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# Predicting the leachate generation from wet phosphogypsum stack using a water-balance-analysis based model

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# ABSTRACT

Leachate from wet phosphogypsum (PG) stack should be properly managed to mitigate the negative environmental impact of phosphoric industry. Accurate prediction of leachate amount is the prerequisite for efficient leachate management. In this study, a model using water balance analysis to predict leachate production from wet PG stack is established. The extruded water, which is related to PG deformation, is innovatively introduced as a variable in the model to account for the porewater's contribution. Model simulation suggested that at the early stage, fresh water need to be added to PG to facilitate the transfer or PG slurries; however, as the leachate accumulates in the tailings pond, a net discharge of PG is required starting at the fourth year for the studied PG stack. Model simulation also indicated that the leachate generation increased gradually over time and that the leachate generation in each month could deviate from the average leachate generation during the life cycle of the stack. The model output matches with measured values reasonably well, which confirmed the model's accuracy. Sensitivity analysis indicated that average precipitation and evaporation are the two most important factors that determine leachate generation rate. Monthly leachate generation rates vary significantly within the year, as the precipitation and evaporation vary in different seasons. The highest leachate generation rates were reached in rainy seasons and the lowest rates were reached in wintery months. This study could be used to optimize the PG leachate managements and to mitigate the PG related pollution to the environment.

# 1. Introduction

Phosphogypsum (PG) is an industrial by-product associated with phosphoric acid production (Silva et al., 2022). It has been estimated that 5 tons of PG is generated for each ton of phosphoric acid produced (Hentati et al., 2015), and that ca.  $2-3 \times 10^8$  tons of PG are produced globally per year (Macías et al., 2017; Parreira et al., 2003; Tayibi et al., 2009; Yang et al., 2009). Typically, PG is stacked in tailing ponds, and wet stacking is by far the most popular large-scale PG disposal method. However, the leachate generated by the wet stacking is a major source of pollution and can cause serious environmental pollution and ecological damage if not handled properly (Adeoye et al., 2021; Agency, 2013; Cánovas et al., 2018; Gázquez et al., 2014; Pérez-López et al., 2016; Torres-Sanchez et al., 2020; Wali et al., 2014; Zhang et al., 2007). Therefore, stricter environmental standards have been introduced in China to regulate the environmental quality of leachate effluent.

To effectively manage the leachate derived from PG tailing ponds, it is of crucial importance to accurately estimate the leachate generation rate, which should be known as a priori to design the leachate treatment facilities (Guerrero et al., 2019; Millán-Becerro et al., 2019; Xu et al., 2019; Zhan et al., 2017a, 2017b). Many studies have been published to elucidate the environmental impact and potential applications of PG waste (Bisone et al., 2017; Cánovas et al., 2018), as well as to introduce advanced leachate treatment techniques and methods (Cheng et al., 2020; Khoo et al., 2020); however, to the best of author's knowledge, few studies have been reported on the accurate estimation of PG leachate generation rate. Leachate production rate has been estimated using over-simplified water mass balances, which only considers precipitation and evaporation (Grugnaletti et al., 2016; Qian et al., 2002; Schroeder et al., 1994; Xu et al., 2012) or empirical correlation-based methods which derived from landfill leachate estimation studies. Considering that PG stacks contains significant amount of porewater

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Received 29 January 2022; Received in revised form 11 April 2022; Accepted 16 April 2022 Available online 18 April 2022 0013-9351/© 2022 Elsevier Inc. All rights reserved. whose mobility is closely related to the physical characteristics of the stack and that the inherent differences between PG stack and the municipal landfills, the modeling approaches tend to give leachate production rates that deviate from the actual ones.

In recent years, a more detailed water-balance based modeling strategy that considers inflow, rainfall, evaporation, leakage and retained water has been proposed (CHU and TONG, 2008; Wissa and Fuleihan, 1993). A crucial improvement of this modeling strategy is that leakage and retained water, which can vary appreciably in each year even for the same PG stack, were taken into consideration. However, a major drawback of the of above-mentioned studies is that the extrusion of pore water from saturated wet PG stack was not considered: since wet PG stack will deform considerably over the years through a series of physical reactions under its own pressure (Mi et al., 2015; Zheng et al., 2019), it typically releases a relatively large portion of its porewater in the form of extrusion water into leachate, and the overlook of the extrusion water will inevitably result in deviation in the leachate prediction results from the measured ones.

The overall objective of this study is to establish a water-balancebased model to predict the production rate of PG leachate. Herein, the extruded water derived from the deformation of PG stack into the water balance analysis is innovatively incorporated, and an equation to estimate the extruded water by measuring consolidation settlement characteristics is proposed. Moreover, the practical calculation formulas of rainfall inflow and evaporation are put forward based on the threedimensional structure, meteorological conditions, and the annual rising height of the PG stack. The accuracy of this new model was verified using measured data from a large-scale wet PG stack in Guizhou, China. The leachate predication model presented in this study could be used as an effective tool to achieve the sustainable management of leachates from PG stacks. In addition, this study could be employed as a guide for the effective treatment of leachates from other industrial solid waste (e. g., red mud and manganese residue) as well.

