Enhancing Oil Recovery in Sandstone Core Samples Using Zeolite, Sodium & Potassium Hydroxide, Silica, Aluminum Addition to Formation Water

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Abstract

This research project explores the effectiveness of adding zeolites to formation water for enhancing oil recovery. The demand for fossil fuels, particularly oil, remains significant for meeting global energy needs. , water flooding plays a vital role in increasing oil production by maintaining reservoir pressure and displacing oil from pore spaces, leading to improved ultimate oil recovery. Zeolites, known for their porous structure and ion-exchange properties, have gained prominence in numerous industrial applications, including EOR.

This research investigates the impact of adding zeolites to formation water on oil recovery. The research issue arises from the recognition that formation water alone may not efficiently recover oil due to oil properties and rock characteristics. The aim of this study is to determine whether the inclusion of zeolites in formation water can enhance oil recovery. Experiments are conducted on sandstone core samples obtained from a Libyan field in the Murzuq basin,

The experimental results demonstrate that the addition of zeolite, sodium hydroxide, potassium hydroxide, silica, and aluminum significantly improves oil recovery at higher temperatures for sandstone core samples. Furthermore, the inclusion of sodium hydroxide yields superior oil recovery compared to potassium hydroxide. Using 15% of sodium and potassium hydroxides yields better results than other percentages, although the underlying cause is not explored in this study. Additionally, the combination of zeolite, sodium and potassium hydroxides, silica, and aluminum enhances oil recovery, warranting further investigation into the underlying mechanisms.

Keywords:- Enhanced, Oil Recovery, Zeolite, formation water, Potassium Hydroxide

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تعزيز استرداد النفط في عينات الحجر الرملي الأساسية عن طريق اضافة الزيولايت وهيدروكسيد الصوديوم والبوتاسيوم والسيليكا والألومنيوم الى مياة الخزان

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الملخص

يستكشف هذا المشروع البحثي مدى فعالية إضافة الزيوليت إلى مياه التكوين لتعزيز استخلاص النفط. ويظل الطلب على الوقود الأحفوري، وخاصة النفط، كبيرا لتلبية احتياجات الطاقة العالمية. يلعب غمر المياه دورًا حيويًا في زيادة إنتاج النفط من خلال الحفاظ على ضغط الخزان وإزاحة النفط من المسام، مما يؤدي إلى تحسين عملية استخلاص النفط في نهاية المطاف.

وقد اكتسب الزيوليت، المعروف ببنيته المسامية وخصائص التبادل الأيوني، شهرة في العديد من التطبيقات الصناعية، بما في ذلك الاستخلاص المعزز للنفط.يبحث هذا البحث في تأثير إضافة الزيوليت إلى مياه التكوين على عملية استخلاص النفط. تنشأ مشكلة البحث من إدراك أن مياه التكوين وحدها قد لا تستعيد النفط بكفاءة بسبب خصائص الزيت وخصائص الصخور. الهدف من هذه الدراسة هو تحديد ما إذا كان إدراج الزيولايت في مياه التكوين يمكن أن يعزز عملية استخلاص النفط.

أجريت التجارب على عينات من الحجر الرملي تم الحصول عليها من حقل ليبي في حوض مرزق. واظهرت النتائج التجريبية أن إضافة الزيوليت وهيدروكسيد الصوديوم وهيدروكسيد البوتاسيوم والسيليكا والألومنيوم يحسن بشكل كبير من استخلاص الزيت عند درجات حرارة أعلى لعينات الحجر الرملي الأساسية. علاوة على ذلك، فإن إدراج هيدروكسيد الصوديوم يؤدي إلى استخلاص فائق للزيت مقارنةً بهيدروكسيد البوتاسيوم. يؤدي استخدام 15% من هيدروكسيدات الصوديوم والبوتاسيوم إلى نتائج أفضل من النسب الأخرى، على الرغم من عدم استكشاف السبب الأساسي في هذه الدراسة. بالإضافة إلى ذلك، فإن مزيج الزيوليت وهيدروكسيدات الصوديوم والبوتاسيوم والسيليكا والألومنيوم يعزز عملية استخلاص النفط، مما يستدعي إجراء مزيد من التحقيق في الآليات الأساسية.

