EFFECTS OF PARAFFIN WAX PRECIPITATION DURING COLD WATER INJECTION IN A FRACTURED CARBONATE RESERVOIR

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ABSTRACT

This study investigates potential effects of paraffin wax precipitation while waterflooding oil from an offshore fractured carbonate reservoir using unheated seawater. Although initial reservoir temperature is 130 deg. C, continuous injection of 8 deg. C seawater propagates a cold temperature thermal front from the water injection wells. Paraffin wax precipitates from the reservoir oil when chilled to temperature below 25 deg. C. Could this be problematic with respect to water injectivity and oil recovery? What is the nature and distribution of precipitated wax in this rock? How does the chilled temperature front propagate in relationship to the waterflood front? Is there incentive to heat the injection water? These are questions that this investigation was undertaken to answer.

Laboratory waterflood tests were conducted on analog outcrop cores and reservoir cores using synthetic seawater and reservoir oil. Several scenarios were tested; continuous waterfloods beginning with residual oil saturation and temperature reduction in steps from 65 deg. C to 10 deg. C, and waterfloods starting with 10 deg. C temperature and different initial oil saturation magnitudes. Oil recovery and water relative permeability were measured. After each test, while maintaining cold temperature, core chips were imaged using an ESEM to identify whether paraffin wax was present in the pore system and if so, how it was distributed. Thermal effects were included in waterflood simulations to evaluate progression of the temperature front relative to the waterflood front and to predict effects of reservoir cooling on oil recovery.

Paraffin wax was identified in cores after each laboratory test. Wax occurred in masses that were unevenly distributed in the porous media. Reducing temperature after flooding cores to S_{or} improved rather than reduced water injectivity. Even though wax precipitated when temperature fell below the oil cloud point, as temperature was reduced, the volume of liquid oil left in the core shrank, increasing water saturation and water relative permeability. This result was consistent with field experience. In waterfloods starting with temperature below 24 deg. C and oil saturation greater than residual, water entry pressures were higher, but once water flow was established, oil recovery was fairly efficient despite paraffin wax precipitation. Waterflood simulations, including thermal effects, showed that progression of the chilled temperature front lagged the waterfront to the extent that oil was efficiently recovered before regions became cold enough to cause

wax to precipitate. With respect to this particular waterflood scenario, there is insufficient incentive to consider heating the injection water.

INTRODUCTION

The original temperature of the giant chalk petroleum reservoir of this investigation is 130 °C. Figure 1 shows viscometer measurements for dead reservoir oil (oil without solution gas), live oil, and brine at various temperatures. Brine and live oil trends are fairly consistent from high to low temperature, but one can easily discern that “dead” oil trends from measurements with 2 different viscometers change abruptly with temperature below 25 °C. The “exact” viscosity of the dead oil is questionable below 25 °C. Using one type of viscometer, an oil viscosity of 46 cP was recorded with 10 °C temperature. Using an identical oil sample at 10 °C but viscometer of different shear rate and closer spacing between the spinning portion of the viscometer and wall, an oil viscosity of about 1700 cP resulted. Others [1, 2] have shown that the oil cloud point, or temperature at which wax begins to crystallize or precipitate, can be inferred from such an inflection point on a viscosity-temperature plot. Comparing live and dead oil trends of Figure 1, one can appreciate the effect of solution gas or “light ends” on viscosity and infer that wax precipitation is influenced by oil composition. Dead oil data of Figure 1 gives impression that wax precipitation should be avoided when attempting to quantify typical reservoir fluid flow behavior, especially as the average pore throat size in this chalk is smaller than 1 micrometer. For over 2 decades, corefloods to characterize flow in this reservoir have been performed with protocols to avoid wax precipitation.

The reservoir is under active waterflood with daily injection of significant volumes of cold (5 °C) seawater. Recent surveys show that continuous injection of cold seawater has reduced temperatures in the reservoir tens to hundreds of meters from injection wells to as low as 10 °C. Whereas wax had previously been a concern regarding produced fluids and laboratory methods, wax may also be precipitating within the reservoir where temperatures are cold.

