.69$	0.9918
	I	$\log(\text{Co}) = -1.001 \log(\text{L/S}) - 1.2372$	0.9988
	L	Below detection limit	
Cd	A	$\log(\text{Cd}) = -0.869 \log(\text{L/S}) - 1.8821$	0.9977
	B	$\log(\text{Cd}) = -0.7958 \log(\text{L/S}) - 2.5053$	0.9882
	G	$\log(\text{Cd}) = -0.9772 \log(\text{L/S}) - 2.1308$	0.9876
	I	Below detection limit	
	L	$\log(\text{Cd}) = -0.828 \log(\text{L/S}) - 2.3004$	0.9955
Se	A	$\log(\text{Se}) = -0.5362 \log(\text{L/S}) - 0.9123$	0.9977
	B	$\log(\text{Se}) = -0.5651 \log(\text{L/S}) - 1.1754$	0.9795
	G	$\log(\text{Se}) = -0.7364 \log(\text{L/S}) - 0.5576$	0.9979
	I	$\log(\text{Se}) = -0.7748 \log(\text{L/S}) - 0.3016$	0.998
	L	$\log(\text{Se}) = -0.7448 \log(\text{L/S}) - 0.413$	0.9976
Mo	A	$\log(\text{Mo}) = -1.0087 \log(\text{L/S}) - 0.8572$	0.9944
	B	$\log(\text{Mo}) = -0.8507 \log(\text{L/S}) - 1.4736$	0.9795
	G	$\log(\text{Mo}) = -0.9035 \log(\text{L/S}) - 1.2703$	0.9979
	I	$\log(\text{Mo}) = -1.0139 \log(\text{L/S}) - 0.9726$	0.998

Concentration (mg/L)	Drywall	Equations	R ²
DOC	L	$\log(\text{Mo}) = -1.0115 \log(\text{L/S}) - 1.0808$	0.9998
	A	$\log(\text{DOC}) = -0.9571 \log(\text{L/S}) + 3.3017$	0.9939
	B	$\log(\text{DOC}) = -1.0155 \log(\text{L/S}) + 3.3068$	0.9979
	G	$\log(\text{DOC}) = -0.9745 \log(\text{L/S}) + 3.1164$	0.9904
	I	$\log(\text{DOC}) = -0.9643 \log(\text{L/S}) + 3.1459$	0.996
Mg	L	$\log(\text{DOC}) = -0.865 \log(\text{L/S}) + 3.002$	0.9967
	A	$\log(\text{Mg}) = -0.8495 \log(\text{L/S}) + 1.7856$	0.9985
	B	$\log(\text{Mg}) = -0.9669 \log(\text{L/S}) + 2.0227$	0.9992
	G	$\log(\text{Mg}) = -0.9889 \log(\text{L/S}) + 2.3248$	0.9993
	I	$\log(\text{Mg}) = -1.0446 \log(\text{L/S}) + 1.7952$	0.9975
K	L	$\log(\text{Mg}) = -0.9048 \log(\text{L/S}) + 2.5742$	0.9986
	A	$\log(\text{K}) = -0.9978 \log(\text{L/S}) + 2.5148$	0.999
	B	$\log(\text{K}) = -1.0494 \log(\text{L/S}) + 2.6601$	0.9962
	G	$\log(\text{K}) = -0.5221 \log(\text{L/S}) + 1.5792$	0.9876
	I	$\log(\text{K}) = -0.9829 \log(\text{L/S}) + 1.5168$	0.998
P	L	$\log(\text{K}) = -0.9821 \log(\text{L/S}) + 1.519$	0.9967
	A	$\log(\text{P}) = -1.1092 \log(\text{L/S}) + 0.0321$	0.988
	B	$\log(\text{P}) = -0.9589 \log(\text{L/S}) - 0.9228$	0.9994
	G	$\log(\text{P}) = -0.2833 \log(\text{L/S}) + 0.0459$	0.9067 (invalid)
	I	$\log(\text{P}) = -0.4741 \log(\text{L/S}) + 0.0647$	0.9983
Si	L	$\log(\text{P}) = -0.4988 \log(\text{L/S}) + 0.1101$	0.992
	A	$\log(\text{Si}) = -1.0146 \log(\text{L/S}) + 1.3088$	0.999
	B	$\log(\text{Si}) = -0.73196 \log(\text{L/S}) + 1.0971$	0.9878
	G	$\log(\text{Si}) = -0.9783 \log(\text{L/S}) + 1.0915$	0.9975
	I	$\log(\text{Si}) = -0.8894 \log(\text{L/S}) + 0.95$	0.9928
Ba	L	$\log(\text{Si}) = -0.73326 \log(\text{L/S}) + 2.6642$	0.9574 (invalid)
	A	$\log(\text{Ba}) = -0.1958 \log(\text{L/S}) - 0.9493$	0.9127 (invalid)
	B	$\log(\text{Ba}) = -0.4155 \log(\text{L/S}) - 0.7541$	0.9384 (invalid)
	G	$\log(\text{Ba}) = -0.2332 \log(\text{L/S}) - 0.3143$	0.8898 (invalid)
	I	$\log(\text{Ba}) = -0.6017 \log(\text{L/S}) - 0.7721$	0.9952
Fe	L	$\log(\text{Ba}) = -0.5295 \log(\text{L/S}) - 1.0261$	0.9843
	A	$\log(\text{Fe}) = -0.9186 \log(\text{L/S}) + 0.9871$	0.9482 (invalid)
	B	$\log(\text{Fe}) = -0.8008 \log(\text{L/S}) + 0.3974$	0.9392 (invalid)
	G	$\log(\text{Fe}) = -0.5467 \log(\text{L/S}) - 0.1125$	0.7513 (invalid)
	I	$\log(\text{Fe}) = -0.5181 \log(\text{L/S}) + 0.1155$	0.8485 (invalid)
	L	$\log(\text{Fe}) = -0.1585 \log(\text{L/S}) - 0.9264$	0.3528 (invalid)

Logarithmic concentration linear dependence of the logarithmic L/S ratio relationship can be applied if the corresponding constituent minerals exist in an unsaturation state ($\text{SI} < 0$), at least for drywall. This assessment is based on the chemical species in the leachate. Based on these assumptions, the composition of the pore water for each drywall sample tested as might be expected in a landfill may further be estimated based on the assumed L/S. In this case, the L/S ratio has been estimated from the water absorption capacity determined from the monolithic leaching test (ML). Using this approach, the average L/S was 0.44 (0.16 to 0.55), and this value was assumed to represent drywall pore water concentrations in a landfill environment; the concentrations of leachate are presented in Table 4-8 from these equations. As expected, significant correlations (Shapiro-Wilk Normality Test, Significance Level = 0.05) between the total amount and the concentration at pore volume for most constituents were observed.

Table 4-7: Pore water concentration of drywall (mg L⁻¹)*

	Average	Min	Max
Sr	10.0	5.2	16.6
B	11.5	7.3	17.7
Si	375	15.2	1800
Mn	4.1	2.0	6.9
Cu	6.3	0.30	12.2
Zn	5.6	0.956	20.5
Ni	0.21	0.066	0.38
Co	0.20	0.045	0.56
Cd	0.017	0.005	0.023
Se	0.62	0.094	1.51
Mo	0.23	0.056	0.53
P	1.71	0.21	3.21
Mg	580	110	2000
DOC	3600	2500	4900

* The pore water concentration was estimated by the corresponding linear equations, and the pore volume (L/S) was determined by the ML test.

