



Self-sealing evaporation ponds for small inland desalination facilities and containment equivalence concepts in Texas

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ABSTRACT

Evaporation ponds are a low-maintenance option for disposing of desalination concentrate. Substantial savings can be achieved in Texas if exemptions are granted in the construction of pond liners. Currently approved liners include a ~0.9-m-thick layer of in situ or compacted clay (with hydraulic conductivity $<10^{-7}$ cm/s) or a geomembrane liner >30 mil (0.075 cm). An alternative liner may also be used if it can be demonstrated to achieve and maintain equivalent containment capabilities with the preapproved liners. We examine (1) the possibility of incorporating a low-permeability layer into the pond-liner system as a liner component or possibly as the liner itself as the pond water starts precipitating minerals, sealing any liner defect, and (2) the ability of the newly-formed minerals to, at minimum, plug liner defects. Assessment of previous laboratory experiments suggests that precipitation of a specific claylike mineral (sepiolite) could have many advantages. From geochemical calculations for assumed evaporation pond parameters, after 5 years of operation, an average precipitate thickness (mostly calcite and gypsum) is approximately 0.38 cm, containing about 7% sepiolite. Our analysis suggests that the precipitant, even with a conductivity $>1 \times 10^{-7}$ cm/s, could efficiently plug defects of the geomembrane, allowing a thinner geomembrane to be used. On the other hand, the modest thickness of precipitant suggests that, to achieve equivalent containment, the precipitated material needs to have a conductivity $\ll 1 \times 10^{-7}$ cm/s to impart the required properties to a scaled-down liner and to be successfully substituted in part or all of the clay liner. However, even if legal requirements are not fully met, self-sealing deposition could be advantageous in settings where an additional defense-in-depth layer is needed, such as areas with an underlying unconfined aquifer sensitive to contamination. In both cases (plugging defects or developing a blanket-like liner), cost remains an issue.

Keywords: Evaporation ponds; Sepiolite; Self-sealing mechanisms; Containment equivalence; Brackish water; Waivers

1. Introduction

This paper presents the results of a study funded by the Texas Water Development Board (TWDB) [1]. It was

undertaken to explore the conditions under which self-sealing evaporation ponds become financially attractive. Regulatory agencies are apparently favorable to such an approach [1]. Texas and other southwestern states in the US are facing population growth accompanied by a

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decreasing conventional water resource base. Inland desalination of brackish water (in most cases of salinity $<5,000$ mg/L) can bring an additional resource to the mix needed to meet this challenge. However, in many cases, disposal of desalination concentrate remains an environmental and cost issue. Disposal methods [2] include evaporation ponds, surface-water body (lake, river, ocean) or municipal sewer outfall, land application, deep-well injection into saline formations or oil and gas fields [3], and zero-liquid discharge. Reduction in pond costs could make evaporation ponds an attractive solution in small communities with needs of $<3,800$ m³/day (1 million gallons a day, MGD), especially in the semi-arid southwestern area of the US. The basis of the article is to examine whether natural clays, particularly sepiolite, a magnesium-rich clay-like mineral having the property of precipitating directly from solution, could (1) seal pond bottom defects without operator intervention and so provide further containment despite the defects or (2) act as a liner component or possibly as the liner itself by incorporating a low-permeability layer (precipitant) into the pond-liner system. Previous laboratory studies have suggested such possibilities.

Evaporation ponds rely on solar energy to reduce the volume of liquid waste by evaporating water. They operate best in climatic environments with limited rainfall and high evaporation rates. In Texas, net evaporation rates follow general weather patterns, and, except for a limited band along the Louisiana border, these rates are positive (Fig. 1). As evaporation proceeds, the remaining liquid becomes more and more concentrated, leading to precipitation of minerals at the bottom of the ponds. The nature of precipitating minerals is site-specific and a strong function of the outfall chemical composition. Evaporation ponds are typically designed to contain or at least limit leakage into the subsurface. In Texas, typical regulatory prescriptive requirements for evaporation ponds include (1) in situ clay, at least ~ 0.9 m (3 ft) thick with hydraulic conductivity of 10^{-7} cm/s or less; (2) compacted clay, at least ~ 0.9 m (3 ft) thick with hydraulic conductivity of 10^{-7} cm/s or less; or (3) geomembrane liner, at least 30 mil (~ 0.075 cm) thick with an underlying leak-detection system.

A self-sealing evaporation pond would allow cracks, holes, and other defects of the clay or geomembrane liner to seal quickly, with no local intervention of the operator through evaporation-induced precipitation of a sealing material. This self-sealing mechanism may make desalination facilities more affordable if it lowers costs associated with the installation and maintenance of pond liners. Cost can be reduced by decreasing the amount of compacted clay to ≤ 0.9 m (3 ft) or by eliminating the need for a leak-detection system beneath a geomembrane liner. This approach could also make all ponds more secure by

adding safeguard redundancy. According to Texas regulations, a waiver, that is, an exemption or softening of the rules, from prescriptive rules is possible when (1) neighboring shallow aquifer water quality will not be degraded by leakage from the pond (discharged water quality $>$ aquifer water quality), (2) a containment system that would be equivalent to prescriptive rule containment is suitable, or (3) the groundwater beneath the pond is monitored.

Because the success of a self-sealing pond relies greatly on the capacity of the pond water to precipitate the appropriate components, a large part of this paper discusses evaporation pond geochemistry. The study is three pronged: (1) sampling and analysis of actual evaporation ponds in Texas and review of natural systems to provide support to point 2; (2) desktop geochemical analysis providing the amount and nature of the material precipitating from solution as water evaporates from the pond by using a numerical geochemical model; and (3) integration of the geochemical results into an equivalent containment study leading to a high-level-cost/saving analysis. In addition, only field and laboratory experiments can provide actual hydraulic conductivity data needed to support the study. Because experiments were not performed in the course of the study, several publications have supplied the needed information instead.

2. Methodology

2.1. Field analyses

As of 2005, there were 10 public water supply (PWS) desalination facilities in Texas with design capacities ≥ 95 m³/d (0.025 MGD), whose main concentrate disposal mechanism was evaporation pond [4]. Currently in Texas no data contrasting feedwater or concentrate chemical composition are publicly available, although information about permeate composition is more readily available. In order to partly fill the data gap, we conducted a small field sampling program that included four facilities (Fig. 2) — all of which use reverse osmosis, as do the vast majority of Texas PWS desalination facilities. The Texas PWS facilities with evaporation ponds are small except for that of Abilene ($\sim 30,000$ m³/d, 8 MGD), Horizon Regional MUD ($\sim 6,100$ m³/d, 2.2 MGD), and Brady ($\sim 5,700$ m³/d, 1.5 MGD), which were all visited for this study. We took samples of feedwater, concentrate, and pond water, all of which were analyzed for major elements, and we sampled bottom sediments for X-ray analysis.

We complemented our field investigation of evaporation ponds by sampling sediments and standing water of some saline lakes of the Texas Panhandle.

