



GHGT-12

# The CO<sub>2</sub>-PENS Water Treatment Model: evaluation of cost profiles and importance scenarios for brackish water extracted during carbon storage.

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## Abstract

Extraction of in-situ water is one of the options for minimizing the impact of large-scale CO<sub>2</sub> injection in saline aquifers or during enhanced oil recovery (EOR). The amount of water to be produced could be significant depending on in-situ conditions and injection parameters. Evaluating the costs of treatment is complex, as the quality of the water may vary considerably from treatments based on well-known seawater chemistry, including reverse osmosis. We evaluated a brackish-salinity water to be extracted from a future CO<sub>2</sub> injection and storage location in eastern China for prototype treatment costs for both cooling water and boiler water final treatment goals. Costs for treatment of the water, excluding costs for organic pretreatment, were within the range of previously analyzed costs for higher-salinity waters (US\$1.53-6.20) but are likely to be lower when economies of scale are included for a full-scale, higher volume treatment facility. Importance analysis lends insight into process factors that may not contribute the highest unit costs to treatment but on whole are very important to total system costs. We found that the acid rate for pretreatment, zero-liquid discharge disposal, feed water temperature, and water transportation costs, were the most important factors within total system costs for this analysis.

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*Keywords:* extracted water , carbon storage, desalination, membrane treatment, thermal treatment

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## 1. Introduction

Extraction of in-situ water is one of the options for minimizing the impact of large-scale CO<sub>2</sub> injection in saline aquifers or during enhanced oil recovery (EOR). The amount of water produced could be significant depending on

in-situ conditions and injection parameters. Evaluating the costs of treatment is complex, as the quality of the water may vary considerably from well-known seawater chemistry; treatments may include membrane methods such as reverse osmosis (RO) or thermal methods such as multiple-effect distillation (MED) or multi-stage flash distillation-thermal vapor compression (MSF-TVC). Salinities are expected to vary widely depending upon the location and formation chosen for carbon storage (1-5); if the formation is associated with oil and gas production or enhanced oil recovery (EOR) then hydrocarbons may also need to be considered in the treatment train. Inorganic constituents, particularly divalent ions, are known to form mineral scale that interferes with desalination treatments including both membrane and thermal systems, so pretreatments to remove inorganic minerals must usually be included. Transportation costs also must be included in order to move the water from the extraction site to the point of treatment, and then to move treated product waters to the point of use, and waste concentrate or waste solids to a point of disposal. Onsite storage of water adds costs and can impact the choice of treatment as well.

To date our modeling efforts have been focused on the United States. Because of this, various model parameters and treatment choices are based on known or assumed regulatory limitations. For example, injection of CO<sub>2</sub> is not allowed into a reservoir where formation fluids have salinity less than 10,000 mg/L TDS, therefore the extracted water will normally be at least this salinity (6). In addition, the types of disposal processes that will be needed are defined not only by the regulatory classification of the water but the climate. For example, water extracted from economic oil and gas formations is classified as “produced water” (PW) in the U.S., and is exempt from certain regulations, but must be disposed in a Class II-type reinjection well. The costs associated with this type of disposal well differ from other classes of disposal and thus are applied based on the user’s specification of the water type to be treated (produced or non-produced). Regional climate affects disposal related to evaporation ponds. Ponds are normally used in the more arid western U.S., versus the more humid eastern U.S. So location in the model becomes a proxy for climate and the user must include this information.

For this paper we chose a CO<sub>2</sub> test injection location outside of the U.S., in Tianjin, China. This analysis is part of a larger pre-feasibility study for the U.S.-China Clean Energy Research Center (CERC) as a part of the GreenGen project. Because the study was conducted outside of the U.S., inputs to the model and interpretation of the results are affected by the different possible water quality scenarios, different discharge scenarios, and alternative disposal possibilities. While resulting costs are based upon U.S. cost databases, the use of a potential future CO<sub>2</sub> storage location provided validation of the model processes and useable costs for alternative scenarios that would not be considered in the U.S.

