

A New Rapid Brine Release Extraction Method in Support of Lithium Brine Resource Estimation

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Abstract

Lithium brine mining via groundwater extraction and concentration in large evaporation ponds accounts for approximately half of the world's lithium production. Lithium brine mineral resources and reserves are typically located in large lacustrine evaporite closed basins (salt pans or salars) associated with high-angle faulting and hydrothermal fluids containing lithium migrating into the basins where they are concentrated by up to 2 orders of magnitude. Lithium concentrations can vary laterally and vertically across a lithium deposit and the host aquifers typically consist of highly heterogeneous layered sediments. Thus, knowledge of the relative lithium concentrations and the drainable porosity and potential flow contribution from the different lithological facies is essential for the resource estimation and to support groundwater modeling.

As a first step in determining economic viability, the lithium brine deposit is evaluated using statistically representative measurements of depth specific brine sample lithium concentrations, as well as core samples to determine drainable porosity (specific yield) of the host aquifer materials. Whereas aquifer pumping tests can provide data on large-scale aquifer hydraulic characteristics, results typically cannot resolve explicit estimates of mineral grade and drainable porosity for multi-layer aquifer systems - such as lithium concentrations and specific yield of fine-grained hydrogeologic units versus coarse-grained hydrogeologic units. Consequently, brine mineral resource estimation requires supporting data from both field and laboratory testing programs to estimate the lithium concentrations associated with the various lithologies in concert with the ability to drain brine from the various lithological layers.

We present a rapid brine release (RBR) test based on a modified soil water characteristic curve (SWCC) method to determine specific yield characteristics of core samples collected during exploration

drilling. The laboratory method takes less than one week and dozens of samples can be run simultaneously using various core sample types (i.e., sonic, HQ, PQ wire line diamond drill core,). To date this method has been used to determine specific yield characteristics on hundreds of samples from eight different brine deposits in North and South America. Case studies from Clayton Valley Lithium Project, Nevada, USA (Pure Energy Minerals) and Minera Salar Blanco (Maricunga Joint Venture Project), Chile are presented.

Background and Method

Specific yield (S_y) is assumed to be equivalent to the amount of brine solution that may be released under gravity drainage conditions from groundwater pumping of the brine deposit. The corresponding amount of water retained is referred to as specific retention (S_r) and the sum of the specific yield and specific retention is equal to the total porosity (P_t) which is the ratio of the volume of pores to the bulk test sample volume.

Laboratory methods to determine brine release/specific yield range from moisture retention characteristic (MRC/SWCC) methods (ASTM D6836-16, 2016), and centrifugal tests (ASTM D6836-16, 2016) to simple suction methods (Relative Brine Release Capacity, RBRC, Stormont et. al., 2011), to establish drainage, S_y and P_t . Traditional SWCC tests are time consuming and expensive; centrifugal and RBRC tests are rapid, but could result in significant errors due to unknown equilibrium times and/or uncontrolled boundary conditions. GeoSystems Analysis, Inc. (GSA) has developed a Rapid Brine Release (RBR) test based on a modified SWCC method and equipment (Figure 1) to determine the specific yield characteristics of core samples collected during exploration drilling. The laboratory method takes less than one week and dozens of samples can be run simultaneously using various core sample types (i.e., sonic, HQ or PQ diamond core, Figure 2).

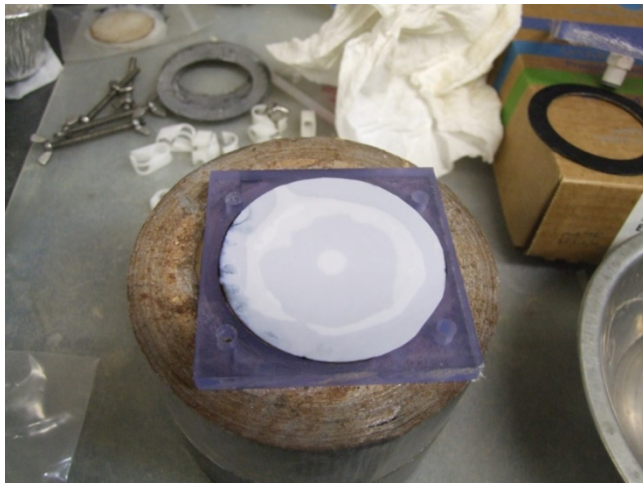


Figure 1. Test cell assembly with micropore filter paper at bottom



Figure 2. HQ core and test ring

The RBR method used by the GSA Laboratory is based on the SWCC method for direct measurement of total porosity (Flint and Flint, 2002, MOSA Part 4 Ch. 2, 2.3.2.1), specific retention (Romano and Santini, 2002, MOSA Part 4 Ch. 3, 3.3.3.5), and specific yield (Cassel and Nielson, 1986). A simplified Tempe cell design (Modified ASTM D6836-16) is used to test intact core samples (Figure 3). These cells can be arranged to handle large number of tests simultaneously (Figure 4). Brine release drainage is measured at -100 to -150 mbar and -330 mbar of soil water matric potential, where:

1. Brine release at -120 mbar is assumed to approximate drainable porosity from sandy sediments and macropores, (-150 mbar suggested by Nwankwor et al., 1984 and -100 mbar suggested by Cassel and Nielsen, 1986)
2. Brine release at -330 mbar represents the S_r for intermediate to finer texture sediments (Cassel and Nielsen, 1986)

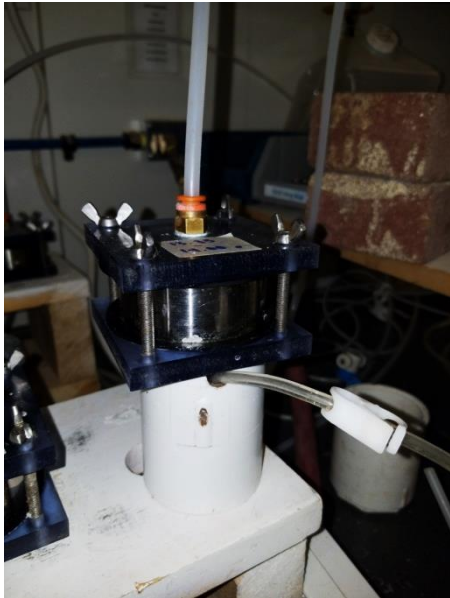


Figure 3. Simplified Tempe Cell



Figure 4. Simultaneous testing of forty cells

RBR Test Cells have a standard diameter of 6.35 cm by 2.5 cm length. HQ core samples can be tested directly or prepared by driving 6.35 cm diameter stainless steel liners into undisturbed sonic and HQ core samples using a hydraulic press in order to preserve the integrity of the core sample. PVC end caps are then placed on either side of the sample to create the RBR Test Cells. The PVC caps contain gaskets to provide an air-tight test cell that maintains constant air pressure and allows continuous solution outflow through the membrane (Figure 3).

After sample preparation, the RBR Test Cell is then saturated with either a brine solution prepared to mimic the chemical composition of the brine solution found within the deposit or native brine samples

from the deposit. Saturation is achieved by repetitively applying brine solution from the bottom of the test cell and then applying a vacuum (-30 to -700 mbar) from the top of the test cell to assist the saturation. Any standing brine solution is carefully removed from the top of the test cell prior to starting the test.

Each saturated RBR Test Cell is transferred to a test rack for the pressure extraction procedure (Figure 4) for three pressure steps as follows. Zero pressure is applied for a day and any free water due to core over-saturation is removed during this step. Two sequential pressure steps, at 120 mbar and 333 mbar (Romano and Santini, 2002, MOSA Part 4 Ch. 3, 3.3.3.2), are used to approximate brine solution release at -120 mbar and -333 mbar of matric potential.

The 120 mbar pressure step is maintained for two days and the 333 mbar step is continued until the sample reaches equilibrium (another two to four days). Test cells are weighed prior to saturation, after saturation, and then two to three times daily to determine brine solution loss over time. Samples are oven dried after the final step to determine S_r , dry bulk density (ρ_b), and P_t (Flint and Flint, 2002, MOSA Part 4 Ch. 2, 2.3.2.1), where S_r is the volume of water retained by the sample under -333 mbar soil water matric potential.

Brine solution release volumes at the 120 mbar and at 333 mbar pressure steps are estimated as the difference of the brine weight divided by the brine solution specific gravity (i.e., 1.2 g/cm³) between the initial cell assembly mass and the mass after each pressure plate step (Romano and Santini, 2002, MOSA Part 4 Ch. 3, 3.3.3.5). The S_y is assumed to approximate the volume of solution released between saturation to -333 mbar divided by the total sample volume. The S_y value is calculated as follows:

$$S_y = \frac{w_s - w_{333 \text{ mbar}}}{A * L * Bsg} \quad (\text{Equation 1})$$

where w_s is the saturated weight, $w_{333 \text{ mbar}}$ is the weight at 333 mbar, A is sample core area, L is sample length, and Bsg is the specific gravity of the brine solution. Sample material from the test cell is then oven dried at a low temperature for five days to determine the residual brine content and bulk density.