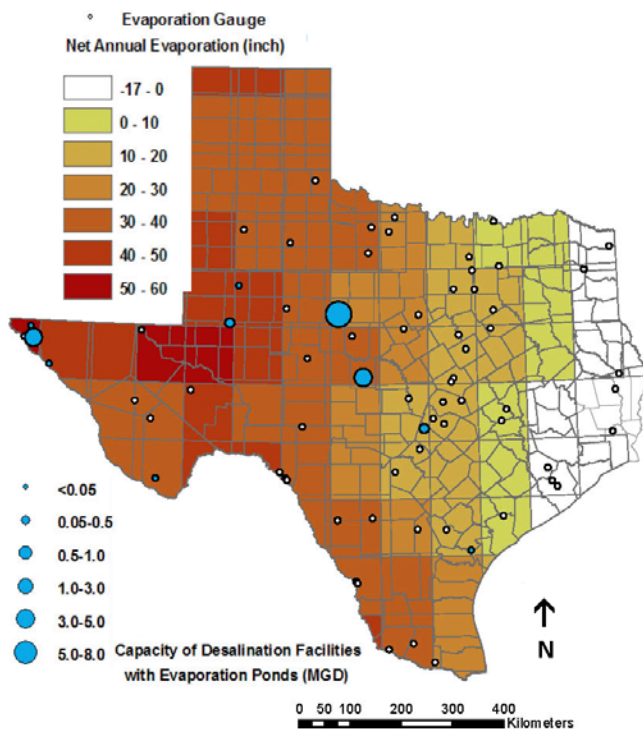


Fig. 1. Net average annual evaporation rates across Texas from a low-salinity water body. Net evaporation rates are high in the arid west of the state, ≥ 100 cm/y ($40''$ /y). Desalination facility capacity from [4]; annual precipitation and gross lake evaporation rate from TWDB website [5]; salinity correction factor of 0.9 is applied to gross lake evaporation rate to account for water salinity. (1 MGD = $3,785$ m³/d).

2.2. Geochemical modeling

To determine amount and nature of the precipitant, feedwater composition is needed. Brackish groundwater is available across the state, but brackish surface water is also an option in the northeast quarter of the state. We selected from the TWDB groundwater electronic database [5] all samples with a total dissolved solids (TDS) $>1,000$ and $<5,000$ mg/L, which were representative of possible candidate locations for desalination facilities and encompassing the salinity range of current plants. Only the most recent samples for each unique location with an electrical balance in the -5% – 5% range, with pH in the 5 – 9.5 range, and of appropriate reliability were retained. The number of database samples totaled 12,720, including surface water samples selected by following the same criteria. In addition, only those samples in areas with positive net annual evaporation rates were retained.

The samples were distributed among the surface water group and 19 groundwater groups, which were tailored specifically for this study and corresponded roughly to TWDB-defined aquifers [6]. Geochemical modeling was performed on only one sample in each group chosen as

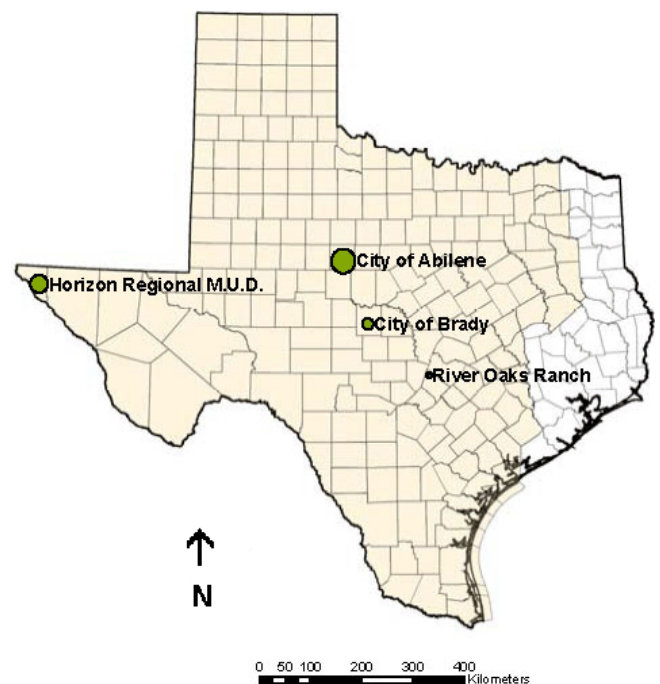


Fig. 2. Location of sampled evaporation ponds: River Oaks Ranch (Hays County, 530 m³/d design capacity), City of Brady (McCulloch County, $5,700$ m³/d, City of Abilene (Taylor County, $30,000$ m³/d, Horizon Regional MUD (El Paso County, $6,100$ m³/d). Gray area represents the counties where net evaporation is positive (salinity correction factor of 0.9 is applied to gross lake evaporation rate).

the “central” sample. It was defined as the sample with concentrations closest in some sense to the median concentration of each element for all samples of the group.

Whereas feedwater chemical composition is widely available, little public information is available about membrane concentrate composition. In this report, we followed the procedure presented in Nicot and Chowdhury [3] to compute the likely range of membrane concentrate composition. It was calculated simply by increasing all concentrations fourfold (recovery of 75%). In general, divalent ions are rejected at a higher rate than monovalent ions, but the error by assuming the same rejection rate decreases as the recovery increases. It follows that this assumption would be valid for the slightly brackish waters considered in this study. As described later, bicarbonate concentration requires a different treatment.

The US Geological Survey-developed code PHREEQC [7] was used in the modeling exercise. The increasing ionic strength of pond water as the pond matures requires the use of the Pitzer thermodynamic database [7]. Thermodynamic information for relevant mineral species not present in the Pitzer database was imported from the LLNL database [7], especially minerals with elements such as aluminum and/or silica in their structure. Such an

addition renders results of the study more quantitative than if only the Pitzer database had been used.

Numerical geochemical modeling mimics the operation of an evaporation pond, with balanced steady input and evaporation. Evaporation is modeled by retrieving water from the system, keeping all the dissolved solids in solution, and the evaporated mass is replaced by the exact same mass of concentrate, increasing, in effect, the dissolved solid loading of the system (see [1] for details). So that the likelihood of precipitation of self-sealing material and the amount thereof could be understood, several sets of geochemical calculations were conducted, with and without additives.

For reasons described later in the paper, we chose to investigate sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2(\text{OH}_2)_2 \cdot 4\text{H}_2\text{O}$), a magnesium-rich, mostly aluminum-free clay-like mineral. To help in sepiolite accumulation, precursor minerals can be injected [8] in the concentrate stream the same as any other additive, such as antiscalant or acid. Magnesium salt (MgCl_2 or $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and sodium metasilicate (Na_2SiO_3), both laboratory and industrial compounds, could be used (e.g., [9]).

As in all predictive geochemical simulations, the modeler has the difficult choice of deciding which minerals will be allowed to precipitate. This choice has a large impact on results and is guided by experience, conservatism relative to expected results, and consideration of analogs. Because of the focus on precipitation of sepiolite, there is a need to manage precipitation of other magnesium minerals during the numerical simulations. Magnesium-rich minerals relevant to this work can be divided into two groups: magnesium carbonates (hydrated forms that generally precipitate first) and magnesium-rich phyllosilicates/clays. Magnesium sulfates and chlorides are more soluble and require evaporation levels not reached in this work to precipitate. The latter group of minerals could use up magnesium before sepiolite had a chance to precipitate. Estimating neoformed clay mineralogy through geochemical modeling is notoriously difficult, and the approach taken in this work was to assume that mostly sepiolite clay would precipitate. It gives an upper bound on the amount of nonswelling clay that can precipitate. Minerals of the clay/phyllosilicate family allowed/not allowed to precipitate in some of the simulations were Ca-montmorillonite, celadonite, talc, and saponite—all individual representatives of different subfamilies.

Assumption of an open/closed system could also bring different sets of results. The system is obviously open for water, but gas-phase behavior is not as clear. Two cases were considered: (1) bicarbonate/ CO_2 being free to evolve with no interaction with the atmosphere (base case) and (2) bicarbonate concentration being controlled by atmospheric CO_2 concentration (380 ppm).

The following assumptions were also made (for details see [1]): (1) some thermodynamically stable minerals will not precipitate for kinetic reasons (e.g., dolomite- $\text{CaMg}(\text{CO}_3)_2$); (2) temperature is maintained at 25°C ; (3) pH is maintained at 8.5, the most favorable for sepiolite precipitation; (4) aluminum concentration needed for clay precipitation in some runs is controlled by diasporite (AlOOH), assumed to be windblown; (5) all minerals will precipitate at a saturation index of 0; (6) no silica is allowed to precipitate as quartz, low-temperature phases, or amorphous silica to favor clay precipitation; and (7) poorly crystalline sepiolite is assumed to precipitate in all runs as an acknowledgment of the impact of kinetics.

