Residence time distribution (RTD) of water flooding activity in oil recovery using vertical sand column: Radiotracer approach

N Othman1*, W H B Wan Kamal2, N S Jasni3, N R Rosli4, R Yahya1, N H Yusoff4, M A S Mohd Yusos1, L N Shah Dahing1, M R Shari1, H Hassan1, A AMahmood1, A M Terry1, N Abdullah1

1Plant Assessment Technology (PAT), Industrial Technology Division, Malaysian Nuclear Agency, 43000 Kajang, Selangor, Malaysia.
2Medical Technology Division, Malaysian Nuclear Agency, 43000 Kajang, Selangor, Malaysia.
3Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), 40450, Shah Alam, Selangor, Malaysia.

*noraisyah@nm.gov.my

Abstract. Waterflooding is a common secondary recovery oil extraction method that can enhance oil recovery up to 45 percent overall recovery factor. Waterflooding is commonly used due to its availability, cost effectiveness and simplicity. Radioactive tracer was introduced to get the optimum Residence Time Distribution (RTD) model which indicates the mechanism of the system. Radiotracer Gallium-68 (Ga-68) is a positron emitting radioactive material, which is eluted from parent Germanium-68 (Ge-68) generator to study the water flooding activity inside the 15 μm grain size of sand pack column oil recovery study. The sand was cleaned, occupying a Perspex sand pack column of 30 cm length and 5 cm diameter arranged in vertical position. The water inlet and tracer were injected from the bottom of the column, assisted by a syringe pump, with the flow rate optimized at 3.5 ml/min in order to push the saturated oil inside the column. Four Sodium Iodide (NaI) scintillation detectors were installed accordingly and attached to 12-channel data analyzer (DAS) to acquire signals of the emitted positron from the Ga-68 solution and monitored by a laptop. The activity utilized was 766 μCi/3ml and the half-life of Ga-68 was 68 minutes with penetrative energy of 511 keV. Initial experience of using Ga-68 was eluting it with 0.05 M HCl for 90μCi/3ml and directly inject it using pulse injection at the upstream of the column. Nonetheless, there was no indication of tracer arrival at the output after several hours which indicated the sole Ga-68 behaves as sand tracer thus, some modification was made to the respective Ga-68 solution. Chelating with DOTA-NHS solution was the second experience with Ga-68, which produced satisfactory result. A very vivid signal was retrieved at the output and RTD model analysis was carried out. The results indicated that the vertical sand pack column behaved as a Perfect Mixer with Parallel Model.

1. Introduction

Water flooding is a form of oil recovery in which continuous water injection mechanism is adopted and the overall recovery factor is about 35 to 45 % original oil in place [1]. The induced pressure in the presence of water is required to displace oil from the reservoir rock into the producing well. The extraction of residual oil requires modification in reservoir characteristics in which water flooding is
most used for enhanced oil recovery [2]. Water flooding within Malaysia fields such as Tapis and Guntong had been proven to increase the overall oil recovery [3]. Common accessibility of water, ease of connection with water, retention of hydraulic head in injection well, water that able to move through an oil-bearing formation, and efficiency of water in sweeping the oil can be counted as the factors of popularity for waterflooding.

To evaluate the effectiveness of the waterflooding, sweep efficiency evaluation need to be done. Sweep efficiency is important to indicate whether trapped oil from primary recovery is displaced by the injected water or not. If the sweep efficiency for waterflooding is low, it means that the water injected to reservoir is insufficient to drive the oil towards production well. The knowledge of the total/swept efficiency is not a simple task because the reservoirs are underground formations and therefore remote to man and conventional tools. Moreover, the petroleum potential in Malaysia is mainly fractured basement rock reservoir located offshore and characterized by a fracture system of very high heterogeneity in porosity and permeability. In addition, fluid flow in most reservoirs is anisotropic. The reservoir structures are usually layered and frequently contained significant heterogeneities leading to directional variations in the extent of flow [4]. Hence, the effective fluid movement can be difficult to predict. The complexity of the reservoir structure introduces a considerable uncertainty in the reservoir model and fluid flow simulation.

