

RESULTS OF A TRACERLESS CORE INVASION STUDY USING MULTIVARIATE CURVE RESOLUTION

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ABSTRACT

The goal of a core invasion study is to determine the amount of coring fluid contamination contained in the formation water of a core sample. Since contamination may affect the physical properties of the core and decisions about the future test program, the level of contamination must be known. Typically a tracer, such as deuterium or tritium, is used in the coring fluid and the level of contamination determined by measuring the level of the tracer in the extracted plug sample water. In this case, the tracer did not reach the wellsite in time for the coring run and was not used. The operator asked if a core invasion study could still be conducted. Westport used Multivariate Curve Resolution (MCR) to determine the level of contamination in the core.

Multivariate Curve Resolution (MCR) uses the difference in chemical fingerprints between multiple components of a mixture to determine the concentration of these components. One component is the coring fluid while the other component is formation water. Therefore MCR is particularly well suited for determining the concentration of coring fluid contamination (fluid invasion) contained in a core sample.

Because MCR is based on the natural fingerprints (the more different the better), no tracer need be added a-priori. The analysis can be performed even when the pure coring fluid or uncontaminated formation water is not available. This is possible because constraints can be placed on the mathematical solution including positive concentration and/or positive chemical information. Multiple natural constraints such as geochemical knowledge, as is available with formation water, greatly improve the determination. Since the pure coring fluid is available for analysis, the MCR procedure is even more applicable.

In this study 48 cores and 5 coring fluids were analyzed to obtain a chemical fingerprint in the form of mass spectral data. After screening, variation information, as determined by Principal Component Analysis (PCA), was used to select suitable masses for fingerprinting. MCR was used to determine the concentration of coring fluid in the core. The further interpretation identified natural tracing properties of the coring fluid, which is compared to the MCR results.

INTRODUCTION

Westport Technology received 150 core plugs for analysis. Additionally 5 coring fluid samples were received. A core invasion study was desired, however coring fluid lacked tracers necessary to conduct a conventional study. It was suggested that a fingerprinting technique called Multivariate Curve Resolution (MCR) could provide a quantification of coring fluid contamination within the cores. The application of MCR to determine core invasion is an extenuation of a commercially performed petroleum geochemistry technique already established for reservoir continuity studies. Analysis proceeded in two batches. The first batch proved the concept of MCR for invasion studies. The second batch yielded additional information that an unusually high concentration of cesium in the coring fluid acted as a natural tracer and contributed to the MCR with a majority of the influence.

METHODS

Multivariate Curve Resolution attempts to decompose an experimental response matrix R into the products of a concentration matrix C and the transposed pure component spectral matrix (or responses) S^T with a residual known as error E defined by Tauler, 1994 (1):

$$R=C*S^T+E \quad (1)$$

Alternating least squares is an iterative technique used to minimize the residual with respect to a model (MCR in this case). MCR requires an initial estimation of the initial concentrations of pure components, an initial estimation of the pure component, and a known number of components. Although the number of components can be estimated many ways, principal component analysis is a particularly well suited method for this application using a method by Tauler 1993 (2). Principal component analysis (PCA) decomposes a data matrix into orthogonal vectors called eigenvectors and a matrix of scores. The eigenvectors of PCA obtained through singular value decomposition (SVD) of the variance-covariance matrix are diagonally such that the first element along the diagonal describes the maximum amount of variation with each successive diagonal element describing the greatest amount of remaining variation. At some point successive principal components describe random variation. Principal components describing real information in an ideal system describe the dimensionality of the dataset as described by Jackson, 1991 (3). This dimensionality for the mixing of components should describe the number of components mixed. For core invasion, the components are the pure formation waters and the coring fluid. Therefore determination of the number of relevant principal components should determine the number of pure components to be used as the input for the multivariate curve resolution of the core invasion study dataset. For the rotation of the MCR response matrix into the concentration and pure spectral response matrix there is rotational ambiguity (an infinite number of solutions) as described by Diewok, 2002 (4). Knowledge of the number of components responsible for the response is necessary and sometimes sufficient for determination of the pure component response matrix. In this situation, Tauler, 1993 (2) mentions that additional constraints must be applied. Universal constraints that can be applied are non-negativity of individual component

responses and non-negativity of concentrations. Other physical constraints can include any individual response. For instance the coring fluid is explicitly known and can be held fixed in the MCR model. Often constraints such as these and those defined in Diewok, 2002 (4) are enough to remove the rotational ambiguity completely.

