

THE EFFECTS OF FREEZING ON TRACER DISTRIBUTION IN CORES

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Abstract When oil fields are evaluated as candidates for enhanced recovery techniques, it is essential to have a realistic estimate of remaining oil in place. In some instances, especially heavy oil reservoirs with low salinity formation waters, oil saturations are measured by core analysis. In these cases it is necessary to determine the extent of mud filtrate invasion in the core, and the common practice is to add a tracer to the mud and analyze the core for the tracer. The usual wellsite procedure is then to freeze the core or core samples to prevent tracer diffusion, on the assumption that freezing immobilizes fluids.

We tested the assumption that freezing immobilizes fluids and found it to be false. For our experiments we used both cores and sandpacks saturated with brines of known composition and then froze them in either dry ice or liquid nitrogen. They were then subsampled, and the fluid composition of the subsamples was determined by geochemical techniques.

Freezing with dry ice causes more migration than freezing with liquid nitrogen. However, in all cases, fluid migration occurs and leads to incorrect assessment of the amount of mud filtrate invasion. The ultimate consequence is that oil saturations are in error. This miscalculation could significantly impact the economic viability of an enhanced recovery project. To avoid such miscalculations, we recommend that tracer analysis samples and subsamples be taken at the wellsite.

INTRODUCTION: THE USE OF TRACERS IN CORE ANALYSIS

Saturation is a key input to oil field economics, especially when evaluating tertiary recovery projects. Saturation is also very difficult to assess, and two things in particular work against obtaining accurate data from cores. First, cores are invaded by mud filtrate to varying degrees, and, second, they lose fluids by pressure blowdown when they are raised to the surface.

To estimate the amount of filtrate invasion, tracers can be added to the mud and then the amount of tracer can be measured in the core. The problem of pressure blowdown will not be addressed in this paper.

Various tracers have been used since Horner (1935) suggested adding arsenic acid or acetone to the mud. Pyle and Jones (1936) used dextrose and felt the method had merit and should be expanded. In some cases the chloride concentration of core samples has been used as a qualitative indication of mud filtrate invasion, provided there is enough contrast between the chloride concentration of the formation water and that of the mud (Caraway and Gates, 1959). Sayre (1959) was awarded a patent for the use of iodine-131 and other radioactive tracers in filtrate invasion studies. Armstrong and Lovelace (1961) found that tritiated water worked well as a tracer.

In recent years various tracers have been added to both water- and oil-based muds, most commonly to help determine remaining oil saturation, a parameter critical in evaluation of enhanced oil recovery projects. Typically tracers are used in conjunction with pressure coring, and consequently the cores are frozen. Even when conventional core has been cut with a tracer, the core, or segments of the core, has been frozen (Hensel, 1984; Brown and Marriott, 1988). The oil field wisdom appears to be that the tracer will diffuse if the core is not frozen and that freezing immobilizes the fluids. Wisenbaker (1947), in his first description of core freezing, claimed that "freezing effectively anchors each particle of oil and water in the particular place it occupies".

On the contrary, much evidence in the soil science, permafrost, and ground freezing literature indicates that moisture migration is a fundamental characteristic of the freezing process (e.g., Tystovich, 1973). Water freezes to produce pure ice, and organic and inorganic solutes are excluded. It seems unlikely that tracers should behave

differently and be immobilized by the freezing process. Movement of the tracers as a result of freezing could give erroneous indications of the amount of filtrate invasion in core.

PROCEDURES

A series of experiments was completed to test the assumption that tracers are immobilized by freezing. Cores and sandpacks were used with potassium salts as the tracers. The cores and sandpacks were about 4" in diameter, which is the average size of oil field cores. We attempted to simulate the oil field practices of initial transport in dry ice, arrival at the lab, and some storage in a freezer before sampling.

The cores and sandpacks were saturated with brines of known compositions and were then frozen by either burying them in dry ice or immersing them in liquid nitrogen. Once frozen, they remained buried in dry ice for about one day to simulate the transport time from the field to the lab. They were then removed from the dry ice and stored in a 0°F (-18°C) freezer for about ten days.

The frozen cores and sandpacks were sampled for tracer analysis. We wanted to prevent thawing during sampling, as this might have caused fluid migration. We also wanted to avoid condensation on the samples. For these reasons the sampling was done in the freezer. The cores and sandpacks were oriented so that the subsamples were from a single plane within them. They were marked into five equal slices along their length, and the first slices were carefully cut using a hammer and chisel. Each slice was cut down its center, again using a hammer and small chisel, and five samples were taken down the diameter of each slice (Figure 1). Subsequent slices were cut and subsampled the same way.

