

Evidence of Multi-Component Ion Exchange in Dolomite Formation during Low Salinity Waterflooding

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Abstract. Low salinity waterflooding is a technique performed in many oil reservoirs around the globe. The technique is simply implemented by injecting water with very low ionic activity compared to formation water into an injection well. The injected water will increase reservoir pressure that is compulsory to drive oil moving toward production well. More than just maintaining reservoir pressure as obtained from conventional waterflooding, low salinity water creates shifting of surface condition, resulting in additional amount of liberated oil. Nevertheless, exact oil recovery mechanisms are still discussed. Among these proposed mechanisms, Multi-component Ion Exchange (MIE) together with wettability alteration is believed to be a major mechanism leading to higher oil recovery compared to conventional waterflooding. In this study, detection of calcium and magnesium ions which are Potential Determining Ions (PDI) for carbonate reservoirs are detected during the coreflood experiment. Dolomite rock sample is used to represent carbonate formation and detection of previously mentioned ions is performed by complexometric titration of the effluents. From the study, it is observed that during conventional waterflooding and low salinity waterflooding at low temperature of 30 degrees Celsius, calcium and magnesium ions in the produced water is increased compared to the amount of these ions in the injected water. This incremental of ions can be explained by the dissolution of calcium and magnesium from dolomite which is chemically composed of calcium magnesium carbonate. At this temperature, the portion of calcium ion is always less than magnesium ion even though the amount of calcium ion is higher than magnesium ion in injected water. However, at higher temperatures which are 50 and 70 degrees Celsius, ratio of calcium and magnesium ions in injected and produced water is reversed. Disappearance of magnesium ion in the effluent is more obvious especially at 70 degrees Celsius and by low salinity waterflooding. This can be explained that at lower temperature, calcium ion disappears to form of calcium carboxylate complex with oil and at higher temperature, magnesium ion disappears as magnesium can start to form magnesium carboxylate complex with oil and hence, the amount of both calcium and magnesium ions is decreased compared to lower temperature. In dolomite reservoir, since both calcium ions and magnesium ions are provided from dissolution mechanism, the benefit from multi-component ion exchange will occur at high temperature as both calcium and magnesium ions will be consumed for oil recovery mechanism.



1. Introduction

Waterflooding is a technique chosen to perform in most oilfields around the globe. The technique is also known as a secondary recovery where reservoir pressure is maintained by means of the injected water. Oil production is therefore, prolonged as the source of driving force for liquid production is maintained. Nowadays, waterflooding is further modified. Many studies were performed to investigate effects of compositions of injected water. In summary, oil recovery mechanisms obtained from low salinity waterflooding can be categorized into: 1) fine migration together with oil droplets due to salinity shock [1]; 2) reduction of interfacial tension due to dissolution mechanism of rock together with rising of pH value of water [2]; and 3) Multi-component Ion Exchange (MIE) between rock surface and surrounding water together with wettability alteration [3]. Most studies have discovered the extension of explanation on the last mechanism and have pointed out that this mechanism may be the one that can explain most cases obtaining additional oil recovery by means of low salinity waterflooding. In nature, dolomite surface tends to be attracted by carboxylic acid in oil. As dolomite surface which is one of the most commonly known carbonate rocks appears to be positively charged in neutral condition, this attracts negatively charges of carboxylic acid in oil to be adsorbed onto dolomite surface [4]. Once direct adsorption occurs, crude oil prefers to stick with non-polar part of carboxylic acid and hence, surface is covered by oil, turning rock surface to oil-wet. Oil is therefore, immobile and this condition turns to be unfavourable for oil production. When salinity of injected water is lower than that of formation water, several mechanisms occur, shifting surface equilibrium to new conditions. Three ions in water including calcium ion, magnesium ion and sulphate ion are known as Potential Determining Ions (PDI) and they are responsible for oil recovery mechanism by low salinity waterflooding in carbonate reservoir [5]. When injected water contains adequate amount of sulphate ion, negative charge from this ion will neutralize positive charge of dolomite surface, causing less attraction force between rock surface and adsorbed carboxylic acid. Together with the function provided by sulphate ion, calcium ion will assist oil recovery mechanism by forming calcium carboxylate complex, inducing acid in crude oil to release interaction with rock surface and to form new complex. Combining effects of both sulphate ion and calcium ion results in liberation of attaching oil on rock surface and crude oil can be produced. In addition to this combining of effects, appropriate amount of calcium ion would favour dissolution mechanism of calcium element on dolomite surface and hence, desorption mechanism of adsorbed oil can be accelerated. That means, the amount of calcium ion in injected water should be less compared to formation water in order to favour dissolution mechanism of calcium element. However, the amount of calcium ion should be adequate to form calcium carboxylate complex which is one of the major oil recovery mechanisms. In the past studies, it is observed that magnesium ion can also assist the MIE mechanism. Nevertheless, the mechanism only appears at higher temperature. Magnesium ion will replace calcium ion in the calcium carboxylate complex to form magnesium carboxylate complex, resulting in more amount of calcium ion to initiate oil recovery mechanism.

