Interplay between Rock Permeability and the Performance of Huff-n-Puff CO₂ Injection

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ABSTRACT: The CO₂ huff-n-puff experiments are often conducted on a rock sample with a given permeability. However, there is a need for understanding the production performance of CO₂ huff-n-puff over a range of rock permeability values. In this study, CO₂ huff-n-puff corefloods were conducted by using 30 cm long artificial cores over a permeability range between 0.7 and 240 mD. After that, the cores and produced oil were analyzed by NMT tests and gas chromatography tests. The effects of rock permeability on primary parameters, such as ultimate oil recovery, gas and oil ratio (GOR), pressures, residual oil distribution, and produced oil composition, were studied in detail. The experimental results indicate that the overall CO₂ huff-n-puff efficiency increases with permeability, while the production dynamics also changes with permeability. The oil production is greater and realized faster in high permeability core samples than low-permeability rocks; hence, maintaining the same production efficiency for low-permeability samples needs more production cycles and a longer production time. Fortunately, the GOR of CO₂ huff-n-puff in low-permeability samples is lower, which is favorable in long-term production. In contrast, a larger produced GOR is realized in high-permeability core samples, especially beyond the optimal cycle. Moreover, although the CO₂ front occurs at a shorter distance from the inlet as rock permeability decreases, CO₂ huff-n-puff can simultaneously produce oil from different pore sizes of different permeability core samples. The permeability of core samples also has a significant influence on the composition of the produced oil. The CO₂ extraction capability is stronger in samples with a lower permeability.

1. INTRODUCTION

Supercritical CO₂ has been studied for many years as an important improved oil recovery agent,1−4 because of its superior characteristics such as low viscosity, higher density (than other gases), and better miscibility with oil. CO₂ has been widely used in many oil fields all over the world.5−8

However, continuous CO₂ injection in tight formations becomes of limited “accessibility” and contact surface with in situ oil is challenging both economically and technically. Therefore, application of CO₂ huff-n-puff as an effective EOR method in tight low-permeability reservoirs has lately become appealing in liquid-rich shales.

Traditionally, applications of CO₂ huff-n-puff have been mainly performed on high-pressure reservoirs or in reservoirs where miscibility can be easily achieved.9−11 In addition, some researchers have reported that for higher pressure difference between the huff process and the puff process, a higher oil recovery is often observed.12−14 However, in some low-pressure reservoirs, such as the Changqing oil field in China, the miscibility can be hardly achieved/maintained at the reservoir conditions.15−17

Furthermore, the existing studies of CO₂ huff-n-puff in low-pressure reservoirs are mostly related to high-permeability systems or heavy-oil reservoirs. The performance evaluation of the CO₂ huff-n-puff process in low-pressure low-permeability reservoirs is limited in the literature.

It has been well-documented that more huff and puff cycles will likely contribute to higher oil recovery.18−20,25 However, the most fraction of produced oil occurs in the first few cycles, and different researchers presented different opinions on the optimal huff-n-puff cycles based on their experimental results.21−23 Similarly, the larger pressure difference between the huff process and the puff process positively contributes to the cumulative oil production; however, the incremental oil recovery becomes less pronounced when the pressure difference is very large.24

On the soaking time, the recommendations are inconsistent. Some researchers have reported that the longer the soaking
time, the better the efficiency of CO₂ huff-n-puff. It is argued that the impact of soaking time on the oil recovery varies at different conditions. However, most of the research studies related to the CO₂ huff-n-puff have been performed in a given permeability or smaller permeability ranges with few studies of CO₂ huff-n-puff efficiency encompassing a broad permeability range.

In this paper, a total of six CO₂ huff-n-puff experiments with the permeability range between 0.7 and 240 mD were conducted to investigate the relation between the rock permeability and the CO₂ immiscible huff-n-puff efficiency using a 30 cm-long cylindrical core holder. We also investigated the relation between the efficiency of CO₂ huff-n-puff process and the number of the injection cycle. Moreover, the produced gas and oil ratio (GOR) was monitored, and nuclear magnetic resonance (NMR) tests and gas chromatography (GC) tests were conducted to evaluate the production performance.