As each individual rock sample was collected, it was broken into smaller chips in a cleaned mortar and pestle. The rock chips were transferred to pre-weighed, one inch-diameter centrifuge tubes and capped. There was no reason to break up the sandpack samples since these disintegrate naturally on thawing. When the sampling was complete, the samples were moved from the freezer and allowed to thaw. Measured volumes of water were added to the tubes, the samples were centrifuged, and the extracts were analyzed for K⁺ using inductively coupled plasma (ICP) spectroscopy or for Cl-

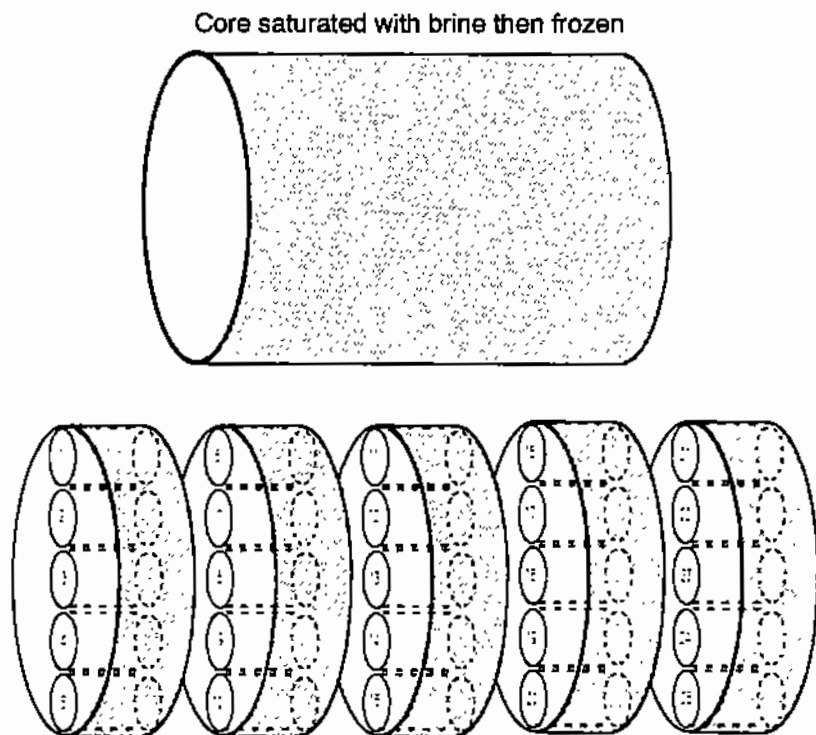


FIGURE 1 Sampling scheme for the cores and sandpacks.

using chloride titration. Both the ICP and chloride titration analytical methods are accurate to within 0.5%. Accuracies were confirmed by analyzing standards that were run with each set of experimental data.

EXPERIMENTS

4" Berea Core

A 4" by 8" core of structureless Berea sandstone was cut and then dried in a vacuum oven at 240°F (116°C). We chose Berea because it contains little clay and the clay is kaolinite. The rock therefore has a low cation exchange capacity (0.007 meq/g), and cation exchange with the potassium tracer in the brine should be minimal.

The core was evacuated in a vacuum desiccator. While under vacuum, a valve was turned so that the brine dripped in from the top of the desiccator. The brine filled the core and eventually filled the desiccator until the core was submerged.

The brine used for this experiment was 6% KBr. We chose this composition for a couple of reasons. First, being so concentrated, the effects of cation exchange would be minimal. Second, we hoped that the brine would have a sufficiently large X-ray cross section to see as concentration differences on computer tomography (CT) scans. The core was CT-scanned three times: dry, saturated, and frozen. Unfortunately differences in KBr concentration before and after freezing could not be resolved from the CT-scan data. Subsequent experiments did not include CT-scanning of KBr.

The Berea core was wrapped in plastic film and aluminum foil, and buried horizontally in dry ice so that it would freeze uniformly from all sides. The sample remained in the freezer in the chest of dry ice for one day and then in the freezer, in the same orientation, for a couple of weeks.

The frozen core was sampled along a vertical plane. Ice samples were also scraped off the surface of the core at the top, bottom, and two ends. Subsamples from the frozen core were analyzed for K⁺ concentrations using ICP.