Particle density, (PD , volumetric mass of the solid) can also be estimated from the P_t and bulk density measurements since the volume of the test cell is known:

$$PD = \frac{\rho_b}{(1 - P_t)} \quad (\text{Equation 2})$$

where PD is the particle density in g/cm³.

Case Studies

Clayton Valley Lithium Project (Blois et. al., 2017)

GSA tested 48 HQ-size core samples from three boreholes at Clayton Valley using the RBR lab method. From this samples set, 10 duplicate samples were sent for RBRC testing by DBS&A (Albuquerque, NM) and 5 samples were sent to Vista Clara (Mukilteo, WA) for testing using a Nuclear Magnetic Resonance (NMR) laboratory method (Behroozman et. al., 2015). Lithologies ranged from fine sand to silt and ash deposits. Results from boreholes CV-7 (A) and CV-8 (B) shown in Figure 5 indicate:

- RBR values of total porosity were higher than the NMR Corona method potentially due to initial brine content of the samples upon receipt and laboratory re-saturation methods used for the NMR laboratory method.
- Except for one anomalous measurement comprised of pellet ash, S_y measurements were in agreement. The anomaly may be related to the high proportion of ash in the sample and re-saturation conditions used by each of the labs.
- Coarser volcanic ash and fine sand material showed higher S_y and P_t , and lower particle density
- RBR method results for all 48 samples showed a mean S_y of 6.9%

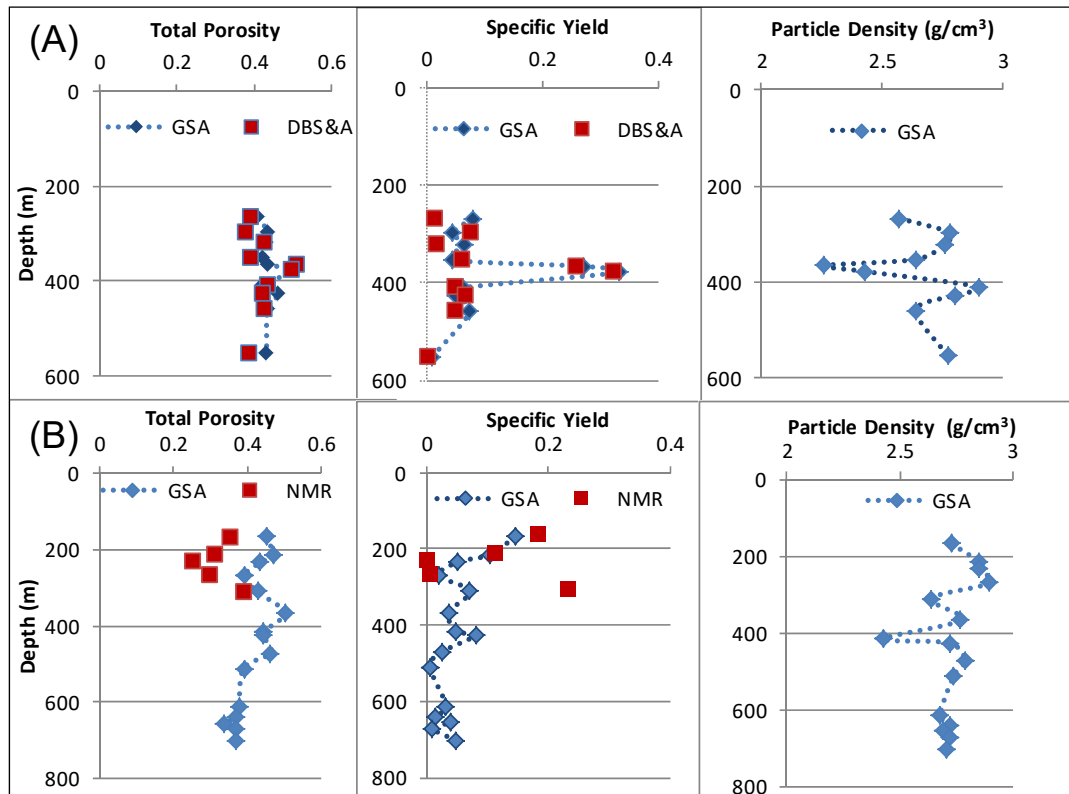


Figure 5. Comparison of RBR (GSA), RBRC (DBS&A) and NMR (Vista Clara) methods for total porosity and specific yield and GSA particle density estimates for (A) CV-7 and (B) CV-8

Comparison of RBR and RBRC methods showed generally good agreement for S_y of volcanic ash sediments, and comparable results, though frequently lower S_y values were observed using the RBRC method for fine-grained, low specific yield sediments. This may be due to longer equilibrium times required for the finer grained materials.