Introduction

Much of the energy needed today comes from fossil fuels, and oil reservoirs are one of its largest sources. However, the production of these resources has many challenges, and it is not possible to produce most of the original oil-in-place (OOIP) with the primary methods. Several recovery methods are used to improve oil recovery. They are called Enhanced Oil Recovery methods (EOR)[1].

Water flooding is an essential technique used in EOR operations to increase the production of oil from reservoirs. Injection of water helps in increasing the reservoir pressure to its initial level and maintain it near that pressure. In addition, water displaces oil from the pore spaces and improves the ultimate oil recovery[2].

The displacement efficiency depends on many factors such as oil viscosity and rock characteristics. Therefore, in order to improve that efficiency, several chemicals were tested and proved its efficiency, added to water during water flooding. For example, smart water injection, carbonated water injection, injection of surfactant solutions, polymers, alkalis and mutual solvents can be considered as various methods of chemical water injection. In addition, sometimes to increase the performance of chemical water, a combination of several types of additives and foam injection is recommended according to the structure of the reservoirs[3].

The Objectives of The Research

A. Formation water without additives might not have great efficiency in recovering oil due to oil properties and rock characteristics.

B. The current research aims to investigate whether adding Zeolites to formation water would improve oil recovery.

C. The experiments in this research will be carried out for sandstone formation using 3 core samples form a Libyan field in Murzuq basin.

D. The researcher hypothesizes that adding zeolite to formation water will improve its characteristics and subsequently enhance oil recovery.

E. Several fields in Libya are being subjected to water injection, If zeolite has proven its efficiency, and improved oil recovery than the daily production rate of the country will drastically be increased.

Zeolites are a group of naturally occurring or synthetic crystalline minerals composed of aluminum, silicon, and oxygen. They have a unique porous structure with regular channels and cavities that can accommodate a variety of cations, such as sodium, potassium, calcium, and magnesium. Due to their high adsorption capacity and ion-exchange properties, zeolites have gained importance in various industrial applications, including enhanced oil recovery (EOR).

In this research, the effect of adding zeolites to formation water in improving oil recovery is investigated.

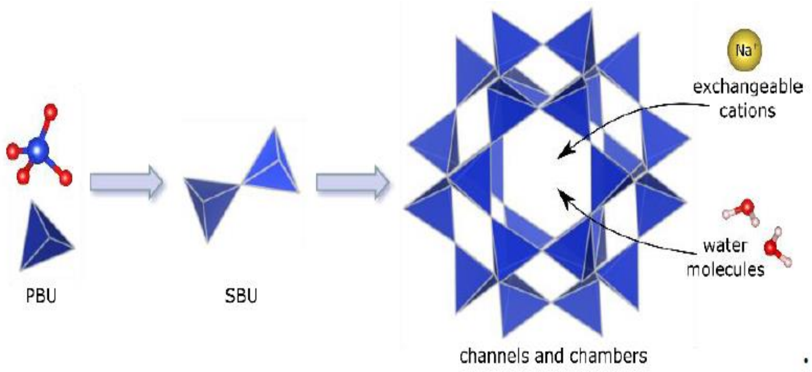

Fig. 1 Scheme of Zeolite Structure[8]

2.Experimental Part

The materials used in this research project experiment includes:

1. Core samples: Three sandstone core samples, from a Libyan field in Murzuq basin was used.
2. Reservoir oil sample: A 40.1 API and 0.8243 gm/cc oil sample was used for the experiment. 3.2 shows the oil sample used for this research project.
3. Reservoir water sample: Use one sample of reservoir water with for our study. shows the reservoir water used for this research project while Table 1 shows the properties of the reservoir water.

