Physicochemical Modifications in Geomaterials and Their Leachates Extracted from Acidic Attack

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Abstract. Exposure of geomaterials to acid leachates may cause chemical species desorption, mineral dissolution, and metal leaching. This study seeks to understand the changes in the physicochemical composition of liquid extracts resulting from the exposure of four different geomaterials (uniform fine sand, basalt residual soil, kaolin, and bentonite) to a blank solution (distilled water) and sulfuric acid solutions at the concentrations of 0.01, and 1.00 mol/L. It was also investigated the relationship between alterations in both chemical and mineralogical constitutions of geomaterials. The elemental composition of the geomaterials was determined by X-ray fluorescence. In the liquid extracts, Na, Mg, Al, K, Ca, Fe, and Mn concentrations were obtained by inductively coupled plasma atomic emission spectrometry, as well as pH and electrical conductivity were evaluated. pH and electrical conductivity data showed that bentonite had buffering capacity until 0.01 mol/L concentration and higher ion dissolution with increasing acid concentration. Acidic attack by the 1.00 mol/L solution resulted in the solubilization of the constituent metals, corresponding to reductions in elemental composition and alterations in geomaterials mineralogy.

Keywords: clayey, metal solubilization, mineralogy, silty and sandy soils, sulfuric acid.

1. Introduction

Anthropogenic processes may cause modification in soil behavior due to contamination by acidic solutions, which, under extreme conditions ($\text{pH} < 1$), result in significant volumetric variations and structural changes in soils (Chavali *et al.*, 2018). Considered chemically aggressive, acidic leachates from industrial and mining solid wastes constitute a considerable source of environmental impact, causing changes in soil structure, as increased hydraulic conductivity and reduced reactive power. Acidic pH solutions increase the mobility of dissolved contaminants, which have the main destination at soil and water resources (Agbenyeku *et al.*, 2016; Candeias *et al.*, 2014; González-Fernández *et al.*, 2018; Grande *et al.*, 2018; Hueckel *et al.*, 1997; Knop *et al.*, 2008; Pecorini *et al.*, 2017).

Usually, geomaterials are used in waste containment liner systems, as mixtures of clayey soils and cement, with or without bentonite added, to improve hydraulic and reactive properties of contention barrier (Ghadr & Assadi-Langroudi, 2018; Gueddouda *et al.*, 2016; Hassanlourad *et al.*, 2016; Mao *et al.*, 2018; Miguel *et al.*, 2017; Morandini & Leite, 2015; Verástegui-Flores & Di Emidio, 2014; Wang

et al., 2018, 2016). It has been recognized that high plasticity clayey soils are likely to lose structure when in contact with leachates containing multispecies contaminants, thus reducing their impermeability potential (Amadi, 2011). Therefore, for the efficient performance of liner systems, properties of the geomaterials must not be compromised over time by the exposure to acidic leachates (such as mining drainage). Therefore, the study of the interaction between clay soil constituents and high acidity solutions, focusing on changes in chemical and mineralogical composition, is fundamental for the correct management, as well as the treatment of contaminated soils (Agbenyeku *et al.*, 2016).

Several studies in the literature reporting the effects of exposure of geotechnical materials to chemically aggressive solutions (Agbenyeku *et al.*, 2016; Chavali *et al.*, 2017, 2018; Hamdi & Srasra, 2013; Li *et al.*, 2013; Liu *et al.*, 2015; Miguel *et al.*, 2017; Sucha *et al.*, 2002; Verástegui-Flores & Di Emidio, 2014), indicate, in general, that contact with acidic waters causes soil pH reduction, metal dissolution, chemical species desorption (Agbenyeku *et al.*, 2016; Miguel *et al.*, 2017), and cation exchange reactions

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with partial mineral dissolution (Chavali *et al.*, 2018), in addition to changes in hydraulic conductivity in clayey soils (Hamdi & Srasra, 2013; Li *et al.*, 2013; Liu *et al.*, 2015) and modifications in their mechanical properties (Hassanlourad *et al.*, 2016). However, Chavali *et al.* (2018) highlight that most of these studies evaluate soil contamination by inorganic acidic solutions with pH under natural conditions ($3 < \text{pH} < 6$). However, this pH range covers natural pH values in some Brazilian soils, such as Cerrado soils (pH 3.75–4.85) (Leite *et al.*, 2006; Leite *et al.*, 2018) and basalt residual soil (pH 5.5) (Korf *et al.*, 2020).