4" Berea core results (Figure 2)

CT scans showed the rock to be structureless with essentially uniform porosity. Porosity was measured as 20%.

Figure 2 shows the K⁺ concentrations as a percentage of expected values. The results indicate that there has been movement of the tracer, but the direction of movement is not clear. In the left half of Figure 2, there appears to have been migration away from the

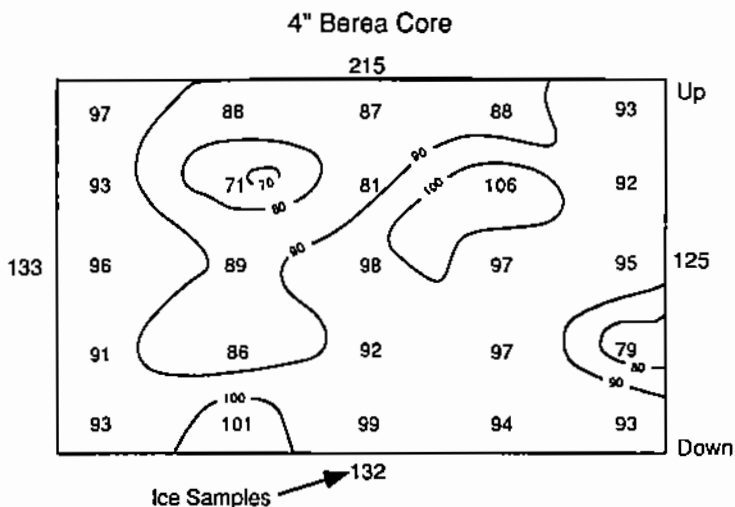


FIGURE 2 Berea core K^+ distribution after freezing in dry ice.

low value of 71%, and in the right half of the figure, there is a high concentrated around the value of 106%. The difference between these two samples is equivalent to 21 000 ppm K^+ out of the original 60 000 ppm.

All of the ice samples have high concentrations of K^+ compared to that expected (assuming the original brine of 6% KBr).

4" Sandpack - Coarse Sand

At this point we carefully reviewed our procedures and one significant question that arose was whether or not the Berea core had been completely saturated. The rock had about 600 md permeability, and the saturation techniques used should have been adequate to saturate the cores. However, to ensure that incomplete saturation was not a problem, sandpacks were prepared for the next experiments. The sandpacks were made by slowly adding sand to the brine; therefore, saturation was certainly complete and uniform.

The top was cut off a 4" diameter plastic bottle, and the bottle was filled about a third full with 3.75% KCl brine. Since we planned not to CT-scan the samples, we used the more common salt KCl instead of KBr. The concentration of K^+ is about the same in a 3.75% KCl solution as in a 6% KBr.

Coarse (16-30 mesh) Ottawa sand was slowly added to the brine. To dislodge air bubbles and ensure good packing, the bottom of the bottle was repeatedly tapped as the sand was added. The top of the bottle was taped on and the sample was buried vertically in a chest of dry ice and placed in the freezer. After a day the bottle was removed from the dry ice and remained in the freezer for two weeks until it was sampled.

To determine how long it actually takes to freeze a 4" sandpack, an additional sample was made and a thermocouple was placed through the neck of the bottle to its center. The sandpack was then buried in dry ice and the temperature was monitored through a chart recorder. The results indicate that it takes 20 to 30 minutes to freeze to the center of a 4" sandpack in dry ice.

The sandpack was sampled in the freezer. The top of the bottle was removed and the rest of the bottle was slit down its side until the sample could slide out. There was a centimeter or so of ice at the top of the sandpack. The ice was made up largely of clear crystals with a thin veneer of 'snowy' ice on top (Figure 3). Each ice type was sampled from the top, plus a little ice was also scraped off the bottom of the sandpack.

Results (Figure 4)

Figure 4 shows a very strong concentration of K^+ toward the center top of the sample. The distribution is a bull's-eye centered on a value that is 278% of the original K^+ concentration. The clear ice has about half of the original K^+ concentration, while the 'snowy ice' has almost three times the original concentration. The ice sample from the base of the sandpack had 474% of the original K^+ concentration.