2.3. Containment equivalence and cost analysis

Whether the self-sealing approach works depends on the chemical nature of the precipitate and how the precipitate structures itself. Some precipitates (e.g., clays) may need less accumulation because of an intrinsically smaller permeability. Strictly speaking, to be efficient as a liner, a precipitate should not necessarily have a hydraulic conductivity $<1 \times 10^{-7} \text{ cm/s}$ but provide containment equivalence in the sense that total leakage through the system stays the same. Both clay and geomembrane liners are considered in the containment equivalence section. In a high-level cost analysis, we used a very general approach with data previously published [2,10].

3. Results

3.1. Review of analogs and experiments

General well-known rules can be drawn in the chemical evolution of an evaporation pond despite the complex chemical interactions and site specificity. Fairly well established precipitation sequences have been commonly observed in both man-made (membrane and thermal desalination) and natural systems. Major ions making up most groundwater—fresh or saline—are Ca^{+2} , Mg^{+2} , Na^+ , K^+ , SO_4^{-2} , HCO_3^- , and Cl^- , to which SiO_2 can be added as a major neutral molecule. They form the bulk of the minerals precipitating when the solution is progressively concentrated. As seen in the extensive geologic record, evaporation of seawater yields the following precipitation sequence of major minerals: calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)/anhydrite (CaSO_4), and halite (NaCl). Calcite precipitates right away, gypsum precipitates only after approximately 80% of seawater has been removed, and halite does so when ~90% has evaporated. The same is true for the saline lakes observed in Texas and elsewhere in the southwestern US where the first major minerals to precipitate are calcite and gypsum, sometimes accompanied by minor clays. Other relevant cations in

natural systems are potassium and magnesium. Potassium concentration is controlled mostly by interactions with clay minerals. At high ionic strength, not seen in this study, it will also precipitate in sylvite (KCl) and other evaporites.

Many saline lakes in the western US behave like natural evaporation ponds. The groundwater they receive naturally is equivalent to pond feedwater. Sepiolite has been observed ([11–13]) in lake sediments in eastern New Mexico and the Texas Panhandle. Our sampling of saline lake sediments failed to provide evidence of large-scale sepiolite precipitation but did show traces of the mineral [1]. Sediments are mostly detrital (abundant quartz and some illite, feldspars, kaolinite, and smectites), with a generally small fraction of chemical origin (calcite, gypsum, and, sometimes, minor sepiolite). It can be concluded that sepiolite does precipitate in natural conditions analogous to those of evaporation ponds and that it can be expected to precipitate in the ponds if environmental conditions are right.

No laboratory experiments were performed in the course of this study, but several researchers and technologists have performed tests and experiments on self-sealing materials. Donahe [14] and Brady [8] observed the precipitation of sepiolite gel by mixing sodium metasilicate and magnesium chloride. Others have observed that poorly crystallized sepiolite precipitates readily in alkaline solutions [9,15]. Precipitation rates seem fast [16] when adequate ions (Si and Mg) are present in sufficient concentration. Data [14] suggest that sepiolite was produced with an observable decrease in vertical permeability of the soil, although still not meeting regulatory requirements. Turner et al. [17] observed the precipitation of calcite and gypsum in laboratory experiments and during a pilot scale test in the El Paso, Texas, area. Hydraulic conductivity reduction was achieved but not to the extent desired. In another study, conductivity of a preparation containing 20% sepiolite was measured at values of $\sim 10^{-6}$ cm/s [18], that is, above the required threshold for a prescriptive liner but possibly sufficient to develop containment equivalence.

3.2. Insights from field analyses

Table 1 provides results from chemical analyses of the four sampled facilities. Their feedwater TDS concentration is consistent with that of inland Texas facilities and averages $\sim 1,800$ mg/L [4]. TDS of the concentrate in the pond can be expected to be three to four times that of the feedwater (at 75% recovery). On the other hand, the pond water TDS is low, barely twice that of the concentrate, which might be due to recent rain events (River Oaks Ranch and Abilene) or to limited evaporation because of constant leakage. Except that of River Oaks Ranch, all

other ponds were observed with little water in them, which might also be due to operations (e.g., Abilene also has the option of sending concentrate to the municipal sewer).

Bottom sediments (Table 2) show material similar to that of the saline lake-bottom sediments, but they are dominated by calcite and/or gypsum, with some wind-blown detrital minerals. The fact that reduced- or low- O_2 conditions have been observed in the sampled ponds suggests that exchange between the pond bottom, where mineral precipitation is most likely to take place, and the atmosphere is sometimes slow. Some ponds (e.g., Horizon MUD and Abilene) show abundant marshland vegetation, whose decay explains the low dissolved oxygen reading. Others (e.g., River Oaks Ranch and Brady) display slimy surfaces, suggesting abundant algal and microbial activity.

From these observations, it can be determined that actual evaporation ponds do not behave as simply as suggested by desktop studies, for example, pond TDS is very low in all cases, and that little sepiolite is present in pond sediments suggesting the need of additives to sustain its precipitation.

3.3. Geochemical calculations

A quick calculation can be done to estimate maximum amount of precipitates. The mass of precipitate on a unit surface area at time t is $C_{TDS} \times e \times t$; that is, with a feedwater concentration of 1,500 mg/L, concentrate TDS C_{TDS} is 6 kg/m³, and a net evaporation rate e of ~ 75 cm/y for 30 years, ~ 137 kg/m². If material density is $\sim 2,400$ kg/m³, it translates into a precipitant thickness of ~ 5.7 cm, or 8.2 cm if one assumes a porosity of 30%. This calculation is consistent with results presented next.

Out of the 20 defined groups, four stand out in their composition (Fig. 3): Capitan Reef, Bone Spring/Victorio Peak, Permian Evaporite, and Brazos River Alluvium. Central values of all other groups occupy a relatively compact area of the trilinear plot. They tend to plot toward the sodium and potassium apex, with calcium being generally second in molar concentration, and toward the chloride apex, with sulfate second in anion abundance. As representative examples, results for the Rio Grande Alluvium aquifer and the Capitan aquifer are given in more detail. A net average annual evaporation rate (Fig. 4) was computed for each of these water groups. It varies from <25 cm/y over the Brazos Alluvium aquifer to ~ 130 cm/y in the Pecos Valley aquifer and the Bolson aquifer of far west Texas. A weighted average of net evaporation rates for all samples is ~ 75 cm/y.

