Estimating Sulfate Effective Diffusion Coefficients of Stabilized Fluorogypsum for Aquatic Applications

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Abstract: The sulfate release from solidified/stabilized fluorogypsum was measured to develop the effective diffusion coefficients (D_e) as a parameter to assess the dissolution potential in aquatic applications. Specimens from 11 compositions consisting of 60–90% pH-adjusted fluorogypsum (pFG), 2–10% Type I/II portland cement (PC), and 0–38% Class C fly ash (FA) were exposed to solutions of 30 $g\,L^{-1}$ (saltwater), 15 $g\,L^{-1}$ (brackish water), and 0.5 $g\,L^{-1}$ (freshwater) total dissolved solids (TDS). The effects of composition and salinity, measured as the TDS, on the sulfate D_e were determined to select the compositions for use in various aquatic environments. The results indicated that the solidified/stabilized pFG had a lower dissolution potential in saltwater and freshwater in comparison with brackish water. On the basis of the low D_e and low critical times (the time when the diffusion out of the specimen equals the precipitation onto the specimen), a composition of 80% pFG, 10% PC, and 10% FA is recommended as an alternative to limestone in saltwater and freshwater applications.
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Introduction

Coastal land loss has been identified as a major concern in the southeastern US (Morton 2003). In particular, the state of Louisiana lost approximately 3,500 km^2 of coastal land from 1956 to 2006 (Barras et al. 2008). The degradation of natural oyster reefs has also been identified as a major concern for Louisiana due to the decrease in their economic benefits and in coastal protection (Grabowski and Peterson 2007; Kirby 2004). Therefore, addressing the land loss and the loss of natural oyster reefs is a high priority in coastal regions (Couvillion et al. 2011; CPRA 2012).

In Louisiana, the establishment of natural oyster reefs has been shown to provide sustainable shoreline protection (Piazza et al. 2005). Piazza et al. (2005) suggested that the construction of natural oyster reefs is limited by the availability of oyster cultch. As an alternative to oyster cultch, limestone accounts for nearly half of the nonnative material used for the construction of artificial oyster reefs (Furlong 2012). However, limestone is not locally available in coastal Louisiana and needs to be transported from other states, which substantially affects the cost of artificial reef construction (Rusch et al. 2005).

Locally available economical alternatives to limestone are needed to decrease the cost for coastal applications. Industrial by-product gypsums have been studied for various applications and may provide an economical component in construction materials for aquatic applications (Guo et al. 2001; Rusch et al. 2005; Wilson et al. 1998). Two industrial by-product gypsums—phosphogypsum, obtained from the production of phosphoric acid, and fluorogypsum, obtained from the production of hydrofluoric acid—are available in large quantities in US coastal regions, with estimates ranging from millions to billions of tons (Korcak 1998; Tayibi et al. 2009).

The extensive study of phosphogypsum (PG) indicated that this material needs to be solidified/stabilized (S/S) with Type II PC and Class C FA and fabricated with pressurization before its potential implementation in aquatic environments (Guo et al. 2004, 2003, 1999; Rusch et al. 2002). The beneficial reuse of PG in aquatic applications may reduce the risk of radon transmission while it provides a much needed substrate for coastal applications (Guo et al. 2001). However, the use of PG is restricted by the US Environmental Protection Agency (EPA) to agricultural applications (Alcordo and Rechcigl 1993). Therefore, the use of alternative gypsums and fabrication methods to decrease costs should be explored for immediate use.

Fluorogypsum (FG) is generated as a by-product of the combination of fluorspar with sulfuric acid. Approximately 894,000 t of FG are produced each year in the US. (Lassen et al. 1992). The EPA has determined that the chemical concentrations in FG are not expected to pose a risk to human health and the environment (USEPA 1990). Due to the acidity of FG, lime or circulating fluidized bed ash (CFB) is blended with fluorogypsum to adjust the pH to approximately 7 or 8 (Garg and Pundir 2014; LA Ash, Inc. 2017). The resulting pFG, also referred to as blended calcium sulfate,

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has found use in dry applications as a road bed material (Wang et al. 2004; Wu et al. 2010). Similarly to other gypsums, the pFG must be stabilized to be used in aquatic environments, due to its solubility (2.0–2.5 $\mathrm{g\,L^{-1}}$) in concentrated sodium chloride solutions (Bock 1961).

For applications in aquatic environments, the dissolution potential of a composition of pFG solidified/stabilized with PC and FA (sFG) may be assessed by estimating the effective diffusion coefficient (D_e) (Guo et al. 2001). Gypsum is composed of approximately 56% sulfate; therefore, most of the mass loss in sFG can be attributed to the sulfate release. Hence, the sulfate D_e, estimated from the sulfate release, can be used as a proxy to assess the dissolution potential (Guo et al. 2004) of sFG for aquatic applications. To fully describe the dissolution potential of sFG, other factors such as potential water intrusion, specific surface area, and rupture development (Rusch et al. 2002) should be considered in combination with the sulfate D_e.