As expected, the amount released by drywall composition increased with an L/S ratio decrease, as the constituents can be described by the linear dependence of composition logarithmic amount on the logarithmic L/S ratio (e.g., Ca, S, Sr, Ba, Sr, and Se in sample A) (Figure 4-18). These compositions usually come from one single dominant source of minerals (Table 4-1, 4-2, and 4-5) and do not relate to saturation status.

If the leached constituents originate from different minerals, the assumption of linear dependence may not be valid. For example, the linear dependence between the logarithmic released P amount and logarithmic L/S ratio for samples I and L was determined valid, whereas no clear patterns were observed for samples A and B (Figure 4-19). The linear dependence between the logarithmic released Si amount and logarithmic L/S ratio was also observed only for sample B, not the other samples (Figure 4-20).

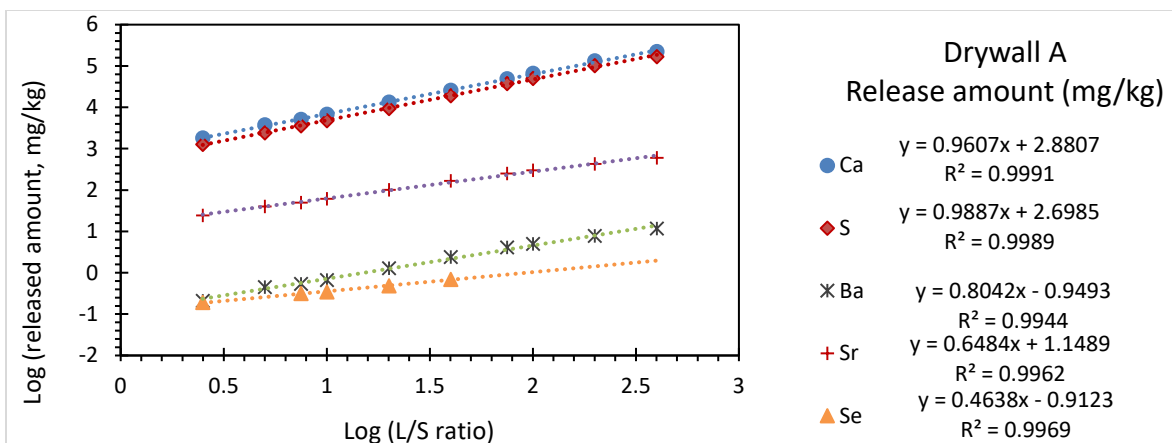


Figure 4-18: Effect of L/S ratio on the release amount of Ca, S, Ba, Sr, and Se from Drywall- A

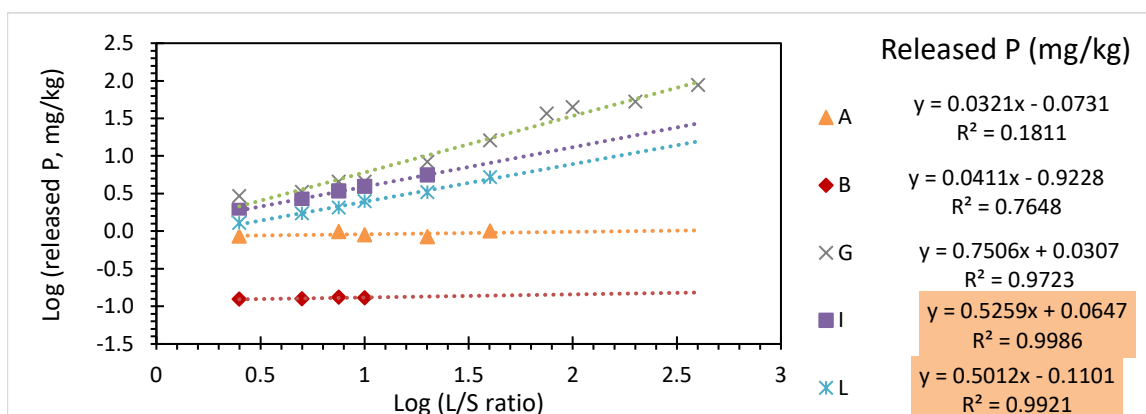


Figure 4-19: Effect of L/S ratio on the release amount of P from different drywall leachates

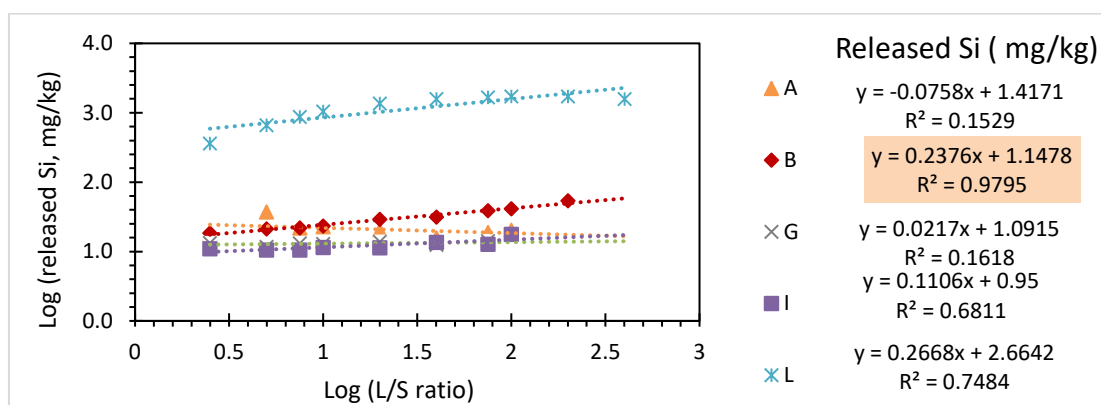


Figure 4-20: Effect of L/S ratio on the release amount of Si from different drywall

leachates

The corresponding mineral information can be found in Table 4-4 (P) and Table 4-3 (Si), respectively. The plots for the release amount of S, Ca, B, Ba, Sr, and Se from the different drywall samples are presented in Figures 4-20 to 4-26, and no general patterns can be applied directly.

Despite the differences noted above, in general, the minerals in drywall are quite simple and similar (Table 3-11). There were almost no differences among all samples relative to calcium and sulfate release (Figure 4-21 and 4-22). These observations suggest that the patterns of the constituent concentrations and mineral phases in a drywall source are more complex than the concentrations in leachate, and the linear dependence of the logarithmic amount on the logarithmic L/S ratio needs further confirmation for each circumstance (each composition with its corresponding minerals). In addition, the compositions in leachate usually are not controlled by a single mineral.