Investigators [3, 4] describe that significant formation damage and loss of brine injectivity can occur when cold-water injection causes wax to precipitate in situ. Although operational experience with the field of this study indicates that water injectivity increases rather than decreases with time, knowing that wax likely precipitates in cold regions near seawater injection wells leads one to speculate on how wax precipitation influences water injectivity and oil recovery. What is the nature and distribution of precipitated wax in this rock of average pore throat size smaller than 1 micrometer? If wax severely blocks matrix pores, could much of the injected water be channeling through the natural fracture system? Could this be problematic with respect to water injectivity and oil recovery? How does the chilled temperature front propagate in relationship to the waterflood front? Is there incentive to heat the injection water? These are questions that this investigation was undertaken to answer.

EXPERIMENTAL

Two series of experiments were performed to investigate effects of cold temperature wax deposition on fluid flow and retention. The first experiment, performed with a chalk core from an analog outcrop with pore size distribution similar to reservoir core, investigated how wax precipitation influences water injectivity near water injection wells. The second experiment was performed using reservoir chalk cores to look at another extreme - where cooling takes place before oil has been significantly recovered from the rock.

Flow Apparatus

The flow apparatus (coreholder, valves, tubing, pressure regulators) was assembled within a large temperature-controlled water bath. Temperature within the bath was easily controlled within the range from 10 to 66 °C.

Fluid Properties

Chalk-equilibrated synthetic seawater was used as brine for this investigation. Whole reservoir oil that had been stored under an Argon gas cap was used for this work. The oil was filtered through chalk at 66 °C prior to conducting coreflood experiments.

The cloud point temperature of the 'dead' whole oil is approximately 25 °C from viscosity data of Figure 1. The cloud point for the dead oil as determined by cross-polar microscopy (CPM) is 25 °C. Cloud point for a live sample of the reservoir oil at 276-bar pressure, determined with a solids detection system (SDS), is 24 °C. For this oil, live and dead oil cloud point temperatures are similar. Near injection wells, where copious volumes of seawater continually flush past residual oil, eventually that oil will likely be "dead", or void of solution gas. With this in mind, tests reported here were conducted using 'dead' whole oil, anticipating that such tests would provide useful information relating to performance within this reservoir.

Water Injectivity – Cooling During Waterflood at S_{or}

This experiment investigated change in water injectivity when residual oil within the rock cools below the cloud point temperature and wax precipitates. A 3.8-cm diameter by 7.6-cm long analog outcrop chalk plug was used for this test. The outcrop chalk is a good analog to reservoir material with similar porosity, permeability, and pore size distribution. Porosity was 35%. The permeability of the plug to brine was 1.5 mD at temperatures from 10 to 66 °C.

Oil Permeability at S_{wr}

The plug was driven to residual brine saturation with air in a high-speed centrifuge. Air was displaced from the core by brief vacuum evacuation. Brine saturation was 13% after flooding with 66 °C whole stock tank oil. Immediately after the oil flood, the permeability of the plug to oil was 1.2 mD. After aging the plug for 5 days at 66 °C, the permeability of the plug to oil was still 1.2 mD.

Brine Permeability at S_{or} as the Plug Cooled

At the 66 °C test temperature, the plug was waterflooded at an injection rate of 0.5-mL/hr, approximating a flood advance rate of 0.03 m/day. This rate was selected to yield higher residual oil saturation than one might expect close to brine injection wells, increasing the likelihood that adverse effects of wax precipitation could be identified. At the end of the 66 °C waterflood, brine saturation was 62 %. Permeability to brine was 0.075 mD, yielding a brine relative permeability of 0.05 (expressed as a fraction of the original permeability of the plug to brine under conditions of complete brine saturation).