#### **Nomenclature**

BW	brackish water
PW	produced water
SW	saline water
WTM	CO <sub>2</sub> -PENS Water Treatment Model
RO	reverse osmosis
NF	Nanofiltration
MSF-TVC	Multistage Flash Distillation-Thermal Vapor Compression
MED	Multiple Effect Distillation

## 2. Data and Methods

### 2.1. CO<sub>2</sub>-PENS Water Treatment Model

Previously, we have shown that a variety of desalination technologies may be feasible depending upon water quality, temperature, and site conditions, using a system model, the CO<sub>2</sub>-PENS Water Treatment Model (WTM) for assessment of geologic CO<sub>2</sub> storage operations (4, 7, 8). This integrated system model is designed to be used as a tool to determine effective water treatment/disposal options that predict various treatment processes and associated costs while taking into account the specifics of sequestration site parameters and operational conditions. The WTM uses literature-based costs and processes to perform high-level, system-scale analysis based on user input information. Water extraction results obtained from CO<sub>2</sub> injection simulations, literature values for oil and gas produced water, and brackish ground-waters, are used to demonstrate the applicability of the model to various time scales, fluid chemistries, and volumes extracted. The WTM is intended to provide screening analysis capabilities for site assessment, but not detailed engineering analysis of a specific treatment scenario. Advantages of the model include the ability to include varied potential inputs such as variable total dissolved solids (TDS) content, variable waste disposal options, and variable transportation scenarios. We also use importance analysis to show the relative importance of different stochastic inputs under given scenarios and site conditions.

The WTM was developed using the GoldSim<sup>®</sup> platform (8, 9). GoldSim<sup>®</sup> is used to develop analysis models that perform multi-realization, probabilistic simulations. A FORTRAN code captures the logic of treatment process selection and is linked within GoldSim<sup>®</sup>. GoldSim utilizes custom data elements for input of user-specified parameters including stochastic distributions. The WTM captures all decision points; both stochastic range and constant data input values. Figure 1 shows a model schematic diagram including user-specified and model-calculated factors. Recently we expanded WTM capability to address pretreatments for organic foulants, TDS composition effects on inorganic pretreatment choices (acid, antiscalent, or both), and a bimodal transportation model that includes truck and pipeline transport (10). The WTM includes the effects of regulation on multiple disposal choices; effects of location (regional climate) and water type on disposal choices. Treatment choices are selected based on influent water volume, temperature, and composition. The WTM includes two modes for pretreatment costing: a generic cost mode for pretreatment based on literature-reported treatment costs (8) and a scaling potential mode that accounts for scale-forming ion concentrations in the influent (11). For CO<sub>2</sub> storage applications, costs are calculated in terms of US dollars/ton of CO<sub>2</sub> stored; for water treatment applications costs are calculated in terms of US dollars/m<sup>3</sup> of water treated.

The model includes four main parts: (1) pretreatment (organic, inorganic); (2) primary treatment processes (RO, thermal (MSF or MED-TVC), and nanofiltration (NF) methods), considering different energy cost scenarios, chemical costs, energy recovery, and scaling potential analysis; (3) concentrate disposal (with various methods depends on location; water type, quality and volume); and (4) storage (tank, pond) and transport (pipeline or truck).

### 2.2. Tianjin Site Features and Data

The site is located near Bohai Bay, southeast of Beijing and in the immediate vicinity of the Huaneng GreenGen IGCC facility in Binhai New Area near Tanggu. Figure 2 shows the site location and structural features in the area.(12). Additional site information can be found in (13).