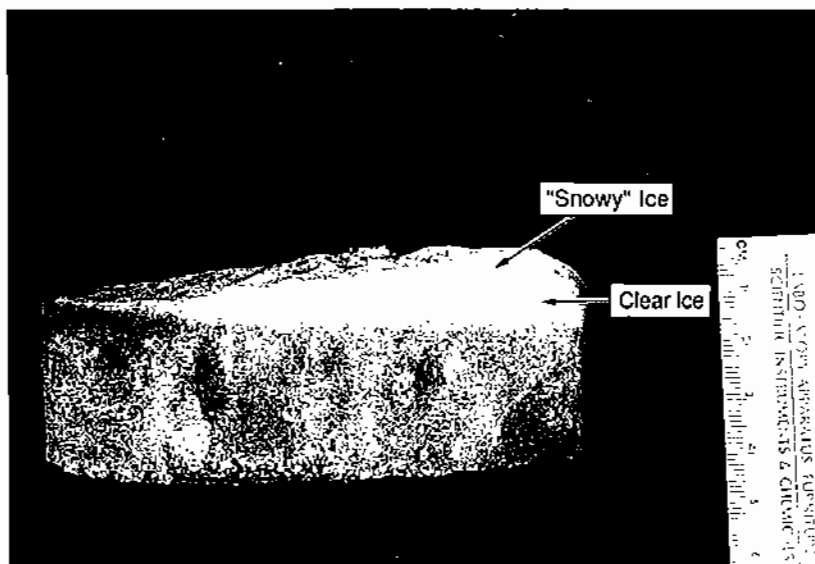


FIGURE 3 Ice sample from top of fine sandpack in dry ice.

4" Sandpack - Coarse Sand

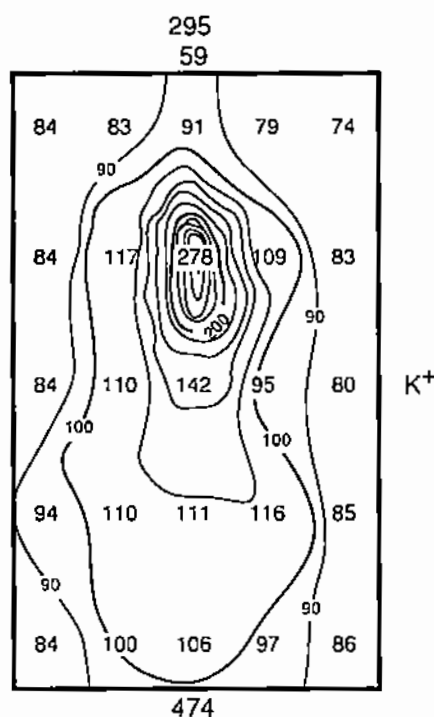


FIGURE 4 Coarse sandpack K⁺ distribution after freezing in dry ice.

4" Sandpack - Fine Sand

This sandpack was made of fine (100-120 mesh) Ottawa sand with 3% KCl brine. Two ice samples were taken from the top surface, but there was not enough ice for samples from other surfaces.

Results (Figure 5)

The K⁺ distribution is similar to that in the coarse sandpack in that it shows concentration toward the center top of the sample. The

4" Sandpack - Fine Sand

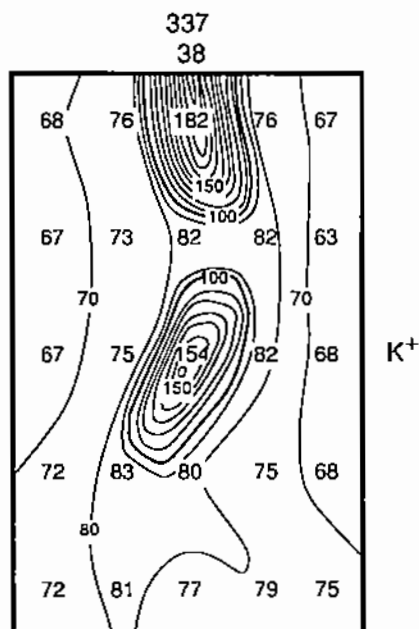


FIGURE 5 Fine sandpack K⁺ distribution after freezing in dry ice.

distribution has two bull's-eyes: one around the central value and one around the central value in the top sampling layer. Both of these samples have over twice as much K⁺ as the original solution. The ice shows a low concentration at its base and 337% of the original K⁺ toward the top.

4" Sandpack - 5-Layer

This sandpack was made of alternating coarse and fine layers to determine whether grain-size layering influences fluid migration during freezing. In addition to the sandpack samples, there were two

ice samples from the top of the sandpack and one very small one from the base.

Results (Figure 6)

The K^+ distribution is concentrated toward the center of the sample with a bull's-eye in the second lowest and topmost layers. There is little consistent difference between the fine and the coarse layers. The lowest fine layer has a concentration at its center of 169% of original K^+ , which is higher than the two surrounding coarse layers. The higher fine layer actually has less K^+ than original and less than the two surrounding coarse layers.