In limestone where its composition is only calcium carbonate, oil recovery mechanism by means of low salinity water may be principally induced by calcium ion. However, dolomite which is composed of both calcium carbonate and calcium magnesium carbonate can be more complicated since magnesium ion may take part in oil recovery mechanism. This study is therefore, performed to study activity of both calcium ion and magnesium ion during the MIE mechanism by detecting the amount of both ions during oil recovery mechanism during both conventional waterflooding (salinity is equal to that of formation water) and low salinity waterflooding. Since temperature is a parameter differentiating activity of calcium ion and magnesium ion, coreflood experiment together with complexometric titration are performed at different temperatures. Appearance and disappearance of both ions during oil recovery mechanism will not only indicate their functions in MIE, but will also indicate appropriate conditions for low salinity waterflooding in dolomite reservoir.

2. Oil Recovery Mechanisms by Low Salinity Water

Low salinity waterflood is a technique recently discovered compared to other chemical enhanced oil recovery techniques. Reducing ionic strength or salinity of injected water induces a shift of surface equilibrium in both sandstone and carbonate formation. As a result, rock surface tends to be more water-wet and oil is liberated from rock surface. For both types of reservoirs, it is important that salinity of injected water must be less than that of formation water. In most studies, it is discovered that the higher the difference between injected and formation water, the better shifting of surface equilibrium and as a result, the better amount of oil to be recovered. A more sophisticated study also investigated effects of particular ions especially in sandstone formation. It is discovered that, not only total salinity should be concerned; certain ions should be removed from injected water. Reduction of calcium ion from injected water results in dissolution of bridging divalent ion between sandstone surface and adsorbed oil layer. Moreover, Srisuriyachai and Peerakham [6] also found that increasing of potassium ion in injected brine causes faster MIE mechanism as hydrated size of potassium is smaller than of sodium due to less amount of water of hydration [7]. Table 1 summarizes ionic properties of cationic ions in formation water including sodium ion, potassium ion, calcium ion and magnesium ion.

Table 1. Ionic properties of cationic ions in formation water including ionic and hydrated radii.

Cation	Ionic radius (pm)	Hydrated radius (pm)
Sodium ion	116	450
Potassium ion	152	300
Magnesium ion	86	800
Calcium ion	114	600

The amount of potassium ion in seawater which is around 369 ppm [8] is adequate to replace divalent ions during the MIE mechanism. However, total salinity of injected water should be kept as low as possible. That means seawater could only work in case that formation water is extremely high. In recent study, not only properties of injected water should be concerned, water composition of formation water also indicates effectiveness of low salinity waterflooding. In sandstone formation, potassium ion can be enriched due to several reasons. Presence of potassium ion results in strong interaction between sandstone surface and adsorbed oil layer. This eventually causes a very strong oil-wet condition and hence, effects from low salinity water are difficultly obtained. When amount of sodium ion is dominant over potassium ion, effects from divalent ion appears. From table 1 it can be seen that ionic radius of magnesium is smaller than of calcium ion. This results in a strong interaction between sandstone surface and adsorbed oil layer. In summary, formation water of sandstone formation should contain less amount of potassium ion and less amount of magnesium ion to favour oil recovery mechanism by low salinity water. For injected water, reduction of calcium and adequate amount of potassium ion are desirable but total salinity must be kept at lower concentration compared to formation water. Figure 1 illustrates effects of ions in formation water on strength of adsorption where figure 2 demonstrates oil recovery mechanism by collaboration between potassium ion and calcium ion in sandstone formation.

