iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 8 Issue: VII Month of publication: July 2020

DOI: https://doi.org/10.22214/ijraset.2020.30595

# The Effect of Asphaltene Precipitation during $CO_2$ Injection for Light Oil Reservoir

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***Abstract: This paper focused on the asphaltene precipitation problem under dynamic induced by carbon dioxide injection. In spite of being $Co_2$ one of common used methods in oil reservoir, it may change the crude oil properties and increase the chances of having asphaltene precipitation. The existence of asphaltene in precipitation shape, flocculation or deposition may change the crude oil composition and reduce the oil recovery. The effect of the asphaltene on reservoir characteristics has the major concern and the damage that occurred by asphaltene can cause formation sever. Thus, this research makes effort to achieve and understand the asphaltene precipitation phenomena created by carbon dioxide injection. Therefore, a light crude oil sample was selected since the light oils are favour to have asphaltene precipitation issue. The presence of carbon dioxide under various injections flow rates are investigated among this research. The results indicated that the precipitated of asphltenehas significant effectas the pore volume of gasinjected greater. Furthermore, it was observed that asphaltene precipitation more sensitive to the injection flow rate0.8 cc/min.***
***Keywords: Asphaltene, precipitation; injection flow rate; $CO_2$injection, enhanced oil recovery***

## I. INTRODUCTION

This document is it is widely known that carbon dioxide flooding application has obtained the main interest in the tertiary recovery for enhanced oil recovery. During the oil production, asphaltene precipitation becomes serious problem to production system and reservoirs. This related to understand the phenomena of asphaltene precipitation, flocculation and deposition[1-3].Researches in the recent time has shown that suitable equipment is probable to investigate the asphaltene behaviour at carbon dioxide flooding and their effect on reservoir formation. [1].

In the first stage asphaltene precipitation problems occur in production facilities, then tubing, lateron, the deposition of asphaltene start with bottom-holeand extend to large region in the reservoir [2].Since 1837, Boussingault introduced asphaltene, nevertheless questions about asphaltene unanswered due to its complicated nature.Initially it is essential to know the term of asphaltene in order that asphaltene definition itself has some confusion. To study this confusion, the asphaltene should be extracted first. Various techniques of extracting asphaltene create different asphaltene. While several scientists place an argument that asphaltene may change properties, consequently, it should be studied in place or it should be extracted. As result theasphaltene definition itself is bit contentious [2]. Based on IP 43 standard, the content of asphaltene is percentage by weight of wax free material insoluble in n-heptane but soluble in hot benzene [5].The classical definition of asphaltenes is relying on the properties of crude oil residuum in different solvent [7].

Theories have been studied on asphaltene initial conditions of precipitation. The first theory is the alteration of resin and asphalteneratio, this acting will lead the asphalteneto be unstable and begin to precipitate. While the initial conditions of crude oil like pressure, temperature and compositions may change theasphaltene instability state inner the crude.

Seemingly, resins leading role as peptizing agents in asphaltene precipitation. This peptizing agents work as forces to accumulate together asphaltene micelles to reduce their overall surface free energy Asphaltene micelles will get large as the amounts of solvents are added to crude oil and this process defeats Brownian forces and favour for Asphaltene micelles to precipitate [8].

The most significant that the highest amount of asphaltene content not indicated to high risk of deposition ,however, the light oils is with less asphaltene content are more interest to have asphalten precipitation. [10, 11].

Asphaltene precipitation classified to three stages, the first one called precipitation, it is occurs once the solid particles has distinct phase when they come out of solution. At this step the size of solid particles are bit small.

Flocculation is the second stage, the size of the small particles grow larger than before in first process. Third stage which called deposition is where the particles are so larger and no longer supported by the liquid. [12, 13].

Some factors such as pressure, temperature, and compositioneffects the stability of asphaltene in the crude oil. The factors changes might impact the stability andoccurasphaltene precipitation [16, 15]. This phenomenon is normally happen during gas flooding in enhanced oil recovery (EOR).

