



Investigation of Barium Sulfate Precipitation and Prevention Using Different Scale Inhibitors under Reservoir Conditions

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ABSTRACT

In this work, scaling tendency and amount of precipitation of barium sulfate (BaSO_4) were determined; the process is depending on temperature, pressure and mixing ratio of injection and formation of waters. Results showed that BaSO_4 precipitation is largely dependent on mixing ratio. Temperature and pressure had no influence on BaSO_4 precipitation. Different scale inhibitors, including a new inhibitor package, were used for preventing BaSO_4 precipitation. The new scale inhibitor consists of three different acids such as phosphonate acid, hydrochloric acid solution, isopropyl alcohol, ammonium chloride and water. In addition, the lowest interfacial tension on the boundary of oil and new inhibitor occurred at 10% of hydrochloric acid. Furthermore, effect of temperature, mixing ratio of waters and barium concentration on the inhibition efficiency of BaSO_4 formation was studied. Results showed that the new inhibitor has the highest efficiency for preventing BaSO_4 precipitation at any temperature, mixing ratio and barium concentration. Moreover, formation damage due to BaSO_4 formation with and without scale inhibitors was determined by core flood tests. In the presence of new inhibitor, the damaged rock permeability ratio was improved from 0.59 to 0.924.

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1. INTRODUCTION

Deposition of inorganic salts in reservoirs and oilfield equipment leads to a decrease in production rate of the well, equipment service life and rock permeability [1]. There are different reasons for scaling in each oil reservoir because of difficult conditions for salt deposition [2]. The most common types of salts in the oil reservoirs are carbonate (CaCO_3) and sulfates (CaSO_4 and BaSO_4).

The injection of water into the reservoir for pressure maintenance has been used in the oil industry for many years [3]. When injected water comes into contact with formation water in the reservoir, sulfate type of inorganic salt is formed. The injected water often contains sulfate ions (SO_4^{2-}), and the formation water contains barium cations (Ba^{2+}). In this case, mixing two waters causes precipitation of barium sulfate. During

waterflooding, formation damage and rock permeability reduction because of scale deposition often occur in oil reservoir [4]. A change in temperature and flow rate has a profound effect on formation damage and reduction of rock permeability due to inorganic salt deposition [5, 6].

Prediction of salt deposition is the first step for scale management in oil reservoirs [7]. It is possible to estimate the probability of salt formation and the amount of its precipitation if a system is in equilibrium [8]. There are various models for determining the probability of salt precipitation. The saturation index (also called scaling index) (SI) with ions is often used to predict the scale precipitation under reservoir conditions. If $\text{SI} > 0$, an inorganic salt is deposited, and if $\text{SI} < 0$, there is no risk of scale formation. SI is determined using the following expression [9, 10]:

$$SI = \log\left(\frac{[Ka][An]}{K_{sp}}\right) \quad (1)$$

where SI is the saturation index; [Ka] and [An] are the concentration of cations and anions in mol/L,

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respectively; K_{sp} is the solubility product in mol^2/L^2 . K_{sp} depends on the pressure, temperature and ionic strength of the solution.

Oddo and Thomson [9] developed a model to determine the values of saturation index for different kinds of inorganic salt. It is a polynomial equation, which is a function of temperature, pressure, and ionic strength (Equation (2)):

$$SI = \log([Ka][An]) + a_1 + a_2T + a_3T^2 + a_4P + a_5I^{0.5} + a_6I^{0.5}T + a_7I \quad (2)$$

where T is the temperature in °F; P is the pressure in psi; a_1 , a_2 , a_3 , a_4 , a_5 , a_6 , and a_7 are the empirical coefficients; I is the ionic strength in mol/L.