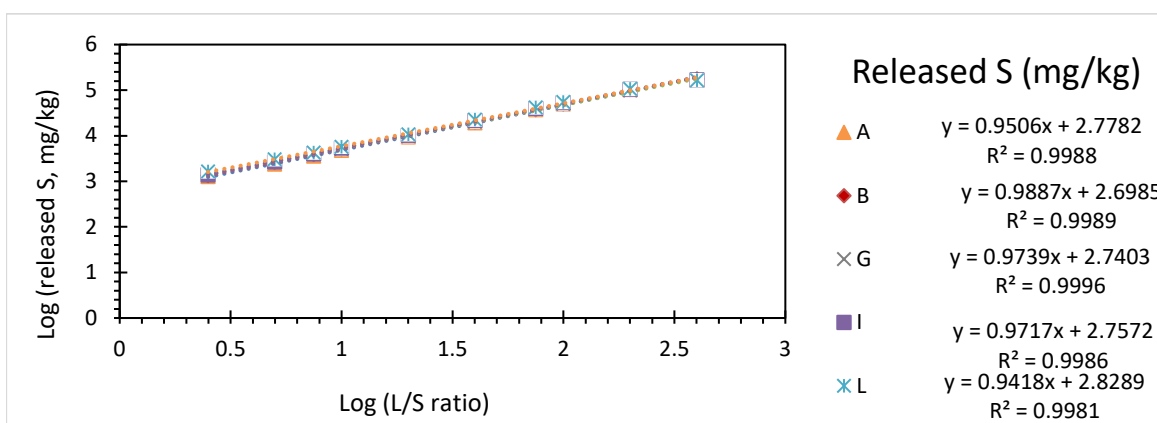


Figure 4-21: Effect of L/S ratio on the release amount of S from different drywall leachates

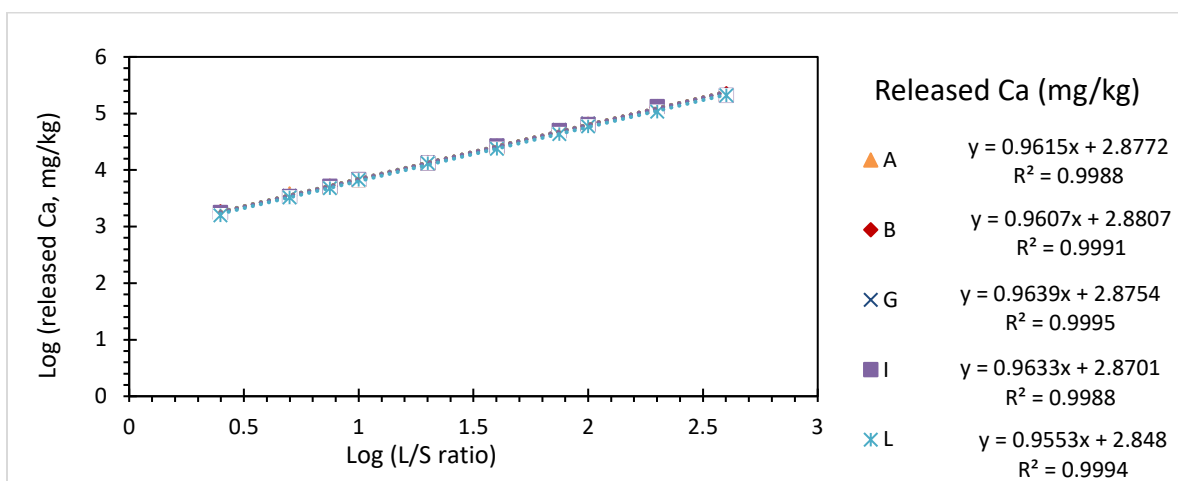


Figure 4-22: Effect of L/S ratio on the amount of Ca released from different drywall leachates

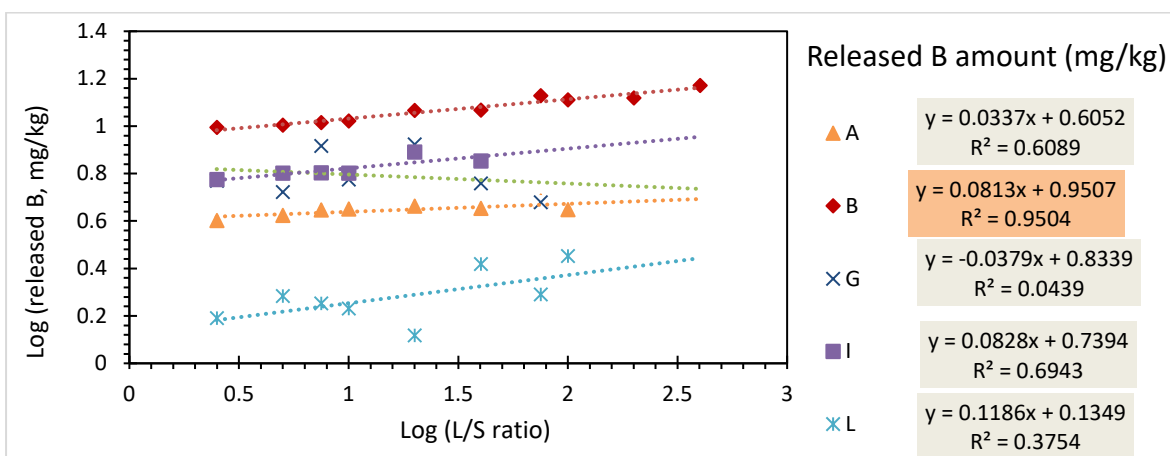


Figure 4-23: Effect of L/S ratio on the amount of B released from different drywall leachates

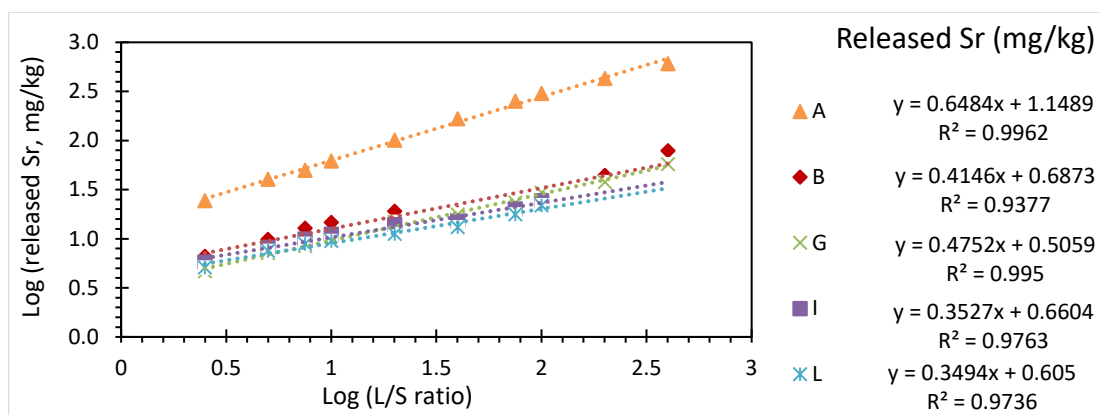


Figure 4-24: Effect of L/S ratio on the amount of Sr released from different drywall leachates

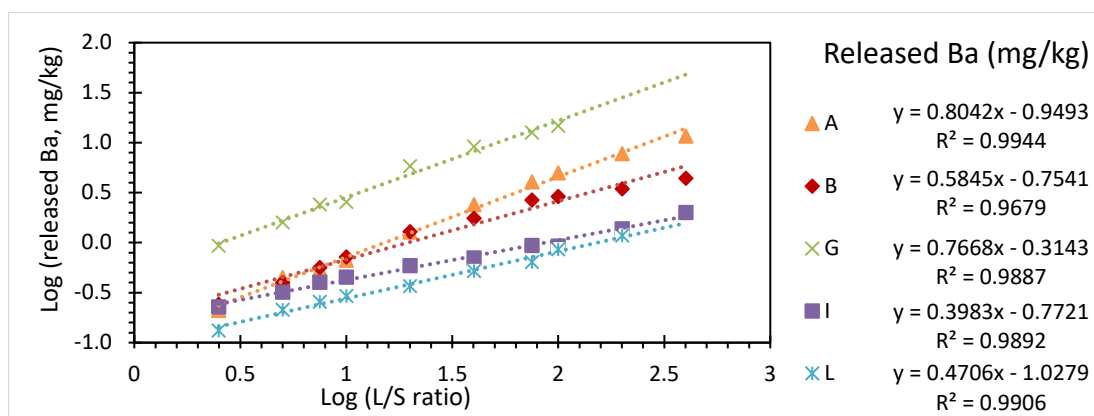


Figure 4-25: Effect of L/S ratio on the amount of Ba released from different drywall leachates