Several studies have indicated the relationship between the D_e and the effective diffusion depth to describe the surface integrity for the prediction of long-term survival (Duedall et al. 1983; Guo et al. 2001). Many studies of a similar nature have examined the diffusion of ions (for example, chloride) into the concrete (Gowripalan et al. 2000) or polymer (Chin et al. 1999) structure. This study focused on the diffusion of sulfate out of sFG specimens as an indication of its dissolution potential. The objective of this study was to determine the effect of composition and salinity on the dissolution potential of sFG by estimating the sulfate D_e. This information is crucial to determine whether a given sFG composition can be appropriate for aquatic applications. This study also provides a framework for future studies that optimize the composition of sFG for aquatic applications.

Materials and Methods

A modified procedure based on the EPA Method 1315 (USEPA 2013) was adopted here to obtain the sulfate release of sFG. The EPA Method 1315 has been used to measure the mass transfer release of constituents of potential concern (COPC) from the concrete with the fly ash replacement of cement (Garrabrants et al. 2014). Thus, this method was shown to provide a reliable framework for obtaining the leaching characteristics of cement and fly ash-based materials. Several modifications to this method were included to address the testing of sFG, as described in the following subsections.

Materials and Specimens Preparation

The components pFG, PC, and FA, obtained in Louisiana, were oven dried at 45°C for 14 h to remove the free water (Turk and Bounini 1984). Table 1 provides the mass of 21 cations and sulfate in each component. Each component was then sieved (US standard sieve #18) to recover the particles with less than a 1-mm diameter to ensure that the materials were homogeneous within small specimens. The dried and sieved pFG (60–90%) was combined with the dried and sieved PC (2–10%) and FA (8–38%) to produce the 11 compositions provided in Table 2. The materials' cost per ton of each composition is also provided for comparison to the cost per ton of limestone. The cost per ton of pFG is significantly less than the cost per ton of FA and PC. Therefore, to reduce costs, the compositions with higher amounts of pFG should be preferred. A detailed economic analysis that includes, for example, the cost of production, transportation, and coverage based on density is needed for a direct comparison between pFG and limestone; however, that is outside the scope of this work.

Table 1. Mass of the identified cations and sulfate in each of the components: pFG, Type I/II PC, and Class C FA

Ion	pFG	PC	FA
Al	428	24,557	79,920
As	3.66	6.17	7.73
B	293	45.5	565
Ba	46	374	3,389
Ca	246,665	405,715	189,059
Cd	0.631	0.9	1.662
Co	1.34	7.99	20
Cr	2.64	112	71
Cu	2.79	89.7	105
Fe	521	23,421	36,588
K	190	3,314	3,078
Mg	249	15,667	33,319
Mn	39	885	120
Na	398	1,717	10,994
Ni	10	39.8	44.1
P	68.2	490	1,054
Pb	3.29	24.1	20.1
Si	52	179	171
Sr	30.2	415	1,946
V	21.2	75.9	109
Zn	5.66	959	97.4
SO_4	624,511	40,837	46,649

Note: Units of each value are in $\mathrm{mg\,kg^{-1}}$; chloride is below the detection limit; common oxidation numbers for each ion are presented.

Table 2. Composition of pFG, PC, and FA as percentages of dry weight and materials cost per ton, based on cost per ton of each component

pFG (%)	PC (%)	FA (%)	Materials cost [t (USD $\mathrm{ton^{-1}}$)]
90	10	0	16.20 (14.70)
90	2	8	10.03 (9.10)
80	10	10	21.38 (19.40)
80	6	14	18.30 (16.60)
80	2	18	15.21 (13.80)
70	10	20	26.57 (24.10)
70	6	24	23.48 (21.30)
70	2	28	20.39 (18.50)
60	10	30	31.75 (28.80)
60	6	34	28.66 (26.00)
60	2	38	25.57 (23.20)

Deionized (DI) water was added to the mixture of pFG, PC, and FA in a volume based on 20–25% of the dry mass assuming a 1:1 ratio of mass (g) to volume (mL). Approximately 100 g of the wetted mixture was then set in a 3.6-cm-diameter by 6.1-cm-long cylindrical mold for 24 h. After 24 h, the specimens were removed and placed in sealable bags at 100% humidity and cured for 28 days at 21 ± 2°C. All specimens were then air dried at 21 ± 2°C for 7 days before the start of the dynamic leaching test.