In addition, scaling tendency (ST) is used for prediction of salt formation under static conditions. In the case of scaling tendency, a salt is formed if ST value is greater than one. However, scaling tendency and saturation index of waters are strongly related to each other. ST is presented by the following formula [11]:

$$ST = 10^{SI} \quad (3)$$

Control of salt precipitation is one the main works during water flooding [10]. All technologies of scaling control can be divided into prevention and removal technologies. Currently, inhibitory protection of oil reservoirs and wells from scaling is the most effective technology for preventing inorganic salt precipitation [12]. Scale inhibitors reduce the propensity of water to form salt deposits during the process of crystal formation. Moreover, the scale inhibitors prevent the precipitation of salt, disrupting thermodynamic stability of a nucleus. The effectiveness of scale inhibitors is associated with the degree of solution supersaturation with salts. At higher degrees of super saturation, scale inhibition becomes more difficult [1, 13]. Corrosion rate of scale inhibitor packages could be reduced by addition of corrosion inhibitors to the solution [14]. An effective scale inhibitor could prevent fully inorganic salt precipitation in the reservoir and production equipment.

In this work, the prediction and inhibition of barium sulfate were investigated. For this purpose, ST and amount of precipitation of BaSO_4 was determined at different temperatures, pressures and mixing ratios of waters. Inhibition efficiency of different scale inhibitors, including a new inhibitor package, was evaluated depending on temperature, mixing ratio and barium concentration. Change in the rock permeability due to

barium sulfate deposition was determined conducting core flood experiments under reservoir conditions.

2. MATERIALS AND METHODS

2. 1. Prediction of Salt Deposition For prediction of barium sulfate formation OLI Studio program was used. This software provides a set of methods of qualitative and quantitative analysis for scaling prediction under reservoir conditions.

Furthermore, it allows predicting the scaling formation in the presence of carbon dioxide. The procedure of scale prediction in this software consists of the following stages: the reservoir pressure and temperature evaluation; analysis of the ionic content and pH of the waters depending on their mixing ratio and calculation of scaling tendency and amount of salt precipitation. The input data consist of the pressure, temperature, ionic content of formation and injection waters, and the volume mixing ratios of the waters. The program is run separately for each desired reservoir pressure and temperature.

In this work, the scaling tendency and amount of barium sulfate precipitation were determined depending on temperature, pressure and mixing ratio. Properties of the used synthetic formation (FW) and injection (IW) for prediction and inhibition of barium sulfate are presented in Table 1.

2. 2. Interfacial Tension Measurement For determining the required concentration of acid solution (HCl,5%) in the new inhibitor, interfacial tension on the boundary of oil and the inhibitor solution was measured. For this purpose, a mass concentration of 5%-HCl solution was increased from 0% to 15 %. The used oil was an Iranian light type. The measurement was done using a tensiometer, which analyzed the shape of drops. The analysis consists of measuring drop length and width. Therefore, the interfacial tension was determined by measuring dimensions of the suspended drop. The drop was balanced if the measured interfacial tension value remained unchanged within 10 minutes. One of the advantages of this method is that it requires no previous calibration. However, for smaller drops, this method requires an enlargement factor for accurate measurement.

TABLE 1. Properties of formation and injection waters

Water	pH	Ionic concentration (mg/L)							Total dissolved solids (mg/L)	
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Ba ²⁺	Cl ⁻	SO ₄ ²⁻		HCO ₃ ⁻
1 (FW)	7.02	42066	1836	469	703	208	69315	233	62	114892
2 (IW)	7.10	11002	348	323	1425	0	20138	2479	74	35789

2. 3. Inhibition Efficiency of Scale Inhibitors

For prevention of barium sulfate deposition, the following scale inhibitors were used: HEDP (etidronic acid or 1-hydroxyethane 1,1-diphosphonic acid), DTPMP (methylene phosphonic acid), PPCA (phosphino polycarboxylic acid), ATMP (aminotrimethylenephosphonic acid) and a new scale inhibitor. More details about the new scale inhibitor are presented in previous works [12, 15, 16] for preventing CaCO_3 and CaSO_4 scale formation.

Jar test was applied for determining the inhibition efficiency. The purpose of this test is to determine the effectiveness of scale inhibitor for preventing salt deposition. Therefore, the effect of temperature, pressure and mixing ratio on the inhibition efficiency of barium sulfate deposition was determined. The steps of experimental studies to determine the performance of scale inhibitors by jar test under static conditions are as follows [1]:

For each test, 100 mL of injection water was poured in two glass bottles (100 mL of injection water in each bottle). The scale inhibitor with a concentration of 30 mg/L was added in one of the bottles. The bottles were shaken and then placed in an oven at the desired temperature for 2 hours. After 2 hours, the formation water was added in the solutions at a required volume ratio to obtain working solutions with the required mixing ratio of formation and injection waters. A concentrated solution of potassium hydroxide was added to the working solutions to change their pH. The working solutions were shaken for 2 minutes and then placed in the oven at the desired temperature for 24 hours. After 24 hours, the working solutions were removed from the oven and then filtered through the filter paper. After that, the working solutions were immediately analyzed for the residual content of barium ions. The ion concentrations of the working solutions were determined using Capel equipment.