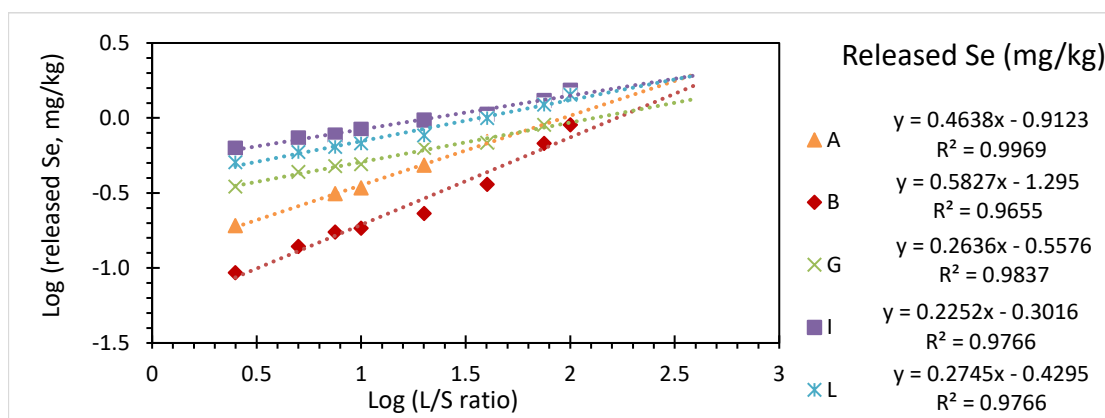


Figure 4-26: Effect of L/S ratio on the amount of Se released from different drywall leachates

4.3. Monolithic Leaching Tests (MLs)

The monolithic leachate test was conducted to study the mass transfer rates of inorganic constituents contained in the drywall board, as a monolithic material, under diffusion-controlled release conditions, as a function of leaching time. The experiments were conducted following EPA M1315 (tank leaching test). The dynamic pH and conductivity EC in the leachate are presented in Figure 4-27. In general, the EC patterns from the five samples were very similar and increased with time, whereas pH in leachate was found to be related to the sample tested. Significant pH changes (>2.5 units) during the leaching process were observed for sample L, which may relate to its mineral composition (e.g., a small amount of carbonates).

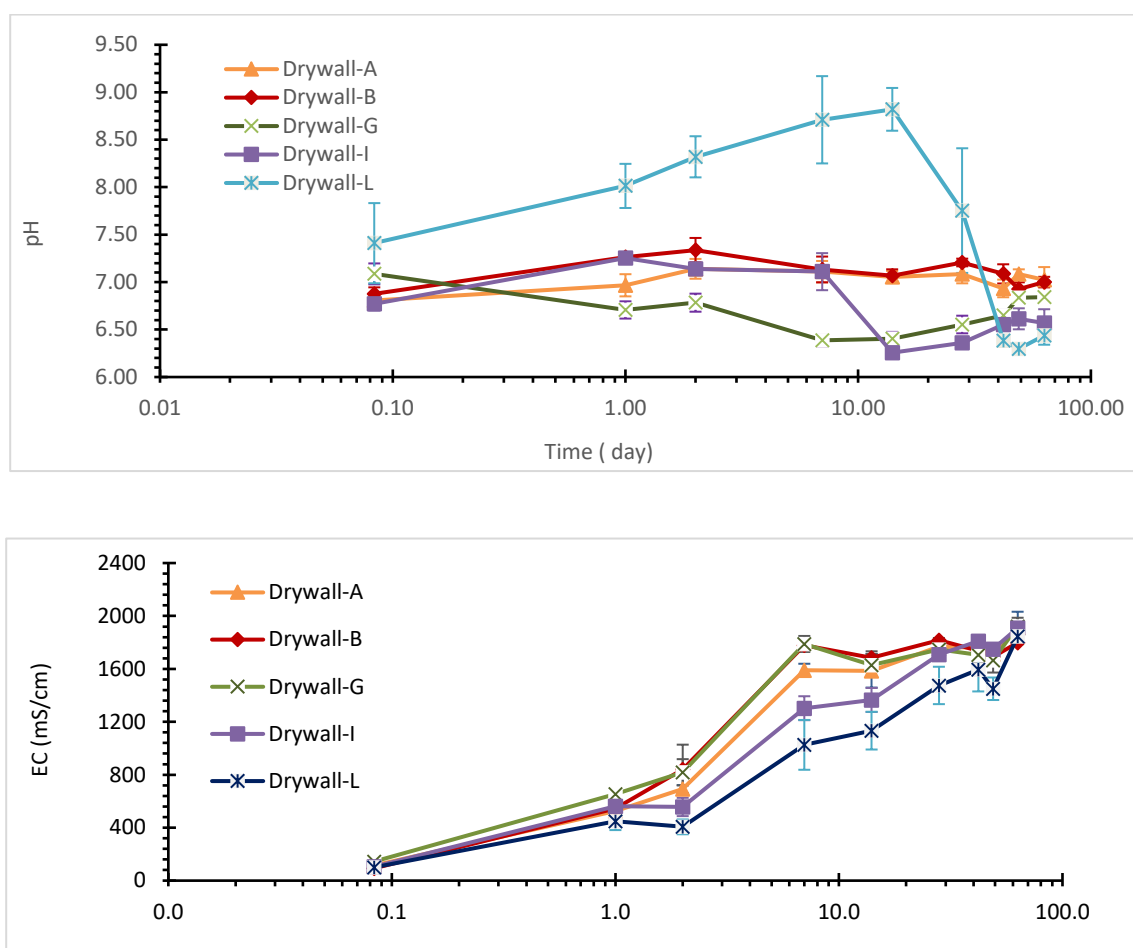


Figure 4-27: Kinetics of pH and EC in M1315 leaching process

The results for cumulative released constituent masses (or loss composition, $P_{\text{cum-Mi}}$, %) are summarized in Table 4-9, based in the cumulative constituent mass measured in the ML tests and the masses of the total constituents presented earlier. Different size membranes (0.05, 0.45, and 5 μm) were used for the filtration; however, no filter size impact was noted in elemental concentration and the data represent the average of the three filter sizes ($p > 0.05$). In addition, as several elements were below detection limits, only 11 constituents (Ca, S, Sr, Ba, Mg, Si, Fe, Mn, Zn, P, and DOC) in five samples were compared. As expected, the amount released ($P_{\text{cum-L}}$) was related to the mineral composition and the specific sample source. There was almost no difference for the dominant constituents in drywall, Ca, and SO_4 , but significant differences were observed for the minor constituents (e.g., Sr and Ba (Table 4-9)).