2. RESULTS AND DISCUSSION

2.1. Influence of Permeability on CO₂ Huff-n-Puff Efficiency. Six synthetic core flood experiments were investigated to evaluate the relationship between the CO₂ huff-n-puff efficiency and the rock permeability. The ultimate oil recovery factor ($R_u$) of CO₂ huff-n-puff as a function of permeability is shown in Figure 1.

As shown in Figure 1, the ultimate oil recovery of CO₂ huff-n-puff proportionally varies with permeability. Thus, the CO₂ huff-n-puff performs much better in core samples with higher permeability. However, this graph can be divided into two sections intersecting at $K = 17$ mD:

- In the first section ($K > 17$ mD), the ultimate oil recovery factor of the experiments smoothly varies with permeability (albeit, at a lower slope) with only less than 10% recovery change for the permeability values more than 200 mD.
- In the second section ($K < 17$ mD), the variation of CO₂ huff-n-puff efficiency with permeability is significant, with nearly 15% recovery changes in the 17 mD permeability range.

2.2. Relation between CO₂ Huff-n-Puff Efficiency and Cycles. The oil production in each cycle is investigated in detail to evaluate the relation between the CO₂ huff-n-puff efficiency and the permeability values. The cumulative oil recovery factor ($R_c$) as a function of huff-n-puff cycles is presented in Figure 2.

The cumulative oil recovery factors for different permeability core samples increase with the number of huff-n-puff cycles, as shown in Figure 2; however, their trend is different. With the increase of huff-n-puff cycles, the cumulative oil recovery factors for high permeability core samples rapidly increase at the beginning and then flat off. However, the cumulative oil recovery factors obtained from low-permeability core samples consistently increase with the number of cycles. To demonstrate a more explicit interpretation of the results, Figure 3 shows the oil recovery factor of each cycle ($R_e$) as a function of huff-n-puff cycles.
As shown in Figure 3, the oil recovery factors of high-permeability core samples are all large after the first several cycles and increase as the core permeability increases. However, at later huff-n-puff cycles, the oil recovery factors of high-permeability core samples monotonically decrease and that the higher the permeability, the faster the decline is observed.

On the other hand, the oil recovery factor of low-permeability core samples in each cycle is lower and decreases much slowly at later stages. The contribution of the last five cycles in low-permeability samples is bigger than that of high-permeability core samples. Therefore, the CO₂ immiscible huff-n-puff efficiency is higher at the beginning and decreases faster at the subsequent cycles in high permeability samples.

To provide a better understanding of the relationship between permeability and CO₂ huff-n-puff efficiency, the optimal huff-n-puff cycle defined as the cycles needed to produce 80% of the ultimate oil recovery is calculated and plotted in Figure 4.

Figure 4. Optimal huff-n-puff cycle as a function of huff-n-puff cycles.

As shown in Figure 4, the optimal huff-n-puff cycle varies inversely with permeability. It increases significantly below 17 mD, meaning that more huff-n-puff cycles are needed to achieve 80% recovery as permeability decreases. Comparing with Figure 3, the optimal cycles are just at the inflection point of these curves, especially for high permeability core samples. It is worthwhile to mention that the oil recovery factor of the low-permeability core samples (K < 17 mD) is still unstable at the end of ten cycles. Thus, more cycles are needed, and therefore, the optimal cycle is very high below 17 mD.

Consequently, combining with Figures 2–4, the oil production of CO₂ huff-n-puff is greater and faster in the higher permeability core sample. The CO₂ huff-n-puff in low-permeability reservoirs needs more cycles and production time. The reason for observing this phenomenon is because of the slower oil flow with the lower permeability cases. The slow oil flow is the outcome of the interplay between capillary and viscous forces within the pore space.

In this study, owing to the neutral wettability of the synthetic core samples and low viscosity of the oil, the effect of capillary resistance and asphaltene deposition (and consequent pore blockage) is relatively insignificant. Thus, the main factor which affects the seepage resistance is the pore blockage effect. As pressure goes below the saturation pressure during the production period, the dissolved CO₂ is released from the oil phase as bubbles, and the foamy oil flow occurs.

The oil can be produced by the volume expansion of CO₂ as the pressure decreases, which is known as solution gas drive. However, when the bubbles sufficiently grow, the gas bubble forms and potentially can get stuck in the small pore throats; thus, the seepage resistance of the oil molecules will increase owing to the pore blockage effect.