The formations of interest for both sequestration of CO<sub>2</sub> and water extraction are the Guantao Fm. and the Dongying Fm. (14). We used water chemistry for the Dongying Fm. for the modeling, as reported in (14, 15). Table 1 lists relevant water chemistry parameters for the site. The reported formation water salinity is quite low, ~3,000 mg/L TDS, although we allowed for variation in our analysis from 1,300 mg/L to 16,000 mg/L TDS to cover variation in actual site salinity. This is a key difference between the Tianjin site versus our previous analyses, because frequently the salinity is lower than the injection formation limit (10,000 mg/L TDS) for a CO<sub>2</sub> storage site in the U.S.

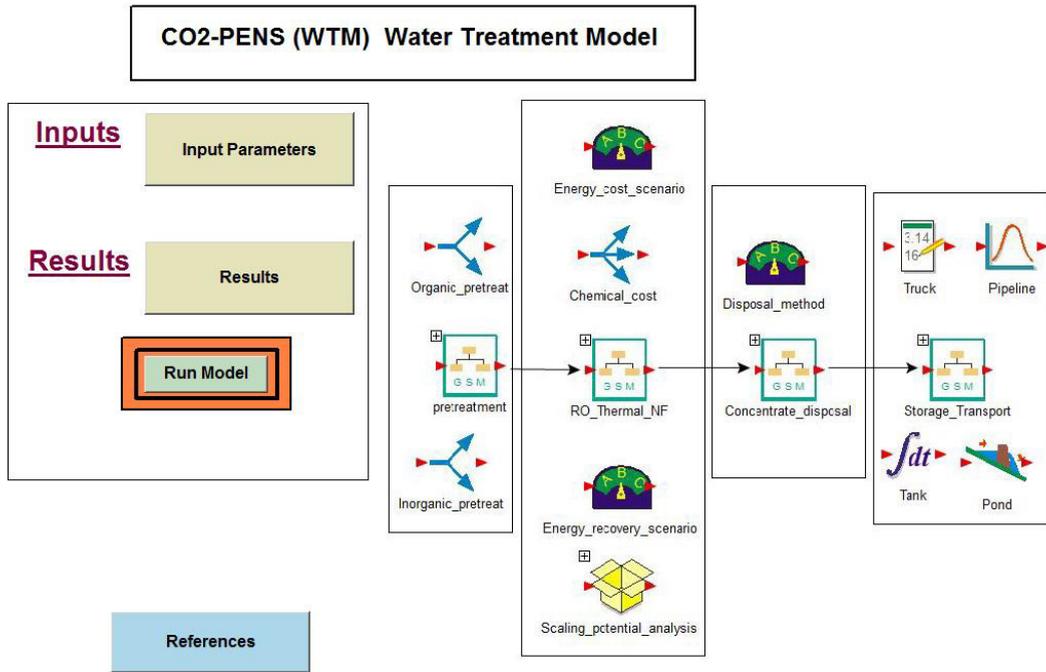


Figure 1. Schematic of the WTM input model structure

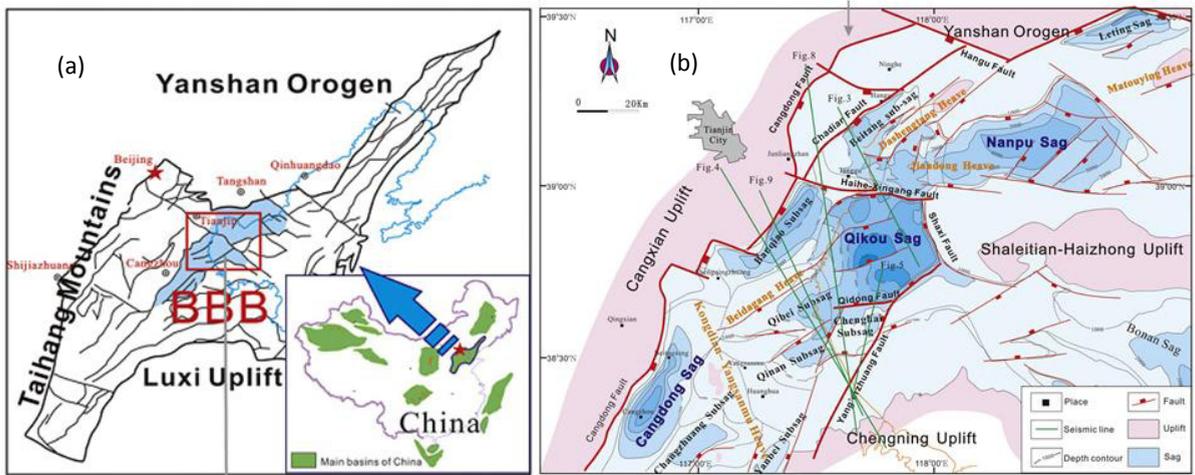


Figure 2. a) Location and structural framework of the Bohai Bay Basin in eastern coastal China with highlighted study area south-east of Tianjin; b) Structural framework of the study area in the immediate vicinity of the Huaneng GreenGen IGCC facility in Binhai New Area near Tanggu. Modified from Zhou et al. 2012.

**Table 1** – Chemical Analysis of Formation Water from the Dongying Fm. Concentration of major elements reported in mg/L. Samples from well Tang 20-2 to the south of Tanggu. Reported depth 2199-2454 meters, with a temperature of 85°C and in situ pH of 8.29. From Meng, 2007.

Cation, mg/L		Anion, mg/L		Other index, mg/L	
K <sup>+</sup>	9.4	Cl <sup>-</sup>	1258.5	Soluble SiO <sub>2</sub>	58.4