#### 2. Materials and methods

#### 2.1. Model framework

A conceptual model of how wet PG stacks were operated is given in Fig. 1. The leachate of PG stack was defined as the contaminated acidic wastewater in contact with PG that needed to be discharged and treated, excluding the wastewater that was recycled from the reservoir area (see text S1). In brief, the monthly leachate generation rate from a wet PG

stack could be calculated using Eq. (1) as follows:

$$L_n = (R_n + P_n + S_n) - (E_n + I_n + Q_n)$$
 (eq 1)

where  $L_n$  is leachate generation rate from a PG stack (cubic meters per month, or, m<sup>3</sup>/mo, the same below),  $R_n$  is net water inflow into slurry (m<sup>3</sup>/mo),  $P_n$  is the precipitation (m<sup>3</sup>/mo),  $S_n$  is extruded water from the PG stack (m<sup>3</sup>/mo),  $E_n$  is evaporation from the PG stack (m<sup>3</sup>/mo),  $Q_n$  is leakage from the stack (m<sup>3</sup>/mo),  $I_n$  is water trapped in the pores of the PG (m<sup>3</sup>/mo). The details regarding to the calculation of  $R_n$ ,  $P_n$ ,  $S_n$ ,  $E_n$ ,  $I_n$ and  $Q_n$  are given in below.

# 2.2. Water balance factor and calculation formula

#### 2.2.1. Precipitation and evaporation

Typically, PG stack is encompassed by a flood-interception ditch to prevent excessive amount of precipitation from entering the stack. The areas that inside the flood-interception ditch can be divided into two parts: the first part is called the working area, and the second part is called the marginal area. A schematic diagram and top-view photos of the studies PG stack is given in the supplementary information (SI).

The precipitation is defined as the rainfall collected within the area of flood-interception ditch, as the precipitation outside of flood-interception ditch will be diverted away. The precipitation inside the flood-interception ditch is estimated using Eq. (2) according to relevant references (Grugnaletti et al., 2016):

$$P_n = P_{avg} \times (C_{L1} \times A_1 + C_{L2} \times A_2) \tag{eq 2}$$

where  $P_n$  is total precipitation within the flood-interception ditch in the nth month (m<sup>3</sup>/mo),  $P_{avg}$  is average annual precipitation (m<sup>3</sup>/mo),  $A_1$  is the top working area (m<sup>2</sup>, see Fig. 1),  $C_{L1}$  is the rainfall infiltration coefficient of top working area (unitless and typically is set to 1.0).

The marginal area is defined as the area within the flood-interception ditch but not occupied by top working area ( $A_2$ ,  $m^2$ ), and the edge of PG heap is covered with soil with the goal of reducing the amount of infiltrated precipitation. In this study, the CL2 is used to calculate the rainfall infiltration. In previous studies that focus on leachate generation from landfills, it has been proposed that CL2 can be calculated as a function of the type of cover, the moisture condition of the surface layer (El-Fadel et al., 1997; Fredlund, 2006; Grugnaletti et al., 2016; Schroeder et al., 1994). However, for most circumstances, a constant empirical value could be set for CL2 without impair the accuracy of the model. For instance, Fredlund assumed the infiltration coefficient could



Fig. 1. The conceptual model of wet PG stack used in this study.

be set to 0.1 for slant slope. Except for the top, the side surfaces of PG stack, which consists of the bulk surface areas that are exposed are slanted, therefore a CL2 value of 0.1 is chosen in this study.

Evaporation from the PG stack could be divided to the part from the surface of top-water and the part from the side surface of wet PG (see Fig. 1). The evaporation rate is determined by several factors, which include the water content of PG, the pore size of the PG, the irradiation of sunlight, the temperature, the humidity of air and the wind speed (An et al., 2018; Neukum et al., 2021; Van Bavel and Hillel, 1976). The evaporation could be determined either using direct in-situ measurements) or using indirect empirical estimations (Dimitriadou and Nikolakopoulos, 2021; Han and Tian, 2018; Zhou et al., 2020). The evaporation could be determined using directly (i.e. based on in-situ measurements) or indirectly (i.e. based on empirical estimation). The evaporation rate is determined based on *in-situ* measurements using previously reported methods (Allen et al., 2005; An et al., 2018; Han and Tian, 2018).

Overall, the evaporation from the PG stack is calculated using Eq. (3):

$$E_n = E_{avg} \times (C_1 \times S_1 + C_2 \times S_2) \tag{eq 3}$$

where  $E_n$  is total evaporation of PG yard in the nth year (m<sup>3</sup>),  $E_{avg}$  is the average annual evaporation(m),  $C_1$  is the evaporation coefficient of open water (dimensionless, and set to 1 in this study),  $C_2$  is the evaporation coefficient of PG surface (dimensionless and is set to 0.57).  $S_1$  and  $S_2$  are the areas of open water surface and PG surface, respectively (m).  $S_1$  is the area of open water surface, and  $S_2$  is the PG surface area (defined as the total surface area of PG stack minus the top surface area of the PG stack).