For carbonate formation, effects of low salinity water are different. In carbonate formation, potassium ion is very small and most of the time it is absent from formation water. Moreover, the interaction of adsorbed oil and carbonate surface can be formed directly due to different charge properties of carbonate surface and carboxylic acid in crude oil. Oil-wet condition in carbonate formation is therefore stronger compared to sandstone surface. In carbonate formation, three ions collaborate together to liberate oil from rock surface. Sulphate ion with negative charge is adsorbed onto positively charged carbonate surface, resulting in reduction of strength of charge. Similar to

sulphate ion, borate ion (BO_3^{3-}) and phosphate ion (PO_4^{3-}) can also provide negative charge [5]. As interaction between rock surface and adsorbed acid is lessened, acid tends to bond with calcium ion in aqueous phase to form calcium carboxylate complex. Dissolution of calcium from rock surface also occurs when salinity of water is reduced. Dissolution of mineral results in disappearance of the adsorbed layer and as a consequence, a new surface without adsorption of oil appears.

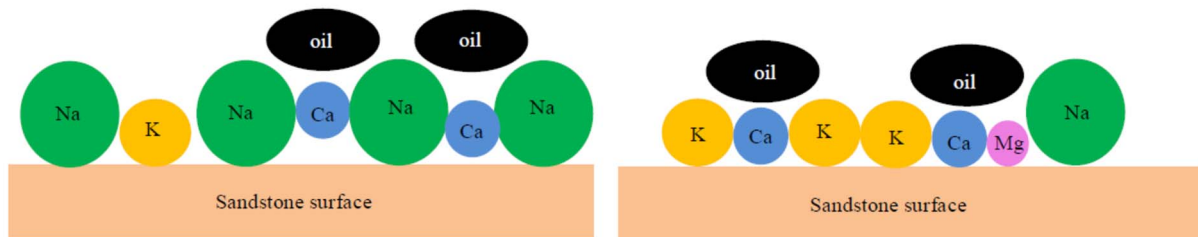


Figure 1. Effects of ions in formation water on oil-wet condition in sandstone; weak adsorption due to large hydrated-size ion (left) and strong adsorption due to small hydrated-size ion (right), [9]

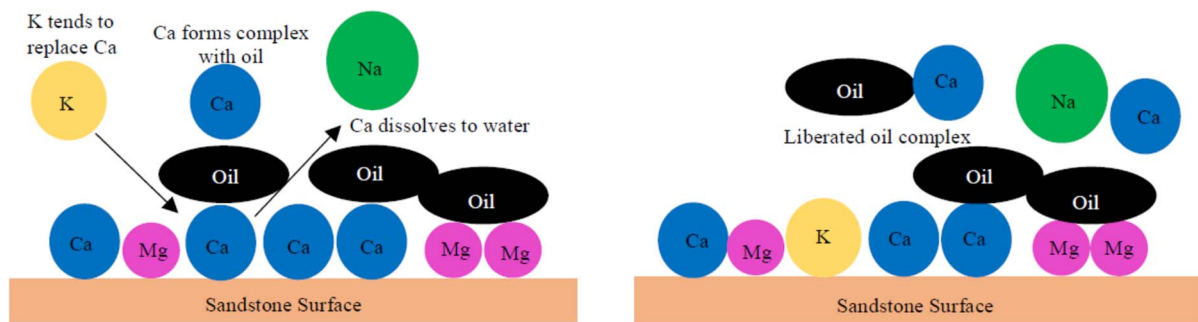


Figure 2. Oil recovery mechanism in sandstone by means of low salinity; replacing of potassium ion onto the site of calcium ion (left) and liberation of oil in a form of calcium carboxylate complex (right), [8]

Once the overall mechanism is completed, oil is liberated and carbonate surface turns to a more water-wet condition again. Magnesium ion can also assist in oil recovery mechanism; however, it can only function at elevated temperature. Magnesium tends to displace calcium ion in calcium carboxylate complex, resulting in more number of available calcium ion to initiate calcium carboxylate complex. Figure 3 illustrates overall mechanism of MIE during low salinity waterflooding in carbonate rock.