PROCEDURE

Twenty-one cores were originally selected as Batch 1 for the invasion study. For batch two, twenty-eight cores were selected. Core 1 at depth 9666.2 yielded all oil so only twenty-seven cores were analyzed for invasion. Water was removed from cores by centrifuging the samples. Recovered fluid mass was measured by the caliper method. When recovered water was greater than 100 micro-liters the mass was rechecked by a conventional gravimetric scale. From Batch 1, 12 samples were diluted by caliper measurements, but in batch all samples were diluted by measurements from a conventional scale. Samples from Batch 1 were diluted by approximately 400 times with the exception of samples 118, 132, and 134 which were diluted by 2000, 12,000, and 15,000 times respectively due to the extremely low volume of water recovered. All Batch 2 samples were approximately diluted by 400 times. Coring fluids were also diluted by 400 times. All dilutions were into 1% HNO₃ using trace metal free vials with 18 mega-ohm water. Samples were analyzed for the complete 260 mass elemental spectrum on an Agilent 7500-i ICP-MS. Samples were analyzed both as prepared and auto-diluted by the ICP-MS by 10X further. Since only comparison between the core fluids' mass spectra and the formation water mass spectra was required, as opposed to quantification, calibration, standard solutions and dilutions were not monitored. For each batch the coring fluids, and diluted core waters were run. A single tune report was generated prior and after sample acquisition to ensure machine parameters did not drift.

DATA HANDLING

Five hundred and twenty mass signals were monitored for each sample and drilling fluid (260 for prepared solution and 260 for auto-diluted solution). Mass channels for which known atmospheric interference existed were removed. Mass spectra were then corrected by a blank solution of the 1% nitric acid solution used for dilution and for dilution factor. Signals were plotted for each sample, at a single mass as a function of dilution factor. The plot was studied to see if there was a linear relationship between mass signal and dilution factor. If it was determined that there was a linear relationship then the mass was removed from the data set because the mass signal was obviously an artifact of dilution. Masses were further discriminated based on a determined signal limit of detection of 50 counts. Further, if the combination of coring fluid and water variation at a particular mass seemed unfruitful the channel was removed. The data was then pre treated differently for two separate discrimination procedures. The first procedure required the retention of only masses for which all coring fluid analysis was significantly above the background for all five coring fluid samples. In the second pre treatment procedure these masses were retained even if the coring fluid signal at a particular mass signal was not significantly different from the background. It was believed that the primary method would lead to a more rigorous answer so long as the coring fluid was

sufficiently different from the formation water. Unfortunately, since this first procedure is based on a fingerprint that is more representative of the original coring fluid additive the contamination could be an underestimation. The secondary pre treatment could be less precise but would not suffer any underestimation problems. If however, the coring fluid and formation water are sufficiently different, then both methods should obtain the same answer. A principal component analysis was performed and a natural separation was found between the core waters and the coring fluid samples as described later. Only masses with significant contribution to this separation were retained.

QUALITATIVE RESULTS

From Batch 1, Figures 1 and 2 show log-log plots of the most dissimilar and most similar coring fluids respectively. What should be noted is linearity over eight orders of magnitude (2-10) by signal mass. This suggests that the coring fluids are in fact extremely similar to each other. In contrast a typical log-log plot is shown in Figure 3 for arbitrary coring fluid-formation water set. The typical low R^2 correlation coefficient between the mud two sets of samples was 0.3 and high 0.6 with most lying closer to 0.45. In effect the coring fluid looks orders of magnitude different from any of the formation waters. It is believed that most linearity (correlation) between the coring fluid and formation waters is due to a sodium and potassium peak that happens to be the highest two signals and thereby weighting the correlation.