Thus, in order to investigate, understand and analyze the mechanisms involved during waterflooding, radiotracer technology can be utilized [5]. Tracer is a tool that accesses and runs across the reservoir, contacting portions of interest and giving information about the total/swept efficiency [6]. Fluid flow and transport behavior inside the reservoir can be specifically described using analysis of RTD Model [7][8]. This RTD models provide the behavior of the reservoir such as the presence of anomalies like dead zone and channeling which will be addressed by the reservoir engineer in order to increase sweep efficiency that leads to increased oil recovery.

2. Methodology

2.1. Ga-68 preparation
Ge-68/Ga-68 generator is typically used in nuclear medicine to produce positron-emitting radionuclide Ga-68. The parent isotope Ge-68 has a half-life of 270.95 days and can be easily delivered to hospitals as a generator, where it can be used as the source of Ga-68 for at least 1 year. Gallium-68 (with a half-life of only 67.71 minutes, difficult to transport) can be easily eluted from the generator any time at the site of application and can be used for different purposes. In this study, Ga-68 was eluted with 0.05 M HCl (solvent) to produce GaCl₃ and the activity was 90 μCi/3ml when it was directly injected inside the sand pack column.

2.2. Ga-68-DOTA-NHS Preparation
Since there was no indication of tracer arrival after 5 half-lives of Ga-68 in the first experiment, modification has been made to the eluted Ga-68 (0.05 M HCl). Firstly, 3 ml of eluted Ga-68 with activity of 9.28 mCi was obtained from the Ge-68 generator. Then, 2 ml of the respective Ga-68 was mixed with HEPES (4-(2-Hydroxyethyl)-1-Piperazinethanesulfonic acid), a buffering agent to prevent a rapid change in pH when acid is added to the solution, using vortex (shaker) to ensure the mixing is homogenous. The activity of the dissolved solution was 6.03 mCi. DOTA (1,4,7,10-Tetraazacyclododecane-1,4,7,10-Tetraacetic acid) was then introduced to chelate with dissolved Ga-68-HEPES. Prior to that, DOTA was heated to 95°C for 10 minutes in order to activate the chelating process of DOTA with Ga-68. About 500 μl of Ga-68 and 100 μl DOTA-NHS were added together and mixed using vortex to ensure homogenous solution in order to produce 68Ga-DOTA. The pH of mixed solution was regulated to 3.9 acidic medium. The activity of chelated DOTA with Ga-68 was 1.142 mCi (600 μl).
2.3. Preparation of radiotracer set up

The sandstone with grain size of 150 μm was pressed manually using surficial weight inside the cylindrical column that was arranged in vertical order. Formation water (original water inside the reservoir) was prepared earlier to be saturated inside the column. About 0.5 g/ml (500 ppm) NaCl solution (saline) was prepared for water flooding activity. Moreover, 180 ml of oil was saturated inside the column and aged for 24 hours to ensure that the oil settled well inside the column. On the next day, about 28.3 MBq/3ml (766 μCi) of Ga-68 was prepared and tappèd at the common line together with water line as shown in figure 1. Thus, during water flooding operation, the valve of Ga-68 and water were opened sequentially. Hence, about 850 ml of water was pumped with constant flow rate 3.5 ml/min using syringe pump continuously to purge out the saturated oil from the column. Prior to that, four NaI scintillation detectors were arranged accordingly and attached to data acquisition system (DAS). The DAS was then connected to laptop for data storage and tracer monitoring. The parameters for each experiment are shown in Table 1.

![Figure 1. Schematic diagram of the experimental setup.](image)

| Parameters                  | Ga-68          | Ga-68-DOTA-NHS |
|-----------------------------|----------------|----------------|
| Q (ml/min)                  | 3.5            | 3.5            |
| V_f (ml): formation water   | 329            | 238            |
| V_w (ml) water flooding     | 850            | 780            |
| Activity of Ga-68 (μCi)/3ml | 90             | 766            |
| Saturated oil, S_or         | 180            | 238            |

The mathematical expression for the First Moment (M1) in discrete form or better known as MRT was calculated using Equation (1). The mathematical expression for RTD is shown in Equation (2). RTD is a fundamental parameter in reactor design which can give information on how long the substrate has been in the reactor and the RTD analysis can help in characterizing the extent of their deviation from ideal behavior.
2.4. Residence time distribution (RTD) model
The mathematical expression for the First Moment (M1) in discrete form or better known as MRT was calculated using Equation (1). The mathematical expression for RTD is shown in Equation (2). RTD is a fundamental parameter in reactor design which can give information on how long the substrate has been in the reactor and the RTD analysis can help in characterizing the extent of their deviation from ideal behavior.

\[ M_i = \int_0^\infty t C_i(t) dt \quad \int_0^\infty C_i(t) dt \]  

(1)

\[ E(t) = \frac{c(t)}{\int_0^\infty c(t) dt} \]  

(2)

where \( C(t) \) is the concentration of radiotracer monitored by NaI scintillation detectors in counts per second (cps) as numerator and denominator is the area under the curve of plotted \( C(t) \). The detected signal was normalized by dividing it by the area under the curve. The RTD models can provide theoretical information or describe the hydrodynamic behavior of the reactor.