Table 4-8: Cumulative release composition (%) in M1315 leaching processing

	Average	STDEV	Min	Max
DOC	5.4	1.4	3.9	7.0
Fe	7.7	8.9	0.6	22.9
Si	15.5	19.4	0.9	49.0
P	18.8	8.5	5.8	27.5
Mg	19.1	17.8	4.4	48.0
Ba	24.8	14.9	10.8	50.3
Mn	39.7	15.4	13.1	52.0

	Average	STDEV	Min	Max
S	43.6	4.0	37.8	47.9
Ca	43.0	3.8	37.3	46.6
Sr	50.3	8.2	40.0	61.5
Zn	63.4	12.9	46.0	72.9

The cumulative released masses of constituents from the drywall samples were plotted as a function of leaching time (Figure 4-28). A general linear dependence between the logarithmic cumulative released compositions ($P_{\text{cum-L}}$ mg m⁻²) and logarithmic total leaching time (t_{cum}) was observed, although there were some differences among the different samples (Table 4-10). For the dominant constituents S and Ca, as well as the minor constituents Sr, Zn, and DOC, the variation of slopes of the best-fit equations were below 20%. For the other minor constituents (Fe, Si, P, Mg, Ba, DOC, and Mn), the variation of slopes was much higher, up to 50%. The variation of intercepts in the equations were much higher compared to the changes in slopes, and there was no link between the intercept and its corresponding total constituent amount in the sample.

Table 4-9: Slopes of the linear equation of the logarithmic cumulative released compositions and logarithmic total leaching time for drywall

	Sample	Slope	r²
S	Drywall A	0.724	0.997
	Drywall B	0.757	0.992
	Drywall G	0.672	0.993
	Drywall I	0.710	0.998
	Drywall L	0.697	0.999
	Overall	0.712	0.982
Ca	Drywall A	0.734	0.997
	Drywall B	0.767	0.994
	Drywall G	0.675	0.996
	Drywall I	0.716	0.998
	Drywall L	0.712	0.998
	Overall	0.721	0.982
Sr	Drywall A	0.736	0.997
	Drywall B	0.721	0.985
	Drywall G	0.631	0.994
	Drywall I	0.647	0.998
	Drywall L	0.653	0.997
	Overall	0.678	0.702
Zn	Drywall A	0.351	0.983
	Drywall B	0.356	0.991
	Drywall G	0.378	0.956
	Drywall I	0.358	0.990
	Drywall L	0.292	0.981
	Overall	0.347	0.568
Ba	Drywall A	0.648	0.996
	Drywall B	0.606	0.992
	Drywall G	0.730	0.995
	Drywall I-1 st period (0-28 d)	0.372	0.985
	Drywall I-2 nd period (28 to 63 d)	0.676	0.992
	Drywall L-1 st period (0-28 d)	0.314	0.976
	Drywall L-2 nd period (28 to 63 d)	0.711	0.980
	Overall	0.554	0.619

	Sample	Slope	r²
Fe	Drywall A	0.348	0.967
	Drywall B	0.241	0.973
	Drywall G	0.401	0.962
	Drywall I-1 st period (0-7d)	0.383	0.964
	Drywall I-2 nd period (28 d-63 d)	1.482	0.970
	Drywall L-1 st period (0-28 d)	0.327	0.987
	Drywall L-2 nd period (28 d-63 d)	1.965	0.965
Si	Drywall A	0.359	0.989
	Drywall B	0.450	0.980
	Drywall G	0.371	0.992
	Drywall I	0.338	0.994
	Drywall L-1 st period (0-42 d)	0.882	0.992
	Drywall L-2 nd period (42 d-63 d)	0.059	0.977
P	Drywall A-1 st period (0-42 d)	0.227	0.984
	Drywall A-2 nd period (42 d-63 d)	0.644	0.964
	Drywall B	0.227	0.992
	Drywall G	0.625	0.986
	Drywall I	0.677	0.999
	Drywall L-1 st period (0-28 d)	0.594	0.994
	Drywall L-2 nd period (28 d-63 d)	1.259	0.990
DOC	Drywall A	0.436	0.982
	Drywall B-2 nd period (0-7 d)	0.488	0.994
	Drywall B-2 nd period (7 d-63 d)	0.223	0.994
	Drywall G	0.309	0.992
	Drywall I	0.483	0.985
	Drywall L-1 st period (0-28 d)	0.262	0.993
	Drywall L-2 nd period (28 d-63 d)	0.911	0.973
Mg	Drywall A-1 st period (0-2 d)	0.615	1.000
	Drywall A-2 nd period (2 d-63 d)	0.282	0.994
	Drywall B--1 st period (0-2 d)	0.627	0.996
	Drywall B-2 nd period (2 d-63 d)	0.109	0.983
	Drywall G-1 st period (0-2 d)	0.845	0.998
	Drywall G-2 nd period (2 d-63 d)	0.244	0.976
	Drywall I-1 st period (0-2 d)	0.563	1.000
	Drywall I-2 nd period (2 d-63 d)	0.377	0.958
	Drywall L-1 st period (0-2 d)	0.934	0.998
	Drywall L-2 nd period (2 d-63 d)	0.546	0.997
Mn	Drywall A-1 st period (0-2 d)	0.566	1.000
	Drywall A-2 nd period (2 d-63 d)	0.230	0.979
	Drywall B--1 st period (0-2 d)	0.528	1.000
	Drywall B-2 nd period (2 d-63 d)	0.208	0.987
	Drywall G-1 st period (0-2 d)	0.659	0.999
	Drywall G-2 nd period (2 d-63 d)	0.445	0.988
	Drywall I-1 st period (0-28 d)	0.534	0.996
	Drywall I-2 nd period (28 d-63 d)	0.202	0.994
	Drywall L-1 st period (0-28 d)	0.337	0.958
	Drywall L-2 nd period (28 d-63 d)	1.224	0.937