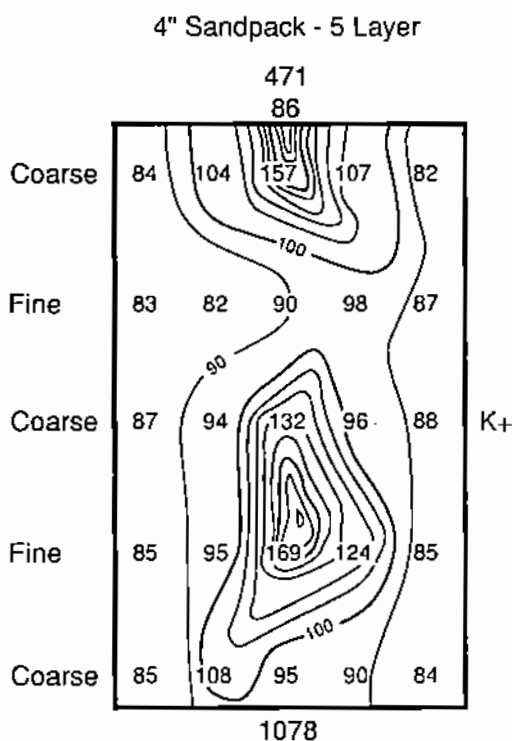


FIGURE 6 5-layer sandpack K^+ distribution after freezing in dry ice.

Layering has not had a noticeable influence on the K⁺ distribution.

The ice sample from the base of the sandpack had over ten times the expected K⁺ concentration. The ice at the top was layered like that on the coarse sandpack and was composed of a low concentration layer (86% of expected K⁺) overlain by a high concentration layer (471% of expected K⁺).

One question that remained was whether rapid freezing, regardless of other core damage that it could cause, would result in less fluid movement than freezing in dry ice. To test this, another sandpack of fine sand was prepared. Fine sand was chosen because, in the previous experiments, it had been much easier to chisel than the coarse and had usually broken along very straight planes.

4" Sandpack - Fine Sand, Liquid Nitrogen

A test sandpack was fitted with a thermocouple to determine how long it takes to freeze to the center of a 4" sandpack using liquid nitrogen. The thermocouple was monitored through a chart recorder, and the sandpack was lowered into a vacuum flask of liquid nitrogen. Freezing took about 10 minutes.

The sandpack for tracer analysis was slowly lowered into the liquid nitrogen until it rested on the curved base of the vacuum flask. An insulated lid was used to cover the flask and was only removed so that additional nitrogen could be added to keep the sample submerged. After about 20 minutes the sandpack was then transferred to a chest of dry ice and moved to the freezer. After one day it was taken out of the dry ice and stored in the freezer for ten days before sampling. We noticed, while chiseling this sandpack, that it was more brittle than those that had been frozen in dry ice. It also felt dryer and more friable.

In addition to the sandpack samples, two ice samples were taken from the top surface.

Results (Figure 7)

There was far less salt migration in this sandpack than in those frozen in dry ice. However, there was still over 10% extra K⁺ at the

4" Sandpack – Fine Sand
Frozen in Liquid Nitrogen

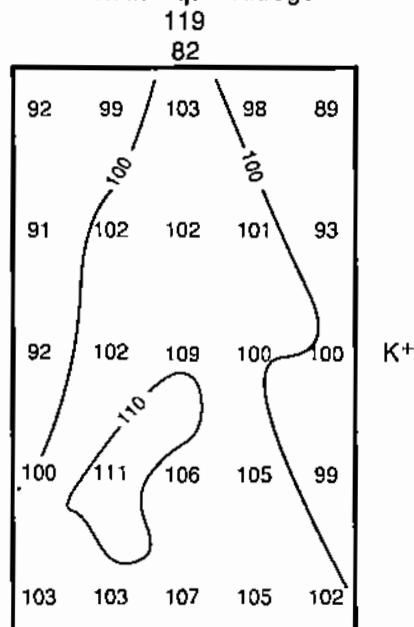


FIGURE 7 Fine sandpack K⁺ distribution after freezing in liquid nitrogen.

center of the sandpack and 10% too little around the edge. The concentration was toward the center and base and was cone-shaped.