Thus, further studies are needed to evaluate changes in soils in contact with more aggressive acidic solutions at pH below 1, such as those from mine drainage storage ponds, where water evaporation causes the increase in hydrogen ion concentration (Liu *et al.*, 2013). These wastewaters contain sulfuric acid molecules generated by the oxidation of sulfide minerals in the presence of oxygen and water. A decrease in pH increases the solubility of soil and rock constituents (Knop *et al.*, 2008). Also, it may occur acidic contamination of soils not only by sulfuric acid from spills or leaks (Chavali *et al.*, 2018) but also by acid mine drainage (AMD) from mining in coal plants (Liu *et al.*, 2013) and mining of metallic sulfide ores (Blowes *et al.*, 2014; Luo *et al.*, 2020).

Therefore, this study seeks to shed light on the alterations in geotechnical materials as they are exposed to different concentrations of sulfuric acid with pH lower than 1, by investigating the changes in the physicochemical composition of the liquid extract resulting from the exposure of four geomaterials to sulfuric acid solutions, as well as the changes in the elemental composition and its relationship with the mineralogy of each geomaterial tested. A better understanding of the alterations in geomaterials as a result of the acid attack may be helpful in designing and modeling of compacted barriers, as well as predicting the response of foundation soils.

2. Methodology

2.1. Materials

In this study, the following geomaterials were used: Osorio Fine Sand (OFS), Basalt Residual Soil (BRS), Kaolin (KAO), and sodium Bentonite (BEN). The sand was collected in a natural deposit in the municipality of Osorio, in the Rio Grande do Sul state, in southern Brazil, and it is considered uniform fine sand (ABNT, 1995; ASTM, 1993). The Basalt residual soil was collected at the Experimental Geotechnical Field of the Technology Center (CETEC) of the University of Passo Fundo (UPF), in the Rio Grande do Sul state, Brazil. It is characterized as a Humic Dystrophic Red Latosol (Streck *et al.*, 2008), with high clay content, classified as low plasticity clay (ASTM, 1993). The Kaolin was purchased from a mineral products supplier located in the municipality of Pântano Grande, in the state of Rio

Grande do Sul, Brazil. This material is commercially known as “pink kaolin” and is classified as a low plasticity inorganic silt (ASTM, 1993). Sodium bentonite of white color was obtained from a supplier located in the municipality of Soledade, in the state of Paraíba, in northeast Brazil, and is classified as a high plasticity inorganic clay (ASTM, 1993). Sulfuric acid used in the experiments was grade P.A., Merck brand with purity 95–97 % and density 1.84 g.cm^{-3} .

2.2. Methods

The preparation of the geomaterials testing samples followed the standard NBR 6457 (ABNT, 2016). The acidic attack on the geomaterials was simulated by a batch testing adapted from ASTM D4646 - 03 (ASTM, 2008). In these tests, the following variables were considered: sulfuric acid concentration at 0.00 mol/L (pH of distilled water equal to 7 ± 2), 0.01 mol/L (pH 2) and 1.00 mol/L (pH 0), and four geomaterials (OFS, BRS, KAO and BEN), resulting in 12 experimental treatments. The batch tests procedures were as follow:

- Insertion of samples of each material into a 2000 mL Erlenmeyer flask at a soil-solution ratio of 1:20;
- Horizontal continuous shaking at 215 rotations per minute for 24 h at $22 \pm 5 \text{ }^{\circ}\text{C}$;
- Decantation and centrifugation of samples to separate solid and liquid phases. The supernatant centrifugation process was performed in a centrifuge under 3000 rpm for 10 min (USEPA, 1996). Subsequently, the liquid extract was filtered through a $0.45 \text{ }\mu\text{m}$ nitrocellulose membrane;
- Drying of the resulting solid material, in porcelain capsules, in an oven at a temperature of 40 to $50 \text{ }^{\circ}\text{C}$, until constancy of mass. After, each sample was macerated in porcelain crucibles until a powdery material was obtained and placed in properly sealed and identified plastic bags.