The seepage resistance caused by the pore blockage effect is more pronounced in low-permeability rocks because of the presence of smaller pore size distribution. Thus, during the production/puff stage, the pressure drops at lower rates, and the local pressure drawdown is smaller than that in high permeability cores. Therefore, the oil production is less and slower in low-permeability core samples. Figure 5 shows the pressure difference between both ends of cores during the first puff period of each experiment as a function of time.

Figure 5. Pressure difference as a function of time.

2.3. Influence of Permeability on the Relevant Parameters of CO₂ Huff-n-Puff. As mentioned before, the permeability of core samples has a significant influence on the CO₂ huff-n-puff efficiency, especially below 17 mD. For further analysis, the relationship between permeability and CO₂ huff-n-puff and different parameters including the produced GOR, location of the CO₂ front, and the composition of the produced oil are studied using NMR and GC.

2.3.1. GOR Analysis. The produced GOR can be used to evaluate the economy of CO₂ huff-n-puff. Figure 6 indicates the produced GOR as a function of huff-n-puff cycles.

As shown in Figure 6, the GOR of these experiments varies with the number of cycles as well as the rock permeability. For samples with higher permeability, it can be clearly seen that the corresponding curves can be divided into three stages:

1. During the first stage (oil production period), the primary produced fluid is oil associated with limited gas production; hence, the GOR in this section is very low.
2. During the second stage of production, after passing the optimal cycles (shown in Figure 4), the GOR rapidly
ramps up. It is due to replacement of the original oil phase with the injected gas inside the pore space.

3) Finally, when the huff-n-puff cycles are repeated for many times, the produced GOR essentially remains unchanged as no oil production occurs, and a stable gas production is realized.

However, as for the low-permeability core samples, it can be seen that the first section is much longer than high-permeability core samples, and the lower permeability core samples have a more extended oil production period. As mentioned in Figure 4, the oil recovery factor of the low-permeability core samples is still unstable at the end of ten cycles. Hence, it can be inferred that the CO₂ huff-n-puff in low-permeability core samples may be still well in the first section, especially for the case of 0.4 mD core sample.

In conclusion, the produced GOR (equivalent to the separation cost) of oil production will dominate when the huff-n-puff cycles exceeded the optimal cycle. Thus, the production cycles of CO₂ huff-n-puff need to be accurately controlled, especially in high-permeability core samples. Meanwhile, the GOR in the low-permeability cases slightly increases with cycles. Therefore, the GOR of CO₂ huff-n-puff in low-permeability core samples is relatively lower, which is favorable to the long-term exploitation of tight or low-permeability reservoirs.

2.3.2. Residual Oil Distribution Analysis. As previously shown, less oil is produced at a slower rate in low-permeability core samples, especially below 17 mD, even at the end of ten cycles. To further investigate this observation, at the end of core flood experiments, the core samples were cut into five equal smaller blocks (6 cm per block) for NMR testing.

Figure 7 presents the NMR T₂ spectra of different positions of small core sections. For each test, another 6 cm core sample (drilled from the same core sample) saturated with oil and brine was also tested as the original NMR T₂ spectra.

It can be seen from Figure 7 that the NMR T₂ amplitude reduction within the rock samples near the inlet is higher than...
that of further from the inlet. The CO₂ huff-n-puff performs very good at the vicinity of the inlet, and farther away from the inlet, the CO₂ huff-n-puff efficiency drops.

Moreover, although these artificial cores are homogenous, there is still some microheterogenous cores in them. The two peaks in Figure 7 mean the different pore sizes. (The higher one represents the micropore, and the lower one represents the macropore.) Therefore, the T2 spectra, regardless of the sample pore size distribution, are always lower near to the inlet, indicating that the CO₂ huff-n-puff can simultaneously extract oil molecules out of different size pores. This is consistent with the results of former research studies.25–29

A small lateral deviation of this T2 spectra can be detected at a closer inspection, which may be due to the oil redistribution during CO₂ huff-n-puff. When the gas is injected/produced into/out of the pore space for several times, oil molecules may be displaced and redistributed because of pore scale phenomena. This phenomenon may occur at a local scale and often has a minimal impact on the overall efficiency.