# 2.2.2. Net water inflow

The net water inflow represents the water that bring into the stack by the PG slurry, which is the water content of PG after the filter in the production workshop. Therefore, based on the experimental measurement of water content, Eq. (4) is firstly proposed in this study, to calculate the net water based on the water content of PG and the total mass of PG:

$$R_n = \frac{m_0 \times w_d}{(1+w_d) \times \rho} = m \times w_d \tag{eq 4}$$

where  $R_n$  is net water inflow value in the nth year (m<sup>3</sup>),  $m_0$  is the mass of initial PG discharged into the stack each year (t),  $w_d$  is moisture content of PG slurry being transported to the stack (%), and  $\rho$  is the density of pore water (t/m<sup>3</sup>), m is the dry mass of PG being discharged to the stack (t).

#### 2.2.3. Retained water

The retained water is the saturated filling water in the newly added PG pores in each calculation period, which is essentially the pore water content of saturated PG. Therefore, based on the measured water content of saturated PG and simple multiplication, Eq. (5) is proposed to calculate retained water:

$$I_n = \frac{m_s \times w_0}{(1+w_0) \times \rho} = m \times w_0 \tag{eq 5}$$

where  $I_n$  is retained water value in the nth year  $(m^3),\,m_s$  is the mass of saturated initial PG discharged into the stack each year (t),  $w_0$  is moisture content of saturated initial PG (%), and  $\rho$  is the density of pore water (t/m<sup>3</sup>), m is the dry mass of PG being discharged to the stack\_

# 2.2.4. Leakage water

The bottom of the wet PG stack is usually lined with impervious geomembranes; however, pinholes would typically exist after geomembranes were deployed which would allow the leachate to filtrate through the geomembranes. In this study, a previously reported equation (Wissa and Fuleihan, 1993; Chou et al., 2021) is used to predict the leakage through pinholes:

$$Q = \frac{4 \times k_m \times r_d \times h}{1 + \frac{4 \times i \times k_m}{\pi \times r_d \times k_c}}$$
 (eq 6)

In Eq. (6), Q is the leakage rate through pinholes  $(m^3/mo)$ ;  $k_m$  is the effective coefficient of permeability of the gypsum immediately above the liner (m/a);  $k_v$  is the vertical coefficient of permeability of gypsum in the hole (m/a); h is the hydraulic head across the liner (m);  $r_d$  is the radius of the hole (m), and t is the thickness of the geomembrane (m).

# 2.2.5. Extruded water

The PG pores in wet PG stack decrease with time under the action of stress, and water is discharged from saturated PG pores. The PG pile will sink because of pore water discharge, which is the consolidation settlement characteristics. The annual extruded water is the sum of the extruded water of each layer in PG stack. The extruded water value is equal to the sum of the extruded water in each layer in the nth month. The extrusion water in each layer can be modeled as the void ratio change rate of PG in the nth year multiplied by the volume of PG at the end of the previous year, which can be calculated using Eq. (7):

$$S_n = \sum_{i=n,j=1}^n S_{i,j} = \sum_{i=n,j=1}^n \left[ V_{i-1,j} \times \frac{(e_{i-1,j} - e_{i,j})}{(1 + e_{i-1,i})} \right] + V_0 \times \frac{(e_0 - e_{n,n})}{(1 + e_0)} \quad (eq \ 7)$$

where  $S_n$  is the total amount of extruded water in each age (layer) of PG in the nth month (m<sup>3</sup>), and  $S_{i,j}$  is the extruded water volume of the jth layer in the ith month (m<sup>3</sup>).

Assuming the volume of the PG solid particles does not decrease during the stacking (i.e. the distance of the PG particles would decrease but no the volume of particles per se), then the volume of the jth layer of PG in the ith month could be calculated using Eq. (8):

$$V_{i,j} = V_0 \times \frac{e_{i,j} + 1}{e_0 + 1}$$
 (eq 8)

where  $V_{ij}$  is the PG volume of the jth layer in the ith month,  $V_0$  is the initial volume of the PG being stacked each month,  $e_{ij}$  is the void ratio of the jth layer PG in the ith month.

# 2.3. PG characteristics and laboratory test

The test PG samples were acquired from a PG stack in Guizhou, China. The stack was put into use since October 2013 with a designed service life of 6 years, which ended in 2019. The bottom of the stack was lined with High Density Polyethylene (HDPE) geomembranes of 1.5 mm thickness. According to the statistics provided by the local meteorological station, the average annual precipitation and evaporation in the tailing pond area are 1166.1 mm and 628.8 mm, respectively. The floodinterception ditches of the studied PG stack encompass cross-section areas of 241,702.1 m<sup>2</sup> and 458,498.86 m<sup>2</sup>, respectively. The relationship between the yard elevation, top surface area and storage capacity is shown in the Supplementary Information (SI). The leakage evaluations described herein conservatively assumed a frequency of 10 defects per hectare of HDPE membrane, with each defect being modeled as a circular hole with a diameter ranging from 2 to 20 mm. The detailed testing procedures as well as more information on PG characteristics could be found in previous publications (ASTM, 2011; Meng et al., 2016). Consolidation settlement characteristics are expressed by stress-strain-time relationships measured according to standard methods (ASTM, 2011). More than 20 undisturbed PG cores samples were taken from four different parts in the stack, and the stress-strain curve of the studied PG in the pressure range of 50-400 kPa was determined. The relationship between pore ratio and pressure and action time can be obtained by the curve fitting in our previous study (Meng et al., 2016):

$$e = e_0 - c_c \times \log\left(\frac{p}{p_0}\right) - (C_a \times p - k) \times \log\left(\frac{t}{t_0}\right)$$
 (eq 9)

where e is the void ratio of PG;  $e_0$  is the initial void ratio of PG, which is 1.1232 based on experimental results;  $C_c$  is the compression index;  $C_a$  is the recompression coefficient, k is a constant; p is the pressure on PG, and t is time of action.