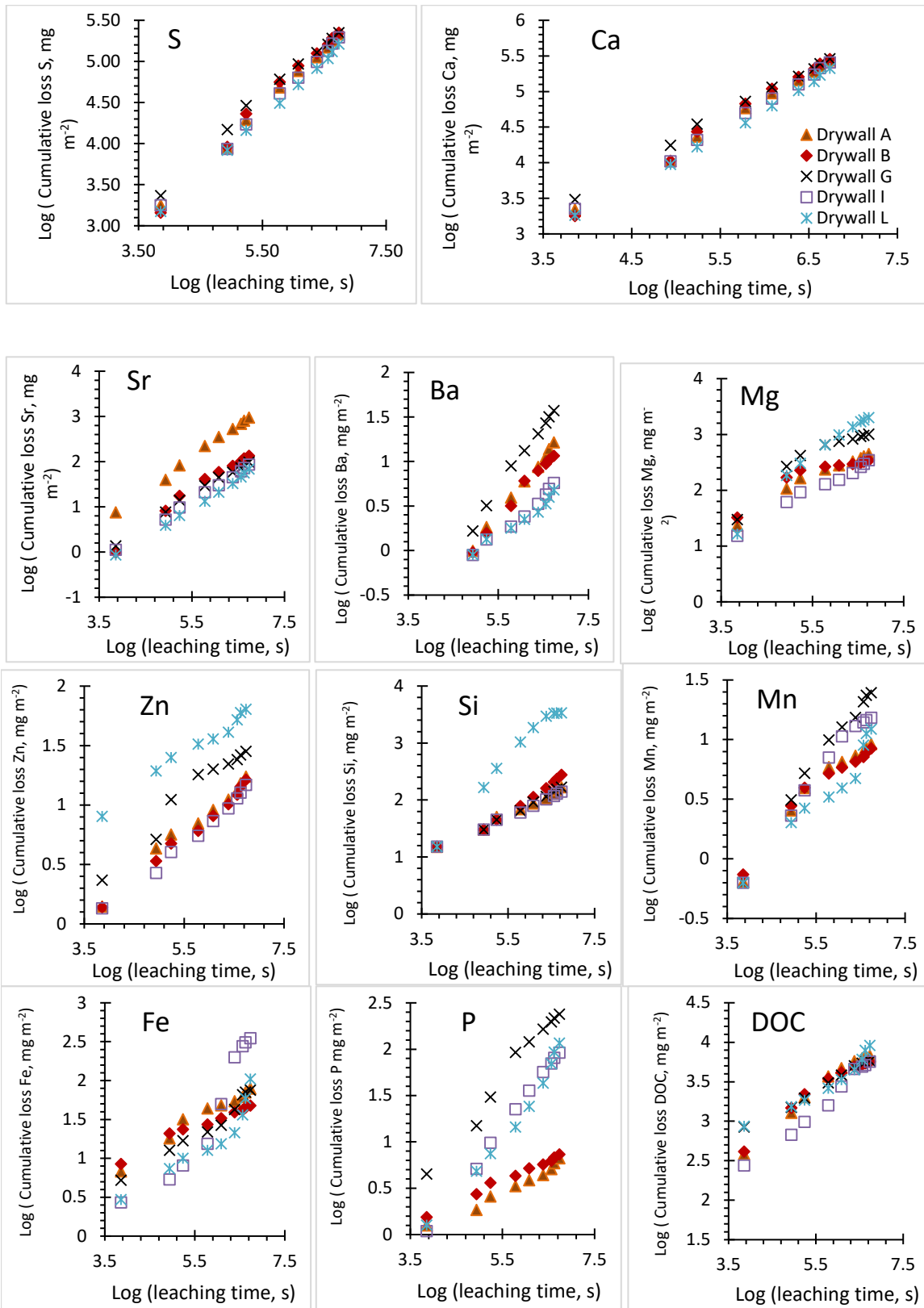
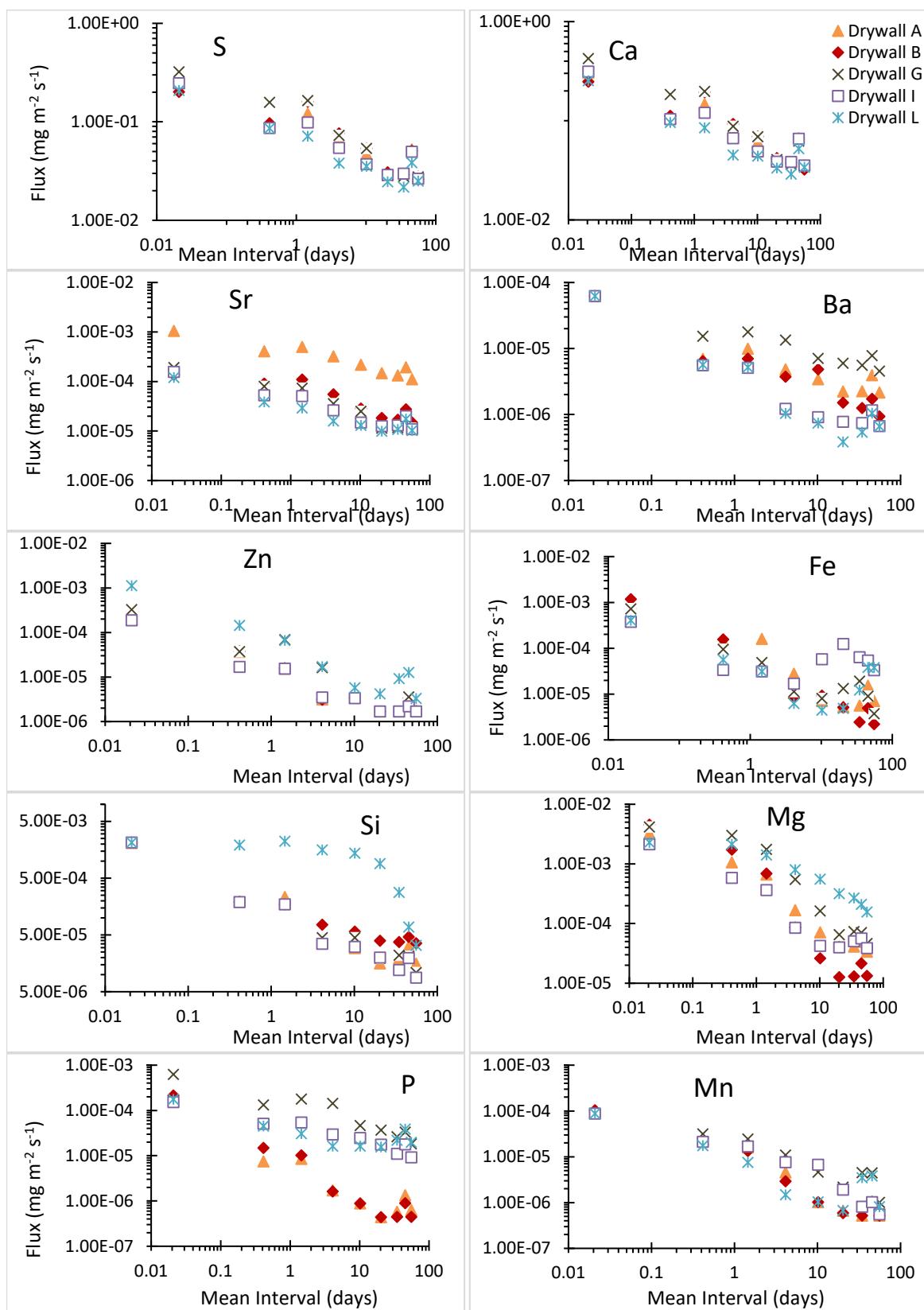


Figure 4-28: Cumulative loss vs total leaching time for the different components in drywall

Typically, leaching is assumed to be diffusion-controlled if the slope of a release equation is 0.5 ± 0.15 (e.g., Zn, and Ba in most drywall). Dissolution or wash-out of mobile species was observed for the dominant constituents in drywall, including S, Ca, and even Sr in all drywall, as the slope of these equations was larger than 0.65. Meanwhile, the behavior of some constituents in drywall might be controlled by multiple mechanisms, as the slopes in the linear equations were changed significantly during the leaching process. A surface wash-off pattern, with initial rapid leaching followed by a lower leaching rate, was observed in some cases (e.g., Mg in all samples and Si in sample L). A delayed release pattern was also observed for Fe in samples I and L, P in samples A and L, and Mn in sample L. In this pattern, a low initial release rate was observed, followed by a higher leaching rate toward the end. A depletion pattern was not common in drywall and occurred only when the composition had been leached out during the initial period (e.g., Si in sample L and Mn in samples A, B, and I).

The interval flux of different constituents was also plotted as a function of mean leaching time (Figure 4-29). Although a linear dependence between the logarithmic flux ($\text{mg m}^{-2}\text{s}^{-1}$) and logarithmic mean leaching time (T) was suggested, the corresponding correlation coefficient (r) was significantly lower than the correlation coefficient of the cumulative released constituents as a function of total leaching time (Table 4-11), especially for the constituents involving two different leaching processes (e.g., Fe, Si in sample L). As stated earlier, several mechanisms may control the leaching behavior of drywall.

Based on the diffusion model, the diffusivity and leachability index of the constituents were calculated (ANS, 1986; Kosson et al., 2002); the results were presented as Table 4-12 and 4-13, respectively. As expected, the highly leachable constituents were Zn, Sr, SO_4 , and Ca, the moderately leachable constituents were Mg and Mn, and the relatively slow-release constituents were P, Fe, Si, Ba, and DOC. However, the mobility of the constituents, especially the minor constituents, was closely related to the minerals in the samples. The variations of D_e or LX were large (e.g., Mg, Fe, and Si) among the different samples. D_e is a dynamic coefficient in the leaching process, and a large variation was observed in the process of leaching for a single sample. The results of D_e for different constituents in sample A are presented in Figure 4-30.