To present dynamic behavior of the CO₂ huff-n-puff process in different cores, a further quantitative analysis is conducted using the NMR T2 data. The area of NMR T2 spectra (integral function) at different positions of each core sample is measured and recorded as $A_n$ and the integral area of the original NMR T2 spectra is named $A_0$. The integral ratio of each section of the core samples is calculated as follows:

$$\text{integral area ratio} = \frac{A_n}{A_0}$$

for $n = 0$ to 30.

This index quantitatively reflects the relative amount of the residual oil in different sections of a core sample. The lower integral ratio indicates the lower oil left behind in the sample and a better CO₂ huff-n-puff efficiency. The results are illustrated in Figure 8.

Figure 8 shows that the integral ratio of the different core samples directly varies with the distance from the inlet, indicating that the oil remained in the core blocks is less, and the CO₂ huff-n-puff efficiency is higher closer to the inlet (wellbore). The difference in the integral ratio of core blocks with a permeability of 0.7 and 6.6 mD is larger than that of samples with a permeability of 17 and 54 mD. That is why the ultimate oil recovery shown in Figure 1 changes very slightly in the high-permeability range.

Moreover, as mentioned before, the oil recovery of 17 and 54 mD core samples both flats off at the end of 10th cycle. Hence, the recoverable oil in these high-permeability core samples has been already produced after 10th cycle, and the residual oil distribution remains unchanged. Thus, the T2 spectra in Figure 7 and the integral ratio variation in Figure 8 of these core samples can be considered as the final residual oil distribution. The T2 spectra of 17 and 54 mD core blocks with a 24–30 cm distance away from the inlet are different from those of original core blocks, and the integral ratio of them is 0.747 and 0.683, respectively. Therefore, it can be inferred that at the end of 10th cycle, the CO₂ front has already reached the end of these core samples. Thus, their actual position of CO₂ huff-n-puff front is much longer than 30 cm.

However, the integral ratio of 0.7 and 6.6 mD core section shows a different trend than the above. The T2 spectra of 0.7 and 6.6 mD core sections at the furthest distance from the inlet (24–30 cm) only have small divergence with that of the original core block. The integral ratio measured from the T2 spectra of them is 0.952 and 0.943, which are very close to 1.0 (it is worth mentioning that the integral ratio of 6.6 mD core blocks is slightly bigger than that of 0.7 core blocks which is opposite to our understanding; nevertheless, the difference between them is only 0.009 with the error of less than 1%, within the acceptable range).

Hence, the residual oil at further sections from the core inlet is the same as that observed in the original sample. Thus, we can infer that only a fraction of CO₂ may find its path deeper in the sample because of diffusion, and essentially, the CO₂ huff-n-puff efficiency in these parts can be ignored. If we define the CO₂ huff-n-puff distance as the region where 10% of the original oil has been produced, the observed CO₂ huff-n-puff distance of 0.7 and 6.6 mD core samples in this study is between 12 and 18 and 18–24 cm, respectively. Therefore, the CO₂ huff-n-puff distance becomes shorter as the permeability decreases.

In conclusion, CO₂ huff-n-puff can simultaneously extract oil from different pore sizes indifferent to the core permeability. Macroscopically, as permeability decreases, the huff-n-puff distance becomes shorter at the end of 10 cycles. However, owing to the low GOR of CO₂ huff-n-puff in low-permeability core samples, it is practically, possible to continue the huff-n-puff process with more production cycles.

2.3.3. Composition Analysis of Produced Oil. After analyzing these core samples at the end of experiments, the produced oil was collected and sampled for further investigation of the changes in the oil composition with the rock permeability. Figure 9 demonstrates the results of the composition analysis. The original oil composition is also listed for the comparison.

Many researchers have shown that CO₂ extraction is one of the main mechanisms of CO₂ huff-n-puff.53 Resulting from the CO₂ extraction, the composition of the produced oil due to CO₂ huff-n-puff indicates a noticeable difference from that of the original oil.

Figure 9 can be divided into three sections. In section A, the content of C4–C11 in the produced oil is less in the lower permeability core samples than that of the original oil because

![Figure 8. Integral ratio of each core block as a function of the distance from the inlet.](https://dx.doi.org/10.1021/acsomega.0c01343)
the C4—C12 extracted by CO₂ is so mobile that it is easy and independent from the process efficiency. Thus, the less C4—C12 found in the produced oil means the stronger CO₂ extraction.