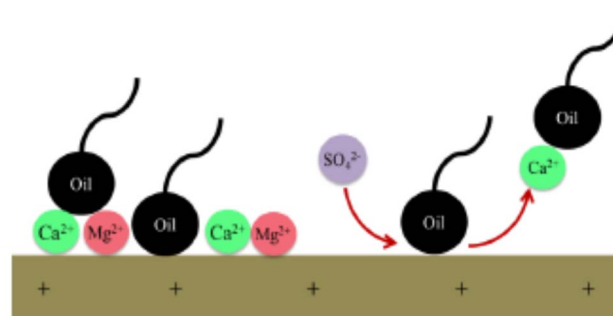


Figure 3. Oil recovery mechanisms during low salinity waterflooding in carbonate illustrating adsorption of sulphate ion and forming of calcium carboxylate complex

3. Methodology

Observation of MIE through detection of divalent ion is performed by the use of coreflood apparatus together with complexometric titration. In this study, Silurian dolomite core samples are utilized to represent reservoir rock. Core samples are cut into cylindrical shape with diameter of 1.5 inches and length of 5 inches. Porosity of rock samples varies from 15-18 percent whereas; absolute permeability greatly varies from 6-400 mD which is a result from irregular pore structures. However, this study mainly emphasizes on surface chemistry and inject rate is relatively small and hence, effects from permeability is diminished. n-dodecane represents hydrocarbon phase in this study. In order to induce oil-wet condition, oleic acid, representing carboxylic acid, is added into n-dodecane at the concentration of 5.0 acid number. This high acid concentration oil is used to ensure strongly oil-wet condition through acid adsorption onto rock surface. After the maximum adsorption occurs, n-dodecane with oleic acid at 1.0 acid number is used to flush the excess acid. Formation water and injected water are synthetically prepared from different salts. Seawater is used to represent injected water in this study. Formulations of formation water and seawater are summarized in table 2.

Table 2. Formulations of formation water and seawater which is utilized as injected water.

Ionic species	Seawater (ppm)	Formation water (ppm)
Sodium ion	10.813	39.620
Potassium ion	369	-
Magnesium ion	1.157	6.977
Calcium ion	304	11.484
Chloride ion	17.386	101.657
Sulphate ion	4.844	236
Hydrogen Carbonate ion	127	154
Total	35.000	160.128

Core samples are cleaned by toluene reflux followed by methanol reflux to remove heavy and light non-polar compounds, respectively. After drying process at 60 degrees Celsius in oven, dry samples are weighed and saturated with formation water. Porosity and absolute permeability are calculated. To restore the oil-wet condition, acid oil is injected into core samples using coreflood apparatus. Once the irreducible water saturation stage is obtained, samples are aged for two weeks to complete the wettability alteration process. Prior to performing waterflooding, acid oil with acid number of 1.0 is injected to flush excess acid that can dramatically consume certain ions in injected brine. Conventional waterflooding process is firstly performed by using formation water as injected water. This process is performed to simulate water reinjection process where salinities of formation water and injected water are equal. That means, only a physical displacement mechanism is expected. Oil recovery factor is detected as a function of pore volume of injected water and effluent is collected for titration process. After oil recovery is constant, seawater is injected to simulate low salinity waterflooding. Again, oil recovery factor is detected and effluent is taken for complexometric titration. Figure 4 depicts schematic diagram of coreflooding apparatus [6]. Complexometric titration is performed in two steps. First total hardness, which is the summation of calcium ion and magnesium ion, is identified. Effluent sample is added by ammonium chloro-ammonium hydroxide buffer solution together with a pinch of Eriochrome Black T (EBT) indicator. Solution is titrated with a known concentration of ethylene diamine tetraacetic (EDTA) and the end point is observed from changing colour from red to blue. The second step is performed by adding 30 percent sodium hydroxide in effluent sample until pH value reaches 11 and the solution is swirled vigorously to precipitate magnesium ion. A pinch of hydroxynaphthol blue (HBN) is added into solution as an indicator and solution is titrated with a known concentration EDTA to identify the concentration of calcium ion remained. The end point is detected when colour is changed from red to blue. The difference between ion concentration of the first and second steps is considered a concentration of magnesium ion. The experiment is performed at three different temperatures which are 30, 50 and 70 degrees Celsius.