Liquid extracts were physical-chemically characterized through the determination of pH and electrical conductivity. pH was determined by pH meter, model HI 2221 Hanna brand, glass body Ag/AgCl electrode with ceramic junction, diameter 9.5 mm, pH range 0 to 13 and temperature 20–40 $^{\circ}\text{C}$. Electrical conductivity was determined by microprocessor conductivity meter, model DM-32 Digimed brand with conductivity cell/sensor DMC-010M (range $0.001 \text{ }\mu\text{S.cm}^{-1}$ to 2 S.cm^{-1} and resolution 0.001/0.01/0.1/1). Also, Na, Mg, Al, K, Ca, Fe, and Mn concentrations were determined for the experimental treatments corresponding to the extremes of the acidic range concentration (0.00 mol/L and 1.00 mol/L) by inductively coupled plasma atomic emission spectrometry (Shimadzu-branded ICP-AES). The pattern solution used to running at ICP-AES was multi element standard XXI for ICP Certipur Merck brand (30 elements in diluted nitric acid- HNO_3).

The chemical compositions of the geomaterials, before and after the acidic attack, were determined by X-ray fluorescence spectrometry (XRF), in a pressed sample, with the STD-1 calibration, allowing for the non-standard analysis of the chemical elements comprised between fluoride and uranium in a Bruker S8 Tiger spectrometer.

The mineralogical constitutions were determined by X-ray diffraction (XRD), by the powder method, in a Bruker X-ray diffractometer, model D8 Endeavor, with a position-sensitive detector. The identification of the crystalline phases was obtained by comparing the sample diffractogram with the International Center for Diffraction Data (ICDD) PDF2 database using the X'Pert High Score software.

3. Results and Discussion

Figure 1 shows the pH and electrical conductivity results of the liquid extracts for the four tested geomaterials. The pH results of the OFS, BRS, and KAO remained close to the initial pH of the acidic solutions to which they were exposed. BEN presented pH above neutrality, especially the sample submitted to the 0.01 mol/L solution (pH 2), due to the acid buffering power associated with the high cation exchange capacity of this soil (Nessa *et al.*, 2007). BEN also presented the highest pH value (0.41) amongst the geomaterials tested at 1.00 mol/L concentration (pH 0). Similar results were observed by Liu *et al.* (2013), who

evaluated that acidic leachate from three sodium bentonites had pH ~ 2 at lower concentrations (0.015 mol/L to 0.25 mol/L), and pH ~ 0 at higher concentrations (0.5 mol/L and 1 mol/L).

The results indicate that bentonite has a higher acid neutralization capacity at 0.01 mol/L solution (pH 2). This condition may contribute to the attenuation of contaminants from acidic leachate. According to Yong *et al.* (1990), smectite soil (*e.g.* bentonite) shows significant resistance to pH changes due to its high cation-exchange capacity (CEC). The H^+ adsorption from smectite-contamination leachate occurs mainly by cation exchange, and when exchange sites are unavailable, the pH decreases rapidly. On the other hand, kaolinite soil does not show considerable resistance to pH changes (Yong *et al.*, 1990), which was observed in BRS and KAO samples.

In general, all geomaterials presented a positive correlation between electrical conductivity and concentration of sulfuric acid, which indicates a higher concentration of dissolved ions in the liquid extracts at 1.00 mol/L. The results of metals concentration by ICP-AES (Table 1) and the XRF (Table 2) indicate the solubilization of the chemical constituents of geomaterials. For the OFS, the significant electrical conductivity measured in the liquid extract of the sample at 1.00 mol/L, is probably due to the presence of hydrogen ions (H^+) in the solution, which did not bind to the active sites of the soil minerals, since quartz has low reactivity to sulfuric acid.

Table 1 shows the metals concentrations in the liquid extract resulting from the geomaterials tested at the extreme values of the concentration range (0.00 mol/L and 1.00 mol/L). These results are consistent with the chemical constitution of the samples (Table 2), demonstrating that exposure to the 1.00 mol/L solution of sulfuric acid caused loss by solubilization of the constituent metals of the geomaterials, mostly aluminum (Al), iron (Fe), calcium (Ca), and magnesium (Mg), in addition to sodium (Na) for the bentonite liquid extract. Knop *et al.* (2008) reported that these metals are commonly mobilized in rocks or soils due to the leaching of sulfuric acid present in acidic mining drainage.