Triplicate specimens of each composition were exposed to solutions representative of the three aquatic environments: saltwater (30 $\mathrm{g\,L^{-1}}$), brackish water (15 $\mathrm{g\,L^{-1}}$), and freshwater (0.5 $\mathrm{g\,L^{-1}}$). The solutions were prepared by mixing Instant Ocean sea salt (Instant Ocean, Blacksburg, Virginia) with DI water and measuring the salinity as TDS with a HACH sensION5 (Hach, Loveland, Colorado) conductivity meter.

Dynamic Leaching Test

The dynamic leaching tests were performed according to the following steps in a modified version of EPA Method 1315: (1) each specimen was suspended in 850 mL of solution, based on a $9 \pm 1{:}1$ ratio of solution volume (mL) to specimen surface area (cm^2); (2) the specimen was then transferred into a freshly prepared solution according to the following exchange schedule: 0.08, 0.29, 1, 2, 3, 4, 5, 7, 10, 14, 21, 28, 35, 42, 49, 63, and 77 days. The number of time intervals was increased in comparison with the ordinary EPA Method 1315 in order to accommodate an expected increased flux of sulfate. In particular, this modification added time intervals at 0.29, 3, 4, 5, 10, 21, 35, and 77 days; (3) at each exchange time interval, the volume, temperature, pH, oxidation-reduction potential (ORP), and conductivity of the eluate (that is, the solution remaining after the specimen had been transferred) was measured by a Myron L Ultrameter III (Myron L Company, Carlsbad, California); and (4) a 30-mL specimen of completely mixed eluate was filtered through a 0.45-μm hydrophilic polypropylene GH Polypro membrane disc filter (Pall Life Sciences, Westborough, Massachusetts), and the sulfate concentration was measured by spectrophotometry (SmartChem 170 discrete analyzer, Unity Scientific, Milford, Massachusetts). The temperature was maintained at $21 \pm 2°\mathrm{C}$ for the dynamic leaching test.

Other modifications to EPA Method 1315 included (1) the use of simulated saltwater ($30\ \mathrm{g\,L^{-1}}$), brackish water ($15\ \mathrm{g\,L^{-1}}$), and freshwater ($0.5\ \mathrm{g\,L^{-1}}$) as the solvent system to obtain representative mass releases of specimens exposed to these environments (by contrast, EPA Method 1315 refers only to the use of DI water); and (2) the reduction of the minimum sample size from 5 to 3.6 cm in the direction of the mass release. Preliminary analysis by scanning electron microscope (SEM) to observe the diffusion depth indicated that the specimens adhered to semi-infinite diffusion processes.

EPA Method 1315 uses a simple diffusion model to approximate the leaching behaviors in a semidynamic system. In this simple diffusion model, a zero surface concentration of a COPC is assumed. A model that includes a nonzero surface concentration assumption is needed when the COPC has a measurable concentration in the system. Guo et al. (2004) specifically developed a model for this purpose.

The general diffusion equation for one-dimensional flux under a non–steady-state condition is defined by Fick's second law

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C = concentration of the COPC; t = time; D_e = effective diffusion coefficient of the COPC; and x = one-dimensional length coordinate. Under the conditions

$$C = \begin{cases} C_x \neq C_b, C_0 & \text{at } F(t) > 0, x > 0, t \geq 0 \\ C_0 = C_b & \text{at } F(t) = 0, t > 0 \end{cases}$$

where C_x = concentration at position x; C_b = bulk concentration; C_0 = surface concentration as x moves into the block from $x = 0$ to $x \to \infty$; and $F(t)$ = release of the COPC at t and under the condition $x \to 0$, Guo et al. (2004) utilized a full leaching model, developed by de Groot and van der Sloot (1992) from the solution to Fick's second law (Crank 1956), with a nonzero surface concentration assumption

$$F(t) = K_1(C_b - C_0) + K_2(C_b - C_0)\sqrt{t} + K_3(C_b - C_0)t + e_i \tag{2}$$

where the statistically determined parameters are denoted as K_1 (length), which represents the surface wash-off process; K_2 ($\mathrm{length\,time^{-0.5}}$), which represents the diffusion process; and K_3 ($\mathrm{length\,time^{-1}}$), which represents the long-term kinetically controlled dissolution/precipitation process. The e_i denotes the error term, that is, the residual. In this study, the K_1 parameter associated with the surface wash-off is assumed to be negligible as the specimens were prerinsed in solution before their submersion. Regressing Eq. (2) with K_1 equal to 0 on the cumulative mass release versus time enables the determination of the two parameters K_2 and K_3 that describe the leaching processes. To estimate D_e, the rate constant of the diffusion process, K_2, is used

$$D_e = \pi \left(\frac{K_2}{2}\right)^2 \tag{3}$$

Guo et al. (2004) also showed that the critical time (t_c), that is, the time in which the diffusion out of the specimen equals the precipitation on the specimen [Eq. (4)], can be estimated by differentiating Eq. (2) with respect to time and setting the daily flux equal to zero, that is, $(\mathrm{d}F/\mathrm{d}t) = 0$

$$t_c = \left(\frac{K_2}{2K_3}\right)^2 \tag{4}$$

Results and Discussion

The pH measured during the experiments ranged from 7.92 to 8.67, from 8.06 to 8.67, and from 7.64 to 11.35, in saltwater, brackish water, and freshwater, respectively. The measured ORP ranged from 133 to 330 mV, from 134 to 358 mV, and from 80 to 304 mV, in saltwater, brackish water, and freshwater, respectively. The measured conductivity ranged from 37.40 to 54.00 mS/cm, from 20.82 to 33.5 mS/cm, and from 1.09 to 4.63 mS/cm, in saltwater, brackish water, and freshwater, respectively.