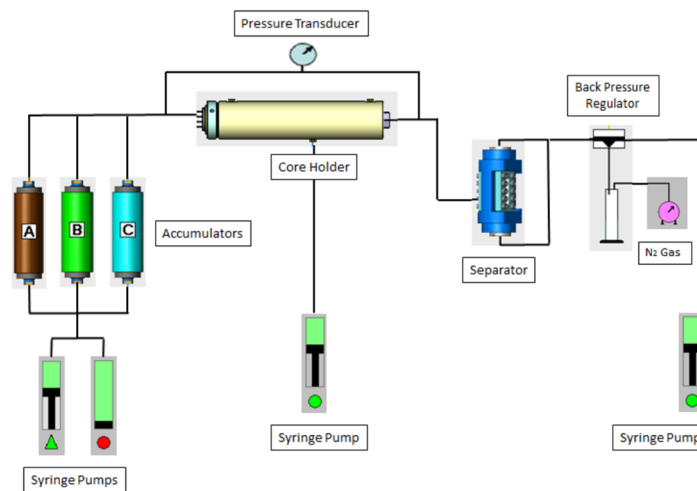


Figure 4. Schematic diagram of coreflood apparatus consisting of major sections which are core holder, fluid accumulators, separator, back pressure regulator and pumps

4. Results and Discussion

Oil recovery factors as a function of injected pore volume of injected water for three different temperatures are shown in figure 5.

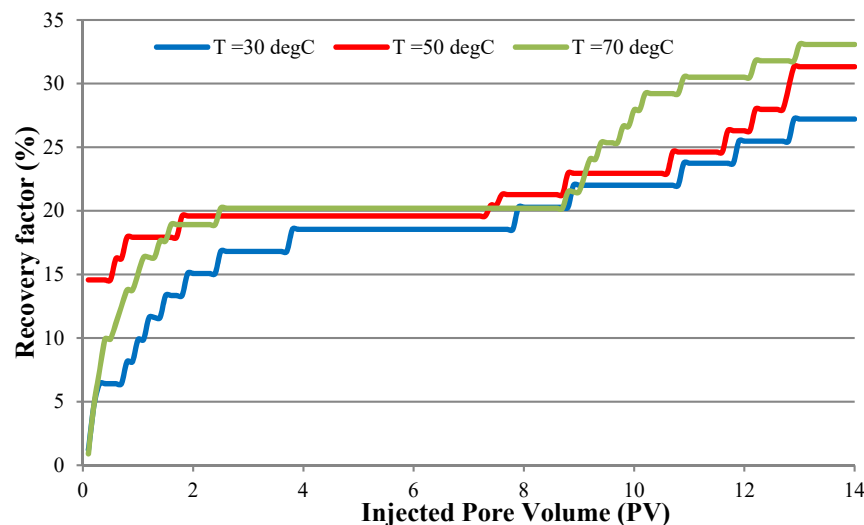


Figure 5. Oil recovery factors from coreflood experiments with various reservoir temperatures as a function of injected pore volume of water

It can be observed from the figure 5 that the highest additional oil recovery factor of about 13% in during low salinity waterflooding (period from approximately 8 PV of water) phase is obtained from the test at temperature of 70 degrees Celsius, whereas 8.5% and 12% additional oil recovery are recovered from the experiments performed at temperatures of 30 and 50 degrees Celsius, respectively. At higher temperature, ion activity is also high especially in aqueous phase. This results in difficulty for rock to form a firm bond with adsorbed layer of oil. Therefore, rock surface is more water-wet and as a consequence, oil can be easily liberated. Moreover, at higher temperature, chemical reaction is faster and hence, both forming of calcium carboxylate complex and mineral dissolution mechanism are favoured. Some literature reviews also explain that at lower temperature, magnesium carboxylate

complex is difficultly occurred and this tends to happen at higher temperature by replacing calcium ion in calcium carboxylate complex, resulting in adequate amount of calcium ion to liberate oil in a form of carboxylate complex. High reservoir temperature is therefore recommended for low salinity waterflooding in dolomite reservoir for several reasons. First, potential determining ions are more active at higher temperature and second, the induced oil-wet condition of carbonate surface maybe not as strong as in low reservoir temperature.

In order to confirm ionic activity at elevated temperature, detection of divalent ions in effluent is performed. Table 3 summarizes the amount of calcium ion and magnesium ion during conventional waterflooding and low salinity waterflooding at three different temperatures.