Gas flooding is one of the oldest methods used for application of EOR (David & Taber, 1992) widely used in light, condensate and volatile reservoirs [25]. There are two major types of gas injection which are miscible and immiscible. The miscible injection mechanism process is occurring when the reservoir fluid and gas have a homogenous phase with new physicochemical properties is formed. The act of continuous injection for the gas would make oil via the miscible front towards the production well [19].

Asphaltene particles when exist in crude oil can destabilize due to various mechanisms. One of the mechanisms is injection of carbon dioxide in the reservoir. Moghadasi*et al.* (2006), conducted on experimental study was conductedto know the influence of carbon dioxide injection on asphaltene precipitation. The asphaltene in the said experimental study was only 0.59 %wt which was considered quite low. The minimum pressure for carbon dioxide with the oil was 5300 psia. The study indicated that the asphaltene started to precipitate as low only 0.54 mole percent of carbon dioxide concentration. The asphaltene precipitation was highest at the bubble point. It was concluded that asphaltene precipitation is dependent on the carbon dioxide gas concentration and rapidly increase from one critical value.

Another study was conducted by (Yang et al., 2006). It was concluded that with increasing injection of carbon dioxide, the precipitated asphaltene mass also increased. With 10 mole percent carbon dioxide injection, the maximum asphaltene precipitation observed was 0.23 mass percent, with 30 mole percent carbon dioxide injection, the maximum was 0.44 %mass, with 50 % mol carbon dioxide injection, the maximum is 0.52 % mass and, with 60 % mol carbon dioxide injection, the maximum is 0.67 % mass.

In 1999 Srivastava *et al.* conducted study on the asphaltene precipitation. It was observed that asphaltene precipitation at 42 molpercent of carbon dioxide concentration and there is a linear increase in asphaltene flocculation with carbon dioxide concentration after that.

In many reservoirs, the miscibility of carbon dioxide with the oil is oscillatory. When then injected carbon dioxide and reservoir oil mixed in any ratio form a single phase they are said to be first contact miscible while due to high pressure and temperature conditions requirement, the carbon dioxide is not always miscible in the reservoir.

Carbon dioxide is greatly soluble in oil and to lesser extent in water. To improves efficiency in oil recovery, carbon dioxide can be eliminates the interfacial tension and capillary forces, in theory, all of the residual oil. Under specific of pressure and temperature conditions and specific oil compositions, Carbon dioxide can develop miscibility through multiple contacts (Parra- Ramirez *et al.*, 2001).

According to Parra- Ramirez *et al.*, 2001, by conducted the experimental study to evaluate the effect of first contact and multiple contact miscibility. It was determined that mostly the asphaltene precipitation on first-contact miscibility is negligible while at multiple contact miscibility the amount of asphaltene precipitation was 3 to 5 times higher than first contact miscibility.

Oil sample growth changes in oil composition after increasing in contact with $CO_2$ concentration. The result of these changes will create instability in structures of micelles for resins and asphaltene fractions and the oil composition change gives instability in resins - asphaltene phases which lead to precipitation to occur [26].

Reports studies form (Chukwudeme & Hamouda, 2009; Al-Qasim, 2011; Alta'ee*et al.*, 2010; Khosravi*et al.*, 2009) the using light oil to predicate asphaltene precipitation by means of static, dynamic test at constant pressure and temperature and effect of $CO_2$ concentration. From their studies they found that asphaltene precipitation were observed at high amount of injected $CO_2$ concentration, and increased rapidly near the bubble point pressure. Their suggestions for high oil recovery were obtained If $CO_2$ gas concentration below critical content point.