However, section B shows a different trend compared to the original oil composition; the content of C11—C20 in the produced oil is more for low-permeability rocks; the produced oil is lighter in the low-permeability samples. In this section, the C12—C20 fraction of the produced oil is mainly composed of two parts. One is the oil produced by solution gas drive, which has little influence on the oil composition. The other is extracted by CO₂, which is responsible for the removal of the light components. Owing to the addition of the extracted oil, the content of C12—C20 is much more than that of original oil, and the proportion of extracted oil is more substantial in lower permeability core samples.

It can be seen from section C that the molar percent of C20—C30 in different produced oil is the same, indicating that CO₂ extraction has less influence on the very heavy oil fractions. Therefore, the GC analysis suggests that the permeability has a significant influence on the composition of produced oil during CO₂ huff-n-puff.

In this study, because the only variable is permeability, the reason for the difference in the composition of the produced oil may be due to the complexity of the pore structure in low-permeability samples. The smaller diameter of the sand particles used in the synthetic cores may lead to the more complex pore distribution. Then, the liquid flowing through this complex pore distribution with a constant pressure will be subjected to significant mixing/dispersion. The oil and CO₂ stirring is stronger in the core pores, representing larger mixing between them leading to a larger effect of CO₂ extraction, and the produced oil is lighter, just as shown in Figure 9.

Moreover, because the CO₂ extraction is one of the major mechanisms of CO₂ huff-n-puff, it can be inferred that the permeability may also have a significant influence on the other mechanisms of CO₂ huff-n-puff. It will be confirmed in our future work.

In summary, the CO₂ huff-n-puff efficiency increases with permeability, but the production dynamic of different permeability core samples is different. The oil production of CO₂ huff-n-puff is greater and faster in higher permeability core samples, and that in tight or low-permeability reservoirs needs more production cycles and production time. Additionally, owing to the larger GOR of CO₂ huff-n-puff in high-permeability core samples, especially after the optimal cycle, the production cycles of CO₂ huff-n-puff need to be controlled accurately. Meanwhile, the GOR of CO₂ huff-n-puff in low-permeability core samples is relatively smaller, which is favorable to the long-term exploitation of tight or low-permeability reservoirs. The NMR analysis of the core samples after core flood experiments suggests that CO₂ huff-n-puff can simultaneously produce oil from different pore sizes of different permeability core samples, but the CO₂ huff-n-puff distance is shorter with permeability decreases. Finally, GC analysis of the produced oil indicates that the permeability of core samples has a significant influence on the composition of produced oil. The capability of CO₂ extraction, as an essential mechanism of CO₂ huff-n-puff, is stronger in the lower permeability core samples.

3. CONCLUSIONS

This work is aimed at gaining a better understanding of the relationship between CO₂ huff-n-puff efficiency and rock permeability. A total of six CO₂ huff-n-puff experiments were conducted using various permeability core samples. Then, for interpreting this variation trend, the relationship between CO₂ huff-n-puff efficiency and cycles was analyzed in detail. Finally, GOR dates, NMR tests, and GC tests were conducted for further investigating the interplay between rock permeability and the performance of CO₂ huff-n-puff.

The major conclusions of the work are as followed:

1. The CO₂ huff-n-puff efficiency increases with permeability, but the production dynamics of different permeability core samples is various. The oil production of CO₂ huff-n-puff is greater and faster in higher permeability core samples, and that in tight or low-permeability reservoirs needs more production cycles and production time.

2. Owing to the bigger GOR of CO₂ huff-n-puff in high permeability core samples, especially after the optimal cycle, the production cycles of CO₂ huff-n-puff should be controlled accurately, especially in high-permeability core samples. However, the GOR of CO₂ huff-n-puff in low-permeability core samples is relatively smaller, which is favorable to the long-term exploitation of tight or low-permeability reservoirs.

3. Microscopically, CO₂ huff-n-puff can simultaneously produce oil from different pore sizes of different permeability core samples. However, macroscopically, with permeability decreases, the CO₂ huff-n-puff distance is shorter.

4. The permeability of core samples has a significant influence on the composition of produced oil. The capability of CO₂ extraction, as an essential mechanism of CO₂ huff-n-puff, is stronger in the lower permeability core samples.