Table 3 presents the results of the regression analysis performed using Eq. (2) on the diffusion (K_2) and dissolution (K_3) processes for all 11 compositions and three salinities considered in this study. Table 4 presents the estimations of D_e and t_c from Eqs. (3) and (4), respectively. Fig. 1 shows a comparison of the 95% confidence intervals for D_e, determined from the 95% confidence intervals of the K_2 coefficient, for each composition and salinity. The significant differences among the D_e of various compositions and salinities are calculated by a one-way analysis of variance on the summary statistics (Larson 1992) of the K_2 parameter using a Tukey adjustment with a significance level of 0.05. The p-values for the comparison of the compositions exposed saltwater, brackish water, and freshwater are provided in Supplemental Data (Tables S1, S2, and S3, respectively).

In the rest of this paper, any given sFG composition is identified by three numbers indicating the percentage content by weight of the pFG, the PC, and the FA, in the form pFG-PC-FA. On the basis of the leaching model [Eq. (2)] with K_1 equal to 0, the measured e_i followed a normal distribution with a p-value larger than or equal to 0.05 ($p \geq 0.05$) for at least one of the Shapiro-Wilk (Shapiro and Wilk 1965), Kolmogorov-Smirnov (Darling 1957), Cramer-von Mises (Darling 1957), or Anderson-Darling (Anderson and Darling 1954) tests for all compositions exposed to each of the three considered salinities, excluding the composition 70-6-24 in brackish water and freshwater. Levene's test (Brown and Forsythe 1974) for homoscedasticity on studentized e_i indicated that three out of 11 compositions exposed to saltwater (80-2-18, 70-10-20, and 60-10-30) had homogeneous ($p \geq 0.05$) or approximately homogeneous variance ($0.025 \leq p < 0.05$). For the specimens exposed to brackish water, only two compositions (90-10-0 and 90-2-8) did not have homogeneous or approximately homogeneous variance. In freshwater, five compositions (80-10-10, 70-10-20,

Table 3. Diffusion (K_2), and dissolution/precipitation (K_3) rate constants for compositions exposed to saltwater ($30\ \mathrm{g\,L^{-1}}$), brackish water ($15\ \mathrm{g\,L^{-1}}$), and freshwater ($0.5\ \mathrm{g\,L^{-1}}$) solutions

Composition, pFG-PC-FA (%)	Saltwater		Brackish water		Freshwater	
	K_2 (10^{-2} cm day$^{-0.5}$)	K_3 (10^{-4} cm day^{-1})	K_2 (10^{-2} cm day$^{-0.5}$)	K_3 (10^{-4} cm day^{-1})	K_2 (10^{-2} cm day$^{-0.5}$)	K_3 (10^{-4} cm day^{-1})
90-10-0	1.34	2.09	1.81	−3.42	1.87	−10.70
90-2-8	1.73	0.25[a]	2.28	−5.28	2.26	−4.36
80-10-10	1.76	−5.41	2.03	−5.66	1.18	−8.40
80-6-14	1.99	−2.78	2.61	−5.90	1.90	−2.27
80-2-18	2.10	−4.00	2.32	−4.13	1.82	−2.29
70-10-20	1.60	−3.97	1.85	−5.03	1.05	−5.16
70-6-24	1.90	−1.61	2.23	−3.90	1.89	−2.64
70-2-28	1.55	−0.55[a]	2.26	−6.38	1.65	−1.96
60-10-30	1.60	−5.24	2.24	−8.93	1.44	−8.23
60-6-34	1.58	−0.15[a]	2.10	−3.32	1.83	−3.85
60-2-38	1.45	−2.41	2.27	−8.04	1.33	−4.10

[a]Not significantly different from 0.