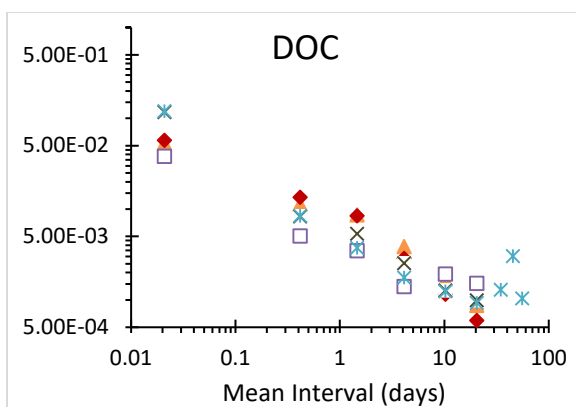


Figure 4-29: Flux vs mean interval time for the different components in drywall

Table 4-10: Slope and r^2 of the equation between logarithmic flux and logarithmic mean leaching time

Sample		Slope	r^2
S	Drywall A	-0.263	0.867
	Drywall B	-0.253	0.795
	Drywall G	-0.325	0.895
	Drywall I	-0.264	0.888
	Drywall L	-0.269	0.916
Ca	Drywall A	-0.253	0.868
	Drywall B	-0.243	0.793
	Drywall G	-0.318	0.912
	Drywall I	-0.254	0.880
	Drywall L	-0.249	0.892
Sr	Drywall A	-0.266	0.913
	Drywall B	-0.300	0.827
	Drywall G	-0.371	0.924
	Drywall I	-0.327	0.923
	Drywall L	-0.298	0.902
Zn	Drywall A	-0.613	0.929
	Drywall B	-0.613	0.927
	Drywall G	-0.697	0.900
	Drywall I	-0.594	0.952
	Drywall L	-0.700	0.909
Ba	Drywall A	-0.383	0.882
	Drywall B	-0.472	0.922
	Drywall G	-0.300	0.922
	Drywall I	-0.551	0.922
	Drywall L	-0.590	0.895
Fe	Drywall A	-0.669	0.887
	Drywall B	-0.787	0.965
	Drywall G	-0.577	0.884

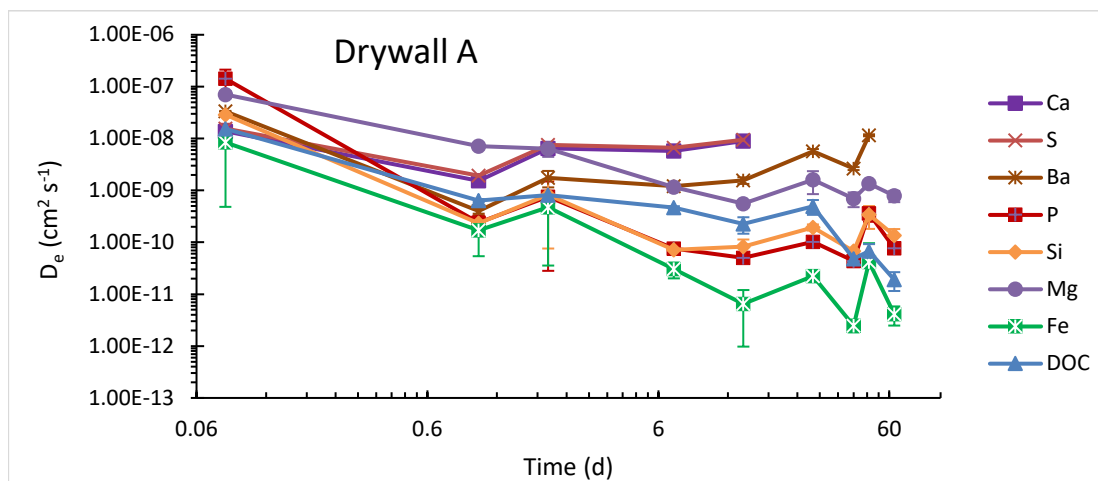
Sample		Slope	r ²
	Drywall I	-0.149	0.185
	Drywall L	-0.373	0.451
Si	Drywall A	-0.606	0.928
	Drywall B	-0.490	0.944
	Drywall G	-0.618	0.967
	Drywall I	-0.657	0.966
	Drywall L	-0.433	0.509
P	Drywall A	-0.699	0.907
	Drywall B	-0.796	0.952
	Drywall G	-0.418	0.910
	Drywall I	-0.326	0.936
	Drywall L	-0.239	0.646
DOC	Drywall A	-0.687	0.946
	Drywall B	-0.745	0.957
	Drywall G	-0.775	0.973
	Drywall I	-0.565	0.917
	Drywall L	-0.537	0.831
Mg	Drywall A	-0.630	0.950
	Drywall B	-0.850	0.918
	Drywall G	-0.647	0.884
	Drywall I	-0.537	0.926
	Drywall L	-0.360	0.867
Mn	Drywall A	-0.709	0.930
	Drywall B	-0.725	0.943
	Drywall G	-0.504	0.875
	Drywall I	-0.628	0.916
	Drywall L	-0.529	0.743

Table 4-11: Weighted arithmetic mean D_e of drywall board (cm² s⁻¹)

	Average	STDEV	Min	Max
S	6.02E-07	3.79E-07	1.98E-07	1.13E-06
Ca	5.54E-07	3.31E-07	1.66E-07	1.01E-06
Sr	4.19E-07	4.58E-07	9.26E-09	1.13E-06
Zn	1.81E-07	1.69E-07	8.35E-09	4.10E-07
Mn	6.49E-08	7.58E-08	1.39E-09	1.86E-07
Mg	5.89E-08	1.29E-07	8.44E-11	2.89E-07
P	4.47E-09	4.17E-09	3.05E-10	9.82E-09
Ba	3.84E-09	2.45E-09	1.45E-09	7.76E-09
Si	3.00E-09	5.84E-09	5.92E-12	1.34E-08
Fe	2.07E-09	4.02E-09	3.73E-12	9.23E-09
DOC	2.09E-10	1.48E-10	6.57E-11	4.49E-10

Table 4-12: Leachability index (LX) of drywall board

	Average	STDEV	Min	Max
Zn	7.0	0.78	6.2	8.1
Mn	7.5	0.92	6.5	8.8
Sr	8.1	0.15	7.9	8.2
S	8.3	0.23	7.9	8.5
Ca	8.3	0.22	8.0	8.6
Ba	8.5	0.41	7.9	9.1
P	8.8	0.51	8.2	9.6
Mg	8.7	1.45	6.3	9.9
Si	9.5	1.09	8.1	11.1
DOC	9.8	0.43	9.2	10.2
Fe	10.3	0.85	9.4	11.6

**Figure 4-30: Dynamics of De of different compositions in drywall A**

The weighted arithmetic means D_e was determined, which is weighted based on the time of leaching; the arithmetic means D_e was often used in other studies. The weighted arithmetic means D_e was surmised to be a more reasonable estimate for leachability than the arithmetic mean. LXs of most constituents in the drywall were between 8 and 9. This finding supports the current management of drywall landfill as Subtitle D landfill (Canada, 1991; Dermatas et al., 2004; Moon and Dermatas, 2007)

The results of the monolithic leaching tests for five different drywall products indicated that the leaching processes occurring during the M1315 laboratory conditions were not controlled by diffusion only, and the dominant constituents, S and Ca (along with some minor constituents, such as Sr), leached out following a dissolution model. While the other leaching models (surface wash-off pattern, delayed-release pattern, and depletion pattern) were also observed for some constituents among the samples, most constituents displayed linear dependence between the logarithmic cumulative released compositions and logarithmic total leaching time. Based on the theory of diffusion, the diffusivity and leachability index of the constituents were calculated. The highly leachable constituents were Zn, Sr, SO_4 , and Ca; the moderately leachable constituents were Mg and Mn; and the relatively slow release constituents were P, Fe, Si, Ba, and DOC. The leachability index of most compositions was between 8 and 9.