Figure 4 shows a principal component analysis of the mud samples with the formation waters. Samples labeled 1-5 are mud samples while remaining samples are sequentially numbered in order of depth. Two items are apparent. First the coring fluids separate naturally from the formation waters. Secondly the sample labeled 12 is an outlier. Sample 12 corresponds to 134, which was the 15,000 time dilution. Interestingly the 10,000 time dilution sample did not separate as an outlier. It was expected that the 10,000 time dilution (132) would not be a problem since it contained 0.7 micro-liters of formation water, and we routinely analyze as little as 1.0 micro-liters. Figure 5 is a secondary PCA with sample 12 removed. It was found that the first 8 PC's were significant with most of the information corresponding to the first 5. No level of discrimination (PC1 to PC8) separated the coring fluid samples attesting to their extreme similarity even between cores. Interestingly it was found that mass 133 corresponding to Cesium contributed most readily to the separation of coring fluids from formation waters. This discovery was made on Batch 2, and only investigated for Batch 2. An estimation of the cesium contained in the coring fluid was approximately 370 ppb (parts per billion) and was consistent for all coring fluid samples. An estimation of the cesium contained in the formation water varied from 70 ppt (parts per trillion) to 5 ppb. The natural abundance of cesium in ocean water is 400 ppt and rarely varies in nature more than an order of magnitude higher or lower than this value. One would therefore expect natural abundance of cesium to be on the order of 40 ppt to 4 ppt. Although the variation of cesium in these formation waters is close to this natural variation it is most likely that the actual natural amount of cesium in these formation waters was around 70 ppt and the additional concentration of cesium was due to fluid invasion. With a coring fluid

concentration of 370 ppb and a maximum formation water concentration of 5 ppb, there is there is added support that the coring fluid invasion in these cores is extremely small.

QUANTITATIVE RESULTS

Multivariate curve resolution was applied to the two pre-treatment groups. Signal non-negativity was one constraint, and drilling fluid end member definition was the other constraint. Concentration was not constrained to positive values so that variation near zero could be identified. Allowing negative concentrations along with the application of two pre-treatment methods served to qualitatively assign a mathematical technique resolution. Tables 1 and 2 show the raw percentage values of coring fluid contamination for Batch 1. Based on the comparison of negative values and repeated values between the table it is generally felt that the technique has about 1% absolute resolution. That is any percentage value below a value of 1 is not significantly different from zero. Therefore no contamination is evident in the cores to a limit of 1%. This is in excellent agreement with the qualitative results. Table 3 shows the maximum percentage of contamination for each sample. Contamination percentage is rounded to the nearest tenth of a decimal.

CONCLUSION

The present study was completed without a control set. That is no samples were contained a defined level of contamination. Also since no set of samples contained a classical tracer it is difficult to define the precision and accuracy of the MCR technique. Fortunately the natural tracer of cesium was identified. Assuming that there was a negligible concentration of cesium in the formation water produces a similar determination as the MCR. This qualitatively suggests that MCR is well suited for the purpose of core invasion determination. This is not surprising since generally MCR improves the more different the fingerprint (response) of individual components. Also this is not surprising since one pure component (the coring fluid) was known. For future work it would be interesting to apply MCR to a dataset with a classical tracer.

REFERENCES

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Table 1. Raw Percentage Values of Coring Fluid Contamination by Method 1

Sample	#1 Mud 51830	#2 Mud 51831	#3 Mud 51832	#4 Mud 51833	#5 Mud 51834
94	0	0	0	0	0
102	0	0	0	0	0
106	0	0	0	0.3235	0.0435
108	0.0196	0.0223	0.0423	-0.0464	0.1581
118	0	0	0	0	0
132	-0.0656	0.0003	0.063	-0.3044	0.0359
134	0	0	0	0	0
138	0	0	0	0	0
268	0	0	0	0	0
274	0	0	0	0	0
276	0	0	0	0	0
278	0	0	0	0	0
282	0	0	0	0	0
286	0.0233	0.1238	0.0529	0.0684	-0.0252
296	-0.0232	0	0	-0.0021	0
298	0	0	0	0	0
305	0	0	0	0	0
307	0.0027	0.0969	0.1024	0.0158	0.0151
310	0	0	0	0	0
314	0	0	0	0	0
318	-0.2435	-0.0698	0.0343	-0.4594	0.165