As a general rule, the following minerals precipitate during numerical simulations: calcite (carbonate with little solubility and a sink for calcium), gypsum (an additional

Table 1
Evaporation pond sampling results

Facility	Sampling location	Temp. (°C)	pH	SiO ₂ (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	TDS (mg/L)
ROR	Well water	NM	NM	12.3	318.1	227.4	77.8	23.7	67.3	1598.4	23.8	2,356
	Concentrate	NM	NM	34.7	1401.3	923.6	312.0	74.9	203.7	6832.0	14.2	9,799
	Pond sample 3	NM	NM	4.1	697.9	1662.1	615.3	147.6	441.9	9651.6	10.2	13,277
	Pond sample 4	NM	NM	4.1	695.4	1770.7	653.2	154.1	439.9	9509.9	10.3	13,240
	Pond sample 5	NM	NM	4.3	746.7	1782.7	661.3	156.9	441.5	9643.5	9.6	13,463
	Pond sample 6	NM	NM	4.9	754.7	1758.8	650.5	153.5	435.3	9547.7	9.5	13,317
Hor.	Well water	24.5	7.94	23.5	94.9	24.7	483.7	10.6	419.0	595.3	76.4	1,736
MUD	Well water	25.3	7.94	31.6	98.0	22.3	493.1	10.6	415.0	593.1	72.3	1,775
	Concentrate	24.3	8.03	70.3	256.5	63.5	1259.7	28.4	997.2	1519.5	35.1	4,230
	Concentrate	24.7	7.96	66.3	189.7	47.2	928.3	22.2	958.9	1461.2	52.0	3,731
	Concentrate	26.0	7.89	106.8	301.5	75.0	1436.3	35.1	1485.9	2344.5	46.0	5,831
	Pond sample 1	21.4	8.57	65.7	257.0	62.1	1280.2	32.1	1169.0	1753.8	12.0	4,664
	Pond sample 2	22.4	8.53	66.5	322.8	81.6	1603.9	42.1	1023.3	1517.6	10.2	4,668
Abilene	Pond sample 3	21.3	8.65	47.8	319.3	80.9	1587.0	44.4	1376.6	1990.7	8.9	5,504
	Well water	23.9	7.88	5.2	82.8	60.6	192.6	10.9	381.9	311.1	84.4	1,130
	Concentrate	24.5	7.36	16.0	311.7	229.8	712.0	39.1	1232.2	1098.1	122.9	3,772
	Pond sample 2	20.3	8.80	2.8	0.0	48.7	1762.2	28.6	2717.3	2127.2	0.0	3,683
	Pond sample 3	20.8	8.41	0.2	278.4	318.4	1843.6	24.5	2743.6	2125.3	8.5	7,318
	Pond sample 4	20.1	8.31	0.7	292.3	328.0	1895.0	23.2	1785.0	1419.7	18.0	7,441
Brady ^a	Well water	25.9	8.40	10.8	44.5	47.6	315.1	17.4	590.1	139.0	42.5	1,245
	Concentrate	24.4	8.32	26.6	114.5	130.0	855.4	48.0	1596.9	364.6	29.9	3,180
	Pond sample	27.5	8.68	12.4	73.8	118.4	810.8	42.5	1641.6	375.3	19.0	3,108

^aConcentrate obtained at the Brady facility does not represent the ultimate concentrate but its composition after one pass.

Notes: Conductivity, temperature, dissolved oxygen, and pH were collected directly in the field using a Quanta model from Hydrolab Corp. Anion analyses were performed at the BEG using ion chromatography. Cation analyses were performed by an external laboratory using the ICP method. Silica analyses were performed at the BEG on a LED photometer using a Vacu-vials[®] kit for silica. NM= not measured; italic (and blue) cells contain data not provided in the source but calculated to approximately match TDS and electrical balance—Feedwater K computed from concentrate K by assuming average concentrate/feed ratio; alkalinity not measured in the field but bicarbonate computed with PHREEQC assuming equilibrium with calcite.

Table 2
Sample pond characteristics

Facility	Design capacity m ³ /d (MGD)	Feedwater source	Nature of pond bottom	Facility start-up year	Geochemical water group	Bottom sediments	Crust/ Efflorescence
River Oaks Ranch	530 (0.14)	Trinity aquifer	Geomembrane liner	1987	Cretaceous limestone	Mostly gypsum with some quartz	Gypsum and some calcite
City of Brady	5,700 (1.5)	Brady reservoir	Local clay/silt material, no liner (exemption under the water quality waiver)	2005	Surface water	Mostly calcite	
Horizon Regional MUD	6,100 (2.2)	Rio Grande alluvium aquifer	Constructed clay liner (mixture of local clay and bentonite)	2001	Rio Grande alluvium	Calcite with some quartz	Gypsum and quartz
City of Abilene	30,000 (8)	Lake Ivie	In situ clay liner (compacted local clay)	2004	Surface water	Quartz with some calcite	

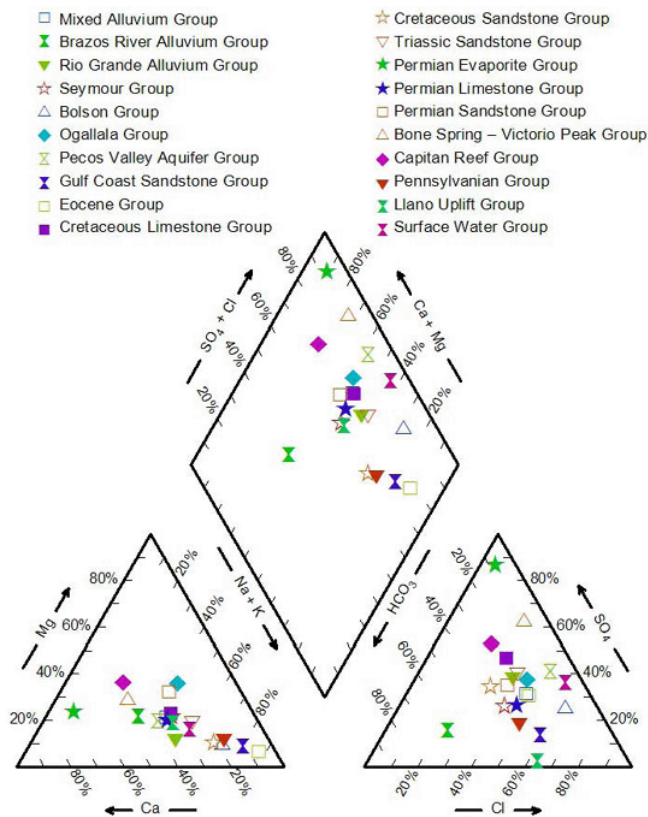


Fig. 3. Piper plot of central values of all 20 water groups. Most groups tend toward a sodium-mixed anion composition. Permian Evaporite water shows a dominant calcium sulfate water, whereas Capitan Reef and Bone Spring/Victorio Peak waters also tend to a less-dominant calcium sulfate composition. Brazos River alluvium has a strong bicarbonate imprint and tends toward a calcium carbonate water type.

sink for calcium), a soluble magnesium carbonate, and a clay or claylike mineral. Calcite is fully or partly replaced by gypsum when sulfate concentration is high enough. The specific magnesium carbonate (nesquehonite, huntite, syngenite) is sensitive to the composition of the aqueous phase. It was verified, however, that some kind of magnesium precipitation occurs independently of the species specified in geochemical simulations and in molar amounts sensibly equivalent. The nature of the clay depends on aluminum availability. In sensitivity runs, we assumed that a magnesium member of clay groups known to precipitate in saline lakes was allowed to precipitate along with sepiolite. In the presence of aluminum, celadonite or Ca-saponite generally precipitates instead of sepiolite. In contrast, sepiolite precipitates preferentially to talc and kaolinite and often Ca-montmorillonite.