Base on experimental result conducted by Sima*et al.* (2011) on the effect of $CO_2$ injection on asphaltene precipitation. Injecting $CO_2$ into the core changed the oil composition by altering in the resin asphaltene ratio of the residual oil. The asphaltene started to precipitate at 0.43 pore volume. Furthermore, the content of asphaltene increased from 0.11 wt% to 0.31 wt% till the end of the flooding operation. At low asphaltene pressure the distance between the surrounding fluid and asphaltene particle is large and then hence more precipitation occurred. it also indicated that asphaltene precipitation was 0.23 wt% at 1.26 pore volume of 2300 psi. However at 2600 Psi, the asphaltene precipitation was 0.19 wt% at 1.27 pore volume (Sima*et al.*, 2011).

In the experimental studies that presented by Alta'ee*et al.*, (2012) to investigate the effect of $CO_2$ injection on asphaltene precipitation. They indicated that the asphaltene precipitated at pore volume 0.33 was 0.024 wt%. Then the $CO_2$ reached to 0.66 pore volumes, the precipitated asphaltene was 0.056 wt%. After that the asphaltene precipitation reached to a final value of 0.078 wt% at 1.66 pore volume.

Others like Kokal and Sayegh 1995, Sarma, 2003 and Srivastava and Huang, 1997 have stated in their studies that by increasing in the $CO_2$ concentration contacted with the oil sample during the injection due to high asphaltene precipitation. The injected of $CO_2$ reason to changes in fluid behavior and equilibrium conditions which drive to asphaltene precipitation.

## II. PAGE EXPERIMENTAL WORK

### *A. The Present work Outline*

The paper represents the impact of carbon dioxide and its flow rate on asphaltene precipitation. Dynamic test has been conducted with several runs at various flow rates and the rest of parameters like pressure, $CO_2$ concentration and temperature were kept constant. To do the dynamic asphaltene precipitation test, relative permeability equipment (core flood) equipment was used in order to recreate reservoir condition. Figure 1.1 gives an example for sample schematic of core flood equipment.

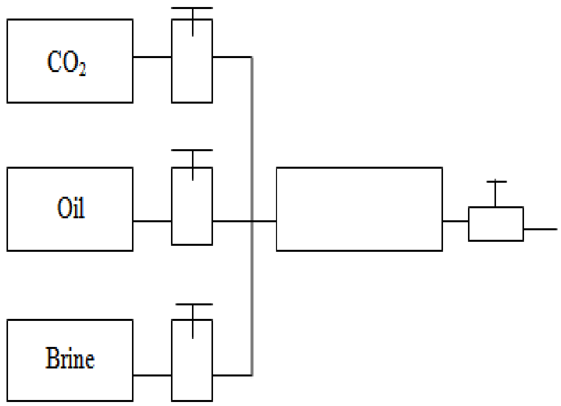


Fig. 1.1 Sample Schematic of Core Flood

### *B. Materials and Equipment*

Since the light oil has long history of asphaltene precipitation problem, therefore in this work a Malaysian light crude oil was selected as oil sample. Asphaltene Initial content value was measured. By Knowing the initial content value of asphaltene to give opportunity to study it variations during carbon dioxide flooding process. Asphaltene content was measured using IP 143 (2004) experimental method. In this Method the sample is mixed well with the n-heptane. This mixture is then heated under reflux. Upon heating, the inorganic material i.e. asphaltene is separated from crude oil. Inorganic material is then collected on the filter paper. Hot toluene is then mixed with the remaining material which makes asphaltene soluble in toluene. The extraction solvent is then evaporated and the asphaltene is weighed. As it illustrated in fig. 2 Helium Porosimeter (Poroperm) was performed to evaluate the core properties.


Fig. 2 Poro-Perm System

In addition, to represent reservoir formation, three Berea sandstone cores were used in this work. Table 1 describe crude oil properties of the selected oil, besides the crude oil viscosity at 98°C was measured using Oswald Viscometer as illustrated in fig 3. The dimensions of the cores were measured before running the core flood. The results of porosity, permeability are shown in Table 2.

ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429
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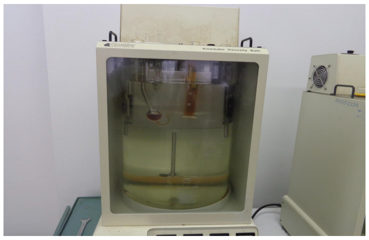

Fig. 3 Oswald Viscometer

TABLE I
CRUDE OIL PROPERTIES

| Sample Name | Malaysian light oil |
|---|---|
| Asphaltene content (wt %) | 37.5 |
| oil viscosity(cp)@98°C | 1.733 |
| Density of oil (gm/cc) @25°C | 0.851 |

TABLE II
Core properties before flooding test

| | Core1 | Core2 | Core3 |
|---|---|---|---|
| Weight | 117.96 | 184.12 | 190.05 |
| diameter | 3.8 | 3.8 | 3.9 |
| Length | 7.3 | 7.55 | 7.4 |
| Kair(mD) | 111.490 | 120.1094 | 116.178 |
| KL (mD) | 38.772 | 41.564 | 40.110 |
| Φ(%) | 18.55 | 18.55 | 18.51 |

## III. EXPERIMENTAL PROCEDURE

Earlier of core flood test in order to set core plugs at original reservoir condition, the core saturated with brine. Saline water was prepared for saturation purpose in this current research. The core sample is filled with brine of 10,000 ppm sodium chloride concentration which is needed for core sample saturation. The injection brine was continued till differential of constant pressure was observed. In the following step, the oil injected to the water saturated core at constant pressure and temperature with different flow rates of injection. This step was carried on until no more water was produced. Within this stage, various flow rate of injection were used 0.4.0.6 and 0.8 cc/min for asphaltene precipitation test induce by carbon dioxide, and it was injected continuously as tertiary recovery after the water injection. The recovery oil was collected at every ten minute until no oil recovery was produced.

## IV. RESULTS AND DISCUSSION

In this study experiments were conducted the core flooding experiments with core-1, core-2 and core-3. It found that as we increase the pore volume injection, the amount of Asphaltene precipitation also increases. Furthermore the flow rate has significant effect on the trend of Asphaltene precipitation. The flow rate has the effect on the amount of Asphaltene precipitation. Three flow rates of 0.4cc/min, 0.6cc/min and 0.8cc/min have the same trend of Asphaltene precipitation that Asphaltene precipitation increased with more fluid injection volume.

TABLE III
Results asphaltene content measurement with flow rate= 0.4 cc/min with initial asphaltene content = 0.3 wt %

| Pore Volume of gas injected (PV) | Asphaltene Content in the Recovered oil (wt %) | Asphaltene Content Precipitated in the Core (wt %) |
|---|---|---|
| 0.25 | 0.29 | 0.01 |
| 0.50 | 0.25 | 0.05 |
| 0.75 | 0.20 | 0.1 |
| 1.00 | 0.17 | 0.13 |

TABLE V
Results Asphaltene Content Measurement With Flow Rate= 0.6 Cc/Min With Initial Asphaltene Content = 0.3 Wt %

| Pore Volume of gas injected (PV) | Asphaltene Content in the recovered oil (wt %) | Asphaltene content precipitated in the core (wt %) |
|---|---|---|
| 0.25 | 0.24 | 0.06 |
| 0.50 | 0.21 | 0.09 |
| 0.75 | 0.16 | 0.14 |
| 1.00 | 0.12 | 0.18 |

TABLE VI
Results asphaltene content measurement with flow rate= 0.8 cc/min with initial asphaltene content = 0.3 wt %

| Pore Volume of gas injected (PV) | Asphaltene Content in the recovered oil (wt %) | Asphaltene content precipitated in the core (wt %) |
|---|---|---|
| 0.25 | 0.22 | 0.08 |
| 0.50 | 0.18 | 0.12 |
| 0.75 | 0.13 | 0.17 |
| 1.00 | 0.11 | 0.19 |