Minera Salar Blanco, Maricunga Lithium Project (Worley Parsons, 2017)

GSA tested 165 PQ samples from four boreholes drilled using sonic methods. From this samples set, 28 duplicate samples were sent for centrifuge testing by Core Laboratories (Houston, TX). Six different lithologies were identified as summarized in Table 1.

Table 1: Maricunga Samples - total porosity and specific yield test results and summary

Material Classification	Core Lab P_t			GSA P_t			Core Lab S_y		GSA S_y	
	N	Mean	SD	N	Mean	SD	Mean	SD	Mean	SD
Clay dominated	6	0.53	0.05	58	0.44	0.08	0.02	0.03	0.03	0.04
Sand dominated	3	0.45	0.08	21	0.38	0.07	0.05	0.04	0.07	0.06
Gravel dominated	3	0.32	0.02	22	0.34	0.06	0.10	0.07	0.17	0.10
Volcaniclastic	13	0.46	0.05	41	0.45	0.06	0.13	0.05	0.15	0.06
Halite	2	0.35	0.08	17	0.33	0.13	0.07	0.05	0.09	0.09
Ulexite	1	0.49	N/A	4	0.35	0.09	0.04	N/A	0.06	0.04

Total porosity and specific yield values were profiled for four boreholes and statistically analyzed for five corresponding lithology types. The Ulexite sample is not shown in Figures 6, 7 and 8 because there were an insufficient number of samples from this lithology type. Figures 6 and 7 compare the values measured by the GSA RBR method and the Core Lab centrifuge method for P_t and S_y , respectively. Figure 8 shows the lithologically classified RBR P_t and S_y distributions and statistics assuming normal distribution.

- The RBR method showed acceptable agreement with the centrifuge test results, though higher S_y values on average were measured by the RBR method, possibly due to longer equilibrium times compared to the centrifuge test.
- Volcaniclastic and gravel materials showed higher S_y values compared to clay, sand, and halite samples.
- Lower particle densities were also observed for volcaniclastic and halite samples (data not shown)