Base-case accumulations were computed with no clay minerals other than sepiolite allowed to precipitate, a fixed pH of 8.5, and CO_2 partial pressure free to drift. These conditions maximize sepiolite precipitation, and

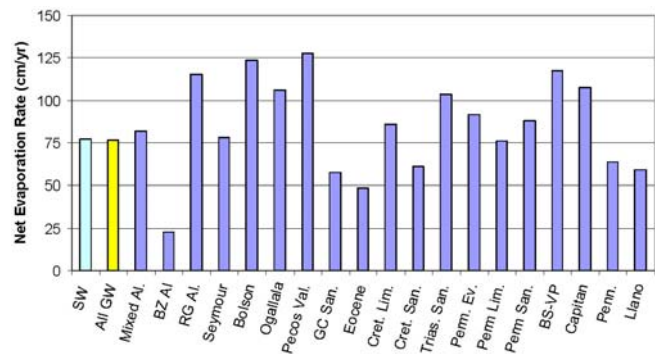


Fig. 4. Net average annual evaporation rate for each water sampling group. Evaporation rate assumed to be 90% of gross lake evaporation rate. Names represent logical abbreviations for the groups given in Fig. 3.

results represent an upper bound of the amount of sepiolite that could precipitate. We assumed a pond depth of either 7.5 or 30 cm (3" or 12"), although this parameter had little impact on accumulation results. For the purpose of comparing results from different water groups, durations of 5 and 30 years after facility opening were examined; 30 years represents a reasonable life span for a pond, and 5 years corresponds to a time interval at which benefits of self sealing should have occurred. At 5 years, with no additives, the average amount of precipitate at the bottom of a pond is 0.38 cm, with a sepiolite volume fraction of 7% (Figs. 5, 6, and 9). The average hides large discrepancies across the state. Bone Spring/Victorio Peak brackish water, as well as Permian Evaporite groups, has the highest accumulation (1.8–2 cm) after 5 years, but a small sepiolite fraction. This result is partly due to high feedwater TDS and, to a lesser degree, to their high local evaporation rates. At early times, higher sepiolite fraction corresponds to smaller accumulation thickness because sepiolite tends to precipitate early. Relative accumulation after 30 years parallels that of 5 years. Average accumulation depth is ~2.5 cm, with a sepiolite fraction of ~6%. Largest accumulations are once again produced by Bone Spring/Victorio Peak brackish water and Permian Evaporite groups (14 and 12 cm, respectively), still with little sepiolite. These accumulation thickness values do not account for porosity.

A set of runs with the addition of a large amount of sepiolite precursor (0.01 mol/L of a blend of MgCl_2 and Na_2SiO_3 in 2:3 proportions, which translates into an approximate doubling of the concentrate TDS) was performed, with clear improvement in accumulation thickness and sepiolite fraction (Figs. 7 and 8). This amount of sepiolite precursors corresponds to an areal loading of 21 kg/m² after 5 years and 127 kg/m² over 30 years (84 kg/m² of sodium metasilicate). Donahe [14] noted in his laboratory experiments that at the application

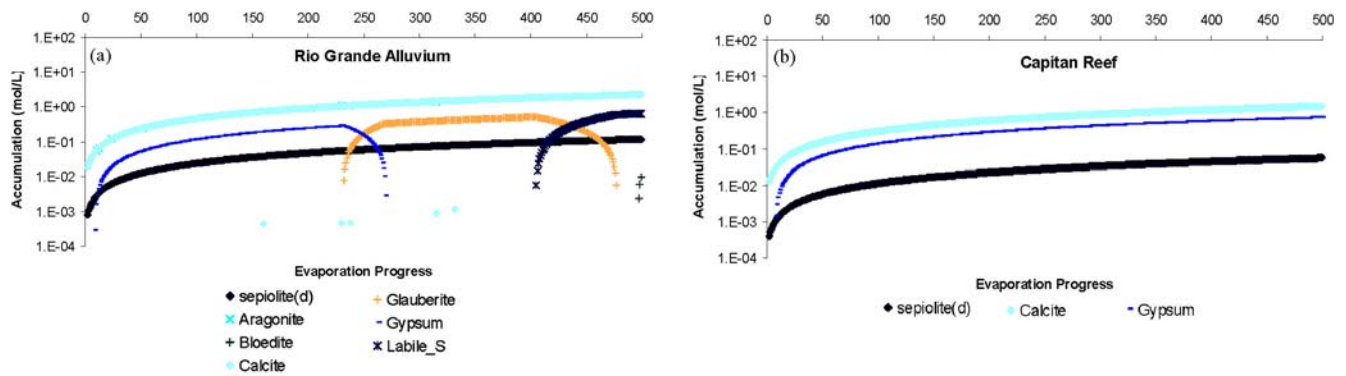


Fig. 5. Mineral suite and molar accumulation as a function of evaporation progress in nonengineered ("natural") conditions for Rio Grande aquifer (a) and Capitan Reef aquifer (b) (aragonite: CaCO_3 ; bloedite: $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$; Glauberite: $\text{Na}_2\text{Ca}(\text{SO}_4)_2$; labile_S: $\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$).

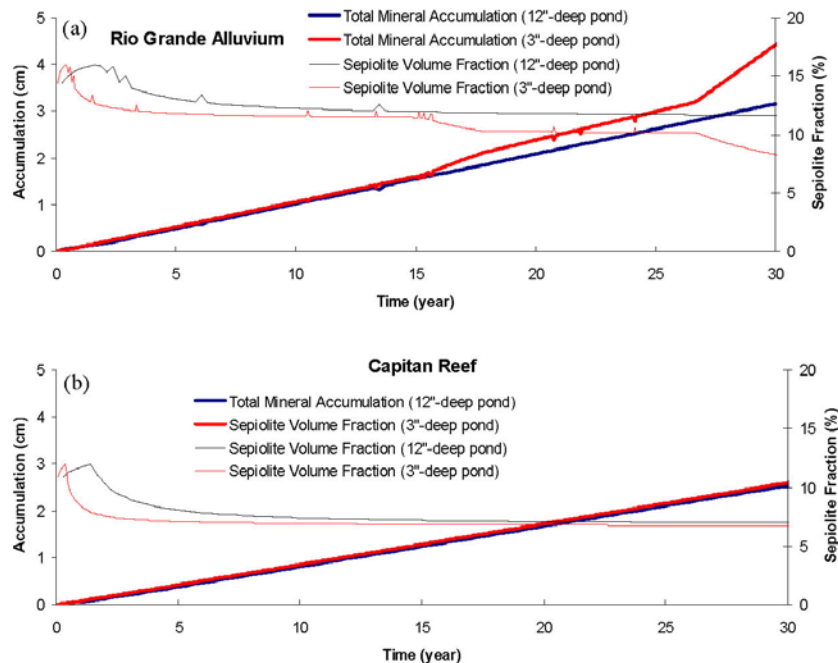


Fig. 6. Total mineral accumulation (assuming no porosity) for different pond depth (3" and 12" [~ 7.5 and 30.5 cm]) in non-engineered ("natural") conditions for Rio Grande aquifer (a) and Capitan Reef aquifer (b).

rate of 8 to 10 kg/m² of sodium silicate, that is, $\sim 10\%$ of the maximum rate used in the simulations, the self-forming liner is capable of supplying, on average, an added resistance to the soil equivalent to ~ 15 cm ($\frac{1}{2}$ ft) of native soil.

To conclude, the most volumetrically abundant minerals to precipitate are calcite, gypsum, and, if engineered correctly, sepiolite. The locus of precipitation is not an output of the geochemical modeling, but precipitation is likely to initiate on the geomembrane liner or within the first few millimeters of the clay liner, at least initially. Nevertheless, the amount of precipitated material remains low, especially early in the life of the pond and, despite considerable geographic variability, typically only a frac-

tion of a centimeter. Addition of chemical additives to the concentrate stream does help in producing a thicker accumulation in proportions commensurate with the added amount.