Brine injection continued (0.5-mL/hr rate) as temperature was reduced to 10 °C in steps. Although no additional oil was produced, brine saturation increased from 62% to 64% as temperature changed from at 66 °C to 10 °C as a result of shrinkage of the in situ oil volume with decrease in temperature. Brine relative permeability increased as the temperature was reduced from 66 to 26 °C, peaked at 0.10 with 26 °C temperature, then dipped somewhat between 26 and 10 °C, ending at 0.09. After 3 additional days of flooding (0.5-mL/hr rate) at 10 °C, brine relative permeability was 0.10; essentially the same as it had been earlier at 26 °C. These results are shown on Figure 2a.

Additional measurements were recorded with higher brine injection rates to see if mobilized wax particles might block pore throats and reduce the brine permeability. Under this scenario, one would expect brine permeability to decrease with increasing rate. The opposite occurred in this case. Higher flow rates yielded slightly higher rather than lower permeability.

Figure 2b shows results from this investigation compared with water relative permeability trends from typical oil-brine tests performed on other chalk samples. Remember that results shown on Figure 2b from this investigation reflect changes in flow capacity and brine saturation resulting from temperature reduction rather than physical displacement of oil from the sample. As shown, results from this investigation are fairly consistent with measurements recorded for other similar samples during relative permeability experiments.

The primary result from this test is that the permeability of the plug to brine at S_{or} increased as the temperature decreased until the temperature fell below the oil cloud point temperature. The increase is consistent with an increase in brine relative permeability with increasing water saturation. Below the cloud point temperature, brine permeability was fairly constant.

The following is an interpretation of these results. A preferential brine flow network was established at S_{or} before the core and fluids were chilled. The mass of oil within the core remained constant as temperature was reduced. Oil density increased as temperature was reduced, yielding lower in situ oil volume and thereby lower residual oil saturation. Unlike water, which becomes less dense (expands) upon freezing, solid wax occupies less volume than its liquid constituents. Apparently solid wax was not mobilized as a result of brine injection. Continuous brine injection insured that volume vacated by oil was replaced by brine, increasing brine saturation and thereby increasing brine permeability.

Post-Test ESEM Inspection for the Presence of Paraffin

The sample was kept cold as it was removed from the coreholder for Environmental Scanning Electron Microscope (ESEM) analyses. Chips were broken from the center of the plug for ESEM imaging. The chalk material was maintained at 10 °C during ESEM imaging using a cold stage. Presence of wax was confirmed by photomicrographs. Wax distribution was uneven, with many pores apparently free of wax. Wax appeared as masses rather than crystals. Some of the wax structures identified were significantly larger than average rock pore dimensions, and appeared to adhere to rock mineral surfaces, as shown in figure 3. Wax is easily distinguished from carbonate core material by EDS (elemental spectral analyses), as shown in Figure 4.

Trapped Oil – Static Cooling with High Oil Saturation Followed by Brine Injection

The objective of these tests was to determine whether brine could be injected into cold reservoir chalk with high initial oil saturation and if so, whether oil would be recovered. Tests were performed using two reservoir core plugs of 2.5-cm diameter by 3.8-cm length. The first plug was of 2.8-mD permeability to brine with 100 % brine saturation. Porosity was 37%. The second plug was of 1.6-mD permeability to brine with 100% brine saturation. Porosity of the second sample was 30%. The brine-saturated plugs were driven to S_{wr} by an air-brine porous plate technique. Air was displaced from the plugs by flooding with Decalin. Decalin was subsequently flooded out with 15 pore volumes of whole stock tank oil at 66 °C to establish initial oil and brine saturations. The plugs were aged for 1 week at 66 °C temperature.