Table 1 Properties of reservoir water sample

Conductivity Electrine CE (mc/cm)	13440
Salinity (ppt)	6.2
PH	8.23
TDS (mg / l)	8810

4. ZSM-5 manufactured zeolite**:**

Fig. 2 Zeolite

5. Silica
6. Sodium Hydroxide
7. Potassium Hydroxide

3.Experiments Procedures:

3.1 Formation Water Preparation:

The treatment process was carried out for water with a TDS of 8810. Using the active ZSM-5 zeolite catalyst, potassium, and sodium hydroxides the TDS was decreased through the following detailed procedures:

Step 1: The first step is to filtrate the formation associated water from sand and oil residuals using paper filters

Step 2: Zeolite was activated before it is being added to filtered water. The activation is carried out by raising the zeolite temperature to 750 °C for two hours.

Fig. 3 Zeolite activation at high temperature

Step 3: Sodium hydroxide with a concentration of 0.2 M was added to a 100 ml of the filtered associated water at different rates of 5%, 10%, 15% and 20%.

Step 4: 1 gm of zeolite was added to the water mixture.

Step 5: The mixture was put in a water bath at 50 °C with a mixer at a speed of 500 rpm for half an hour.

Step 6: The mixture was left in a Polypropylene vial for 24 hours at room temperature as per

Step 7: After 24 hours the water was filtered form the zeolite.

Fig. 4 Filtrating water from silica and zeolite

Step 8: Filtered water was analyzed.
Step 9: The process was repeated again with replacing the sodium hydroxide with potassium hydroxide with a concentration of 0.1M with the same rate and procedure.
Step 10: Another two scenarios were investigated:

Scenario 1 (Cat1): Using 15% sodium hydroxide sample, a 1:1 ratio of pure silica and aluminum was prepared and added to water in order to have a better efficiency in terms of total dissolved solids.

During preparation they were activated at a temperature of 450 °C for a period of two hours. The mixture was then put in a water bath with stirring for half an hour and being left in poly poplin bottle.

Scenario 2 (Cat2): The same scenario was repeated but the 15% sodium hydroxide sample was replaced by the 15% potassium hydroxide sample.

The results of both scenarios were reported. All reported results shall be discussed in the next chapter.

3.2 Core Samples Preparation and Preliminary Measurements:

Step 1: Core Samples Cleaning:

Three core samples were used in previous experiments and might be saturated with oil. Therefore, they were cleaned with toluene by Soxhlet device.

Fig. 5 **Soxhlet device used in core cleaning**

Step 2: Core Sample Drying

Step 3: Core samples bulk volume measurement
Step 4: Core samples saturation in formation water
Step 5: Core samples drying form saturation water
Step 6: Core samples saturation in formation oil
Step 7: Oil density measurement
Step 7: Samples OOIP measurements Wettability Measurement of Filtered Waters

Wettability was evaluated using contact angle measurement through the following steps:
Step 1: Core samples were saturated with oil.
Step 2: Saturated core samples were submerged into three different solutions, filtered formation water, Cat1 and Cat2. Samples are shown in Figure
Step 3: Using a high-resolution camera, drop shots were taken for the three cases.
Step 4: Using image software and the drop shot the contact angle was measured for the three cases.
Step 5: Results of all cases were reported and will be shown in the next chapter.

3.1 Spontaneous Imbibition Test:

Oil saturated core samples were placed inside the test tube.

1. The test tubes were filled with original reservoir water, Cat1 and Cat2 treated water until the core samples were completely submerged.
2. Test tubes orifices were closed using aluminum foil and paper tape in order to prevent oil evaporation.
3. The volumes of produced oil were measured through several steps at different temperatures starting from room temperature, 30 °C, 40 °C, 50 °C, 60 °C and 70 °C. At each step the samples were left for two days.
4. Oil recovery factor was calculated using the following equation:

$$Rf = NP/N*100$$

Where:

Rf: Oil Recovery Factor (fra).
NP: Oil Production (cc).
N: Original Oil In Place (cc)