The cone shape of the K⁺ distribution might be the result of contact with the base of the flask, and possibly the distribution would have been more of a bull's-eye if the sandpack were suspended and entirely surrounded by liquid nitrogen until frozen.

The ice at the top of the sandpack was composed of a layer that had 18% less K⁺ than expected overlain by one that had 19% more K⁺ than expected.

The sandpack data consistently showed tracer migration toward the center of the samples. However, at this point we felt it appropriate to test two more rock samples: another 4" diameter sample frozen in dry ice and a 4" sample frozen in liquid nitrogen.

4" Kaolinitic Sandstone

This sample was a core of structureless, clay-rich reservoir sandstone. The clay is predominantly kaolinite and occurs as individual platelets from 1 to 10 microns across and vermiform masses up to 80 microns long (Figure 8). The core had been preserved in strippable plastic and was still fairly fresh when opened. It was miscibly cleaned by flowthrough of toluene and methanol and then saturated by flowthrough of 3% KCl brine at 5 ml/h.

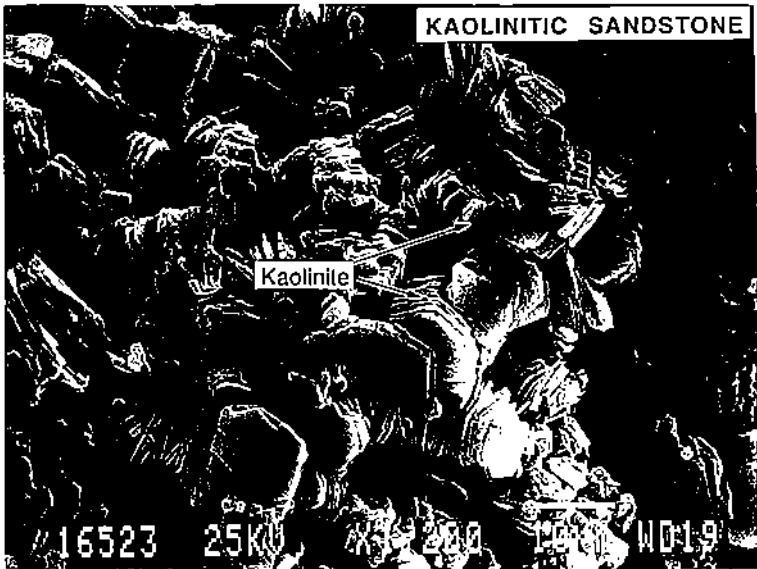


FIGURE 8 Scanning electron photomicrograph of kaolinitic sandstone core.

The core had been cut with KCl mud, so there was a chance that solid KCl remained following cleaning. However, 3% KCl brine is undersaturated and will dissolve the solid salt. For this reason we

continued to flow brine through the sample until the brine flowing out was the same concentration as that flowing in. To monitor this, the effluent brine resistivity was measured by flow through a conductivity cell. Flow was continued until the resistivity of the effluent matched that of the saturating brine. A total of two liters of brine were used. Four pore volumes were displaced, and one pore volume made up the final saturation.

The core was wrapped in plastic film and foil, oriented, and buried horizontally in dry ice. The core was sampled through the vertical plane. Only one ice sample was taken, as there was very little ice on the surface of the core.

Results (Figure 9)

The K^+ distribution is concentrated toward the center of the core. The lowest concentrations are toward the right. The difference between high and low values is 20%, equivalent to 6000 out of the original 30 000 ppm K^+ .

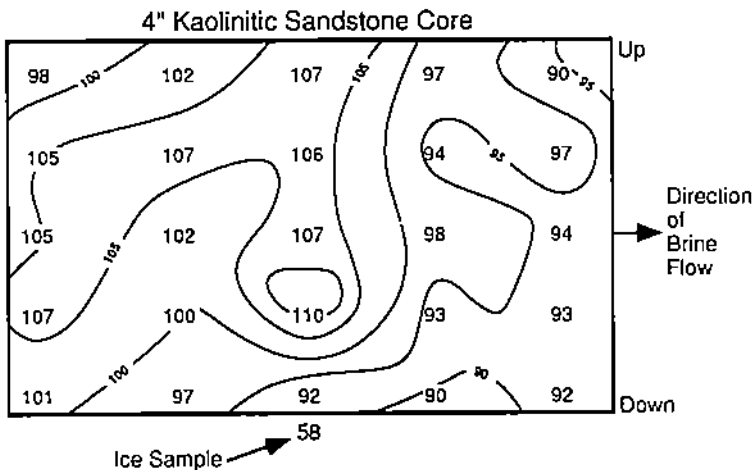


FIGURE 9 Kaolinitic sandstone core K^+ distribution after freezing in dry ice.