The first sample was allowed to spontaneously imbibe brine for two weeks within an imbibition cell at 66 °C. Brine saturation changed from 13 to 40% in 6 days and thereafter remained constant for the remainder of the 2-week spontaneous brine imbibition process. After transfer to a coreholder, the plug was chilled to 10 °C. The threshold pressure required to inject brine at 10 °C for this sample was measured by increasing pressure drop (difference between upstream and downstream pressure) in 0.1 bar steps. At each step, production was monitored for at least 24 hours. Production was not observed until pressure drop increased to 0.6 bar. The core was flooded at this pressure (approximate rate of 0.75 mL/hr) for 107 hours, although all oil produced during this test was recovered during the first 58 hours. Final brine saturation was 63%. Brine relative permeability at this saturation was 0.12. This data point falls close to the trend shown for other samples on Figure 2b.

The second sample was mounted in a core holder and cooled to 10 °C. Initial brine saturation was 27%. The threshold pressure required to initiate brine flow into the core at 10 °C was 0.8 bar. With 0.8 bar pressure drop across the core, production was monitored for 400 hours. During this time, production rate gradually changed from 0.014 mL/hr to

0.043 mL/hr. During the first 274 hours, brine saturation increased to 69%. No additional oil was subsequently produced for the remaining 126 hours of the test. Brine relative permeability was 0.01 with 69% brine saturation. This data point is off trend compared to results of Figure 2b.

Threshold pressure necessary to initiate brine flow through the matrix at 10 °C temperature appears to be related to initial oil saturation. These threshold pressures are different than capillary pressure values for similar chalk samples at similar brine saturation [5].

Figure 5 shows one of the images from ESEM analyses conducted on the plugs while cold and after flow tests were completed. Masses of wax were found to occupy select regions of the pore space, similar to observations for the outcrop core described in the previous section, but with greater abundance. Relative abundance of wax appears to be related to initial oil saturation before cooling.

In summary, threshold pressure for brine penetration appeared to be related to oil saturation magnitude. Once brine flow was initiated, significant oil recovery was attained even though the samples were cooled to 10 °C with high initial oil saturation before flooding with 10 °C seawater. Although wax deposition was noted within the cores, wax did not plug all pores or dramatically change waterflood oil recovery.

These tests looked at a scenario whereby bypassed oil might be chilled below the cloud point before being subject to waterflood. If, because of cooling, a threshold pressure has to be exceeded before brine penetrates a matrix block within this naturally fractured reservoir, brine may preferentially flow through the fracture system and bypass matrix blocks. Simulation was used to check whether this might be a potential scenario.

SIMULATION OF COLD WATER INJECTION

Reservoir simulations were performed using a homogeneous cross-section model (homogeneous radial), typical reservoir fluid flow parameters, reservoir temperature data (initial temperature, fluid specific heat, formation specific heat, thermal conductivity) and PVT data to identify proximity of the "cold temperature" front in relation to the waterflood front. Summary results, shown in Figure 6, show that the temperature front lags the waterflood front significantly. Temperature and brine saturation maps generated by the full field flow model (including effects of heterogeneity) also indicated that the temperature front significantly lags the waterflood front. Position of the waterflood front at various times was studied in detail to identify whether the frontal position between layers might leave moveable oil in cold zones where wax might affect recovery. Temperature and saturation maps at various times were generated. Remaining moveable oil (pore volume times difference between oil saturation and waterflood residual oil saturation) was calculated as a function of time, temperature, effective permeability, and swept area. To gain a sense of how remaining moveable oil is distributed in relationship to reservoir temperature, results were subdivided according to temperature range. To graph results, potentially recoverable oil reserves within particular temperature ranges were calculated by dividing remaining moveable oil in regions within a temperature range by total remaining moveable oil for the year being simulated. Results are shown in Figure 7.

As shown by Figure 7, remaining moveable oil at temperatures low enough to precipitate wax is less than 0.3% of total remaining reserves for the foreseeable future. Cold regions are in the vicinity of brine injection wells. Defining "low" temperature as below 52 °C, about 0.3% of the remaining moveable oil in swept areas is left in low temperature zones by year 2012, and 1.2 % in year 2029.