Table 2. Raw Percentage Values of Coring Fluid Contamination by Method 2

	#1 Mud 51830	#2 Mud 51831	#3 Mud 51832	#4 Mud 51833	#5 Mud 51834
94	0	0	0	0	0
102	0	0	0	0	0
106	0	0	0	0	0
108	0.125	0.0488	0.1695	0.0709	-0.4087
118	0	0	0.4185	0.4446	0.1894
132	0	0	0	0	0
134	0	0	0	0	0
138	0	0	0	0	0
268	0	0	0	0	0
274	-0.1764	0.0872	-0.03	-0.0225	0.0789
276	0	0	0	0	0
278	0	0	0	0	0
282	0	0	0	0	0
286	0	0.0409	0	-0.0051	0.0012
296	0	0	0	0	0
298	0	0	0	0	0
305	0.0708	0	0	-0.0534	0.4509
307	0	0	0	0	0
310	0	0	0	0	0
314	0	0	0	0	0
318	0	0	0	0	0

Table 3. Maximum Percentage of Contamination

Sample	Core	Depth ft	% Invasion
5	1	9634.2	0.3%
9	1	9638.2	0.6%
15	1	9654.2	1.0%
19	1	9658.2	0.2%
23	1	9662.2	0.4%
27	1	9666.2	NA
31	1	9670.2	0.1%
35	2	9674.2	0.0%
39	2	9678.2	0.2%
43	2	9682.2	0.0%
47	2	9686.2	0.1%
54	2	9698.4	0.2%
58	2	9702.2	0.1%
60	2	9704.2	0.0%
66	2	9710.2	0.2%
70	2	9714.2	0.1%
78	2	9726.7	0.1%
82	2	9730.5	0.1%
86	2	9734.2	0.0%
90	3	9737.2	0.0%

94	3	9741.2	0.0%
98	3	9745.2	0.3%
102	3	9749.2	0.0%
106	3	9753.2	0.3%
108	3	9755.2	0.2%
118	3	9765.2	0.4%
132	3	9779.2	0.1%
134	3	9781.2	0.0%
138	3	9785.2	0.0%
154	4	9801.2	0.2%
158	4	9805.2	0.2%
170	4	9817.2	0.9%
174	4	9821.2	0.1%
194	4	9841.3	1.7%
219	4	9867.2	0.5%
264	4	9913.1	0.1%
268	5	9919.4	0.0%
274	5	9927.2	0.1%
276	5	9929.2	0.0%
278	5	9931.2	0.0%
282	5	9935.2	0.0%
286	5	9939.3	0.1%
296	5	9963.3	0.0%
298	5	9967.1	0.0%
305	5	9989.5	0.5%
307	5	9991.3	0.1%
310	5	9995.8	0.0%
314	5	10000.7	0.0%
318	5	10003.2	0.2%