Na <sup>+</sup>	1190	SO <sub>4</sub> <sup>2-</sup>	40.1	Free CO <sub>2</sub>	0
Ca <sup>2+</sup>	8.4	HCO <sub>3</sub> <sup>-</sup>	872.6	TDS	3438.3
Mg <sup>2+</sup>	0.9	CO <sub>3</sub> <sup>2-</sup>	0	Total Solids	3002
NH <sub>4</sub> <sup>+</sup>	3.1	NO <sub>2</sub> <sup>-</sup>	<0.002	COD <sub>Mn</sub>	12.33
Cu <sup>2+</sup>	<0.02	NO <sub>3</sub> <sup>-</sup>	10.66	Total Hardness(as CaCO <sub>3</sub> )	24.5
Mn <sup>2+</sup>	0.02	F <sup>-</sup>	3.5	Permanent Hardness (as CaCO <sub>3</sub> )	0
Zn <sup>2+</sup>	0.37	Br <sup>-</sup>	5	Temporary Hardness (as CaCO <sub>3</sub> )	24.5
TFe	0.42	I <sup>-</sup>	1.25	Negative Hardness(as CaCO <sub>3</sub> )	691.1
TCr	0.003	PO <sub>4</sub> <sup>2-</sup>	0.04	Total Alkalinity(as CaCO <sub>3</sub> )	715.6
Pb <sup>2+</sup>	<0.01	HBO <sub>2</sub> <sup>-</sup>	15.29	Total Acidity (as CaCO <sub>3</sub> )	0
Cd <sup>2+</sup>	<0.001				

### 2.3. Modeling Scenarios

Scenario choices for the Dongying Fm. are shown in Table 2, while an example of the detailed simulation parameters used for modeling are provided in Appendix A. The approximate volume expected from an initial pilot test of the system is 400 m<sup>3</sup>/day. This volume is low compared to volumes treated by most water treatment plants; typical plants are often built to handle over 37,850 m<sup>3</sup>/d (10 Mgal/d). We used two industrial use scenarios for the final treated water, boiler water (final TDS ~150 mg/L), and cooling water (final TDS~1,000 mg/L). One scenario chosen included organic pretreatment, to illustrate the effect that this step has on final costs.