#### 2.4. Model validation and sensitivity analysis

The validity of our model was checked by comparing the model output with the measured data from a large-scale PG tailing pond. As in many PG tailing ponds, the PG stack selected in this paper shares the leachate pipeline and regulating tank with the company's old PG stack. The unsealed site of the old storage site still produces a large amount of leachate, which makes it difficult to accurately measure the leachate generation rate. Therefore, it is difficult to directly verify the leachate model proposed in this paper through the measured data. According to the above analysis, the net inflow and pore intercepted water are relatively fixed, while the evaporation, rainfall, leakage and extruded water are closely related to the change of the height of PG stack. Therefore, the change of stack height is used as a reference to alternatively check the accuracy of this model. The root mean square error (RMSE) was used as an indicator to reflect the goodness of the fit (Chai and Draxler, 2014):

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (X_{mod, i} - X_{obs,i})^2}$$
(eq10)

where RMSE is the root mean square error (unitless), n is the total number of predicted/observed data points,  $X_{mod}$  is the output from the model in the ith year,  $X_{obs,i}$  is the corresponding observed value in the ith year.

In addition, global sensitivity analysis was performed to evaluate the impact of model parameters on the predicted leachate ( $L_n$ ). In short, five parameters, which are  $P_{avg}$ ,  $E_{avg}$ ,  $\omega_d$ ,  $\omega_0$  and  $r_d$ , have been selected to be subjected to sensitivity analysis. The Elementary Effects Test (EET) was employed, and the means of the elementary effects, which reflect the total effect of an parameter over the output, is calculated according to a previous study (Pianosi et al., 2015).

# 3. Results and discussion

# 3.1. Calculation results of the PG stack height

Based on the relationship between elevation and volume of PG stack selected above, as well as the actual monthly storage volume of PG, the relationship between initial storage height and time of saturated PG can be obtained. Using Eq. (9) and the pressure and time of each layer, the pore ratio after monthly settlement of each layer can be calculated, and then the settlement height of each layer can be obtained subsequently.

The theoretical height of PG stack of each month (see Fig. 2) is calculated by subtracting the settlement height from the initial stockpiling height, and the change of the characteristics of PG stack each year is shown in Table 1. The overall rising height curve shows a trend of rapid increase and then gradually slows down. The height of the yard rises sharply in the first year and the first month due to the small bottom area of the valley PG stack and the same volume requires a larger height. The change of the characteristics of PG stack is shown in Table 1. The top surface area reaches the maximum in the 3rd year, which is 47.5 ha. Later on, the top surface area gradually decreased, and when the PG stack was closed in the last year, the top surface area was only 23.3 ha.

# 3.2. Simulating the precipitation, evaporation and leakage

Using the meteorological data, the PG characteristics and surface evaporation, the precipitation, evaporation and the leakage factors in



Fig. 2. Changes in the calculated height of the studied PG stack over the simulation period.

 Table 1

 Shape variation for different stage.

Year	Lift Height (m)	Average top surface area (ha)	Storage volume (10 <sup>3</sup> m <sup>3</sup> )
1st year	29.0	22	216.8
2 nd year	9.1	39.6	513.1
3rd year	8.0	47.5	854.7
4th year	8.5	38.2	1192.3
5th year	10.0	30.2	1606.9
6th year	9.9	23.3	1890.1

the water balance of PG stack were predicted. It can be seen from the calculation results that the annual net water inflow and pore interception water are basically unchanged over the simulated 72 months of 6 years, which are  $8.33 \times 10^4$  and  $15.97 \times 10^4$  m<sup>3</sup>/mo respectively. The evaporation calculated in the light annual top surface area and water surface area of PG, and the rainfall calculated according to the elevation and the location of flood interception ditch, the data of both are shown in Fig. 3 (see Fig. 4).



**Fig. 3.** The calculated leakage (a), evaporation (b) and precipitation rates from studied PG stack over the course of 72 months.



**Fig. 4.** The calculated leachate (a) and extruded water yield (b) from studied PG stack over the course of 72 months.

Both evaporation and precipitation are closely related to the height of PG stack. Our simulation results indicated that both the precipitation and evaporation exhibited a trend of increasing in the first 3 years and then decreasing in the following 3 years. Both evaporation and precipitation reached the highest values in the 3rd year, which can be explained by the fact that both the top work area and the open water area reached the maximum values. Starting from the 3rd year, the precipitation gradually decreased. Although the flood-interception area does not change since the 3rd year, it should be noted that the side areas of the PG stack was covered to reduce the precipitation infiltration. Assuming no measures were undertaken to reduce the precipitation infiltrated into the PG stack, then the estimated precipitation collected within the flood-interception ditch is 295.56  $\times$  10<sup>4</sup> m<sup>3</sup>, which is higher than the actual value (i.e., 231.82  $\times$  10<sup>4</sup> m<sup>3</sup>), and this would result in 63.74  $\times$  10<sup>4</sup> m<sup>3</sup> of precipitation entering the body of PG stack.