This sample had very little ice on its surface. The one sample that we analyzed had a low concentration of K^+ .

4" Boise Core - Liquid Nitrogen

The final experiment was to determine the amount of tracer migration that occurs in a rock frozen in liquid nitrogen. All of the unlaminated Berea had been used, so we chose a sample of structureless Boise sandstone that had similar porosity and permeability to the Berea.

The core was vacuum-saturated with 3% KCl, wrapped in plastic film and foil, and placed vertically in the vacuum flask. Liquid nitrogen was poured into the flask until it covered the sample, and then an insulated lid was held onto the flask. Additional liquid nitrogen was added as needed to keep the sample submerged. After about 30 minutes the sample was removed and buried horizontally in dry ice. It was labeled with arrows to indicate its orientation in both the flask of liquid nitrogen and the dry ice.

We examined unfrozen rock from the same sample in the scanning electron microscope (SEM) and were surprised to find all the grain surfaces covered with authigenic quartz and heulandite (Figure 10). Heulandite is a calcium aluminum zeolite and is very prone to cation exchange.



FIGURE 10 Scanning electron photomicrograph of Boise sandstone core.

Results (Figure 12)

This sample fractured, most likely while it was frozen in the liquid nitrogen. There was one large fracture that cut diagonally across the core from its top end to two thirds of the way down its length (relative to its orientation in the flask of liquid nitrogen, Figure 11). There was a centimeter or so of ice at the top of the sample. The relationship between the ice and the fracture is unclear. There was no visible ice in the fracture and, for the analyses, we avoided sampling the fracture surface itself.

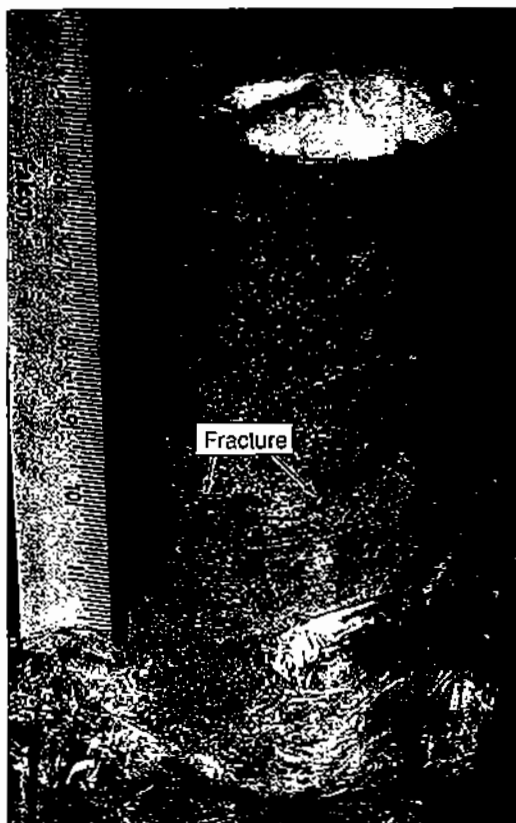


FIGURE 11 The Bolse core fractured when frozen in liquid nitrogen.

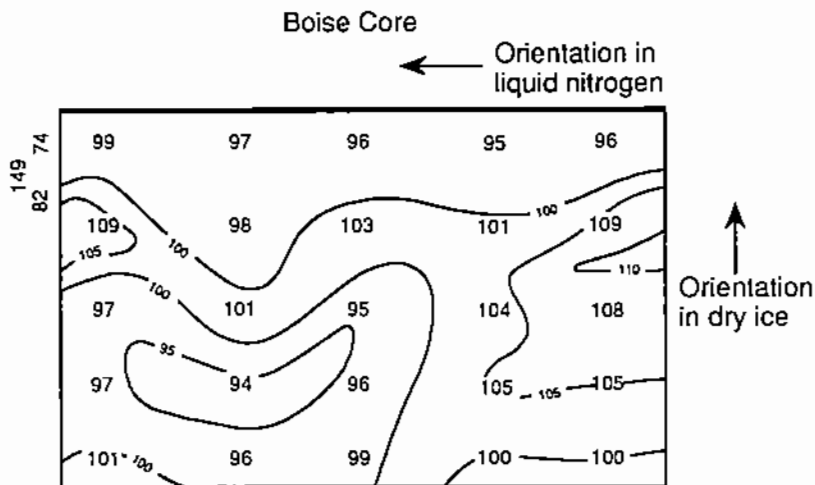


FIGURE 12 Boise Cl- distribution after freezing in liquid nitrogen.