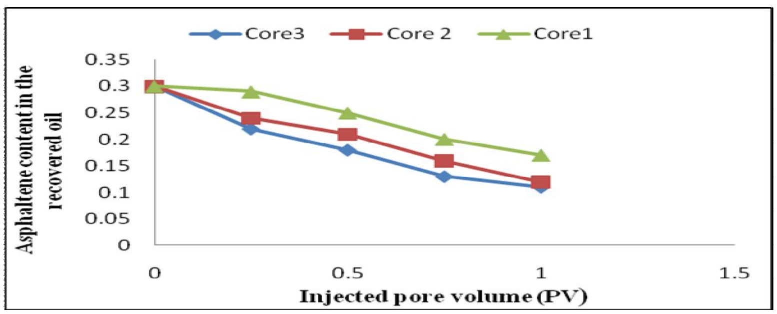


Fig. 4 Asphaltene content in the recovered oil for three cores

Fig. 4 shows the pore volume of injection versus asphaltene content of recovered oil. As can be seen from Fig. 4, in run 1 where the flow rate was 0.4cc/min, the results show that the asphaltene initial point of precipitate at 0.25 pore volume and the amount of precipitated was 0.01%. Asphaltene has more significant once reached to 1.00 pore volume and the asphaltene at this point was 0.13 wt %. Afterward, as the pore volume of injected an upward, the asphaltene content in the recovered oil is kept declined. By comparing with run 2 from previous run ,the flow rate has incremented to 0.6 cc/min, the asphaltene content left in the core was 0.06 wt % at 0.25 pore volume, however, the quantity of asphaltene jumped to 0.18 wt% at 1.00 pore volume.

The percentage of deposition for asphaltene increased more at run 3 with 0.8 cc/min flow rate compared to other runs. At 0.25 pore volume, the asphaltene started to precipitate and extent to 0.08 wt%. While $CO_2$ injection reached1.00 pore volume the asphaltene content collected improve to 0.19 wt %.

It can be observed in this study experiments were conducted the core flooding experiments with core-1, core-2 and core-3. It found that as increase in the pore volume of injection, the amount of Asphaltene precipitation also increases. Furthermore the flow rate has the effect on the amount of Asphaltene precipitation. Three flow rates of 0.4cc/min, 0.6cc/min and 0.8cc/min have the same trend of Asphaltene precipitation that Asphaltene precipitation increased with more fluid injection volume.

Ali and Islam in 1998 stated in their research that influence of flow rate on behaivoir of asphaltene deposition. They found that the asphaltene precipitation depends on flow rate and it takes place near wellbore or inlet of core injection. [l6], [17].

In addition, asphaltene deposition rate is a function of flow rate. They clarified that for a system that depends on flocculation and deposition dependence on flow rate. For the case of fine deposition, allow flow rate translates into less energy for floatation, which typically means that the deposition rate would increase with increasing flow rates [17].

Experimental study did by Bagheriet al. to investigate the influence of flow rate on asphaltene deposition process. It can be concluded from their results that flow rate growth is followed by high amount of asphaltene deposition which induces to reduce in permeability and porosity.

## V. CONCLUSIONS

From the research that has been undertaken, it is possible to conclude that injected $CO_2$would alter the crude oil composition and lead to instable in asphalene and resin ratio. At once the asphalene get altered, this change is favour for asphaltene to precipitate. When $CO_2$ injected continuously, thepore volume of the injected gas increase as soon as crude oil contacts with carbon dioxide for long time, consequence, more aspahlteneprecipitationoccurs. As well as, it is believed that when $CO_2$ injection flow rate increased thus cause increasing of asphaltene precipitation and deposition in light oil reservoir.