4. MATERIALS AND METHODS

4.1. Materials. Oil and brine samples were collected from the Changqing oil field (Shanxi, China). The properties of oil and reservoir are listed in Table1. Table 2 details the properties of the synthetic core samples employed in the CO₂ huff-n-puff...
3.1, 32 The CO2 supplied by Shunda Gas Products Co., Ltd. (Beijing, China) with a purity of 99.9%.

4.2. Experimental Methods. The heat shrink tubing is used to seal the core samples before the tests and reduce the leakage of the supercritical CO2 and the negative impacts of the elasticity of the rubber sleeve on the experiment results. The core flooding assembly is shown in Figure 10. Pump A was used to inject the brine, oil, and gas into the core through a floating-piston transfer cylinder set at a constant velocity of 0.33 mL/min. Pump B was used to apply overburden pressure. Pressure transducers were used to measure the pressure at different pressure taps across the core with results monitored by a computer. An oil and water collector and a gas meter was used to collect the produced oil, brine, and gas. All of these instruments, except the computer and pumps, were placed in a constant temperature oven to ensure that the experiments were done at a constant temperature of 50 °C.

A total of six core flooding tests were conducted using synthetic core samples with different permeability values. In preparation of each core flooding experiment, the dry core was sealed by heat shrink tubing at 120 °C. The sealed core was then saturated with brine in a vessel after vacuuming for 6 h to measure the pore volume. Afterward, the core was placed in the pressure compartment, and the pressure on the outlet was set to the desired value. Then, the oil is injected into the core with a velocity of 0.33 mL/min until no more brine was produced, and the initial oil/water saturation was computed; next, the fluid-saturated core was aged at a reservoir temperature of 50 °C for 24 h.

To start the huff stage (injection), the valve at the outlet of the core was closed, and CO2 was injected at constant pressure until the pressure in the core sample becomes stable, and then, the valve at the inlet was closed during the soaking period for 2 h. After the end of soaking time, the puff stage was started by opening the inlet valve at the desired back pressure for 30 min. Throughout the CO2 huff-n-puff experiments, the pressure along the core, and the volume of produced fluids were monitored. Last but not the least, the procedure was repeated for other core samples with different permeability values until a total of six core flood experiments were conducted.

After that, the core sample was depressurization to atmosphere and then cut into five equal blocks (6 cm per block), and a low-field NMR core analysis system (MacroMR12-150H-I, Suzhou Niumag Analytical Instrument Corp., China) was employed to measure the NMR T2 spectrum. It is

Table 1. Properties of the Oil and Reservoir

| property       | test value |
|----------------|------------|
| density, g/mL  | 0.76       |
| viscosity, mPa·s| 1.5        |
| GOR, m³/m³     | 132.2      |
| saturation pressure, MPa | 7.41 |
| temperature, °C| 50         |
| pressure, MPa  | 10         |
| MMP of CO2, MPa| 20         |

Table 2. Properties of the Synthetic Cores

| number | K (mD) | φ (%) | S_o (%) | length (cm) | diameter (cm) |
|--------|--------|-------|---------|-------------|---------------|
| 1      | 0.7    | 18.5  | 61.9    | 29.8        | 2.48          |
| 2      | 2.0    | 20.0  | 63.9    | 30.3        | 2.51          |
| 3      | 6.6    | 21.7  | 69.2    | 30.6        | 2.53          |
| 4      | 17.0   | 23.2  | 70.6    | 30.4        | 2.56          |
| 5      | 54.0   | 22.4  | 72.7    | 30.1        | 2.52          |
| 6      | 240.0  | 24.5  | 73.1    | 30.5        | 2.47          |

Figure 10. Schematic diagram of the CO2 huff-n-puff assembly.
worth noting that owing to the small puff pressure (3 MPa) and the long period of production (10 cycles), less oil was observed during depressurization. Moreover, we were supposed to study the relation between residual oil distribution with rock permeability. The only concern was the difference between different permeability core samples. Thus, we think the depressurization process has limited influence on the variation of residual oil distribution with permeability. Moreover, to eliminate the influence of the signal of water in NMR tests, Mn²⁺ was added into water before core flooding experiments.

Meanwhile, the produced oil in the core flood experiments was collected and sent for GC analysis according to the oil-phase) to achieve a better CO₂ huff-n-puff efficiency.

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**Notes**

The authors declare no competing financial interest.

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