Model simulation suggested that the leakage peaked at the 36th month of the life-cycle of PG stack, with a peak leakage rate of 0.75  $\times$  10<sup>4</sup> m<sup>3</sup>/mo. Although the leakage rate is relatively small comparing to the precipitation and evaporation rate, it can negatively impact the groundwater quality. This is especially true for this PG stack studied, which is located in Guizhou, China, a region that is known for its Karst aquifer systems, which is conducive to frequent conversion of surface water and groundwater, through precipitation, evapotranspiration and underground seepage.

Intriguingly, model simulation also suggested that the evaporation and precipitation varied swiftly within the same year. The precipitation reached the highest values during May to July in each year due to the higher average precipitation during this period. As shown, the leakage rate initially increases with increased stack height due to the increase in applied hydraulic head. At greater heights, however, the exponential reduction in the hydraulic conductivity of the gypsum above the liner results in a reduction in the leakage rate despite the continued linear increase in hydraulic head (CHU and TONG, 2008; Guerrero et al., 2019; Millán-Becerro et al., 2020; Pérez-López et al., 2016; Wissa and Fuleihan, 1993).

Overall speaking, the amounts of extruded water increased as time elapses, with the monthly average extruded water increased from 3.18  $\times$  10<sup>4</sup> m<sup>3</sup> in the 1st year to 7.35  $\times$  10<sup>4</sup> m<sup>3</sup> in the 6th year, which represents an increase of 2.3 times. It should be noted that site characteristic also plays an important role in determining the amount of extruded water each month. In our study, the PG stack was constructed in a valley that has a very narrow bottom, as a result of that the increase in PG

height in the first month is much larger than the increase in the subsequent 9 months (i.e., from 2 nd month to the 10th month). The sharp increase in stack height led to a higher leachate generation rate in the 1st month, which is  $3.42 \times 10^4$  m<sup>3</sup>, whereas the average leachate generation rate in the following 9 months decreased to  $3.07 \pm 0.19 \times 10^4$  m<sup>3</sup> due to the slower increase in PG height.

# 3.3. Application analysis of the calculation results

The amount of each water balance factor and leachate production in the whole calculation period are shown in Fig. 5. The water quantity from the slurry (i.e. net water inflow) is one of the main sources of the leachate. In our study, the net water inflow is defined as the water in wet PG that was being discharged to the stack. Using a typical water content of 25%, it is estimated that the water being brought into the PG stack is  $8.33\,\times\,10^4$  m³/mo. Interception water and extruded water are not controlled by external factors and do not tend to vary significantly. In order to reduce leachate production in daily operation, the main influencing factors of water balance that can be effectively controlled are rainfall and evaporation. Rainfall can be reduced by controlling the raincutting area, such as adding temporary isolation and drainage measures in rainy season, and evaporation surface area can be controlled to increase evaporation, such as increasing water surface area in sunny days. Because of the relatively low densities (higher void ratios) and correspondingly higher hydraulic conductivities at the lower stack heights, the predicted leakage rates are higher during the early life of the stack than at maturity.

The leachate generated from the PG stack will be returned to the production shops for slurry loading, and the excess leachate will only enter the collection tank for treatment and discharge. The actual leachate yield to be disposed of is the calculated amount. In addition, there is a large difference between the average leachate production in the whole calculation period and in each calculation period. When designing and calculating the scale of leachate treatment facilities, it is necessary to be more realistic and calculate the leachate yield according to different stages. Finally, the goals of PG management policy could successfully be implemented using proper leachate treatment systems to generate a universal system which is cost effective, sustainable, and acceptable to the community (Show et al., 2019).

# 3.4. Model accuracy

The accuracy of the model is validated using the measure height value of the PG stack (see Fig. 6). Using eq (10), the RMSE value was determined to be 1.213, which means that the predicted value is in very



**Fig. 5.** The quantity of water balance factor and leachate yield in the whole cycle. The positive values represent net input into the leachate while the negative value represents decrease in leachate generation.



**Fig. 6.** The calculated and the measured height of PG stack over the course of 6 years.

good agreement with the measured ones. Moreover, the measured and calculated values of the rising velocity of PG stack shown in Fig. 5 are basically consistent, indicating that the model can accurately predict the actual situation of the stack. The missing and inaccurate data in the sixth year were mainly due to the large-scale resource utilization of PG in 2019 when the stack was close to the closure, resulting in an appreciable reduction of the storage volume; however, such abnormalities should not be explained as the model fail to reflect the true situation of the PG stack.