The expressive concentrations of Fe in the liquid extracts were an expected result since this metal is highly soluble in acidic environments. This feature was observed mainly for the BRS, which has significant Fe content in its natural composition (see Table 2). For the specimen SRB at 1.00 mol/L, it was observed a Fe concentration of 458 mg/L, confirming the loss of hematite identified by the XRD analysis (Table 3). According to Sunil *et al.* (2006), Fe leaching from a lateritic soil reduces the bonds between soil particles, resulting in alterations in their mechanical and physical properties, such as reduced compressive strength and maximum dry density and increased optimal moisture content. Also, a high concentration of aluminum was detected in the liquid extracts, corroborating the idea

Figure 1 - pH (a) and electrical conductivity (b) of the liquid extract of the geomaterials tested.

Table 1 - Metal concentration of liquid geomaterials extract (mg/L).

Specimen	Na	Mg	Al	K	Ca	Fe	Mn
OFS 0.00 mol/L	- ¹	0.21	2.31	- ¹	- ¹	0.85	- ¹
OFS 1.00 mol/L	- ¹	1.79	10.03	1.06	2.16	6.94	0.16
BRS 0.00 mol/L	- ¹	0.85	- ¹	- ¹	1.69	0.06	0.24
BRS 1.00 mol/L	- ¹	4.27	418.12	1.99	8.39	458.12	3.00
KAO 0.00 mol/L	- ¹	0.49	7.34	1.47	0.04	1.14	- ¹
KAO 1.00 mol/L	- ¹	12.93	205.98	8.56	14.10	9.57	1.91
BEN 0.00 mol/L	161.98	11.27	96.32	2.64	5.27	38.00	0.05
BEN 1.00 mol/L	332.97	132.99	136.32	8.63	282.50	46.33	0.86

¹: Below detection limit.

Table 2 - Elemental chemical composition of solid extracts of geomaterials (mg/kg).

Specimen	Na	Mg	Al	P	Si	S	K	Ca	Ti	Fe	Mn	Zr	Ba
OFS Pure	900	400	11600	-	435200	100	7100	500	900	2800	-	-	-
OFS 0.00 mol/L	900	300	9900	-	445500	-	6000	400	700	2100	-	-	-
OFS 1.00 mol/L	-	-	5800	-	401600	11300	5100	-	500	2000	-	-	-
BRS Pure	-	2100	128100	500	216900	300	3400	200	9800	74800	300	500	-
BRS 0.00 mol/L	-	1700	109600	400	232300	300	-	300	9400	73400	300	-	-
BRS 1.00 mol/L	-	600	37500	-	94000	63700	-	200	3800	27000	-	200	-
KAO Pure	-	900	189500	100	221600	300	7000	800	900	8200	100	-	500
KAO 0.00 mol/L	-	500	191600	-	216900	-	8900	900	1300	11600	-	-	-
KAO 1.00 mol/L	-	500	128600	-	143500	31800	5600	700	600	6200	-	-	-
BEN Pure	5900	5900	166200	200	217400	100	10300	8400	2200	18300	100	100	400
BEN 0.00 mol/L	2400	5100	130200	-	247300	-	24100	17800	1600	15700	-	200	600
BEN 1.00 mol/L	900	3200	102700	-	162200	35600	7300	1600	1500	12900	-	100	400

that at very low pH values (less than 4.5), this metal is solubilized in the forms of Al^{3+} and AlO_2^- (Miguel *et al.*, 2017).

Spagnoli *et al.* (2012) reported that, in a solution with pH close to 3, Al^{3+} dissolution acts as a coagulant agent in kaolinite, increasing shear strength. According to the authors, the occurrence of clay mineral dissolution in acidic environments is a function of protonation reactions of the hydroxide (OH^-) and oxide (O^{2-}) termination sites, which weaken the bonds that support the aluminum and, consequently, displace it from the structure to the liquid phase as Al^{3+} . In the study of Bakhshipour *et al.* (2016), it was found that the reduction of aluminum and iron contents of a residual soil by acidic leaching increased Atterberg limits and optimum moisture content and reduced shear strength and maximum dry density.