Inhibition efficiency was calculated in accordance with the NACE TM0374-2016 standard using the following expression [13, 17]:

$$E_{inh} \% = \frac{[Ba^{2+}]_2 - [Ba^{2+}]_1}{[Ba^{2+}]_0 - [Ba^{2+}]_1} \cdot 100 \quad (4)$$

where E_{inh} is inhibition efficiency in %; $[Ba^{2+}]_2$ is the concentration of barium in the solution with scale inhibitor in mg/L; $[Ba^{2+}]_1$ is the concentration of barium in the solution without scale inhibitor in mg/L; $[Ba^{2+}]_0$ is the initial concentration of barium in the solution in mg/L.

2. 4. Formation Damage due to Salt Deposition

Core flood experiments were conducted for evaluation

of formation damage because of BaSO_4 precipitation in core samples. The purpose of the experiments was determination of effectiveness of the scale inhibitors in the reservoir under dynamic conditions. Iranian carbonate core samples were used for core flood experiments. The depth, length and diameter of the core samples were about 2500 m, 3.5 cm and 2.8 cm, respectively. The experiments were carried out at a constant reservoir temperature and pressure of 80 °C and 20 MPa using scale inhibitors at 30 mg/L. The permeability of the core samples after injection of the solution containing scale inhibitors was determined. The permeability was calculated using Darcy's law. The damaged permeability ratio was determined as a ratio of final permeability (K_f - after injection) to initial rock permeability (K_0) as K_f/K_0 .

3. RESULTS AND DISCUSSION

3. 1. Scaling Tendency and Precipitation of Barium Sulfate

As shown in Figure 1, scaling tendency of barium sulfate was decreased with increasing temperature at any mixing ratio. However, the amount of precipitation of barium sulfate was insignificantly changed by increasing temperature. Therefore, it can be concluded that the precipitation of barium sulfate is not dependent on temperature, but strongly is dependent on the mixing ratio of waters (IW:FW). Figure 1 presents that in 100% of formation water, the values of scaling tendency of barium sulfate are greater than one at any mixing ratio. Moreover, due to the absence of barium ions in the solution of 100% of the injection water, barium sulfate was not formed at any mixing ratio. As shown in the figure, a maximum value of scaling tendency and precipitation of barium sulfate occurred at a mixing ratio of 60:40 for IW:FW at any reservoir temperature. It should be noted that the solubility of barium sulfate in the water is not dependent on the temperature. Therefore, the scaling tendency and precipitation of barium sulfate was not considerably changed by increasing the temperature. Moreover, the main reason of barium sulfate precipitation is the mixture of incompatible waters containing barium and sulfate ions.

Figure 2 illustrates the dependency of barium sulfate scaling tendency and amount of precipitation on pressure and mixing ratio of waters at 80 °C. The range of studied pressure (0.1-70 MPa) was selected just to investigate the effect of reservoir pressure on the barium sulfate precipitation during water flooding. As shown in this figure, a maximum value of scaling tendency and precipitation of barium sulfate occurred at a volume ratio 60:40 of injection and formation waters at any pressure.