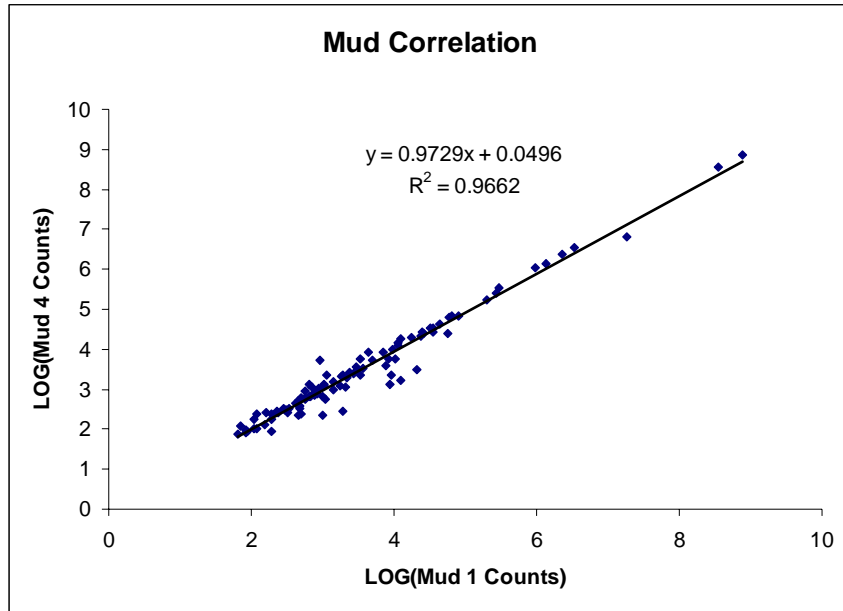


Figure 1. Correlation of Most Dissimilar Coring Fluid

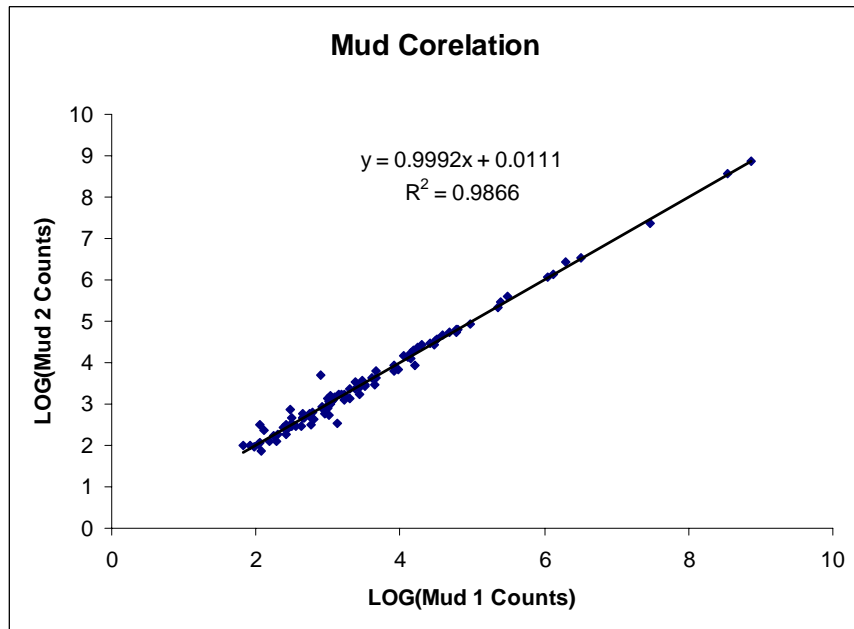


Figure 2. Correlation of Most Similar Coring Fluid

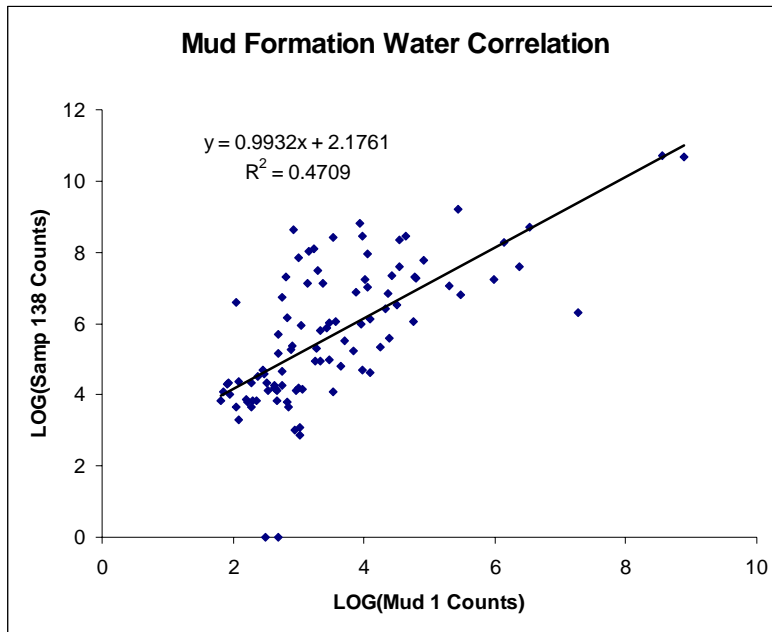