For the BEN sample, the acidic attack resulted in an increase of sodium, calcium, and magnesium in the liquid extract. The desorption of these bentonite elements is supported by the results of the XRF analysis (Table 2). This

feature was probably due to the bentonite high cation exchange capacity (Asof *et al.*, 2017; Caglar *et al.*, 2013; Koch, 2002). According to Liu *et al.* (2013), the concentrations of sodium and calcium in leachates of sodium bentonite reflect hydrogen ion exchanges. The authors reported that around 90 % and 50 % of Na and Ca, respectively, were displaced by H^+ .

Considering the application of bentonite in waste containment liner systems and degraded areas exposed to acid contaminants, the loss of cations from bentonite, as observed in this study, points out to potential changes in expansion capacity, plasticity, microstructure, and permeability (Bouazza *et al.*, 2006; Egloffstein, 2001; Koch, 2002; Mazzieri *et al.*, 2017; Ruhl & Daniel, 1997; Shackelford *et al.*, 2000). Chavali *et al.* (2018) reported that contamination of sodium bentonite by sulfuric acid caused a reduction in the expansion of this clay, where equilibrium expandabilities of 67 % and 50 % were measured at 1 mol/L and 4 mol/L concentrations, respectively. According to the authors, these changes in bentonite are due to the cation ex-

change process, in which sodium ions are replaced by hydrogen ions, whose ionic radius (0.012 Å) is smaller than that of sodium (1.02 Å), resulting thus in smaller expansion. Liu *et al.* (2013), for three sodium bentonites, found that the contact with sulfuric acid solutions (0.015 mol/L to 1 mol/L) caused the displacement of cation ions by hydrogen ions, resulting in a reduction of Atterberg limits and expandability index, which might compromise the hydraulic performance of these geomaterials when applied in waterproofing systems.

The elemental characterization presented in Table 2 is consistent with the metal concentrations found in the liquid extracts, for all geomaterials exposed at 1.00 mol/L, demonstrating expressive reductions of Fe, Al, Mg, Ca, and Na in sodium bentonite.

Table 3 shows the mineralogical compositions of the geomaterials samples. In line with the results of the FRX (Table 2) and ICP-AES (Table 1), a significant reduction of iron occurred for all four geomaterials exposed to the most acidic solution, especially for the BRS, likely due to the acidic attack to the iron oxides adsorbed on the surface of soil particles, evidenced by the loss of hematite (Fe_2O_3) and

the formation of coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) and pyrophyllite ($\text{Al}_2\text{Si}_4(\text{OH})$) in the sample exposed to the 1.00 mol/L solution. For the other geomaterials exposed to the most acidic solution, there was also a significant reduction in the Al content, as well as in the other constituent elements (Table 2), which was corroborated by the loss of albite ($\text{Na}(\text{AlSi}_3\text{O}_8)$) and the formation of gibbsite ($\text{Al}(\text{OH})_3$) in the OFS; the loss of anatase (TiO_2) in the BRS; the loss of calcite (CaCO_3) and hydrobiotite ($\text{KMgAlSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$) in the BEN; and the formation of alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) in the BRS, KAO, and BEN. The hydrate sulfate alunogen present in the samples is explained by the increased sulfur content. Similarly, there was a correspondence between anatase loss in the SRB and calcite loss in the BEN, with a significant reduction in Ti and Ca contents for both geomaterials (Table 2).

The OFS showed lesser chemical reactivity in contact with sulfuric acid compared to the other geomaterials, which is plausible since this soil is mostly composed of quartz. From the works of MacCarthy *et al.* (2014) and Brady & Walther (1989), it may be inferred that the acid concentrations, pH values and temperature conditions used in the present study promoted the dissolution of amorphous silica and that the presence of Fe, Al, Mg, Si, and Na influenced the adsorption rate or the attack of H^+ ions to the active sites of quartz particles.