5. Conclusions

The findings presented in this report provide information regarding the mineral and chemical characteristics of gypsum drywall products and add to the database of existing literature on the subject. A total of 10 drywall samples were collected, and all or a subset of these samples were characterized using multiple analytical procedures, including their leaching behavior by EPA Methods 1315 and 1316. The major findings of this research are highlighted below.

5.1. Drywall Characteristics

Ten drywall products were evaluated for mineral analysis, moisture content, total sulfur, and metal composition, water-soluble sulfur and metals, organic component analysis, and two different leaching tests (M1315, and M1316). Overall, the primary constituents and minerals in drywall are quite uniform, but the composition of minor constituents exhibited a large degree of variability. This variability was attributed to differences in gypsum feedstock, conditions at the processing facilities, and sample processing and analysis.

- MC of the drywall was related to the temperature used for its determination. The average MC of gypsum from drywall measured at 45, 105, 230, 400 and 550 °C was 0.76, 0.35, 13.6, 19.4, 19.7 and 20.8%, respectively. The average MC of the drywall samples tested at 105 °C was 15.36%. The MC results at 150 °C were unstable because calcium sulfate exists at three levels of hydration at that temperature. Samples that were air-dried and not dried at elevated temperatures were employed in this work since the mineral phases can change during the high-temperature MC analysis
- Drywall, including the gypsum core of the drywall board, contains a small amount of organic carbon. The average total carbon and sulfur content of the gypsum samples using a combustion methodology were 0.87 and 17.56%, respectively (air-dry weight basis). Formaldehyde was detected at a concentration range from 500 to 8500 $\mu\text{g kg}^{-1}$, with a median of 1800 and an average of 3700 $\mu\text{g kg}^{-1}$. Tributyltin (TBT) was also detected in some samples, namely, those products manufactured for greater mold control. Polynuclear aromatic hydrocarbons (PAHs) were also detected in some samples, and the presence of PAHs was attributed to the paper fraction of the drywall product.
- The dominant mineral in the drywall products was gypsum, accompanied by small amounts of hemihydrate and anhydrite. Carbonate and silica were also detected.
- The total acid extractable sulfur and metal concentrations of the gypsum core of the drywall samples were investigated using different methods. The average sulfur contents of the gypsum samples using EPA M3051A, 0.25 M HCl extraction (24 h), and 10% HNO₃ at 90 °C were 13.67, 17.65, and 18.34%, respectively. The average calcium contents by these methods were 18.57, 24.50, and 24.03%, respectively. The average strontium content was 140, 175, and 189 mg kg^{-1} , respectively. Re-precipitation is a common occurrence after microwave digestion of materials with high amounts of calcium sulfate minerals, and the re-precipitation was confirmed using digestion experiments in which dilution was conducted at different temperatures. The results suggest that analysts should be cautious of measuring elemental concentrations on gypsum materials using EPA M3051A; use of this method might significantly underestimate the content of sulfur, calcium, strontium, and other compositions. A new procedure of acid extraction (10% HNO₃ at sub-boiling temperatures (90 °C) for 16 h (overnight) was developed in this work and is recommended for future work. The results of extractable sulfur in this new procedure were like the total sulfur concentration measured using the combustion technique and

significantly higher than the total sulfur measured using EPA M3051A. The results for calcium and strontium using the new procedure were also significantly higher than the results obtained from measurement by EPA M3051A.

- Water-extractable sulfur and inorganic element concentrations were studied by repeating a water extraction procedure four times. Very high cumulative water-extractable sulfate and calcium were observed in the gypsum samples tested. The other detectable elements in the water extracts were Sr, Ba, Mg, Fe, P, and Si. The average cumulative water-extractable SO_4 , Ca, and Sr concentrations from the gypsum samples were $54.4 \pm 1.5\%$, $22.1 \pm 0.5\%$, and $193 \pm 211 \text{ mg kg}^{-1}$, respectively. Based on the total sulfur content by combustion, 98.2% of the water-extractable sulfur was in the form of sulfate (SO_4). The average water-extractable calcium and strontium content in the gypsum samples was 90%, and 95%, respectively, when the cumulative water extraction concentrations were compared to those measured using the new acid extraction procedure.

5.2. Leaching Behavior of Drywall

- Kinetic leaching experiments were conducted for periods up to 2 months using five of the drywall products at a fixed liquid-to-solid ratio and room temperature. The chemical concentrations, pH, and conductivity in the leachates were measured and based on the chemical measurements and MINTEQ modeling, the kinetics of the saturation index (SI) of the controlling minerals were assessed. Chemical equilibrium is a dynamic process, and there is no universal time at which chemical equilibrium is reached for all constituents in the leachate. In many cases, a constituent concentration (e.g., calcium) was not controlled by a single mineral phase, and the changes in leachate concentration over time were related to changing mineral phases. An equilibrium time of one week was found appropriate for the work conducted here.
- Liquid-solid partitioning of inorganic constituents from the drywall samples was examined on five drywalls using a modified EPA Method 1316 with ten different L/S ratios (from 2.5 to 400). The linear dependence of logarithmic constituent concentration as a function of the logarithmic L/S ratio was observed and found to be dependent on the saturation index (SI) of the minerals controlling the constituent equilibrium. When the controlling mineral for a leached constituent was in an unsaturated status ($\text{SI} < 0$), the linear dependence was found to be valid for all the samples studied. These relationships were further used to estimate the constituent concentrations in the pore water. The estimated average of pore water concentrations of Sr, B, Ba, Zn, Cu, Mn, Ni, Co, Mo, Cd, and Se were measured at 10, 11.5, 0.29, 5.6, 6.3, 4.1, 0.2, 0.2, 0.23, 0.02, and 0.6 mg L^{-1} , respectively. The linear dependence relationship was demonstrated if the constituent was released from a single mineral phase.
- Monolithic leaching tests were conducted using EPA Method 1315 for five different drywall products. A linear relationship was observed between logarithmic cumulative released constituent concentrations and logarithmic total leaching time. The slopes of the linear equation indicated that the leaching process was not controlled by diffusion. The dominant species (sulfate, Ca), as well as Sr, leached following a dissolution mechanism. A surface wash-off pattern, a delayed-release pattern, and a depletion pattern were also observed for the other minor constituents depending on the mineral source and composition of the gypsum. The diffusivity of the leached constituents, as well as the leachability index, was further calculated. The average weighted arithmetic mean (D_e) of S, Ca, Sr, Zn, Mn, Mg, P, Ba, Si, Fe and DOC from the samples was 60.2, 55.4, 41.9, 18.1, 6.5, 5.9, 0.45, 0.38, 0.30, 0.21, and $0.02 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively. The more highly leachable constituents were Zn, Sr, SO_4 , and Ca; the moderately

leachable constituents were Mg and Mn; and the relatively slow release constituents were P, Fe, Si, Ba, and DOC. The leachability index of most constituents was between 8 and 9.

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