Figure 3. Correlation of Coring Fluid and Formation Water

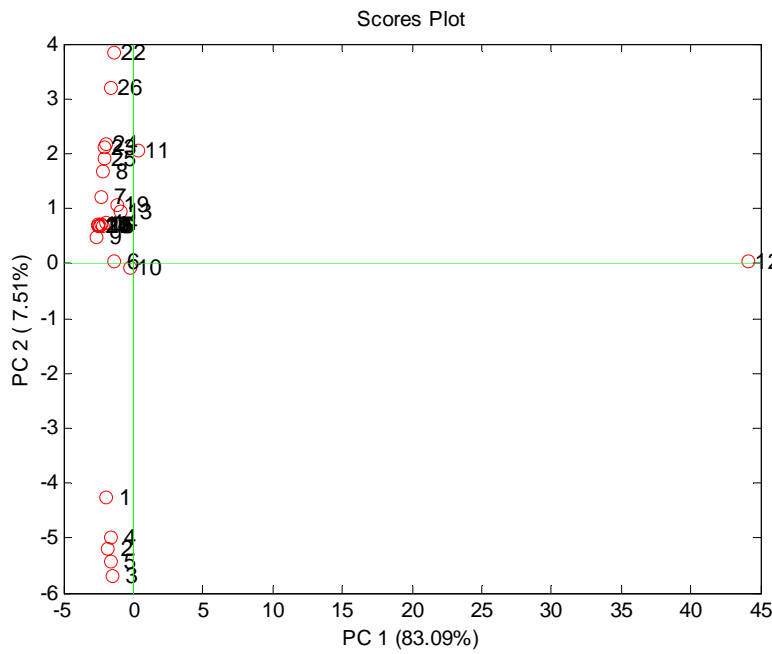


Figure 4. Principal Component Analysis of Mud Samples with Formation Waters

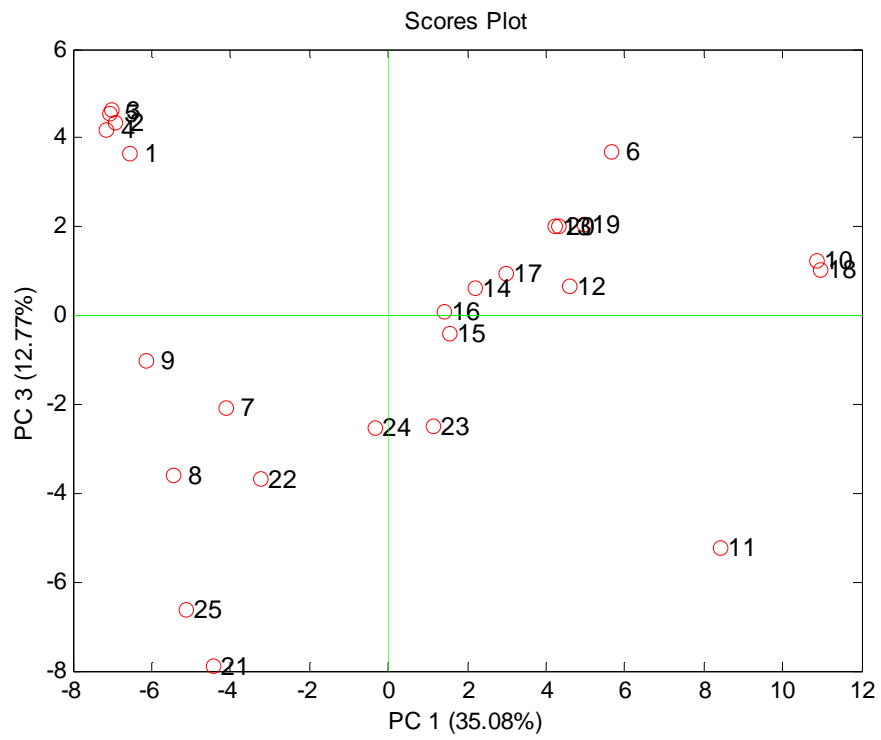


Figure 5. Principal Component Analysis with Sample 12 Removed