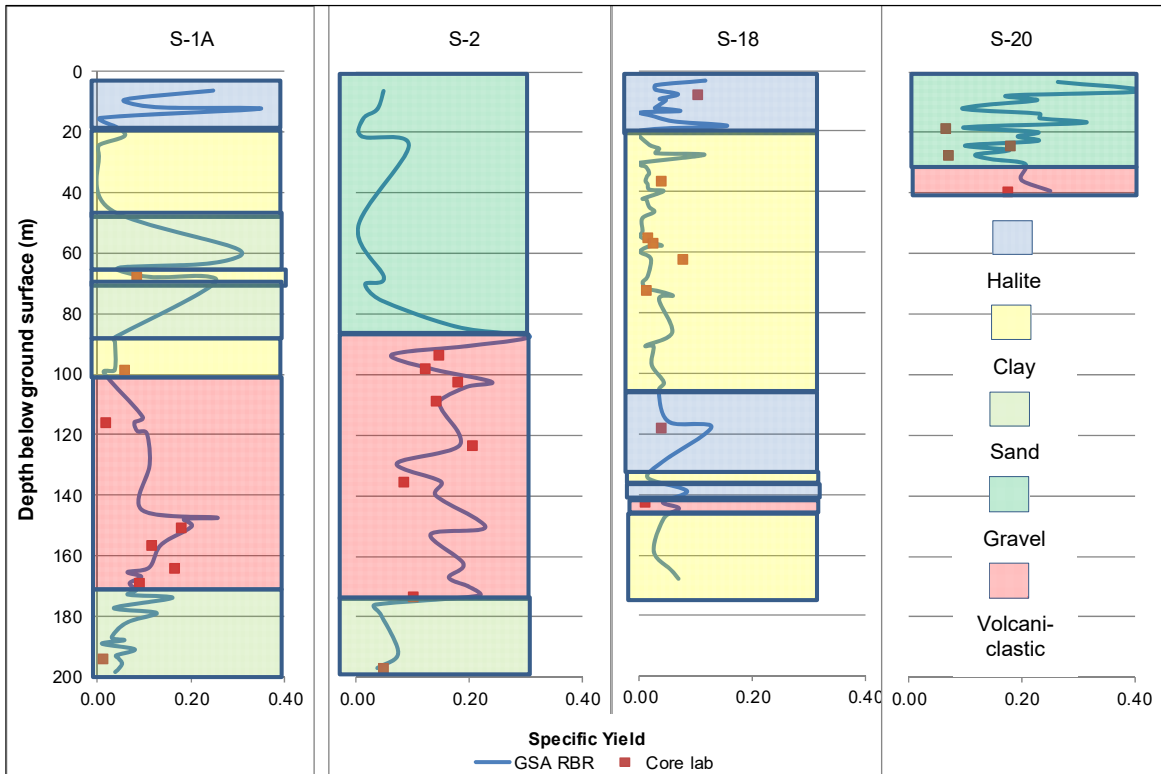


Figure 6. Comparison of GSA RBR and Core Lab measured S_y values

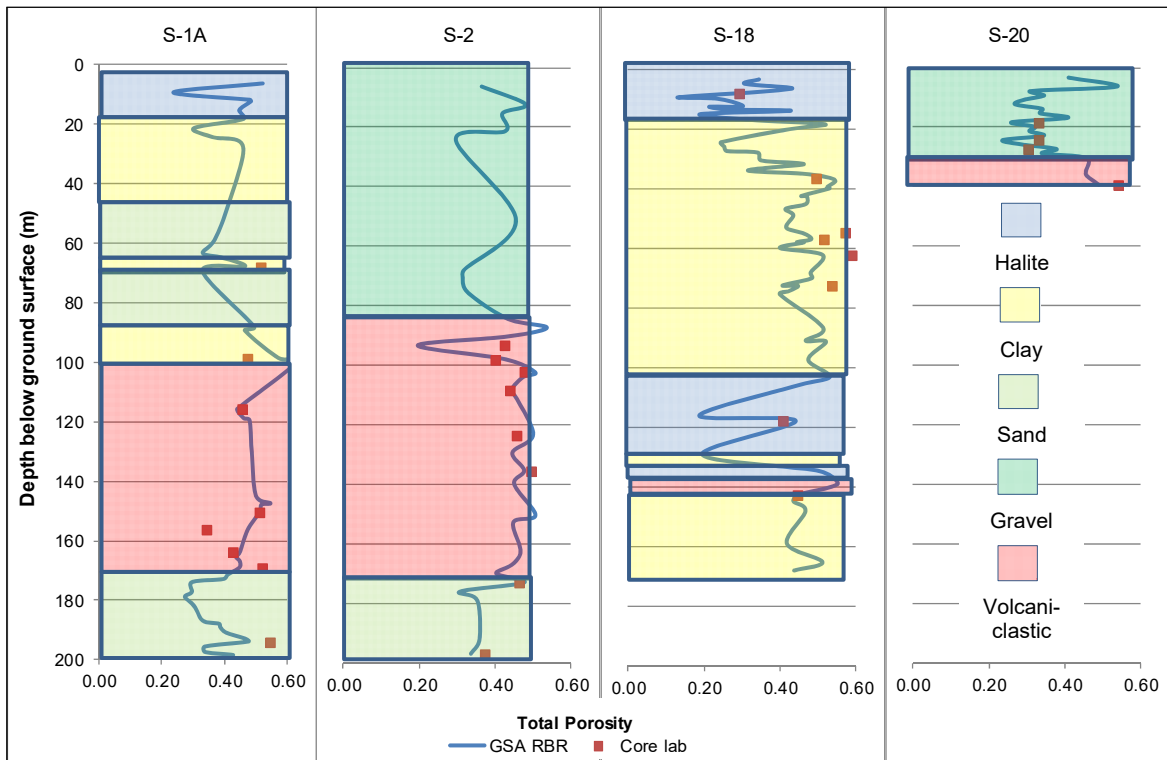


Figure 7. Comparison of GSA RBR and Core Lab measured P_t values

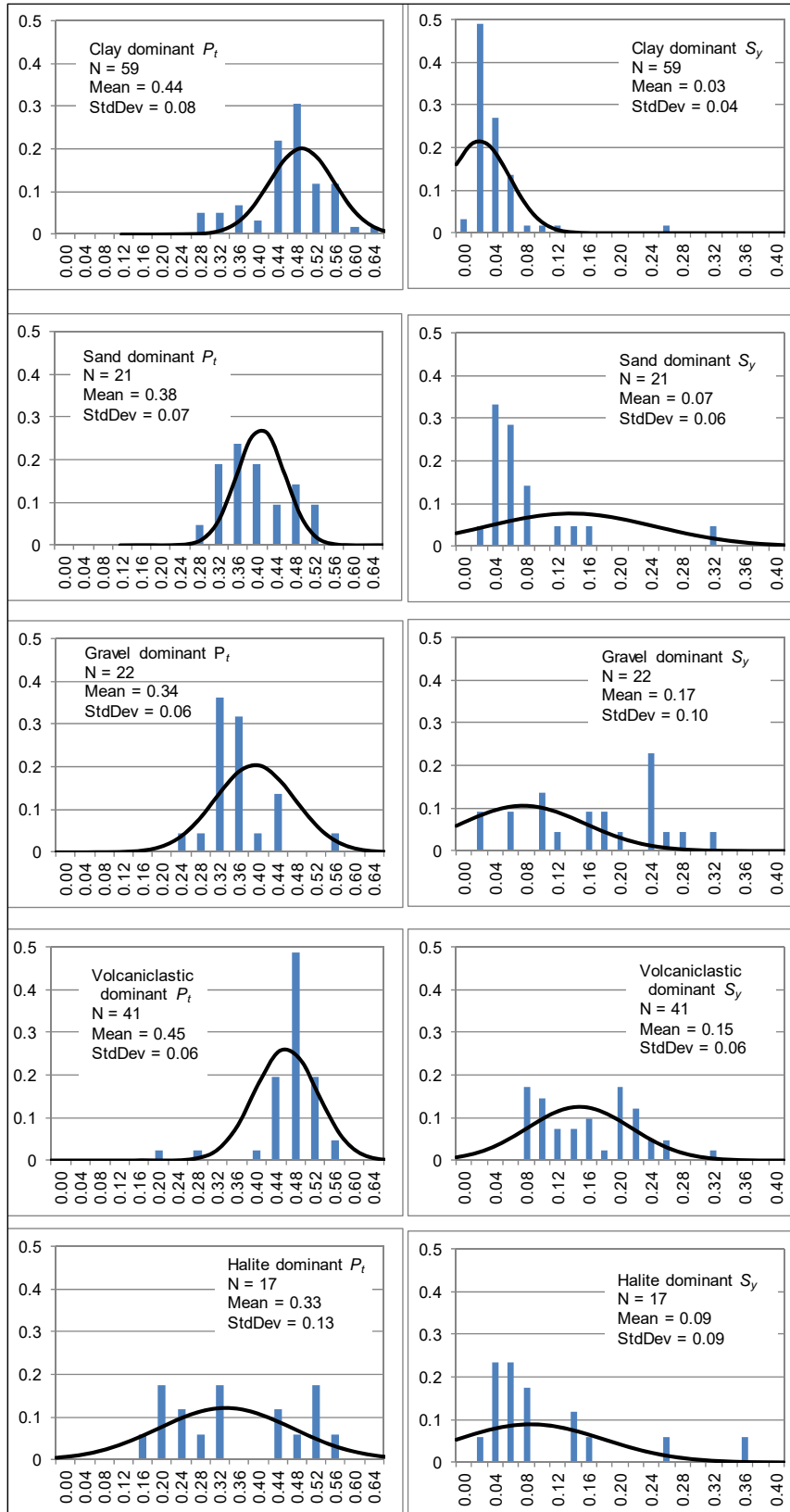


Figure 8. Lithologically classified P_t and S_y distributions and statistics (y-axis is fraction of samples). Curves in plots are the best fit normal distribution

Conclusions

The Rapid Brine Release (RBR) method presented herein is an improvement over existing brine release laboratory test methods. It is based on proven and standard laboratory procedures which allow samples to be measured at equilibrium and two drainage points can be measured. Duplicate sample testing indicates general agreement with other brine release methods though slightly higher estimated drainable porosity values, possibly due to differences in equilibrium conditions. Benefits to this laboratory method include: the use of standard methodology to determine the specific yield which results in higher accuracy and reproducibility; the test is relatively rapid; the ability to test large quantities of samples and variable sample sizes/diameters, and; the ability to calculate/estimate particle density.

Acknowledgements

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