3. Result and discussions
The results will cover the Ga-68 analysis, oil recovery and RTD Models respectively.

3.1. Ga-68-DOTA Analysis
The purity of solution was checked using thin layer radiochromatograph (TLC) scanner which produced about RCP 99.24% that indicated only 0.76% of Ga-68 did not bind with DOTA as shown in figure 2. In this study, the radioactive solution was diluted and 766 μCi/3ml to be injected inside the sand pack column for water flooding activity. Table 2 shows the RCP of chelated Ga-68 and DOTA.

![Figure 2. TLC Scanner results.](image)
| Region       | Start (mm) | Stop  (mm) | Centroid (mm) | RF   | Region Counts | Region CPM | % of Total | % of ROI |
|--------------|------------|-----------|---------------|------|---------------|------------|------------|----------|
| Region 1     | 13.5       | 46.7      | 31.1          | 0.156| 3337.0        | 6674.0     | 0.68       | 0.70     |
| Region 2     | 75.5       | 109.7     | 94.0          | 0.470| 475981.0      | 951962.0   | 96.28      | 99.30    |
| 2 peaks      |            |           |               |      | 479318.0      | 958636.0   | 96.96      | 100.00   |

No increment of radiation signal was found at the outlet of the sand column using D2. Only background reading was received that indicated Ga-68 was adsorbed onto the sand beads. To confirm the theory, the survey meter was run along the column and the counts reading were escalated. Thus, conclusion has been made that Ga-68 is suitable for sand tracking and NOT for fluid tracking and monitoring. Therefore, the modification was made to the existing Ga-68 which was best chelated with DOTA and the data was outlined accordingly.

3.2. Oil recovery
Table 3 shows the percentage of oil recovery from two respective radiotracers. The Ga-68 extracted more oil than chelated DOTA. This result is puzzling since the expected results should be similar. This is because radiotracer will not interfere with any chemical process since it acts as the tracking fluid for easy monitoring during water flooding. Investigation has been carried out and the results were due to negligence in saturating the water inside the column. The water saturation should use formation water and NOT the 500ppm saline water.

| Parameters   | Ga-68 | Ga-68-DOTA |
|--------------|-------|------------|
| Recovered oil (ml) | 120   | 91.8       |
| % oil recovery  | 66.7  | 38.6       |

3.3. Residence time distribution (RTD) models
Figure 3 illustrates the results of the output that has significant information about the process inside the column. It was observed that the data required necessary treatment to ensure only radioactive signals are present. Thus, data treatment as outlined by previous researchers was referred [9]. The RTD curve was then obtained after undergoing the data treatment as well as data transformation as described in Equation 1 [7]. Figure 4(a) to (d) shows the results of RTD optimization of RTD Model by adopting Software by IAEA [1].
Figure 3. Raw data of Ga-68-DOTA-NHS experiment.

(a) Perfect Mixer in Series Model

(b) Perfect Mixer with Parallel Model

(c) Axial Dispersed Plug Flow Model

(d) Axial dispersed with Exchanged Model

Figure 4. (a) – (d) RTD Models of the experimental curve.
Figure 4 shows that all RTD Models fit the experimental results well. These models are the perfect mixers in series model, the perfect mixers in parallel model, the axial dispersed plug flow model and the axial dispersed plug flow with exchange model respectively. Nevertheless, according to Table 4, the Perfect Mixer with Parallel Model fits the experimental curve best as the value of Error Sum of Square (SSE) is the minimum.