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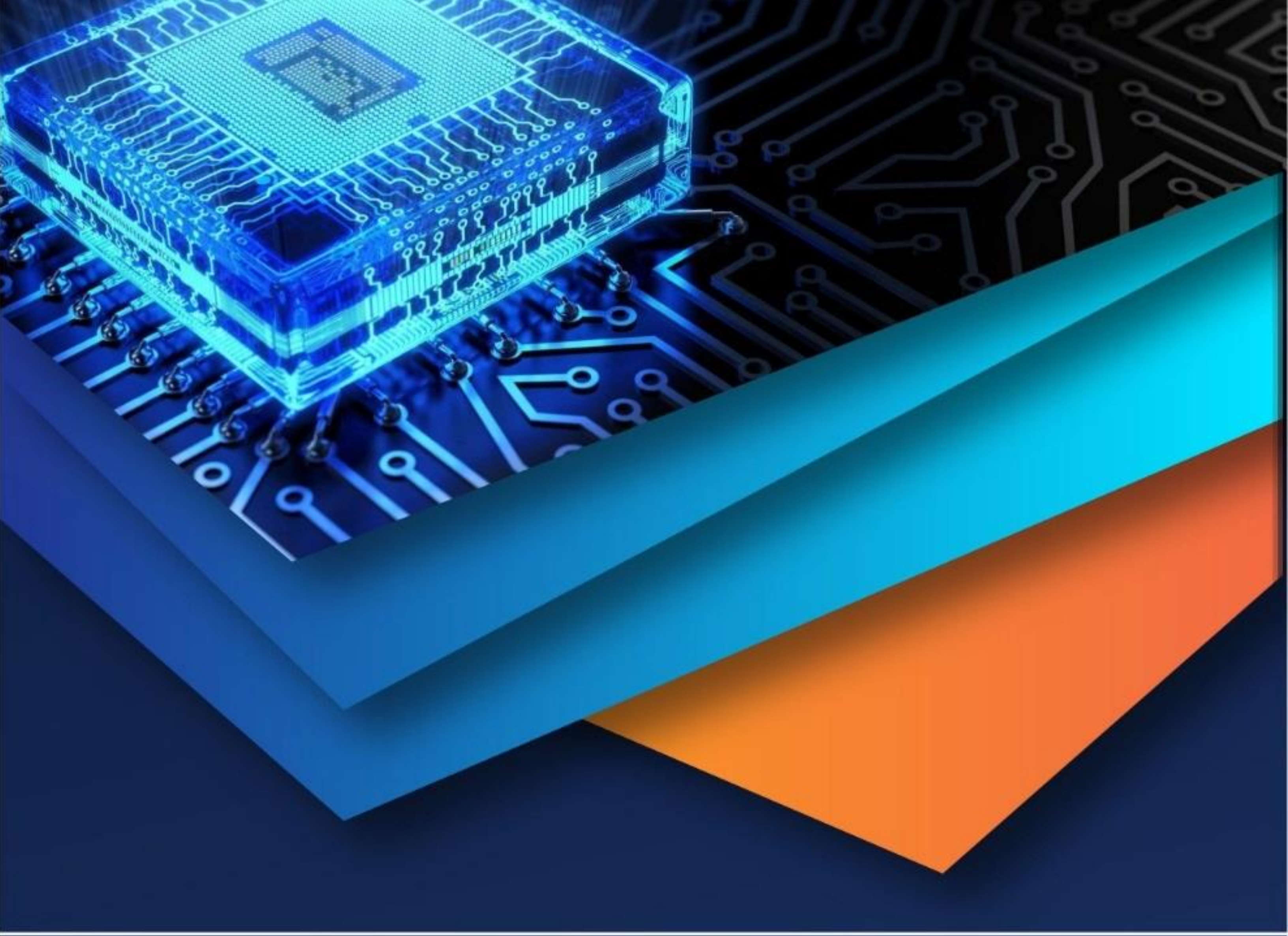

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