EOR Potential

After waterflood, remaining oil in swept areas is still an attractive target for EOR. More than 95% of that target volume will be in areas where temperatures are higher than 52 °C and effective permeability higher than 1 mD. About 90 % of the remaining moveable oil will be in areas where the reservoir temperature is greater than 121 °C.

Although wax precipitation as a result of cold seawater injection is seen to have little impact on waterflood oil recovery, cold regions around seawater injection wells do pose a challenge with respect to potential EOR processes. While the bulk of the EOR target is "hot," EOR designs will need to take into account cold regions in areas surrounding wells that were used for cold seawater injection.

DISCUSSION

For this specific reservoir scenario, results of this investigation describe a cohesive picture about effects of wax precipitation from cold seawater injection. Where oil saturation is low before wax precipitation occurs, wax occurrence has negligible effect on brine injectivity. Wax distribution within the porous media is uneven, with many pores free of wax. Shrinkage of in situ oil volume as a result of cooling yields increased brine saturation, brine relative permeability, and brine injectivity. This result is consistent with field experience. In corefloods starting with temperature below the oil cloud point and oil saturation greater than residual, brine entry pressures were higher, but once brine flow was established, oil recovery was fairly efficient despite paraffin wax precipitation. Waterflood simulations, including thermal effects, showed that progression of the chilled temperature front lagged the waterfront to the extent that oil was efficiently recovered before regions became cold enough to cause wax to precipitate. With respect to this particular waterflood scenario, there is insufficient incentive to consider heating the injection water. However, the presence of cold regions within the reservoir needs to be taken into account when designing and implementing EOR processes.

CONCLUSIONS

Conclusions from this work on effects of paraffin precipitation during cold-water injection in a fractured carbonate reservoir include the following:

1) Wax adheres to some of the chalk mineral surfaces in pores and micro-cracks.
2) Wax abundance is related to oil saturation.
3) With continuous brine flow and low oil saturation, wax precipitation as a result of cooling did not appreciably affect water injectivity.
4) After cooling chalk with intermediate to high oil saturations under static conditions (no flow), threshold pressures had to be overcome to initiate brine flow into the rock matrix. After exceeding "threshold pressures," oil recovery was significant even with low temperatures.
5) Simulations show that the cold front significantly lags the waterflood front.
6) With respect to this particular waterflood scenario, there is insufficient incentive to consider heating the injection water. However, the presence of cold regions within the reservoir needs to be taken into account when designing and implementing EOR processes.