4. Discussion and cost analysis

Self-sealing properties can be imparted to a potentially defective liner in two ways. Dissolved ions will provide material to grow crack-plugging material identical to that of the crack walls, using the crack walls themselves as physical support (in the case of clay liners). However, it is more likely and applicable for both geomembrane and clay liners that the precipitate will passively plug the

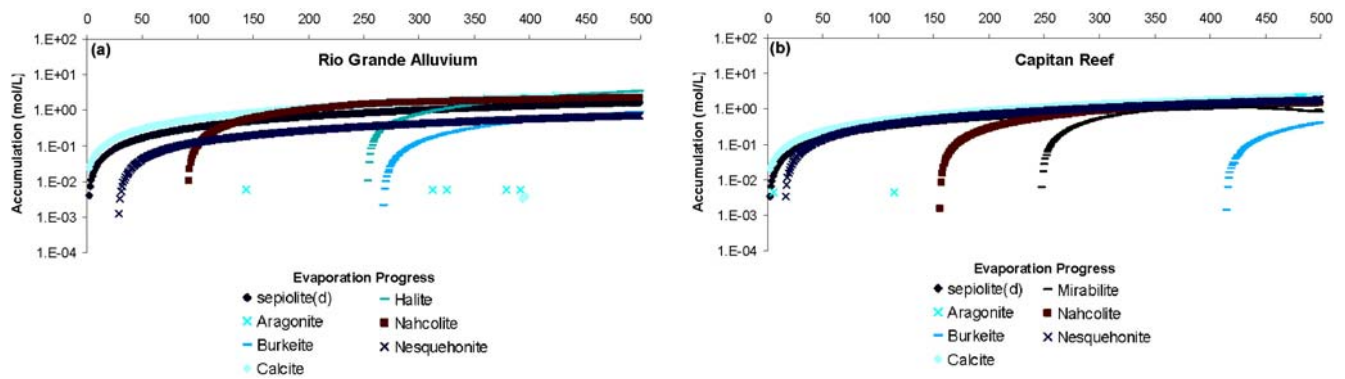


Fig. 7. Mineral suite and molar accumulation as a function of evaporation progress in engineered conditions (addition of 0.01 mol of sepiolite precursor to 1 L of concentrate) for Rio Grande aquifer (a) and Capitan Reef aquifer (b) (aragonite: CaCO_3 ; burkeite: $\text{Na}_6\text{CO}_3(\text{SO}_4)_2$; mirabilite: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; nahcolite: NaHCO_3 ; nesquehonite: $\text{Mg}(\text{HCO}_3)\text{OH} \cdot 2\text{H}_2\text{O}$).

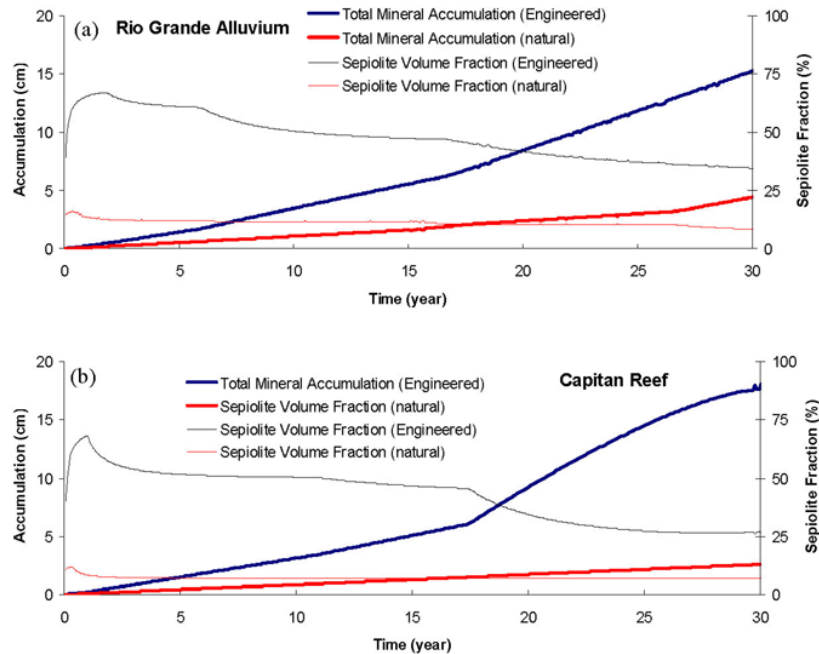


Fig. 8. Comparison of total mineral accumulation (assuming no porosity) in nonengineered (“natural”) and engineered (addition of sepiolite precursor) systems for Rio Grande aquifer (a) and Capitan Reef aquifer (b).

opening regardless of the chemical nature of the opening walls. Modified from Turner et al. [17], we categorized several sealing mechanisms by direct precipitation: (1) deposition of a well-individualized layer on top of the pond bottom; it grows by settling of particles generated in the water; (2) clogging of the pores and openings at the top of pond bottom; this is a variation of the previous case, in which reactions still occur in the main water body; (3) precipitation occurring in the soil pore space, resulting in grain growth and lowering of conductivity.

4.1. Equivalence to clay liner

As authorized by the Texas regulations, some alternate material/process is said to be hydraulically equivalent to

a clay liner if water leakage is not greater than that it would be with a clay liner. This section investigates the properties the precipitate must acquire to satisfy clay liner equivalence. In Texas, the prescriptive clay liner must be at least ~ 0.9 m (3 ft) thick, with a maximum hydraulic conductivity of 1×10^{-7} cm/s. The leakage rate through the saturated soil liner can be calculated using Darcy's equation, $Q/A = ki$, where Q is the leakage rate per pond area A , k is the hydraulic conductivity of the clay liner, and i is the hydraulic gradient defined by $i = (h + t)/t$, where h is the average head of liquid in pond and t is thickness of clay liner (Fig. 10). For values of $k = 1 \times 10^{-7}$ cm/s, $h = 2.8$ cm, and $t = \sim 0.9$ m (3 ft), $i \sim 1$ because h is small relative to t , and $Q/A = ki = 8.6 \times 10^{-3}$ cm/d or ~ 3.2 cm/y. The parameter h represents the average pond depth over the

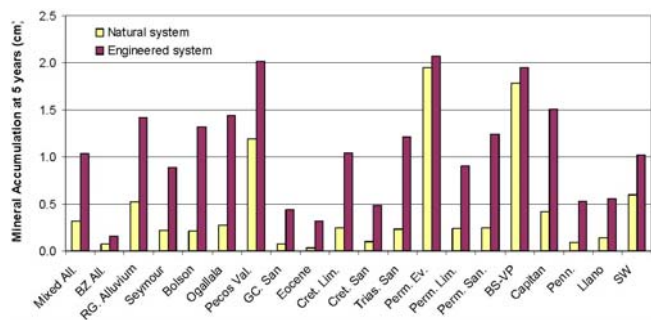


Fig. 9. Comparison of total mineral accumulation at 5 years for nonengineered ("natural") and engineered (addition of sepiolite precursor) systems. Accumulation thickness does not account for porosity.

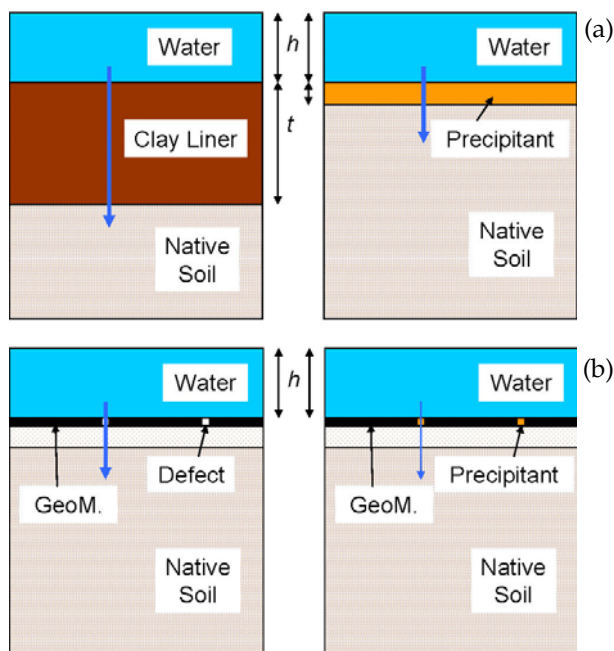


Fig. 10. Containment equivalence (right-hand side) of a prescriptive clay (a) and geomembrane (b) liner.

four sampled facilities but calculated at average conditions.