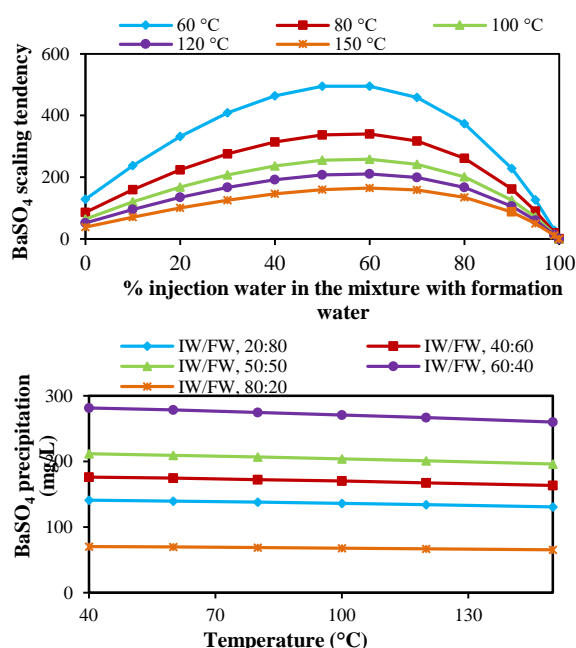


Figure 1. BaSO₄ scaling tendency and precipitation depending on mixing ratio and temperature at 20 MPa

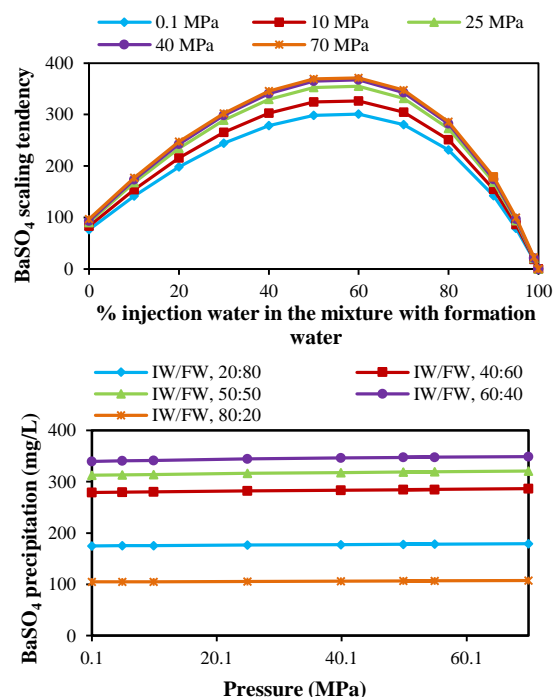


Figure 2. BaSO₄ scaling tendency and precipitation depending on mixing ratio and pressure at 80 °C

Figure 2 depicts that the precipitation of barium sulfate is not dependent on pressure. However, at low pressure (less than 40 MPa), scaling tendency of barium sulfate was increased by increasing pressure. Moreover, at high pressure (more than 40 MPa), scaling tendency remained almost unchanged by increasing pressure. This behavior of barium sulfate precipitation is associated with the solubility. BaSO₄ solubility in water does not depend on pressure changes. The barium sulfate solubility depends more on ion contents of the waters.

3. 2. Interfacial Tension on Boundary of Oil and Inhibitor Solution

Interfacial tension on the boundary of Iranian light oil and a solution of the new inhibitor was measured at different concentrations of 5%-HCl solution (in a range from 0 to 15%). Figure 3 shows the results of interfacial tension measurement. As presented in the figure, a significant decrease in interfacial tension occurred by increasing concentration of 5%-HCl solution in the inhibitor from 0 to 3%.

In this case, interfacial tension was reduced from 29 to 10 mN/m. Interfacial tension was changed from 10 to 5.5 mN/m by increasing concentration of 5%-HCl from 3 to 10%. A further increase in the concentration of 5%-HCl solution (more than 10%) practically did not reduce the values of interfacial tension. By increasing the HCl concentration, interfacial tension on the boundary of oil and the inhibitor solution is related to the oil interaction with acids, as a result of which surfactants (surface-active substances) are formed. The surfactants reduce the interfacial tension.

3. 3. Performance of Scale Inhibitors

Figure 4 presents the effect of the reservoir temperature on BaSO₄ inhibition efficiency. As shown in this figure, in prevention of barium sulfate deposition, the inhibition efficiency varied slightly with an increase in the temperature since the solubility of BaSO₄ is not changed by increasing temperature. The new inhibitor had the highest performance at any temperature. Its effectiveness was more than 89% for preventing barium sulfate precipitation. The high inhibition efficiency of the new scale inhibitor is related to the inhibition properties, which are not dependent on temperature. These properties lead to prevention of the salt crystal formations and deposition at any temperature.

Figure 5 depicts dependency of inhibition performance on the mixing ratio of waters at 80 °C.