**Table 2.** Scenario Choices for Preliminary Cost Assessment

Formation	Salinity Range (mg/L TDS)	Temperature Range (°C)	Scenario ID-Product water quality
Dongying	1300-16000	10-85	Case 1a-Boiler Water
Dongying	1300-16000	10-85	Case 2a-Boiler Water
Dongying	1300-16000	10-85	Case 1b-Cooling Water
Dongying	1300-16000	10-85	Case 2b-Cooling Water
Dongying	1300-16000	10-85	Case 1c-Cooling Water with organic pretreatment
For Cases 2a, and 2b, disposal options include zero-liquid discharge (ZLD), a Class V disposal well, or ocean discharge. For Case 1a, 1b and 1c, we include a Class II disposal well instead of Class V, to illustrate costs associated with produced water disposal. Case 1c also includes organic pretreatment.			

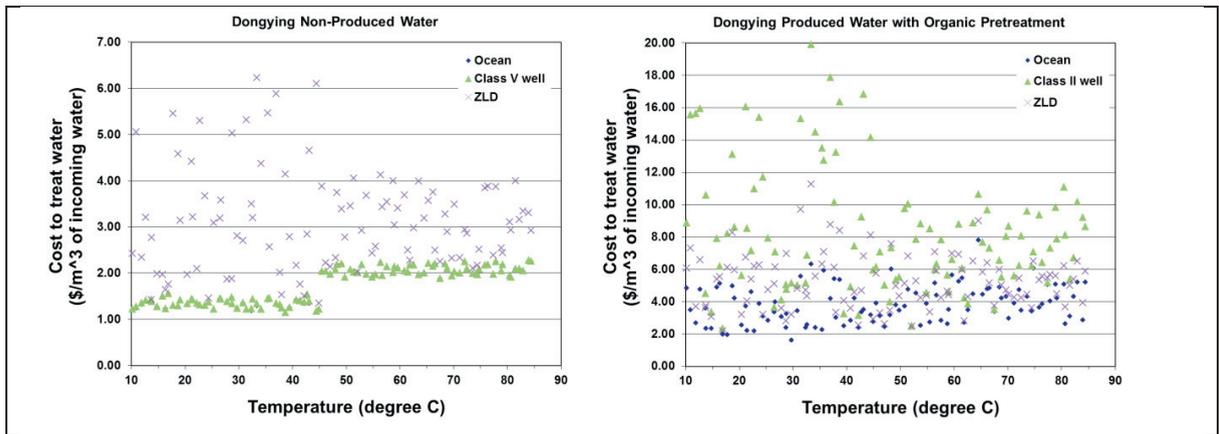


Figure 3. Dongying Fm. case results for non-produced (case 2a, left) and produced water (case 1c, right), plotted by possible disposal scenarios.

### 3. Results and Discussion

The low influent volume ( $Q_{in}=400 \text{ m}^3/\text{d}$ ) for these test cases may result in higher costs because economies of scale cannot be effectively included for transportation, storage, and other processes. However, the costs evaluated are relatively low compared to other site evaluations for higher salinity waters and indicate that extracted water treatment is a feasible option for this location (8). This model shows stochastic best estimates of cost ranges. Figure 3 shows the results for cases 1c and 2a, for the Dongying Fm. Costs ranged from a low of US\$1.12/m<sup>3</sup> for membrane treatments below 45°C (ocean disposal), to a high of US\$6.23/m<sup>3</sup> for thermal treatment and a zero-liquid discharge (ZLD) disposal scenario (left hand Fig. 3) Ocean disposal is typically the cheapest disposal option, because it implies that the salinity of the waste water is compatible with ocean salinity and that there are no other limitations to this discharge. Class V well disposal is a class designated in the U.S. for various industrial wastes, while Class II disposal is for wastes associated with oil and gas produced water. The two classes cover a range of reasonable costs for U.S. disposal of wastes. Inclusion of organic pretreatment and a Class II disposal rate raised the maximum costs for treatment and disposal to approximately ~US\$20.00/m<sup>3</sup>. (right hand Fig. 3).