The precipitant generated in evaporation ponds may be hydraulically equivalent to a clay liner if the thin precipitant layer can limit leakage to 3.2 cm/y. Considering that the average accumulation depth of precipitant generated in the evaporation ponds was calculated to be about 0.38 cm after 5 years of pond operation, the effective hydraulic conductivity of this layer at 5 years would have to be $<1 \times 10^{-8}$ cm/s to provide equivalent containment capability; and even lower to meet the requirement at earlier time. It will be difficult for sepiolite, let alone calcite or gypsum, to strictly meet this hydraulic conductivity criterion for clay liner equivalence. Even if the thickness of

the precipitant layer is increased by chemical amendment of the outfall waters, thereby increasing the thickness of the layer to about 1 cm, the effective hydraulic conductivity of this layer at 5 years would have to be $<2 \times 10^{-8}$ cm/s. If the average pond depth is much higher, e.g., on the order of 30 cm, as is permissible in many cases, the equivalent containment capability must also be higher because of the increased head ($i = 1.33$). In this case, the leakage rate with the prescriptive liner is still 8.6×10^{-3} cm/d, whereas the effective hydraulic conductivity of the precipitant layer would be $<1 \times 10^{-9}$ cm/s.

In the above calculations, it is assumed that the hydraulic conductivity of the clay liner will be no greater than 1×10^{-7} cm/s. In reality, a clayey material exposed to wetting and drying cycles has the potential of developing desiccation cracks. Because of this macrostructure imposed by these cracks, hydraulic conductivity of exposed clay liners has been measured at two or more orders of magnitude higher than that of clay liners prior to exposure. Considering that equilibrium hydraulic conductivity of the exposed clay liner may be on the order of 1×10^{-5} cm/s (despite being $<1 \times 10^{-7}$ cm/s at end of construction), effective hydraulic conductivity of a precipitant layer at 5 years would have to be $<1 \times 10^{-6}$ cm/s to provide equivalent containment capability. This value may be achievable for evaporation ponds in Texas. In conclusion, self-sealing processes could help in mitigating clay liner aging. At a minimum, the precipitant from evaporation ponds can fill cracks that develop in exposed clay liners. As the clay liner ages and develops more and deeper cracks, the average precipitate thickness increases as well possibly balancing the negative consequences of liner aging.

4.2. Equivalence to geomembrane liner with a leak-detection system or groundwater monitoring system

Geomembrane liners are also acceptable material to line bottom and sides of evaporation ponds. The prescriptive geomembrane liner is at least 30 mil thick (~ 0.075 cm) (twice as thick if a high-density polyethylene geomembrane is used). Unlike clay liners, when a geomembrane is selected as a pond liner, the Texas environmental agency requires that the containment capability of the geomembrane liner be monitored by a leak-detection system or groundwater monitoring system. We next compute typical leakage rate through average defects in geomembrane liners that are inflicted during installation or operation (Fig. 10). Flow through defects is the primary mechanism for leakage through a geomembrane (rather than permeation through geomembrane structure). Leakage through a hole in a geomembrane overlain and underlain by relatively high permeability material can be evaluated using Bernoulli's equation [19]:

$$Q = 0.6a(2gh)^{0.5}$$

where Q is leakage rate through one geomembrane hole (m^3/s), a is the area of the circular hole (m^2), g is the acceleration of gravity (m/s^2), and h is the hydraulic head on top of the geomembrane liner (m). For typical values of 0.5 to 1 geomembrane holes per $1,000 \text{ m}^2$, $a = 9.5 \times 10^{-5} \text{ m}^2$ (corresponding to a hole diameter of $d = 1.1 \text{ cm}$), $g = 9.81 \text{ m}/\text{s}^2$, and $h = 2.8 \text{ cm}$, the calculated leakage rates range from 66 to $132 \text{ cm}/\text{y}$. If pond-water depth is higher, the leakage rate is higher too (217 to $435 \text{ cm}/\text{y}$, with a water depth of 30 cm).

Flow through a geomembrane hole can be impeded if the hole is overlain or underlain by a relatively low permeability material, that is, either a composite geomembrane liner (that goes beyond requirements) or a prescriptive geomembrane liner and a precipitant layer. Assuming good contact between the geomembrane and the overlying precipitant, leakage through a geomembrane hole of a precipitant/geomembrane or composite geomembrane liner can be calculated using an equation developed by Giroud [20]:

$$Q = 0.204 \left[1 + 0.1(h/t)^{0.95} \right] d^{0.2} h^{0.9} k^{0.74}$$

where Q is leakage rate through one geomembrane hole (m^3/s), h is the hydraulic head on top of the composite liner (m), t is the thickness of the precipitant component of the composite liner (m), d is the diameter of the circular hole (m), and k is the hydraulic conductivity of the precipitant component of the composite liner (m/s). This equation is not dimensionally homogeneous and must be used with the specified units. The following input parameters were used in the analysis: $h = 2.8 \text{ cm}$, $t = 0.38 \text{ cm}$, $d = 1.1 \text{ cm}$, $k = 1 \times 10^{-6}$ to $1 \times 10^{-4} \text{ cm}/\text{s}$, and 0.5 to 1

geomembrane hole per $1,000 \text{ m}^2$. With these input parameters, calculated leakage rates range from 0.01 to $0.62 \text{ cm}/\text{y}$ (0.0052 and $0.156 \text{ cm}/\text{hole}/\text{y}$ for $k = 1 \times 10^{-6}$ and $1 \times 10^{-4} \text{ cm}/\text{s}$, respectively). These rates are low and significantly lower than leakage through the prescriptive clay liner ($3.2 \text{ cm}/\text{y}$) or the prescriptive geomembrane liner overlain and underlain by relatively high permeability material. However, for a water depth increased to $\sim 30 \text{ cm}$, calculated leakage becomes 0.19 and $5.8 \text{ cm}/\text{hole}/\text{y}$, respectively.

4.3. Conclusions on containment equivalence

As discussed in Section 4.1, a thin precipitant by itself (category (1) modified from Turner et al. [17]) is unlikely to substitute for or be equivalent to a clay liner: it may, however, help in allowing a facility to use a reduced clay liner thickness rather than the prescriptive thickness of $\sim 0.9 \text{ m}$ (3 ft) (Table 3). In the case of a geomembrane liner (Section 4.2), the precipitated material could have a large impact in reducing leakage through defects (category (2) modified from Turner et al. [17]), even if its hydraulic conductivity is above that required for a clay liner. It can be seen that a single $\sim 1\text{-cm}$ -diameter hole in a geomembrane will generate a much higher overall leakage rate than that of a prescriptive clay liner. On the other hand, a defective prescriptive geomembrane liner acting as a composite geomembrane liner, thanks to a layer of precipitant, could behave much better than a prescriptive clay liner.

4.4. Cost analysis

This section analyzes the cost savings owing to the presence of a working self-sealing mechanism relative to a prescriptive liner. The general capital cost of an evapo-