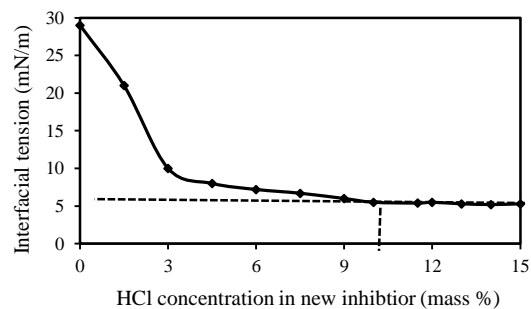


Figure 3. Interfacial tension on boundary of oil and the new inhibitor depending on mass concentration of HCl

A minimum inhibition efficiency of the new inhibitor for preventing barium sulfate deposition was 89%. DTPMP had the highest efficiency among the industrial inhibitors. For all inhibitors, the lowest performance occurred at a ratio 50:50 of waters. The performance of all inhibitors was not strongly affected by changes in the mixing ratio of waters. The high performance of the new inhibitor for preventing barium sulfate formation at any mixing ratio of the waters is associated with the optimum concentrations of three phosphonate acids. The mass concentrations of the new scale inhibitor components were obtained on the basis of a positive synergistic inhibition effect determination under static conditions [16].

Figure 6 shows the inhibition effectiveness of barium sulfate deposition was reduced with an increase in the concentration of barium ions. The performance of the new inhibitor remained unchanged by increasing the barium concentration to 1000 mg/L. At high concentrations of barium ions in the solution (from 1000 to 3000 mg/L), effectiveness of the new inhibitor was reduced to 86.6%. However, the efficiency of industrial inhibitors was significantly reduced by increasing barium concentration. An increase in the concentration of barium ions contributes to the acceleration of the crystallization process and formation of barium sulfate. Therefore, the inhibition efficiency is reduced by increasing the ion concentration in the solution.

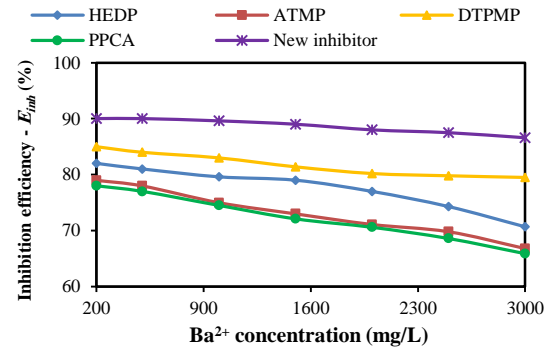


Figure 6. Dependency of scale inhibitor efficiency on Ba²⁺ concentration

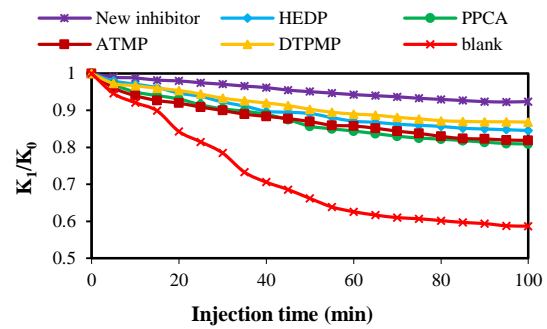


Figure 7. Change in permeability ratio depending on injection time using different scale inhibitors

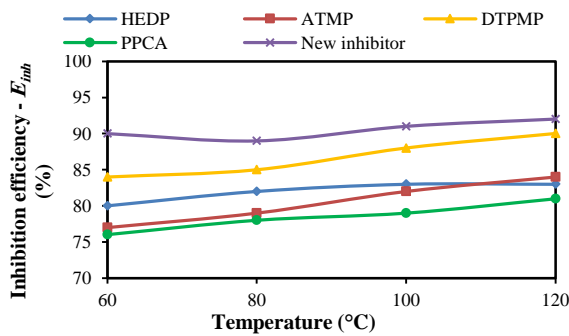


Figure 4. Dependency of scale inhibitor efficiency on temperature

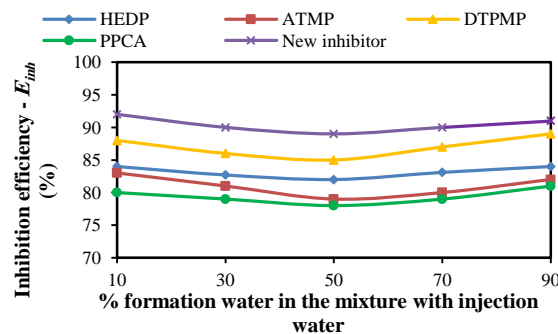


Figure 5. Dependency of scale inhibitor efficiency on content of formation in mixture with injection water