In general, the exposure of the geomaterials to the 1.00 mol/L solution resulted in liquid extracts with higher metal concentrations. These results correspond to the elementary and mineralogical variations of the geomaterials. In this regard, it is important to note that in acidic environments, mineral structure dissolution, cation leaching, anion adsorption, changes in the clay particles edge charges and the diffuse double layer, and the formation of sulfate minerals are able to affect the engineering behavior of soils (Bakhshipour *et al.*, 2016; Chavali *et al.*, 2018). In the present study, the expressive concentration of several metals found in the liquid extracts, especially for the BEN exposed to the 1.00 mol/L solution, correspond to liquids with higher concentrations of multivalent cations. These cations (such as Ca^{+2} and Mg^{+2}) tend to shrink the diffuse double layer in clay particles, causing soil flocculation, macropore formation and consequently increased hydraulic conductivity (Amadi, 2011; Mitchell, 1993; Ruhl & Daniel, 1997).

Spagnoli *et al.* (2012) report that kaolinite has no forces in the double layer because the surface charge is considered neutral. According to Bakhshipour *et al.* (2016), in residual soils consisting mainly of illite, kaolinite, and goethite, acidic contamination does not provoke changes in the diffuse double layer sufficient to promote variations in properties such as Atterberg limits, hydraulic conductivity, and compaction characteristics. In contrast, in smectite clay minerals, both faces have oxide (O^{2-}) terminations, and the edges have hydroxide (OH^-) and O^{2-} terminations. In smectites, the diffuse double layer governs the mechanical prop-

Table 3 - Mineral composition of geomaterials samples.

OFS Pure	OFS 0.00 mol/L	OFS 1.00 mol/L
Quartz	Quartz	Quartz
Microcline	Microcline	Microcline
Albite	Albite	Gibbsite
BRS Pure	BRS 0.00 mol/L	BRS 1.00 mol/L
Quartz	Quartz	Quartz
Hematite	Hematite	Alunogen
Kaolinite	Kaolinite	Coquimbite
Anatase	Anatase	Kaolinite
-	-	Pyrophyllite
-	-	Microcline
KAO Pure	KAO 0.00 mol/L	KAO 1.00 mol/L
Quartz	Quartz	Quartz
Kaolinite	Kaolinite	Kaolinite
Microcline	Microcline	Microcline
Muscovite	Muscovite	Muscovite
-	-	Alunogen
BEN Pure	BEN 0.00 mol/L	BEN 1.00 mol/L
Quartz	Quartz	Quartz
Kaolinite	Kaolinite	Kaolinite
Microcline	Microcline	Microcline
Muscovite	Muscovite	Muscovite
Calcite	Calcite	Alunogen
Hydrobiotite	Hydrobiotite	-

erties, since oscillations in the pH increase the concentration of ions in the double layer. At low pH values, the increase in H^+ concentration causes the reduction of the double layer (Spagnoli *et al.*, 2012).

The available literature suggests that the effects of inorganic acids on different types of geomaterial might include dissolution of minerals, leaching of metals such as iron and aluminum, and high loss of cations, which in turn influence properties such as Atterberg limits, expandability, maximum dry density, optimal moisture content, mechanical strength, and permeability.

4. Conclusions

In this study, the physical-chemical composition of the liquid extracts and the elemental compositions of four geomaterials exposed to sulfuric acid solutions were evaluated and related to changes in their mineralogical constitution. The following experimental findings were achieved:

- The pH values showed that only the bentonite liquid extract reached a pH above neutrality after exposure to the 0.01 mol/L H_2SO_4 solution. Under higher acid concentration, the liquid extracts remained at pH did not present a buffer capacity for that level of acid concentration with values close to the initial value (pH ~ 0);
- The electrical conductivity results showed a positive correlation with the increase of acid concentration, indicating a higher concentration of dissolved ions in the liquid extracts of geomaterials submitted to the 1.00 mol/L H_2SO_4 solution;
- Exposure to the 1.00 mol/L solution of H_2SO_4 resulted in the solubilization of metals, mainly in basalt residual soil and bentonite. The concentrations of metals in the liquid extracts matched the reduction of the geomaterial constituent elements, as well as the alterations in the mineralogical composition, with loss and formation of minerals.

In conclusion, when considering the potential application of the geomaterials studied to constitute impermeable barriers, one should pay attention to the solubilization of metals and loss of minerals in extreme acidity conditions and the associated susceptibility to structural changes and consequent modification in the mechanical properties and hydraulic performance of waterproofing systems.

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