Table 3
Containment equivalence summary

Equivalent containment type	Annual pond leakage rate if minimum pond depth (i.e., 2.8 cm)	Annual pond leakage rate if maximum allowed pond depth (i.e., 0.3 m)
	Rate as computed from rules must be $< 3.2 \text{ cm}/\text{y}$, that is, a leakage rate $< 32 \text{ m}^3/\text{y}/1,000 \text{ m}^2$	
Thin layer of precipitant is equivalent to clay liner	Needs a single precipitant layer with $k < 1 \times 10^{-8} \text{ cm}/\text{s}$ to meet leakage rates derived from rules	Needs a single precipitant layer with $k < 1 \times 10^{-9} \text{ cm}/\text{s}$ to meet leakage rates derived from rules
Prescriptive geomembrane liner with three holes per $4,000 \text{ m}^2$; no precipitant, this is a defective liner	Rate is $99 \text{ cm}/\text{y}$; that is, a leakage rate of $\sim 1,000 \text{ m}^3/\text{y}/1,000 \text{ m}^2$	Rate is $327 \text{ cm}/\text{y}$; that is, a leakage rate of $\sim 3,270 \text{ m}^3/\text{y}/1,000 \text{ m}^2$
1 cm of precipitant with $k = 1 \times 10^{-6}$ to $1 \times 10^{-4} \text{ cm}/\text{s}$ and geomembrane liner and with three holes per $4,000 \text{ m}^2$	Rate is 0.016 to $0.47 \text{ cm}/\text{y}$, that is, a leakage rate of ~ 0.2 to $4.7 \text{ m}^3/\text{y}/1,000 \text{ m}^2$	Rate is 0.57 to $17.2 \text{ cm}/\text{y}$, that is, a leakage rate of ~ 5.7 to $172 \text{ m}^3/\text{y}/1,000 \text{ m}^2$

ration pond is mostly a function of its size (area and depth). Pond footprints vary as a function of net evaporation rate and expected inflow. Major contributing costs are land, earthwork, lining, possible monitoring-system installation, and miscellaneous costs (access roads, fences, etc). Although cost of an evaporation pond is highly site specific, the differences between a general and a self-sealing evaporation pond reside mainly in the chemical nature of pond inflow including additives. Capital (that is, construction) costs could be reduced if some requirements in the facility infrastructure were waived. In that case, the difference in capital cost between using prescriptive liner technology and using an alter-native liner that incorporates self-sealing technology can be significant and balance the additional operation costs. Assuming that the self-sealing mechanism works, examples of such capital cost-saving measures include thinner geomembrane, no leak-detection system or groundwater monitoring system if a geomembrane is used, and two or three clay lifts (23 cm [9"] thick each) instead of the four lifts (that is, ~0.9 m [3 ft]) generally required for constructed clay liners.

Most operational costs for conventional and self-sealing ponds are essentially the same. However, cost of additives could be prohibitive. Cost of magnesium chloride is in the \$0.031 to 0.042/mol-Mg range [21], not including transport costs. An approximate cost of sodium metasilicate is \$0.40/mol Si. Each mole of sepiolite contains three moles of Si and two moles of Mg (~\$1.30/mol). It follows that engineering significant precipitation with additives could come at the prohibitive cost of ~\$4,300/1,000 m³ of permeate if the high seeding rate of 0.01 mol/L of concentrate is used. This cost approximately translates into an annual cost of sepiolite precursors of ~\$10/m² or ~\$300/m² over 30 years (assuming the cited cost of additives).

Relative to capital costs, land and earthwork costs are not significantly different for conventional or self-sealing ponds. Most gain can be made by doing away completely or partly with liners and/or leak-detection systems. According to generic information provided [2,10], costs of prescriptive clay or geomembrane liners are approximately equivalent in 2007. Estimated costs to construct the prescriptive liners are \$12/m² for a ~0.9-m-thick (3-ft) clay liner, and \$11.5/m² for a 30-mil-thick (~0.075-cm) geomembrane liner with geocomposite leak detection system. After adding other costs (land clearing, excavation, construction, etc.), the approximate total capital cost applicable to both liner types is \$13/m². Liner construction costs could be reduced for self-sealing ponds if certain regulatory requirements for liners were waived. Examples of such waivers are:

- use of a 0.6-m (2-ft) thick clay liner rather than a ~0.9-m-thick (3-ft) clay liner, which results in an estimated savings of 30%;

- use of a geomembrane liner with a simple leak detection system, which results in an estimated savings of 45%;
- use of a geomembrane liner without a leak-detection system, which results in an estimated savings of 60%;
- use of a 40-mil-thick (~0.1-cm) HDPE geomembrane rather than a 60-mil-thick (~0.15-cm) HDPE geomembrane, which results in an estimated savings of 17%; and
- use of an excavation utilizing the natural soil as a liner, with no other work required, results in savings of approximately 90% of the capital cost of a prescriptive liner.

Comparing incremental costs or savings generated by a self-sealing pond leads to contrast a maximum incremental saving of 17 to 90% of \$13/m² of capital cost to a maximum incremental cost of \$300/m² of operating cost. Engaging in such activity would make sense only at an additive loading rate of about 5% (0.0005 mol of sepiolite per liter of concentrate) of the maximum considered in Section 3.3 and only if the maximum savings of 90% of capital cost is considered.. Ability to use cheaper additives would obviously make the self-sealing option more attractive.

5. Conclusions

Currently, Texas preapproved pond liners include a ~0.9-m-thick (3-ft) layer of in situ clay or compacted clay or a geomembrane liner of 30 mil (~0.075 cm) having leak-detection monitoring. Alternative liners may also be approved if they can be demonstrated to achieve and maintain equivalent containment within the prescriptive liners. The geochemical analysis performed in this work suggests that at most a few centimeters (but typically <1 cm) of material precipitates at the bottom of the pond after 5 years of operation. Simple engineering of the system may control the nature of the precipitate and increase its amount (e.g., sepiolite) with the caveat that actual ponds do not seem to show much precipitation. This study did not perform hydraulic conductivity analyses, but other investigators have been unable at this point to demonstrate that the precipitant can achieve the prescribed maximum conductivity value of 10⁻⁷ cm/s.

Technical feasibility is closely associated with cost. The challenge is to make self-sealing technology cheaper than the simple, robust, existing technology. The evaporation pond coupled with a generic ~3,800-m³/d (1 MGD) desalination facility has an average surface area of approximately 500,000 m² (~125 acres). This preliminary stage of the research underlines the fact that a cost-effective self-sealing process cannot be implemented right away at any evaporation pond. The cost of the additives is currently

prohibitive. In addition, the amount of material that can be engineered to precipitate is small and of uncertain, but too high hydraulic properties.

The most practical way to make use of self-sealing properties is to exercise the option of demonstrating that the alternative liner will achieve equivalent containment. The greatest savings seems to be associated with obtaining a waiver for leak detection/groundwater monitoring systems that generally accompany a geomembrane liner. Our analysis suggests that the precipitant, even with a hydraulic conductivity $>1 \times 10^{-7}$ cm/s, could efficiently plug holes and defects of the geomembrane. This plugging ability, however, needs to be confirmed by experiments and pilot tests. The other option, applicable to clay liners, of equivalent containment by sheer accumulation of the precipitated material at the bottom of the pond is currently out of reach. The modest thickness of at most a few centimeters of precipitant after a few years of operation suggests that the precipitated material needs to have a hydraulic conductivity much lower than 1×10^{-7} cm/s to impart required properties to a scaled-down liner and be substituted successfully for part or all of the clay liner.

Nevertheless, an immediate benefit of self-sealing properties could be increasing confidence in permitting an evaporation pond constructed to municipal wastewater standards and locating it in an environmentally sensitive area (such as above a shallow groundwater source of potable water). However, self-sealing technology does not seem able to create the sought-after repair effect at a cost smaller than traditional techniques in these sensitive areas. At the opposite end of the environmental spectrum, if the effluent is nonhazardous and local groundwater quality poor, a self-forming single liner may be appropriately constructed by, for example, forcing precipitation of sepiolite through an initially high loading of sepiolite precursors onto a natural clayey or silty soil.

Possible items for future studies include (1) impact of uneven additive loadings through time, for example, initial large loading to immediately reach the required equivalence conditions followed by smaller loadings, (2) investigation of minerals other than sepiolite—specifically the most abundant minerals, calcite and gypsum, whose grain size can be engineered through additives (e.g., [14]). In particular, investigation on how to precipitate calcite in particles as small as possible to reduce porosity and permeability of a clay liner; (3) study of the impact of biomass, both at the bottom of the pond, where reducing conditions may exist, and at the surface, where microorganisms such as diatoms may mobilize most of the silica. Evaporation ponds do not seem to reach salinity levels at which life is not sustainable. Such microorganisms may also mediate the precipitation of useful minerals.

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