Table 4. Error Sum of Square (SSE).

| Models                          | Parameters | SSE           | Ranks (Minimum) |
|--------------------------------|------------|---------------|-----------------|
| Perfect Mixer model            | \(\tau_1\) | 360           | -               | 0.920 \times 10^{-7} | 2 |
| Perfect Mixer with Parallel Model | \(\tau_2\) | 366           | 295             | 0.239 \times 10^{-8} | 1 |
| Axial Dispersed Plug Flow Model | \(J_1\)   | 365           | -               | 0.155 \times 10^{-6} | 4 |
| Axial Dispersed Model with Exchange model | \(J_2\)   | 352           | -               | 0.131 \times 10^{-6} | 3 |

The results also indicated that there were two series of perfect mixers which were arranged in parallel whereby primary series consists of 17 mixers and secondary series comprises with 3 mixers accordingly. No short-circuiting or channeling was found in the model, indicating that the sand was well packed inside the column. No long tail was also observed in the RTD curve, which indicates no dead zone discovered inside the column. Moreover, the RTD model was symmetrical that signifies perfect mixer is achieved and radiotracer was mixed homogenously inside the column.

4. Conclusions

Several highlights have been discovered in this work. Ga-68 independently is a sand tracer and does not blend well with water (fluid). On the other hand, Ga-68-DOTA-NHS can represent the fluid flow but the preparation is quite tedious. Moreover, formation water should not be mistaken as saline water because it affects the percentage of oil recovery. Water flooding is proved to be able to extract residual oil from the vertical column excellently up to 67%.

Based on the RTD Model discussion, the sand column was prepared nicely because there was no indication of common process anomalies found such as dead zone, channeling and short-circuiting. The Perfect Mixers in Parallel Model fits the experimental model well due to minimum value of SSE in comparison with other models.

5. References

[1] Zitha P, Felder R, Zornes D, Brown K, and Mohanty K 2011 Increasing hydrocarbon recovery factors (Soc. Pet. Eng.) 1–9.
[2] Khan I H, Farooq M, Ahmad G D M, Gul S and Qureshi R M 2003 Tracer technology to investigate inter-well communications during enhanced oil recovery (Vienna: Research Contract No. PAK-12949/RBF).
[3] Selamat S, Samsuddin S A and Halim N A 2011 Evaluation and optimization of enhanced oil recovery by WAG injection at Tapis and Guntong fields, Malaysia (SPE 145123).
[4] Mohammadian E, Hamidi H, Azdarpour A and Junin R 2015 Proc. of the Int. Civil and Infrastr. Eng. Conf. 417-424.
[5] Tayyib D, Al-Qasim A, Kokal S and Huseby O 2019 SPE Kuwait Oil and Gas Show and Conference (Soc. of Pet. Eng.).
[6] Melo M A and Almeida A R 2017 SPE Latin America and Caribbean Mature Fields Symposium (SPE-184956-MS) https://doi.org/10.2118/184956-MS.

[7] Othman N, Mohamed Hassan N P, Yahya R, Ahmad Khusaini M A, Shari M R, Hassan H and Mahmood A A 2017 Malaysian J. of Analy. Sci. 21(2) 445–451.

[8] Othman N, Saaid I M, Ahmed A, Yusof N H, Yahya R, Yunos M A S M, Engku Chik E M F, Shari M R, Hassan H and Mahmood A A 2020 ASEAN J. of Chem. Eng. 20(1) 49–56.

[9] Kasban H, Zahran O, Arafah H, El-Kordy M, Elaraby S M S and Abd El-Samie F E 2010 Laboratory experiments and modeling for industrial radiotracer applications Appl. Radiat. and Isot. 68(6) 1049–1056.

[10] IAEA 2008 Radiotracer residence time distribution method for industrial and environmental applications Material for Education and On-the-job Training for Practitioners of Radiotracer Technology, Training Course Series No. 31.

Acknowledgment

The authors would like to thank National Cancer Institute (NCI), Putrajaya for providing the Ge-68/Ga-68 generator which is used to produce positron-emitting radionuclide Ga-68. The authors also would like to thank Prof Jovan Thereska from IAEA, Vienna Prof Tor Bjornstad from IFE, Norway and Dr Quang from CANTI, Vietnam in providing continuous assistance and knowledge contribution throughout this study. Not to forget all PAT colleagues who participated in this experiment. Finally, the authors would like to express their appreciation for the support of the sponsor IAEA Research Contract No: 22898, IAEA Coordinated Research Project F22069 and FRGS with Project No FRGS/1/2018/TK07/MOSTI/02/3.