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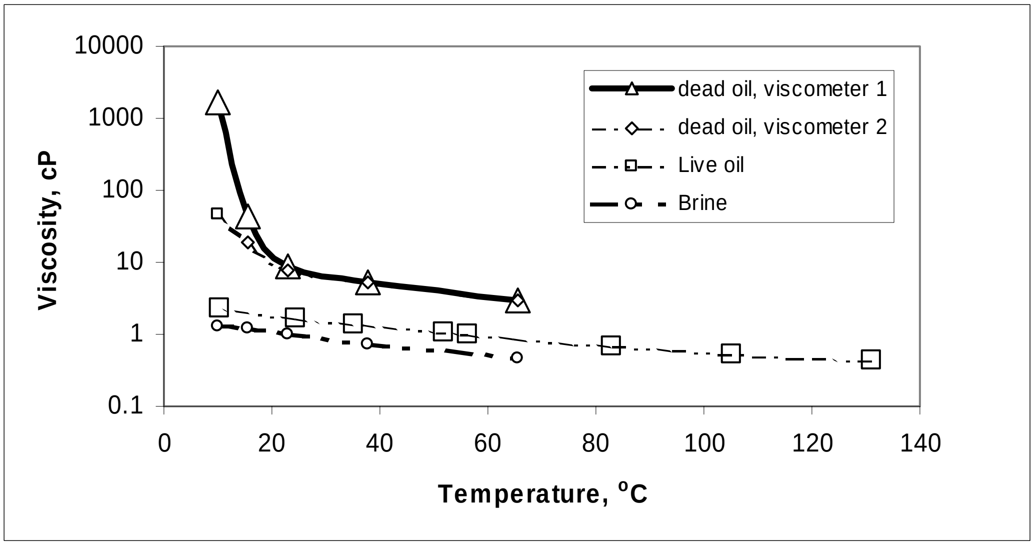
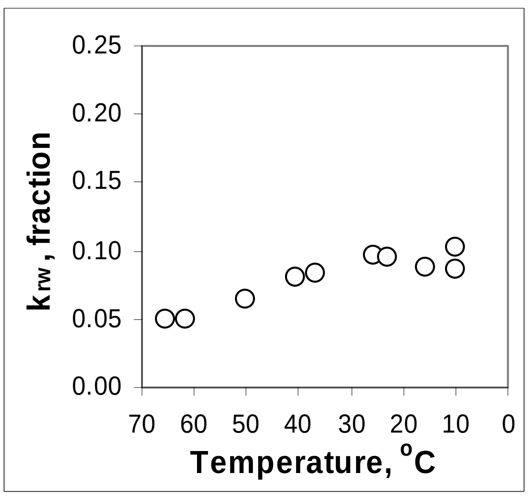
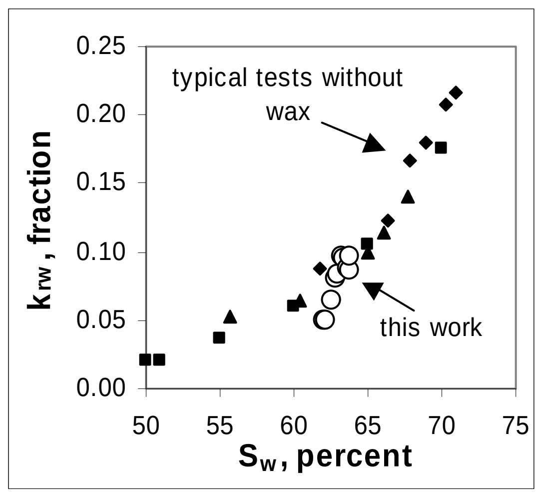


Figure 1. Oil and brine viscosity at various temperatures.

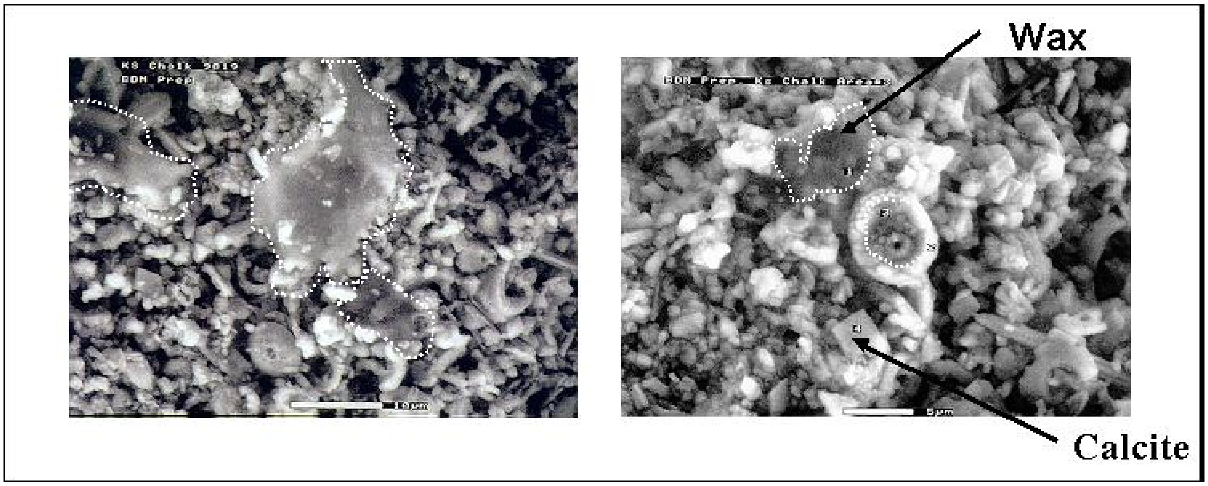


(a)