Expected recoveries from various treatments are all 90% or greater. This is quite good because most of the influent waters are relatively low in salinity (brackish range is from 1,000 to 10,000 mg/L TDS) and as a result fewer passes are needed through membrane systems, and lower membrane osmotic pressures exist, thus reducing electricity costs for high-pressure pumping.

The cost break at  $T=45^\circ\text{C}$  is indicative of a change from membrane methods (RO or NF) to thermal methods. Temperatures above 45°C are not compatible with membrane-based treatment and can degrade membranes. Costs for cases 1a and 1b and for 2a and 2b were the same (not shown) because the treatment methods selected by the model yielded a resulting water quality that met goals for both cooling water and boiler water (less than 150 mg/L TDS). Case 1c shows costs for produced water include not only organic pretreatment but also Class II well disposal (Fig.3 right hand side). The cost ranges for this type of disposal are wide, varying from US\$0.10 to 10.00 per m<sup>3</sup> of influent water), and create a wide variation in costs for this scenario. Pretreatment for organic compounds is necessary for membrane methods but is less critical for thermal treatments; the cost differential may be enough to suggest thermal treatment as a better option, particularly if the relatively high temperature of the influent water can be used as a pre-heating mechanism to save on thermal energy inputs.

Figure 4 shows an importance analysis for Case 2a, non-produced water for boiler or cooling purposes, plotted by waste disposal option. Importance analysis lends insight into process factors that may not contribute the highest unit

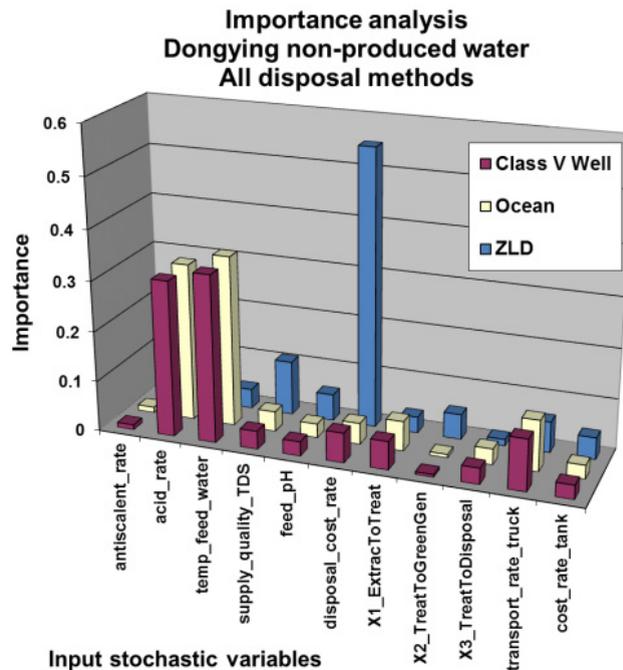


Figure 4. Importance analysis for Case 2a, with no organic pretreatment.

costs to treatment but on whole are very important to total system costs. Zero-liquid discharge disposal is a special case because costs are still evolving for this type of disposal, and can be very high based on the current literature. Feed water temperature is the most important of the input stochastic parameters, because it affects the model choice between membrane and thermal treatment methods. This choice usually means larger variance in costs for treatment. The acid cost rate is nearly as important because it influences pretreatment costs, especially when mineral scale potential is high. Transportation is the next largest contributor to cost variance, indicating that the choice of location for a treatment and disposal facility is crucial. Attempts to reduce transport costs are thus likely not as important as the feed temperature but are even more important than other factors that can have very high cost ranges, including most forms of disposal. The use of importance analysis helps define critical factors for site design, beyond defined cost ranges for specific processes.