Table 4. Bulk sulfate content (C_b), sulfate surface content (C_0), effective diffusion coefficient (D_e), and critical time (t_c) for compositions exposed to saltwater ($30\ \mathrm{g\,L^{-1}}$), brackish water ($15\ \mathrm{g\,L^{-1}}$), and freshwater ($0.5\ \mathrm{g\,L^{-1}}$) solutions

Composition, pFG-PC-FA (%)	C_b (mg cm^{-3})	Saltwater			Brackish water			Freshwater		
		C_0 (mg cm^{-3})	D_e (10^{-13} m^2 s^{-1})	t_c (day)	C_0 (mg cm^{-3})	D_e (10^{-13} m^2 s^{-1})	t_c (day)	C_0 (mg cm^{-3})	D_e (10^{-13} m^2 s^{-1})	t_c (day)
90-10-0	794	2.81	1.63	1,028	1.40	2.96	697	0.046	3.19	77
90-2-8	768	2.67	2.73	119,801[a]	1.33	4.71	466	0.044	4.65	673
80-10-10	746	2.75	2.81	264	1.38	3.76	323	0.045	1.26	49
80-6-14	694	2.41	3.61	1,281	1.20	6.19	922	0.040	3.29	1,754
80-2-18	740	2.70	3.99	686	1.35	4.90	789	0.045	2.99	1,575
70-10-20	667	2.55	2.32	404	1.27	3.11	338	0.042	0.995	103
70-6-24	642	2.40	3.27	3,454	1.20	4.50	814	0.039	3.24	1,282
70-2-28	650	2.54	2.19	20,100[a]	1.27	4.64	314	0.042	2.48	1,775
60-10-30	563	2.37	2.33	233	1.19	4.56	157	0.039	1.89	77
60-6-34	557	2.33	2.27	265,564[a]	1.16	4.02	1,004	0.038	3.05	565
60-2-38	563	2.37	1.92	908	1.18	4.69	199	0.039	1.62	265

[a]Undefined.

70-6-24, 70-2-28, and 60-10-30) had homogeneous or approximately homogeneous variance.

Behavior of Different Compositions in Saltwater

As presented in Table 3, all K_3 values were negative, except the composition 90-10-0. This result implies that dissolution and not precipitation was the dominant process for composition 90-10-0 in comparison with the other compositions. Three compositions (90-2-8, 70-2-28, and 60-6-34) had K_3 values that were not significantly different from 0. This result indicates that the diffusion remained the dominant process throughout the exposure to saltwater of the specimens consisting of these compositions.

The sulfate D_e values ranged from 1.63×10^{-13} to $3.99 \times 10^{-13}\ \mathrm{m^2\,s^{-1}}$ in saltwater (Table 4). These results are consistent with those obtained by Guo et al. (2004) (2.77×10^{-13} to $5.02 \times 10^{-13}\ \mathrm{m^2\,s^{-1}}$) for pressurized briquettes consisting of PG, PC, and FA. The similar range of sulfate D_e values estimated for similar sFG and S/S PG compositions may indicate that the fabrication methods (pressurized versus nonpressurized) did not affect the sulfate D_e. This result also may imply that the decrease in surface porosity obtained using a pressurized fabrication method did not contribute to a decrease in sulfate D_e. However, because many studies have recognized the importance of porosity on D_e (Rozière et al. 2009; Sarkar et al. 2012; Sun et al. 2013), the observed phenomenon could also be explained by the effects of the neutralization of FG. The increase in pH by the addition of lime or CFB ash may have balanced the effects of the higher porosity due to the nonpressurized fabrication of sFG on sulfate D_e, in comparison with the pressurized S/S PG compositions in which the PG was not initially mixed with lime or CFB ash.

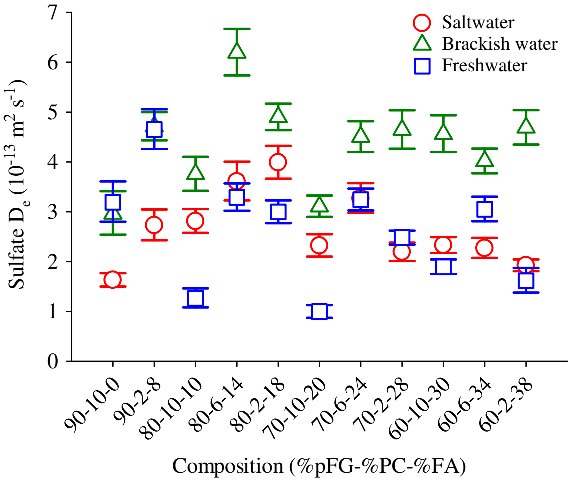

Fig. 1. Comparison of the sulfate effective diffusion coefficient (D_e) with 95% confidence intervals for compositions exposed to saltwater ($30\ \mathrm{g\,L^{-1}}$), brackish water ($15\ \mathrm{g\,L^{-1}}$), and freshwater ($0.5\ \mathrm{g\,L^{-1}}$) solutions.