5. All recovery factor results were reported and shall be presented in the next chapter.

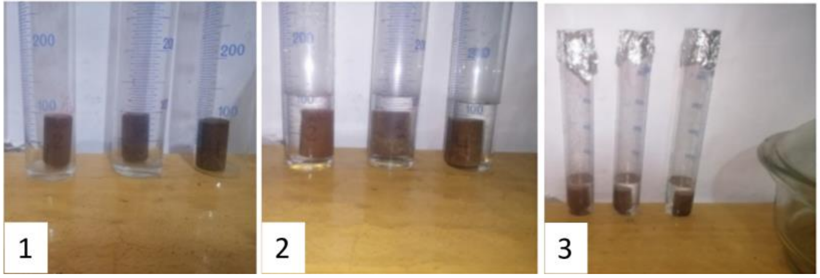

Fig. 6 Spontaneous imbibition test steps

4. Results and Discussion:

4.1 Formation Water Preparation Results:

The results of all of the experiments will be presented and discussed in this chapter.

Starting from Table 4.1 which shows the results of the original formation water sample after filtration. Tables 4.2 to 4.5 show the formation water with the addition of sodium hydroxide with a percentage of 5%, 10%, 15% and 20%.
Form those tables, the higher the percentage of sodium hydroxide the lower the percentage of TDS. are showing the water analysis for different water samples.

Table 4. 1 The Parameters of Original sample

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 ºC	8.23	-	ASTM D-1293
2	Electrical Conductivity , EC	13440	µS/cm @ 25ºC	AWWA 2510
3	Total Hardness	1500	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	750	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	750	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	300	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	182	mg/L	ASTM D511
8	Sodium (Na^{+})	2700	mg/L	ASTM D-2791
9	Potassium (K^{+})	155	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	8810	mg/L	Measured

Table 4. 2 The Parameters of sample with NaOH (5%) (N1)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 ºC	8.21	-	ASTM D-1293
2	Electrical Conductivity , EC	12750	µS/cm @ 25ºC	AWWA 2510
3	Total Hardness	860	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	280	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	580	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	112	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	141	mg/L	ASTM D511
8	Sodium (Na^{+})	2100	mg/L	ASTM D-2791
9	Potassium (K^{+})	140	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	8450	mg/L	Measured

Table 4. 3 The Parameters of sample with NaOH (10%) (N2)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 ºC	8.29	-	ASTM D-1293
2	Electrical Conductivity , EC	12120	µS/cm @ 25ºC	AWWA 2510

3	Total Hardness	310	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	120	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	190	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	48	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	46	mg/L	ASTM D511
8	Sodium (Na^{+})	2275	mg/L	ASTM D-2791
9	Potassium (K^{+})	120	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	7730	mg/L	Measured

Table 4. 4 The Parameters of sample with NaOH (15%) (N3)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 °C	8.29	-	ASTM D-1293
2	Electrical Conductivity , EC	12120	μS/cm @ 25°C	AWWA 2510
3	Total Hardness	310	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	120	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	190	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	48	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	46	mg/L	ASTM D511
8	Sodium (Na^{+})	2275	mg/L	ASTM D-2791
9	Potassium (K^{+})	120	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	7730	mg/L	Measured

Table 4. 5 The Parameters of sample with NaOH (20%) (N4)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 °C	8.75	-	ASTM D-1293
2	Electrical Conductivity , EC	12940	μS/cm @ 25°C	AWWA 2510
3	Total Hardness	Nil	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	Nil	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	Nil	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	Nil	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	Nil	mg/L	ASTM D511
8	Sodium (Na^{+})	1975	mg/L	ASTM D-2791
9	Potassium (K^{+})	705	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	6670	mg/L	Measured

Tables 4.6 to 4.9 show the formation water with the addition of potassium hydroxide with a percentage of 5%, 10%, 15% and 20%.

Form those tables, the higher the percentage of potassium hydroxide the lower the percentage of TDS. are showing the water analysis for different water samples.