#### 4. Conclusions

A brackish-salinity water to be extracted from a future CO<sub>2</sub> injection and storage location in eastern China was evaluated for prototype treatment costs for both cooling water and boiler water final treatment goals. Costs for treatment of the water, excluding costs for organic pretreatment and disposal, were within the range of previously analysed costs for higher-salinity waters (US\$1.00-3.00) and are likely to be lower than predicted when economies of scale are included for a full-scale, higher volume treatment facility. Inclusion of organic pretreatment and relatively high disposal costs (based on U.S. costs and regulations) indicate that a definition of the organic pretreatment needs and disposal cost refinement are necessary for final design cost assessment. Costs were found to be reasonable for potential industrial reuse for both final treatment goals; this was made possible because the lower salinity of the water reduced overall treatment costs. Transportation of to the disposal site was important to overall costs, even if transportation was not the highest cost processes in the system. Careful attention to system location and design is needed to optimize costs and processes.

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## References

1. Bourcier WL, Wolery TJ, Wolfe T, Haussmann C, Buscheck TA, Aines RD. A preliminary cost and engineering estimate for desalinating produced formation water associated with carbon dioxide capture and storage. *International Journal of Greenhouse Gas Control*. 2011;5(5):1319-28.
2. Buscheck TA, Sun, Yunwei, Hao, Yue, Wolery, Thomas J., Bourcier, William, Tompson, Andrew F. B., Jones, Edwin D., Julio Friedmann, S., Aines, Roger D. Combining brine extraction, desalination, and residual-brine reinjection with CO<sub>2</sub> storage in saline formations: Implications for pressure management, capacity, and risk mitigation. *Energy Procedia*. 2011;4:4283-90.
3. Wolery TJ, Aines, R.D., Hao, Y., Bourcier, W., Wolfe T, Haussman C. Fresh Water Generation from Aquifer-Pressured Carbon Storage: Annual Report FY09. Lawrence Livermore National Laboratory, 2009 December 1, 2009. Report No.: LLNL-TR-420857 Contract No.: LLNL-TR-420857.
4. Sullivan EJ, Chu S, Stauffer PH, Pawar RJ. A CO<sub>2</sub>-PENS model of methods and costs for treatment of water extracted during geologic carbon sequestration. *Desalination and Water Treatment*. 2012; published online August 9, 2012. <http://www.tandfonline.com/doi/abs/10.1080/19443994.2012.714727>:1-7.
5. Klapperich RJ, Cowan RM, Gorecki CD, Liu G, Bremer JM, Holubnyak YI, et al. IEAGHG, "Extraction of Formation Water from CO<sub>2</sub> Storage". Cheltenham, GLOS, United Kingdom: IEAGHG, 2012 November 12, 2012. Report No.
6. US. EPA Federal Underground Injection Control (UIC) Class VI Program for Carbon Dioxide (CO<sub>2</sub>) Geologic Sequestration (GS) Wells 2011 [07/29/2014]. Available from: <https://www.federalregister.gov/articles/2011/09/15/2011-23662/announcement-of-federal-underground-injection-control-uic-class-vi-program-for-carbon-dioxide-co2>.
7. Sullivan, E.J., Chu, S., Stauffer, P.H., and Pawar, R.J. Development of a system model of methods, processes, and costs for treatment of water extracted during carbon sequestration. *Energy Resources and Produced Water Conference*; May 25-26, 2010; University of Wyoming, Laramie, Wyoming 2010.
8. Sullivan, EJ, Chu S, Stauffer PH, Middleton RS, Pawar RJ. A method and cost model for treatment of water extracted during geologic CO<sub>2</sub> storage. *International Journal of Greenhouse Gas Control*. 2013;12(0):372-81.
9. GoldSim Technology Group. GoldSim Probabilistic Simulation Environment User's Guide, Version 10.5. Volumes 1 and 2. Issaquah, Washington: GoldSim Technology Group LLC; 2010.
10. Sullivan Graham EJ, Chu S, Pawar RJ, editors. The CO<sub>2</sub>-PENS Water Treatment Module: Cost Profile and Importance Scenario Analysis for Understanding Treatment Processes. Thirteenth Annual Carbon Capture, Utilization, and Sequestration Conference; 2014 April 28-May 1, 2014; Pittsburgh, PA.
11. Dow Chemical. [cited 2013 01/07/2013]. Feed Water Quality Guidelines for Dow Filmtec Membranes]. Available from: [https://dow-answer.custhelp.com/app/answers/detail/a\\_id/3170/~~/filmtec-membranes---feed-water-quality-guidelines](https://dow-answer.custhelp.com/app/answers/detail/a_id/3170/~~/filmtec-membranes---feed-water-quality-guidelines).
12. Zhou L, Fu L, Lou D, Lu Y, Feng J, Shuhui Z, et al. Structural Anatomy and Dynamics of Evolution of the Qikou Sag, Bohai Bay Basin: Implications for the Destruction of North China Craton. *Journal of Asian Earth Sciences*. 2012;Vol. 47:94-106.
13. Ziemkiewicz P, Carr T, Donovan J, Lin L, Song L, Jiao Z, et al. Pre-feasibility Study to Identify Opportunities for Increasing CO<sub>2</sub> Storage in Deep, Saline Aquifers by Active Aquifer Management and Treatment of Produced Water. Charleston, WV: West Virginia University, 2014.