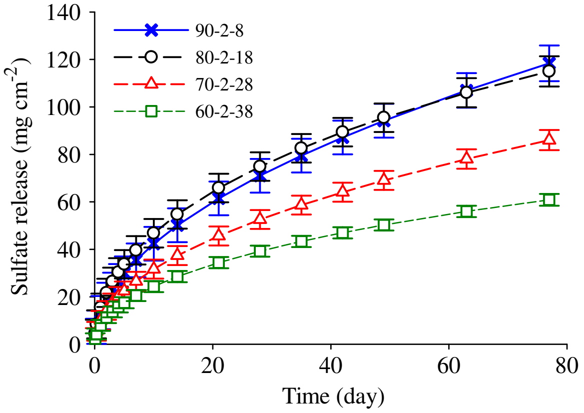

Fig. 2. Sulfate release with 95% confidence intervals for indicated compositions (percentages of pFG-PC-FA) containing 2% PC exposed to saltwater.

For the compositions with 2% PC, the lowest estimated sulfate D_e in saltwater occurred at 60% pFG. The D_e values increased with the increasing pFG content to a maximum of 3.99×10^{-13} m^2 s^{-1} at 80% pFG. This trend of increasing D_e is confirmed by the trend of increasing sulfate release, as shown in Fig. 2. The cumulative sulfate release at 77 days (Fig. 2) for the compositions 90-2-8 and 80-2-18 was not significantly different. This result indicated that the low content of the cementitious material (≤20%) with 2% PC for high contents of pFG (>80%) insufficiently decreased the dissolution potential of the sFG in saltwater. Therefore, the maximum pFG content should be less than 80% when mixed with 2% PC and exposed to saltwater environments.

At 10% PC, the sulfate D_e values followed a similar trend to those at 2% PC, with a maximum D_e occurring in the composition 80-10-10. However, the composition 90-10-0 had the minimum D_e among the compositions with 10% PC exposed to saltwater. The sulfate D_e for composition 90-10-0 was significantly lower in comparison with the D_e corresponding to the compositions 80-10-10, 70-10-20, and 60-10-30, as shown in Fig. 1.

The t_c values for sulfate in saltwater ranged from 264 to 265,564 days. The very large values of t_c for the compositions 90-2-8, 70-2-28, and 60-6-34 indicate that the specimens of these compositions did not reach equilibrium before complete sulfate release at approximately 1,459, 3,142, and 2,143 days, respectively, as determined from Eq. (2). The value of K_3, which is not significantly different from 0 for these compositions, led to the undefined t_c value, which implies the failure to reach equilibrium between the dissolution and precipitation of sulfate. Due to this undefined t_c value, these three compositions are not recommended for use in saltwater applications. A high variability, due to the sensitivity of the K_3 parameter, of t_c is observed. This result indicates that t_c should not be used for a quantitative estimation of the long-term stability. However, this parameter is still useful as a general indication of the long-term stability on the basis of its magnitude. The composition 80-10-10 is recommended for long-term applications in saltwater due to its low critical time (264 days), low sulfate D_e (2.81×10^{-13} m^2 s^{-1}), and cost of materials.

Behavior of Different Compositions in Brackish Water

All the K_3 values for specimens exposed to brackish water were negative (Table 3), indicating precipitation as the dominant long-term process. At 2% PC, no significant differences existed in the sulfate D_e for the various pFG contents. This indicates that 2% PC is not a sufficient PC content to reduce the dissolution potential of sFG in brackish water. A lower surface pH due to a decreased PC content combined with a decreased concentration of ions in brackish water in comparison with saltwater may inhibit the formation of calcium carbonate ($CaCO_3$). The formation of a protective layer of $CaCO_3$ has been suggested (Guo et al. 2001) as a major mechanism to reduce the dissolution potential in saltwater of a similar material, that is, S/S PG. Further investigations based on X-ray diffraction (XRD) and SEM studies are recommended to determine the potential for sFG exposed to brackish water to produce $CaCO_3$ in comparison with saltwater.

At 10% PC, the D_e for the composition 60-10-30 is not significantly different from the D_e for the composition 80-10-10. The D_e for the composition 70-10-20 is lower than the D_e for the composition 60-10-30 but not significantly different from the D_e for the compositions 90-10-0 and 80-10-10 (Fig. 1). Among the compositions with 6% PC, the D_e for the composition 80-6-14 is higher than both 70-6-24 and 60-6-34. However, when the pFG is kept constant at 80%, the D_e for the composition 80-6-14 is higher in comparison with the D_e for the compositions 80-10-10 and 80-2-18. On the basis of these results, it is concluded that the D_e of the sFG compositions exposed to brackish water follow no generalized trends. A combination of competing phenomena (for example, the increased solubility of sFG in brackish water, the pore development because of the increased ion exchange between $CaSO_4$ and NaCl, and the various levels of $CaCO_3$ formation) may explain the lack of generalized trends for the sFG specimens exposed to brackish water.