# 3.5. Sensitivity analysis

A total of five model parameters' impact on the leachate production rate have been analyzed, for 6 years, using elementary effects methods. According to Table 2, Pavg and Eavg consistently exhibited higher elementary effect values than the other 3 parameters, indicating that the average precipitate and evaporation are the two most significant contributors to the leachate production. The W<sub>0</sub> and W<sub>d</sub> only exhibited modest elementary effects, which suggest that the water contents of initial PG and the PG being transferred to the stack did not constitute the major component of leachate. The radius of the pinholes in geomembranes, which is r<sub>d</sub>, exhibited the lowest elementary effect value. This fact suggested that the leakage through the geomembranes in our studied scenario has the most negligible impact on the leachate production. Overall, the sensitivity analysis indicated that the average precipitation and evaporation are the two most important parameters that determine the generation of leachate. Such fact highlights the importance of selecting proper sites for wet PG stack to lower the Pave or increase the Eavy. Moreover, it is also helpful to reduce the leachate generation if temporary precipitation diversion measures could be put in place during the rainy seasons and if the top area of the tailing pond could be increased during the dry seasons to facilitate evaporation.

#### 3.6. Limitations of the modeling approach

Static PG conditions to establish the modeling process have been assumed in above analysis, but surface area change processes could be

attributed to elevation and plane area variation processes over time, resulting in possible changes of evaporation and rainfall infiltration. Furthermore, quality control of geomembrane installation would also not be considered, so the number of pinholes or other structural defects did not vary during the complete period. In fact, geomembrane in many PG stacks in China will not only be destroyed in the construction process, but also be more damaged in the operation process, resulting in more pinholes or holes with larger diameters. Additionally, the foundation and geological conditions beneath the pad were not considered by our model and may affect the leachate prediction, resulting in a subtle change of the leachate generation.

In case of evapotranspiration, tree, shrub vegetation or grassland would be more effective than PG surface, but vegetation types cannot be sufficiently considered by the model. Moreover, the evaporation capacity depends on the water content of PG, determined as a uniform value in this paper, which is different in different regions, so there may be errors in the actual calculation. On the other hand, temporary drainage measures are taken during the rainy season to reduce the amount of rainwater entering the stack; thus, the model overestimates the actual precipitation inflow.

#### 4. Conclusions

Based on the study of water balance and PG consolidation characteristics, a simulation model for the evaluation of leachate generation at PG stacks is herein presented. The applicability of the developed model as a valuable tool to estimate the leachate production at PG stacks have been demonstrated. Based on the results presented in this paper, the following conclusions can be drawn.

The comparison with vary stack height data showed that the proposed model and formula can provide a more accurate description of leachate production. This better accuracy is mainly ascribed to the inclusion in the new model of some key processes for leachate production during the active phase of a PG stack that are neglected in the other model (e.g., PG compression and consolidation, change in PG physicalmechanical properties). The calculation model proposed in this paper can accurately calculate the main sources and total amount changes of leachate, which will play a critical role in the design and daily operation of leachate treatment facilities in PG stacks, such as the construction scale of treatment facilities, stack wastewater operation control and economic cost savings.

In summary, the prediction model allowed to prove the functionality of a PG stack system under the given weather and site conditions. In order to finally validate the leachate in PG stack, more physically and geological based models could give more insight into the variations in geomembrane defects and geological foundations. This step will be part of further research, as well as leachate composition and its impact on the environment. This is a research paper mainly addressed to the scientific and engineering community, but the conclusions could be presented to PG waste stakeholders, such as the fertilizer industry, the local government and decision makers and the general public, affected by PG stacks and seeking alternative management methods.

#### Declaration of competing interest

The authors declare that they have no known competing financial

Table 2

The elementary effects of the selected model parameters on predicted leachate generation.

Parameter	1st year	2nd year	3rd year	4th year	5th year	6th year
Pavg	72,510,630.00	137549658.00	137549658.00	137549658.00	137549658.00	137549658.00
Eavg	35,662,000.00	60,560,560.00	76,122,160.00	60,819,920.00	52,293,460.00	40,946,460.00
w <sub>0</sub>	27,534.33	27,507.59	27,538.87	27,577.32	27,534.64	27,535.65
w <sub>d</sub>	7252.66	7251.01	7252.63	7254.40	7253.72	7251.91
r <sub>d</sub>	0.05	0.06	0.07	0.08	0.09	0.10

interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2022.113338.