Table 3. Concentrations of total divalent ion, calcium ion and magnesium ion obtained from complexometric titration during conventional waterflooding and low salinity waterflooding at different temperatures.

Ionic type	Conventional waterflooding (ppm)				Low salinity waterflooding (ppm)			
	Initial	T=30°C	T=50°C	T=70°C	Initial	T=30°C	T=50°C	T=70°C
Divalent ion	18.164	28.898	25.595	24.150	1.399	10.321	7.844	4.335
Calcium ion	10.940	12.178	12.178	12.385	283	4.335	4.747	3.096
Magnesium ion	7.224	16.720	13.471	11.765	1.116	5.986	3.097	1.239

According to the results shown in the table 3, it can be observed that amounts of both calcium ion and magnesium ion are obviously increased from the initial values. This can be explained by dissolution mechanisms of both calcium and magnesium ions from dolomite itself. However, the increment of magnesium ion is more obvious in all cases. Even though dolomite is composed of both calcium ion and magnesium ion in similar portion, dissolution of both ions is different. Another reason that can be explained here is that a part of calcium ion is consumed to generate calcium carboxylate complex whereas magnesium ion cannot induce oil to produce magnesium carboxylate complex. This behaviour is more obvious at 30 degrees Celsius.

When injected water is switched to seawater, the increasing trend of both ions is slightly changed. The increment of both calcium and magnesium ion is at the same level at 30 degrees Celsius. Concentration of calcium ion increases approximately 4,000 ppm whereas magnesium ion is about 5,000 ppm. This increment of ion ratio is reasonable for the fact that dolomite is composed of both calcium and magnesium ions in similar proportion. And since most of the oil is already produced, only a small fraction of calcium ion may be used to produce calcium carboxylate complex in this case. At elevated temperatures, it can be observed that MIE is a function of temperature. Even when conventional waterflooding is performed, the amount of magnesium ion is remarkably decreased whereas amount of calcium ion tends to be constant. At higher temperature, both calcium ion and magnesium ion can form carboxylate complex. More interesting results are observed when low salinity waterflooding is performed. Amount of magnesium ion starts to decrease and reaches the minimum value at 70 degrees Celsius. Not only magnesium ion, but also calcium ion is decreased compared to other two temperatures. When low salinity waterflooding is performed in dolomite reservoir with high temperature, this condition would yield benefit over limestone as released magnesium ion can undergo forming of carboxylate complex. This reducing trend of both ion concentrations compared to the performance at lower temperature comes together with greater improvement in oil recovery, leading to conclusion of the effects of both ions in forming carboxylate complex at high temperature.

Results from complexometric titration experiment show that changes of proportion of divalent ions would come together with MIE mechanism. During conventional waterflooding, this mechanism may occur but due to equality of salinity between formation water and injected water, a part of mechanisms is inhibited. When low salinity waterflooding is performed, changing in proportion of both divalent

ions compared to initial concentration and compared to conventional waterflooding confirms the occurrence of the MIE mechanism. Great reduction of magnesium ion as well as calcium ion, which comes together with high amount of recovered oil, is also another evidence of MIE that occurs in dolomite at higher temperature.

5. Conclusions

Both calcium ion and magnesium ion are increased in injected water during both conventional waterflooding and low salinity waterflooding as these ions are enriched in formation brine as well as they are the main compositions in dolomite and can naturally dissolve in water. Nevertheless, presence of calcium ion is less compared to magnesium ion during waterflooding process which can be described by favourability of carboxylate complex of calcium and magnesium at different temperatures. Changing injected water also changes the equilibrium. From the study, when low salinity water is injected portion of calcium ion is increased from the period of conventional waterflooding, which can be explained by higher dissolution from rock, and less quantity of calcium ion is consumed from calcium carboxylate complex once remaining oil saturation is less than oil saturation during the conventional waterflooding period. For the effect of temperature, high temperature results in higher amount of recoverable oil. This can be explained by faster chemical reaction. Ions can move faster and reaction is rapidly occurred so calcium carboxylate complex can be generated. Moreover, reduction of magnesium ion during low salinity waterflooding which is tested by complexometric titration can also explain the favourability of generating of magnesium carboxylate complex at higher temperature.

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