The D_e values for brackish water ranged from 2.96×10^{-13} to 6.19×10^{-13} m^2 s^{-1}, with a t_c of 157–1,004 days (Table 4). As a group, the compositions exposed to brackish water had higher values of D_e in comparison with the compositions exposed to saltwater and freshwater. However, the estimated values and variability of t_c for brackish water were generally lower in comparison with those for saltwater or freshwater. This result indicates that the sulfate diffusion out of sFG specimens exposed to brackish water proceeded at a higher rate near the first exposure, therefore reaching equilibrium between the dissolution and the precipitation of sulfate at a faster rate. To examine this claim and provide a recommendation on a sFG composition for use, additional long-term testing of sFG compositions exposed to brackish water is needed.

Behavior of Different Compositions in Freshwater

For specimens exposed to the freshwater solution, all compositions had negative values of K_3, indicating precipitation as the long-term dominant process. The sulfate concentration measured at several exchange intervals for the composition 90-2-8 was consistent with the leaching of gypsum from the recovered construction and demolition debris in DI water (Jang and Townsend 2001). However, this composition resulted in the most sulfate release for all compositions and various solutions tested.

The stabilization of pFG with PC and FA was highly effective when the sFG was exposed to freshwater. Low sulfate releases (≤40 mg cm^{-2}) were observed for compositions containing 10% PC, except for the composition 90-10-0 (Fig. 3). The sulfate releases of the compositions containing 60, 70, and 80% pFG with 10% PC at 77 days of exposure to freshwater were not significantly different. This result indicates that the dissolution potential of sFG had been sufficiently reduced with 80% pFG and 10% PC when exposed to freshwater. However, the sulfate D_e for the composition 60-10-30 was higher in comparison with the sulfate D_e of the compositions 70-10-20 and 80-10-10. In this case, the lower bulk sulfate content in the composition 60-10-30 in comparison with

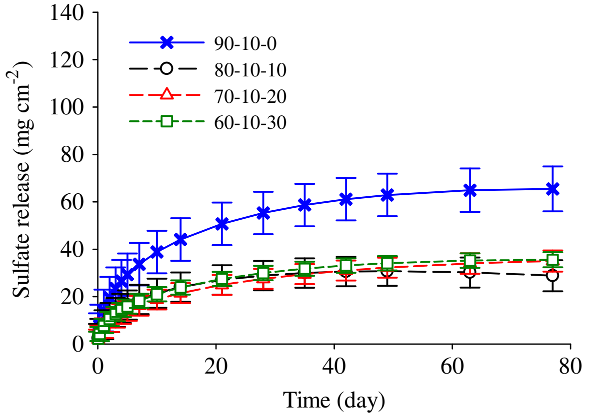

Fig. 3. Sulfate release with 95% confidence intervals for indicated compositions (percentages of pFG-PC-FA) containing 10% PC exposed to freshwater.

the compositions 80-10-10 and 70-10-20 (C_b in Table 4) resulted in a higher D_e despite no significant difference in the sulfate release. Therefore, the use of D_e should be preferred to the use of mass releases to enable a consistent comparison of the compositions with various bulk contents.

At 2% PC, the sulfate D_e values decreased with the decreasing pFG content. There were no significant differences in the sulfate D_e due to the various pFG contents at 6% PC. At 10% PC, the minimum D_e occurred for the 70% pFG content (Table 4). The composition 70-10-20 had the lowest measured D_e among all the compositions, that is, 9.95×10^{-14} $m^2 s^{-1}$. The t_c for the compositions exposed to freshwater had a range of 49–1,775 days. The composition 80-10-10 is recommended for freshwater applications due to a low t_c value (49 d), a sulfate D_e that is not significantly different from that of the composition 70-10-20, and a lower materials cost due to the higher amount of pFG.

Effects of Different Salinities

It is observed that, in general, the sulfate release of sFG at 77 days of exposure as a function of the salinity decreases with the change from brackish water to saltwater, and further decreases with the change from saltwater to freshwater. This trend is clearly shown for the two compositions 80-10-10 [Fig. 4(a)] and 60-2-38 [Fig. 4(b)].

Specimens exposed to brackish water have a higher sulfate release in comparison with specimens exposed to saltwater for all compositions except composition 90-10-0. This result indicates that the solubility of sFG does not increase monotonically with the salinity. This finding is consistent with the experimental and modeling results presented by Meijer and Van Rosmalen (1984), in which gypsum was found to have an initial increase in solubility with the NaCl concentration in water to a maximum before decreasing at higher NaCl concentrations. Meijer and Van Rosmalen (1984) indicated that gypsum becomes saturated in artificial sea water before the maximum solubility of gypsum is reached. However, a saturation of gypsum from sFG does not occur, because of the exchange of water in the dynamic leaching test. This phenomenon allows the maximum solubility of sFG to be observed in brackish water, resulting in a higher sulfate release in comparison with saltwater. The increased dissolution in brackish water may be explained by the interaction of two factors. First, the increased concentration gradient in brackish water in comparison with saltwater results in a higher potential for diffusion to occur. Second, the higher concentration of sodium and chloride ions in brackish water can lead to an increased ion exchange with calcium and sulfate, the main components of gypsum, in comparison with freshwater. Additional SEM and XRD analyses are needed to confirm this explanation.