Table 4. 6 The Parameters of sample with KOH (5%) (K1)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 ºC	8.41	-	ASTM D-1293
2	Electrical Conductivity , EC	13900	µS/cm @ 25ºC	AWWA 2510
3	Total Hardness	1250	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	600	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	650	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	240	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	158	mg/L	ASTM D511
8	Sodium (Na^{+})	2500	mg/L	ASTM D-2791
9	Potassium (K^{+})	320	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	6710	mg/L	Measured

Table 4. 7 The Parameters of sample with KOH (10%) (K2)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 ºC	8.23	-	ASTM D-1293
2	Electrical Conductivity , EC	13120	µS/cm @ 25ºC	AWWA 2510
3	Total Hardness	1000	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	5000	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	5000	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	200	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	122	mg/L	ASTM D511
8	Sodium (Na^{+})	2400	mg/L	ASTM D-2791
9	Potassium (K^{+})	380	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	6700	mg/L	Measured

Table 4. 8 The Parameters of sample with KOH (15%) (K3)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 ºC	8.51	-	ASTM D-1293
2	Electrical Conductivity , EC	12570	µS/cm @ 25ºC	AWWA 2510
3	Total Hardness	720	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	240	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	280	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	96	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	117	mg/L	ASTM D511
8	Sodium (Na^{+})	2275	mg/L	ASTM D-2791
9	Potassium (K^{+})	540	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	5870	mg/L	Measured

Table 4. 9 The Parameters of sample with KOH (20%) (K4)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 °C	8.40	-	ASTM D-1293
2	Electrical Conductivity , EC	12650	µS/cm @ 25°C	AWWA 2510
3	Total Hardness	540	mg/L	ASTM D1126
4	Calcium Hardness as CaCO3	300	mg/L	ASTM D1126
5	Magnesium Hardness as $CaCO_3$	240	mg/L	ASTM D1126
6	Calcium (Cs^{-1})	88	mg/L	ASTM D511
7	Magnesium (Mg^{+2})	78	mg/L	ASTM D511
8	Sodium (Na^{+})	2050	mg/L	ASTM D-2791
9	Potassium (K^{+})	676	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	6030	mg/L	Measured

Table 4.10 shows the formation water with the addition of 15% sodium hydroxide, silica and aluminium. The sample was labelled as Cat1 and was later used for imbibition process.

Table 4.11 shows the formation water with the addition of 15% potassium hydroxide, silica and aluminium. The sample was labelled as Cat2 and was later used for imbibition process.

Table 4. 10 The Parameters of sample with NaOH + Silica+ Aluminum (Cat1)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 °C	7.28	-	ASTM D-1293
2	Electrical Conductivity , EC	11350	µS/cm @ 25°C	AWWA 2510
8	Sodium (Na^{+})	2700	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	5430	mg/L	Measured

Table 4. 11 The Parameters of sample with KOH + Silica+ Aluminum (Cat2)

	PARAMETER	TEST RESULT	UNITS	METHOD
1	pH -Value @ 25 °C	8.27	-	ASTM D-1293
2	Electrical Conductivity , EC	12510	µS/cm @ 25°C	AWWA 2510
8	Potassium (K^{+})	500	mg/L	ASTM D-2791
10	Total Dissolved Solids (TDS)	6760	mg/L	Measured

1.1 Experiments Procedures Results:

Table 4.12 and Table 4.13 show the measurement results of core samples dimensions and bulk volume. Table 4.14 shows the volume of produced fluids in mL for the different samples at temperatures from 30 °C to 70 °C.

Table 4. 12 Core sample dimensions

Sample	D (cm)	L (cm)
1	2.5	3.2
3	2.5	3.3
4	2.5	4.3

Table 4. 13 Core samples bulk volume

Sample	Bulk Volume ($\frac{\pi}{4}.D^{2}).L$	Unit
1	15.70	cc
2	16.19	cc
3	22.08	cc

Table 4. 14 Produced volumes 1from core samples in (mL) at different temperatures

		Temperature (°C)	20	30	40	50	60	70
1	Cat 2	KOH	1	1	1.5	1.5	2	2
2	Cat 1	NaOH	0.5	1	1	1.5	2	2.5
3	Formation Water	F.W	1	1	1	1.5	1.5	1.5

Table 4. 15 Measurements of OOIP in the different core samples using different formation waters

			Original Oil in Place (STB)
1	Cat 2	KOH	$\frac{38.45-34.20}{0.84}=5.05$
2	Cat 1	NaOH	$\frac{52.05-48.25}{0.84}=4.52$
3	Formation Water	F.W	$\frac{42.30-38.09}{0.84}=5.01$

Table 4.16 shows the calculated recovery factor from each sample at different temperatures.