14. Yang F, Pang Z, Lin L, Jia Z, Zhang F, Duan Z, et al. Hydrogeochemical and isotopic evidence for transformational flow in a sedimentary basin: Implications for CO<sub>2</sub> storage. *Applied Geochemistry*. 2013 3//;30(0):4-15.
15. Meng L. *Geothermal Resource Evaluation in Early Tertiary Oligocene in the North of Tanggu District*, . Beijing: China University of Geosciences,; 2007.

**Appendix A. Example case scenarios for Dongying Fm. Boiler water product goal.**

Scenarios-Cases 1a and 2a	Dongying Fm., Boiler water as final product goal.		
Parameter	units	Base Case 1a	Base Case 2a
Location	east/west	east	east
ocean choice		coastal	coastal
produced water?	yes/no	yes	No
Thermal treatment type	MED or MSF	MED	MED
storage	yes/no	yes	yes
Transportation	1=truck/pipe, 2=other	1	1
Transportation method X0	truck or pipeline	truck	truck
Transportation method X1	truck or pipeline	pipeline	pipeline
Transportation method X2	truck or pipeline	truck	truck
Transportation method X3	truck or pipeline	truck	truck
Storage type	tank or pond	tank	tank
<b>Stochastic Variables</b>			
Desired Permeate quality	mg/L	150	150
TDS	mg/L	1300 ~ 16000	1300 ~ 16000
Temperature	°C	10-85	10-85
Pretreatment inorganics-pH	pH units	7.4 ~ 8.6	7.4 ~ 8.6
NTU		5	5
SDI		5	5
NF recovery percentage		75~90%	75~90%
acid rate	\$/m3	8.04e-8 ~ 0.0053	8.04e-8 ~ 0.0053
antiscalent rate	\$/m3	6.91e-9 ~ 0.0053	6.91e-9 ~ 0.0053
Cost of Energy	\$/kWh	0.07	0.07
energy recovery type	various	Pelton	Pelton
Desired Permeate %	50%, 75%, or 90%	50	50
water choice for Q in	fixed or time series	fixed	fixed
Q in	m3/d	400	400
Pretreatment-organics	yes/no	no	no
Disposal type	various	model selected	model selected
Pretreatment-inorganics-use mineral scaling calculations?	yes/no	yes	yes
Distance X0 (CO2-to-inj)	km	0	0
Distance X1 (Qin-Treat)	km	0.1-0.5	0.1-0.5
Distance X2 (Treat-Qperm)	km	12	12
Distance X3 (Treat-Qrej)	km	0.1-2	0.1-2