The trend of a decreasing sulfate D_e based on the three salinities tested for each composition generally follows the sulfate release trend. For all compositions, the sulfate D_e is higher in brackish water than in saltwater (Fig. 1 and Table 4). In addition, the sulfate D_e is higher in brackish water than in freshwater for all compositions except 90-10-0 and 90-2-8.

Finally, of the 11 compositions, four (80-10-10, 80-2-18, 70-10-20, and 60-10-30) had D_e values that were higher in saltwater than in freshwater ($p < 0.0001$, $p < 0.0001$, $p < 0.0001$, and $p = 0.0161$, respectively). However, the D_e values for the compositions 90-10-0, 90-2-8, and 60-6-34 were higher ($p < 0.0001$) in freshwater than in saltwater. The remaining compositions (80-6-14, 70-6-24, 70-2-28, and 60-2-38) presented no significant difference in the sulfate D_e between saltwater and freshwater.

The values of t_c generally increased from brackish water to freshwater to saltwater. Although it is useful for predictions of long-term stability, the use of t_c as a comparison parameter among various salinities and compositions should be avoided due to the high sensitivity of t_c on small changes (and thus on small estimation errors) in K_3. This high sensitivity of t_c on K_3 can produce a

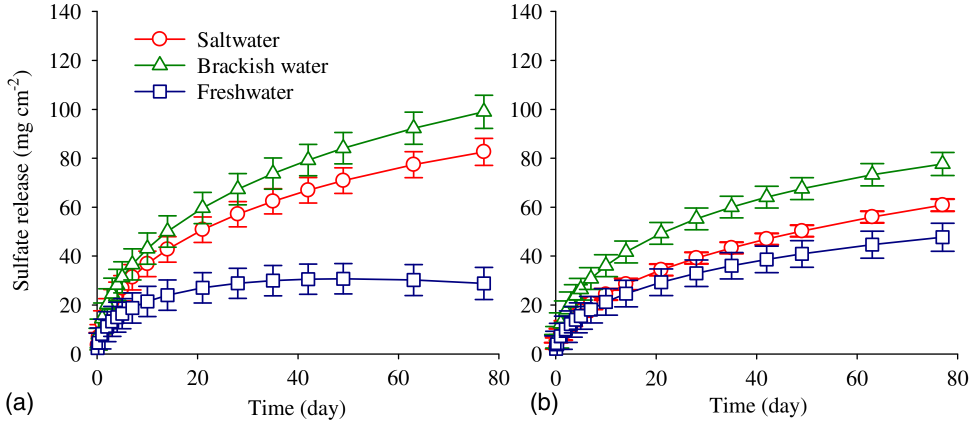

Fig. 4. Comparison of sulfate release in saltwater, brackish water, and freshwater solutions for two representative compositions (percentages of pFG-PC-FA): (a) 80-10-10; and (b) 60-2-38.

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large variability of t_c under different conditions, which can be even more significant for field applications because many competing factors, such as the temperature, flow of water, and influence of aquatic organisms, can affect the equilibrium between a solid and a solution. Therefore, the use of D_e for the quantitative comparison of compositions should be preferred to the use of t_c.

Conclusions

The dissolution potential of several compositions of stabilized/solidified pH-adjusted fluorogypsum was parameterized by estimating the sulfate effective diffusion coefficients. The sulfate effective diffusion coefficients were then used for assessing the potential aquatic applications of stabilized/solidified pH-adjusted fluorogypsum in saltwater, brackish water, and freshwater environments. In a comparison of these three salinities, the results indicated that the majority of the compositions of stabilized/solidified fluorogypsum considered in this study had a lower dissolution potential in freshwater and saltwater environments in comparison with a brackish water environment. None of the compositions examined in this study are recommended for application in brackish water without further investigation. A composition of 80% pH-adjusted fluorogypsum, 10% Type I/II portland cement, and 10% Class C fly ash is recommended for saltwater and freshwater aquatic applications as an alternative to limestone. This composition is recommended due to a low sulfate D_e of 2.81×10^{-13} $m^2\,s^{-1}$ in saltwater and 1.26×10^{-13} $m^2\,s^{-1}$ in freshwater and an expected ceasing of the sulfate release at 264 days in saltwater and 49 days in freshwater as an indication of stability.

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Supplemental Data

Tables S1–S3 are available online in the ASCE Library (www.ascelibrary.org).

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