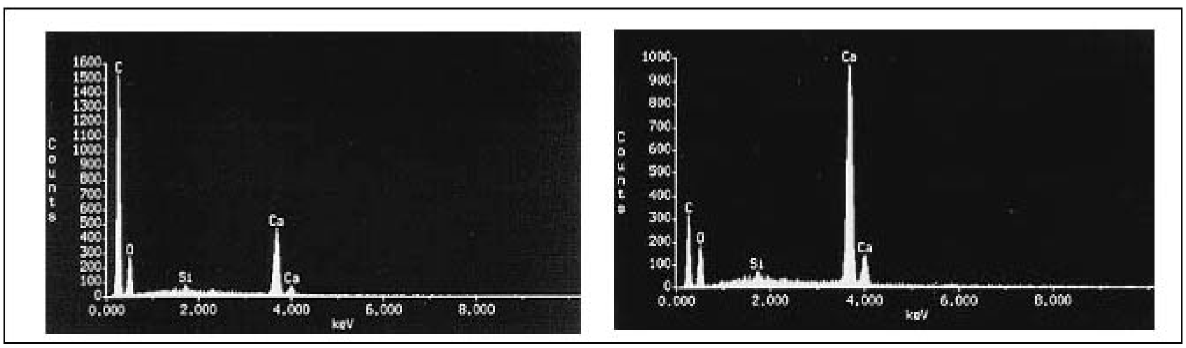
(b)

Figure 2. Brine relative permeability during cooling. (a) k_{rw} versus temperature, (b) k_{rw} versus S_w.



(a) 2000 x magnification (b) 3000 x magnification

Figure 3. SEM photos of wax in pore space. Wax features are outlined with dashes.



a. Wax – large carbon peak b. Calcite – small carbon peak

Figure 4. Elemental spectra analyses (EDS) showing clear distinction between wax and carbonate constituents. Wax is identified by relative magnitude of the carbon peak and by comparison to that of calcium.

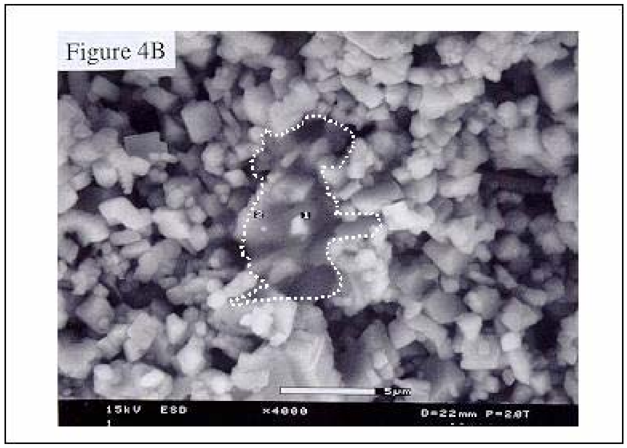


Figure 5. ESEM image after cold water injection into reservoir core. 4000 x magnification. Wax is outlined with dashes.