Since the sample contained heulandite, the K^+ data would be influenced by both cation exchange and the effects of freezing, and the two would be difficult to separate. For this reason we analyzed the samples by chloride titration and compared the chloride concentrations as a percentage of those expected.

The chloride data are shown in Figure 12 and display a concentration toward the center, with the majority of high values at center right. The ice was composed of a layer that had less Cl- than expected overlain by one that had 49% more than expected.

DISCUSSION

In all our freezing experiments, the tracer migrated inwards, away from the freezing source. Of the samples frozen in dry ice, the cores typically showed far less tracer migration than the sandpacks. The outside of the core or sandpack would have frozen first and, as the

ice crystals formed, some salt was trapped, most likely in the form of fluid inclusions, while the rest moved ahead of the freezing front. This would increase the salinity of the remaining liquid and consequently lower its freezing point. Within a sample, therefore, freezing actually takes place over a range of temperatures.

The frozen rocks were tightly wrapped with plastic film, and there was very little ice on their surfaces. At the onset of freezing, brine in the very outermost pores of the samples froze and the salt tracer could easily be expelled at the surface, hence the higher than expected concentration for most surface ice samples. In detail, the sandpacks did not freeze completely uniformly from the outside in. Since the tops of the sandpacks were not in direct contact with the freezing source, the sides would have frozen before the tops. The centimeter or so of ice on top of the frozen sandpacks indicates that there was time for, and room for, water to be expelled upwards. This water would start to freeze from its contact with the cold thermal mass of the sandpack. As the ice formed, the tracer would be excluded, hence the lowermost ice is most pure. Ultimately the final salt-rich layer of water froze to form the thin veneer of 'snowy' ice.

Freezing in liquid nitrogen resulted in less tracer movement than freezing in dry ice. Both the core and the sandpack, frozen in liquid nitrogen, showed about 10% more tracer than expected toward the center of the sandpack and toward the center ends of the core. The extremely low temperature of liquid nitrogen causes rapid freezing. Since heat transfer occurs much more rapidly than mass transfer, the resultant ice crystals are less able to exclude solutes.

The Boise sandstone core was frozen quickly in liquid nitrogen, and, while this resulted in only 10% tracer migration, it also fractured the core. Rapid freezing leads to high-temperature differentials between the surface and interior of samples. This leads to pressure buildup within samples, and fracturing is not uncommon. Lebeaux (1952), for example, reported that most core samples fractured when he froze them using an acetone-dry ice mixture. During all-round freezing, surface pores become plugged with ice, thereby creating a closed system. In matrix-supported, poorly consolidated samples, rapid freezing may lead to local compaction of matrix clays and further complication of the tracer distribution.

The behavior of a tracer on freezing is influenced by many variables including porosity, permeability, pore sizes and heterogeneity, rock/fluid interactions, freezing rate, freezing direction, freezing temperature, storage temperature, storage time, thermal

conductivity, solute concentration, etc. Panday and Corapcioglu (1991) summarized the situation thus: "In fact, a wide variety of complex behavior has been observed in freezing porous media." In our experiments we deliberately used single salt tracers and samples with homogeneous fabric. With more complex rocks and fluids, it would have been difficult to predict expected tracer concentrations and therefore difficult to determine the effects of freezing from the effects of other variables.

We froze relatively small samples, and therefore the freezing was faster than when whole cores are frozen. When whole cores are frozen in dry ice, there may or may not be enough ice to bury each core length. The time taken to freeze a whole core depends upon its size, the reservoir temperature, and the amount of ice. From our experience it takes a minimum of 3 hours to freeze a 3-ft length of 4½-in. core recovered from a 90°F (32°C) reservoir. A core length placed in a chest with a block of dry ice on top of it will not only freeze slowly, but also from one side. The slower a solution freezes, the more able it is to exclude solutes such as tracers, and nonuniform freezing will result in an asymmetrical pattern of tracer distribution.

CONCLUSIONS

From our experiments we draw one conclusion - don't expect that tracers will be immobilized by freezing - and pose one practical recommendation: sample and subsample the cores at the wellsite for tracer analysis. If the cores are subsampled and packed separately, diffusion is no longer a potential problem, because the entire sample will be analyzed.

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