Table 4. 16 Recovery factor for the 3 core samples using different formation water composition

Temperature (ºC)	Sample	RF
30	Cat 2 - KOH	$\frac{1}{5.05} \times 100 = 19.80$
	Cat 1 - NaOH	$\frac{1}{4.52} \times 100 = 22.12$
	Formation Water	$\frac{1}{5.01} \times 100 = 19.96$
40	Cat 2 - KOH	$\frac{1.5}{5.05} \times 100 = 29.70$
	Cat 1 - NaOH	$\frac{1}{4.52} \times 100 = 22.12$
	Formation Water	$\frac{1}{5.01} \times 100 = 19.96$
50	Cat 2 - KOH	$\frac{1.5}{5.05} \times 100 = 29.70$
	Cat 1 - NaOH	$\frac{1.5}{4.52} \times 100 = 33.18$
	Formation Water	$\frac{1.5}{5.01} \times 100 = 29.94$
60	Cat 2 - KOH	$\frac{2}{5.05} \times 100 = 39.60$
	Cat 1 - NaOH	$\frac{2}{4.52} \times 100 = 44.24$
	Formation Water	$\frac{1.5}{5.01} \times 100 = 29.94$
70	Cat 2 - KOH	$\frac{2}{5.05} \times 100 = 39.60$
	Cat 1 - NaOH	$\frac{2.5}{4.52} \times 100 = 55.30$
	Formation Water	$\frac{1.5}{5.01} \times 100 = 29.94$

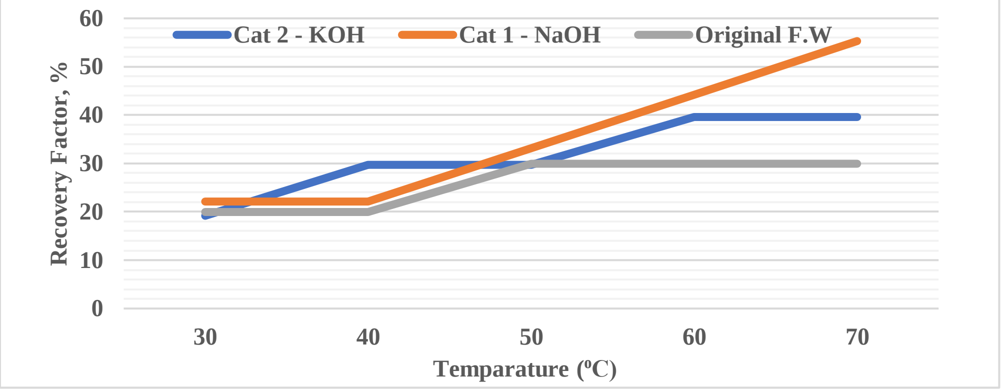

Fig. 7 Comparison between recovery factors using different compositions of formation water

Figure 7 shows the calculated recovery factor from each sample at different temperatures. From the presented results chart, it is very clear that the core samples saturated with Cat 1 formation water exhibit a notably higher oil recovery factor at elevated temperatures compared to Cat 2 formation water and the original formation water.

However, at lower temperatures, Cat 2 formation water was performing better in the oil recovery compared to Cat 1 and original formation water. Additionally, the recovery factor for Cat 1 is still going higher, while Cat 2 and original formation water were stable in recovery.

Conclusions

In conclusion, the experimental findings presented in this research project shed light on the significant influence of adding chemicals to formation water on oil recovery. These are some of the conclusions:

1- For a sandstone core samples, adding Zeolite, sodium hydroxide, potassium hydroxide, silica and aluminum significantly improves oil recovery at higher temperatures.
2- The addition of sodium hydroxide had better oil recovery than potassium hydroxide.
3- Using 15% of sodium and potassium hydroxides gave better results than other percentages of 5, 10 and 20%.

Adding silica and aluminum to the combination of Zeolite, sodium and potassium hydroxides gave better results in terms of oil recovery.

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