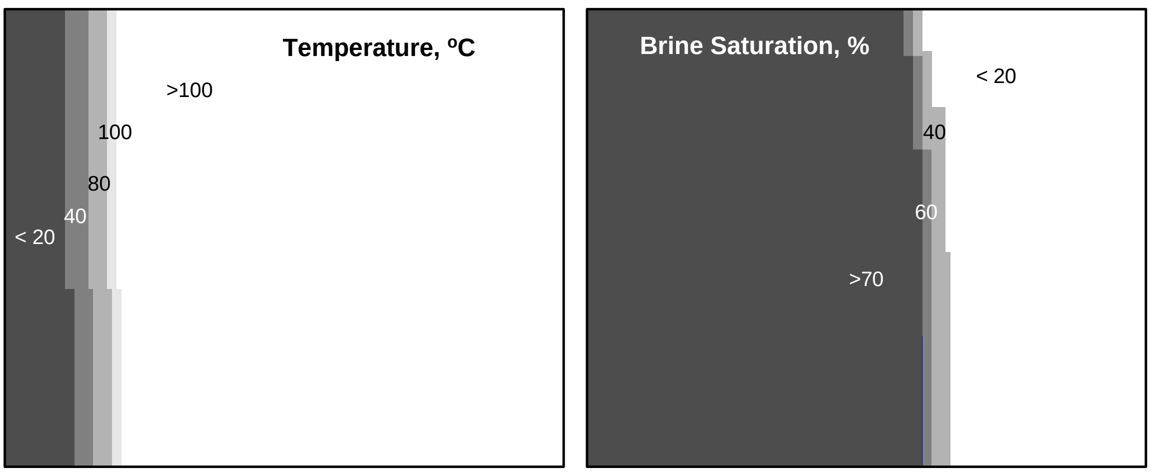


Figure 6. Simulation results, homogeneous cross-section model. Temperature and brine saturation after 9 years of continuous brine injection. Model dimensions are 230 m vertical by 300 m horizontal.

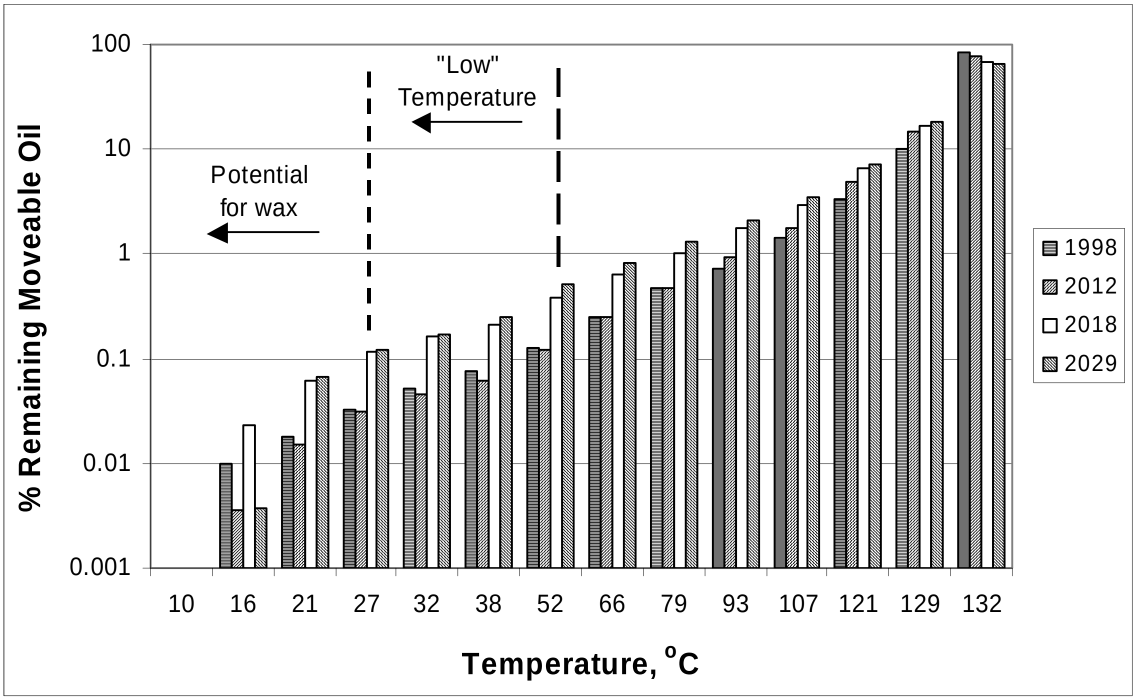


Figure 7. Temperature distribution of remaining moveable oil for various times. Y-axis scale is logarithmic.