3. 4. Change in Rock Permeability Due to Salt Precipitation

Figure 7 depicts dependency of permeability ratio (K_1/K_0) on injection time. As shown in this figure, in a blank case, a high formation damage occurred due to barium sulfate deposition in Iranian core samples. In this case, the rock permeability decreased to 59% of its initial value. By application of the new inhibitor, DTPMP, HEDP, ATMP and PPCA for prevention of barium sulfate in the core samples, the permeability has reached to 92.4, 86.8, 84.6, 81.9 and 80.9% of initial rock permeability, respectively.

Formation damage reduction in the presence of scale inhibitor is related to the prevention of barium sulfate deposition in the core samples during water flooding. Barium and sulfate ions in the presence of scale inhibitor remained soluble in the water during core flood tests. Furthermore, the scale inhibitors caused the dissolution of the formed salt crystals and changed the crystallization process, which leads to blocking of the crystal growth.

4. CONCLUSIONS

Based on the results obtained in this study, the following conclusions can be drawn:

The maximum amount of barium sulfate precipitation occurred in a volume ratio of 60:40

injection and formation waters. Amount of barium sulfate precipitation depends on changes in temperature and pressure, and strongly dependent on the mixing ratio of waters during water flooding. This behavior is related to the solubility of barium sulfate in water. BaSO₄ solubility is not considerably changed with a change in temperature and pressure.

Temperature, mixing ratio and concentration of barium had a negligible effect on the inhibition efficiency of the new scale inhibitor. Interfacial tension on the boundary of Iranian light oil and solution of the new inhibitor had the lowest value at a mass concentration of 10% of HCl.

A decrease in the permeability of Iranian carbonate core samples due to deposition of barium sulfate was up to 59% of the initial permeability without addition of any scale inhibitor. Injection of inhibitors into the core samples sufficiently reduced formation damage due to barium sulfate deposition. The rock permeability in the presence of the new scale inhibitor, DTPMP, HEDP, ATMP and PPCA was 92.4, 86.8, 84.6, 81.9 and 80.9% of initial rock permeability, respectively.

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در این مقاله، وابستگی میزان اشباع و رسوب سولفات باریم به دما، فشار و نسبت ترکیب آب تزریقی به مخلوط تعیین شد. نتایج نشان داد که رسوب سولفات باریم عمدتاً وابسته به نسبت ترکیب آب تزریقی به مخلوط است. تغییرات دما و فشار تأثیری بر تغییر میزان تشکیل سولفات باریم نداشتند. بازدارنده‌های مختلف، از جمله یک بازنده جدید، برای جلوگیری از رسوب سولفات باریم استفاده شدند. بازدارنده جدید شامل سه نوع فسفونیک اسید مختلف، هیدروکلریک اسید، الکل ایزوپروپیل، کلرید آمونیوم و آب است. کمترین کشش سطحی بین نفت و بازدارنده جدید در غلظت ۱۰ درصد هیدروکلریک اسید مشاهده شد. اثر دما، نسبت ترکیب آب‌ها و غلظت یون باریم بر بازده بازدارنده‌ها مورد بررسی قرار گرفت. نتایج نشان داد که بازدارنده جدید دارای بالاترین کارایی برای جلوگیری از رسوب سولفات باریم در هر دما، نسبت ترکیب آب‌ها و غلظت باریم است. علاوه بر این، آسیب سازند ناشی از رسوب سولفات باریم در حضور بازدارنده‌ها و نیز بدون آن‌ها از طریق تست‌های سیلاب‌زنی مورد مطالعه قرار گرفت. در حضور بازدارنده جدید، نسبت نفوذپذیری سنگ از ۰/۵۹ به ۰/۹۲۴ بهبود یافت.

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