#### References

- Adeoye, C., Gupta, J., Demers, N., Adhikari, A., 2021. Variations of radon and airborne particulate matter near three large phosphogypsum stacks in Florida. Environ. Monit. Assess. 193, 284.
- Agency, I.A.E., 2013. Radiation Protection and Management of NORM Residues in the Phosphate Industry. Internat. Atomic Energy Agency.
- Phosphate Industry. Internat. Atomic Energy Agency.Allen, R.G., Pruitt, W.O., Raes, D., Smith, M., Pereira, L.S., 2005. Estimating evaporation from bare soil and the crop coefficient for the initial period using common soils information. J. Irrigat. Drain. Eng. 131, 14–23.
- An, N., Tang, C.-S., Xu, S.-K., Gong, X.-P., Shi, B., Inyang, H.I., 2018. Effects of soil characteristics on moisture evaporation. Eng. Geol. 239, 126–135.
- ASTM, 2011. Standard Test Method for One-Dimensional Consolidation Properties of Soils Using Incremental Loading (ASTM D2435/D2435M-11).
- Bisone, S., Gautier, M., Chatain, V., Blanc, D., 2017. Spatial distribution and leaching behavior of pollutants from phosphogypsum stocked in a gypstack: geochemical characterization and modeling. J. Environ. Manag. 193, 567–575.
- Cánovas, C.R., Macías, F., López, R.P., Nieto, J.M., 2018. Mobility of rare earth elements, yttrium and scandium from a phosphogypsum stack: environmental and economic implications. Sci. Total Environ. 618, 847–857.
- Chai, T., Draxler, R.R., 2014. Root mean square error (RMSE) or mean absolute error (MAE)?–Arguments against avoiding RMSE in the literature. Geosci. Model Dev. (GMD) 7, 1247–1250.
- Cheng, S.Y., Show, P.L., Juan, J.C., Ling, T.C., Lau, B.F., Lai, S.H., Ng, E.P., 2020. Sustainable landfill leachate treatment: optimize use of guar gum as natural coagulant and floc characterization. Environ. Res. 188, 109737.
- Chu, X.-q., Tong, X.-x., 2008. Design Outline of Large-Scale Phosphogypsum Stack [J], vol. 4. Phosphate & Compound Fertilizer.
- Dimitriadou, S., Nikolakopoulos, K.G., 2021. Annual actual evapotranspiration estimation via GIS models of three empirical methods employing remotely sensed data for the peloponnese, Greece, and comparison with annual MODIS ET and Pan evaporation measurements. ISPRS Int. J. Geo-Inf. 10, 522.
- El-Fadel, M., Findikakis, A.N., Leckie, J.O., 1997. Modeling leachate generation and transport in solid waste landfills. Environ. Technol. 18, 669–686.
- Fredlund, D.G., 2006. Unsaturated soil mechanics in engineering practice. J. Geotech. Geoenviron. Eng. 132, 286–321.
- Gázquez, M., Mantero, J., Mosqueda, F., Bolívar, J., García-Tenorio, R., 2014. Radioactive characterization of leachates and efflorescences in the neighbouring areas of a phosphogypsum disposal site as a preliminary step before its restoration. J. Environ. Radioact. 137, 79–87.
- Grugnaletti, M., Pantini, S., Verginelli, I., Lombardi, F., 2016. An easy-to-use tool for the evaluation of leachate production at landfill sites. Waste Manag. 55, 204–219. Guerrero, J.L., Gutiérrez-Álvarez, I., Mosqueda, F., Olías, M., García-Tenorio, R.,
- Bolívar, J.P., 2019. Pollution evaluation on the salt-marshes under the phosphogypsum stacks of Huelva due to deep leachates. Chemosphere 230, 219–229.
- Han, S., Tian, F., 2018. Derivation of a sigmoid generalized complementary function for evaporation with physical constraints. Water Resour. Res. 54, 5050–5068.
- Hentati, O., Abrantes, N., Caetano, A.L., Bouguerra, S., Gonçalves, F., Römbke, J., Pereira, R., 2015. Phosphogypsum as a soil fertilizer: ecotoxicity of amended soil and elutriates to bacteria, invertebrates, algae and plants. J. Hazard Mater. 294, 80–89.
- Khoo, K., Tan, X., Show, P., Pal, P., Juan, J., Ling, T., Ho, S.-H., Nguyen, T., 2020. Treatment for landfill leachate via physicochemical approaches: an overview. Chem. Biochem. Eng. Q. 34, 1–24.
- Macías, F., Cánovas, C.R., Cruz-Hernández, P., Carrero, S., Asta, M.P., Nieto, J.M., Pérez-López, R., 2017. An anomalous metal-rich phosphogypsum: characterization and classification according to international regulations. J. Hazard Mater. 331, 99–108.

- Meng, M., Liu, N., Jiang, P., 2016. Impacts of initial moisture content and consolidation character on leachate generation of wet phosphogypsum stack. Chin. J. Environ. Eng. 10, 2035–2040. Chinese Version.
- Mi, Z.K., Rao, X.S., Chu, X.Q., Cao, P., 2015. Physico-mechanical properties of deposition phosphogypsum. Yantu Gongcheng Xuebao/Chin. J. Geotech. Eng. 37, 470–478.
- Millán-Becerro, R., Pérez-López, R., Macías, F., Cánovas, C.R., 2020. Design and optimization of sustainable passive treatment systems for phosphogypsum leachates in an orphan disposal site. J. Environ. Manag. 275, 111251.
- Millán-Becerro, R., Pérez-López, R., Macías, F., Cánovas, C.R., Papaslioti, E.-M., Basallote, M.D., 2019. Assessment of metals mobility during the alkaline treatment of highly acid phosphogypsum leachates. Sci. Total Environ. 660, 395–405.
- Neukum, C., Morales Santos, A.G., Ronelngar, M., Bala, A., Vassolo, S., 2021. Modelling groundwater recharge, actual evaporation and transpiration in semi-arid sites of the Lake Chad Basin: the role of soil and vegetation on groundwater recharge. Hydrol. Earth Syst. Sci. Discuss. 1–29.
- Parreira, A., Kobayashi, A., Silvestre Jr., O., 2003. Influence of Portland cement type on unconfined compressive strength and linear expansion of cement-stabilized phosphogypsum. J. Environ. Eng. 129, 956–960.
- Pérez-López, R., Macías, F., Cánovas, C.R., Sarmiento, A.M., Pérez-Moreno, S.M., 2016. Pollutant flows from a phosphogypsum disposal area to an estuarine environment: an insight from geochemical signatures. Sci. Total Environ. 553, 42–51.
- Pianosi, F., Sarrazin, F., Wagener, T., 2015. A matlab toolbox for global sensitivity analysis. Environ. Model. Software 70, 80–85.
- Qian, X., Koerner, R.M., Gray, D.H., 2002. Geotechnical Aspects of Landfill Design and Construction. Prentice Hall, New Jersey, U.S.
- Schroeder, P.R., Dozier, T.S., Zappi, P.A., McEnroe, B.M., Sjostrom, J.W., Peyton, R.L., 1994. The Hydrologic Evaluation of Landfill Performance (HELP) Model: Engineering Documentation for Version 3.
- Show, P.L., Pal, P., Leong, H.Y., Juan, J.C., Ling, T.C., 2019. A review on the advanced leachate treatment technologies and their performance comparison: an opportunity to keep the environment safe. Environ. Monit. Assess. 191, 1–28.
- Silva, L.F.O., Oliveira, M.L.S., Crissien, T.J., Santosh, M., Bolivar, J., Shao, L., Dotto, G.L., Gasparotto, J., Schindler, M., 2022. A review on the environmental impact of phosphogypsum and potential health impacts through the release of nanoparticles. Chemosphere 286, 131513.
- Tayibi, H., Choura, M., López, F.A., Alguacil, F.J., López-Delgado, A., 2009. Environmental impact and management of phosphogypsum. J. Environ. Manag. 90, 2377–2386.
- Torres-Sanchez, R., Sanchez-Rodas, D., de la Campa, A.S., de la Rosa, J., 2020. Hydrogen fluoride concentrations in ambient air of an urban area based on the emissions of a major phosphogypsum deposit (SW, Europe). Sci. Total Environ. 714, 136891.
- Van Bavel, C., Hillel, D., 1976. Calculating potential and actual evaporation from a bare soil surface by simulation of concurrent flow of water and heat. Agric. Meteorol. 17, 453–476.
- Wali, A., Colinet, G., Ksibi, M., 2014. Speciation of heavy metals by modified BCR sequential extraction in soils contaminated by phosphogypsum in Sfax, Tunisia. Environ. Res. Eng. Manag./Aplinkos Tyrim. Inžinerija Vadyba 70, 14–25.
- Wissa, A.E., Fuleihan, N.F., 1993. Design and reclamation of phosphogypsum disposal sites. American Institute of Chemical Engineers AICHE Symp. Ser. 89, 149-149.
- Xu, J., Fan, L., Xie, Y., Wu, G., 2019. Recycling-equilibrium strategy for phosphogypsum pollution control in phosphate fertilizer plants. J. Clean. Prod. 215, 175–197.
- Xu, Q., Kim, H., Jain, P., Townsend, T.G., 2012. Hydrologic evaluation of landfill performance (HELP) modeling in bioreactor landfill design and permitting. J. Mater. Cycles Waste Manag. 14, 38–46.

Yang, J., Liu, W., Zhang, L., Xiao, B., 2009. Preparation of load-bearing building materials from autoclaved phosphogypsum. Construct. Build. Mater. 23, 687–693.

- Zhan, L.-T., Xu, H., Chen, Y.-M., Lan, J.-W., Lin, W.-A., Xu, X.-B., He, P.-J., 2017a. Biochemical, hydrological and mechanical behaviors of high food waste content MSW landfill: liquid-gas interactions observed from a large-scale experiment. Waste Manag. 68, 307–318.
- Zhan, L.-T., Xu, H., Chen, Y.-M., Lü, F., Lan, J.-W., Shao, L.-M., Lin, W.-A., He, P.-J., 2017b. Biochemical, hydrological and mechanical behaviors of high food waste content MSW landfill: preliminary findings from a large-scale experiment. Waste Manag. 63, 27–40.
- Zhang, C., Yang, C.-h., Yu, K.-J., Fu, S.-W., Chen, F., 2007. Study on physico-mechanical characteristics of phosphogypsum. Yan Tu Li Xue 28, 461–466.
- Zheng, B., Zhang, D., Liu, W., Yang, Y., Yang, H., 2019. Use of basalt fiber-reinforced tailings for improving the stability of tailings dam. Materials 12, 1306.

# Further reading

Chou, Y.-C., Brachman, R.W.I., Rowe, R.K., 2021. Leakage through a hole in a geomembrane beneath a fine-grained tailings. Can. Geotech. J. 59 (3), 372–383.

Zhou, H., Han, S., Liu, W., 2020. Evaluation of two generalized complementary functions for annual evaporation estimation on the Loess Plateau, China. J. Hydrol. 587, 124980.