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Olga Titova[1],
Natalia Stoliarova[2],
Zoia Hrushak[3],
Tetiana Kravchuk[4]

THE STUDY OF THE PRECIPITATE FORMATION PROCESS IN SILICATE-ALKALI MIXTURE IN THE PRESENCE OF SALT WATER

National Aviation University
Kosmonavta Komarova avenue, 1, Kyiv, 03680, Ukraine
E-mails: [1]kafedra_hht@ukr.net; [2]kafedra_hht@ukr.net; [3]kafedra_hht@ukr.net; [4]kafedra_hht@ukr.net

Purpose: *The aim of this article is investigation of the precipitation process when diluting silicate solution with salt water. The precipitation process changes have been analyzed with pH value increasing of the initial silicate-alkali mixture.* ***Methods:*** *Methods of direct and reverse titration were used for the determination of silicate relative concentration in the supernatant liquid. pH metrics was used for determination pH value change of silicate-alkali mixtures during experiment performance.* ***Results:*** *the precipitation process proceeds more intensively when ratio of silicate and salt water is 40 ÷ 60; the precipitate amount consistently decreases with pH value increase in initial mixture in the result of mixing with salt water; necessary residue concentration of silicate in a solution should be 1.5-2 mass % for a gel formation process; the most significant changes of mixture pH values occurs when salt water content is above 50 %.* ***Discussion:*** *It is necessary to determine silicate concentration in the supernatant liquid (filtrate) for the determination minimal silicate concentration necessary for gel formation when mixing silicate mixtures with salt water. It was determined that silicate amount in the supernatant liquid increases for all ratios of silicate and salt water with pH value increase in the initial mixture, besides it is necessary to increase part of salt water in a mixture with pH value increase for obtaining the same concentration of silicate in the supernatant liquid. It was found, that gel formation (for a mixture with initial pH = 11.72) occurred at silicate residue concentration in the solution equal to 0.25-0.3 from the initial one. Thus, it was found that minimal silicate concentration in a solution may be 1.5-2.0 mass %.*

Keywords: concentration; filtrate; gel formation; pH value; precipitation; silicate-alkali mixture

1. Introduction

The development of oil production at various oil reservoirs, including those placed on the bottom of the world's ocean, is associated with the need for further involvement acceleration into additional production from hard extracted oil reserves at a late exploitation stage. Waterflooding is one of the main methods of increasing production from oil reservoirs [1-3]. In this case efficiency of oil production depends primarily on the completeness of the formation's coverage and the impact of injected water. The presence of highpermeable layers in the productive reservoir causes their high heterogeneity. This leads to a rapid breakthrough of water into production wells and, as a consequence, to deterioration of technical and economic characteristics of reservoir production and decrease in oil recovery.

Improving of oil reservoirs production (when using waterfloating) is connected with redistribution of drainage water flows in the reservoir to increase the reservoir coverage by waterflooding both in capacity and area of the reservoir. Redistribution of flows is achieved by equalizing the acceleration profile (EAP) of the injection wells by reducing the permeability of the highly permeable zones of the reservoir and by increasing waterflooding coverage of the reservoir by complete or partial isolation of the already waterflooded high permeable reservoir zones by the creation of a flow deflecting barrier in the water filtration path [4-5].

2. Analysis of the latest research and publications

One of the most environmental friendly and progressive methods for increasing reservoir coverage is the use of gel-forming compositions based on sodium silicate. [6-9]

A precipitate is formed in the result of interaction between sodium silicate and present in salt water ions of hardness (Ca^{2+}, Mg^{2+}). This precipitate is a mixture of metals silicates and hydroxides insoluble in water. The amount of a precipitate highly depends on conditions of components mixing, that is why it is necessary to study the precipitation process and the influence of salt water on it [10].

Factors causing the intensity of precipitation:

– degree of dilution of silicate composition with salt water;

– the initial pH of the mixture.

3. Purposes and problems of a research

The precipitation process was investigated when diluting silicate solutions with salt water. Changes in precipitation process have been analyzed with increase of pH value of the initial silicate-alkali mixture solution.

4. Materials and methods of research

Methods of direct and reverse titration were used for the determination of silicate relative concentration in the supernatant liquid. pH metrics was used for determination pH value change of silicate-alkali mixtures during experiment performance. Sodium silicate (6 mass %) solution, analogue of sea water with general mineralization 34 g/cm^3 (analogue of Black sea water), sodium hydroxide solution were used as materials for investigation.

5. Research results

Influence of the dilution degree of silicate mixtures with salt water on the formed precipitate amount

The investigation of the precipitation process performed in the following way. The analogue of salt water with mineralization 34 g/cm^3 (analogue of salt water in the Black sea) was added to the initial solution of silicate (6 mass %) in different ratios so that percentage of salt water in mixture had been from 0 to 100 %.

The obtained precipitate was filtrated through the paper filter, washed by deionized water and desiccated until constant mass. After that filters with a precipitate were weighted for the determination a precipitate amount left on a filter.

The performed research shows, that the biggest amount of a precipitate (27.5 g/dm^3) is formed when the content of salt water in a mixture was 60 % (fig.1, table 1).

A highly dispersed precipitate is formed if the salt water content varies from 10 to 30 %; this precipitate may take from 1/3 to1/2 of the total solution volume. Gelled and highly coagulated precipitate was formed in the whole volume of the obtained mixture with further increase of salt water content in a mixture. The formation of such precipitate took place with the salt water content from 40 to 90 %. It is necessary to mention that precipitate's low dispersion didn't stop the solution filtration.

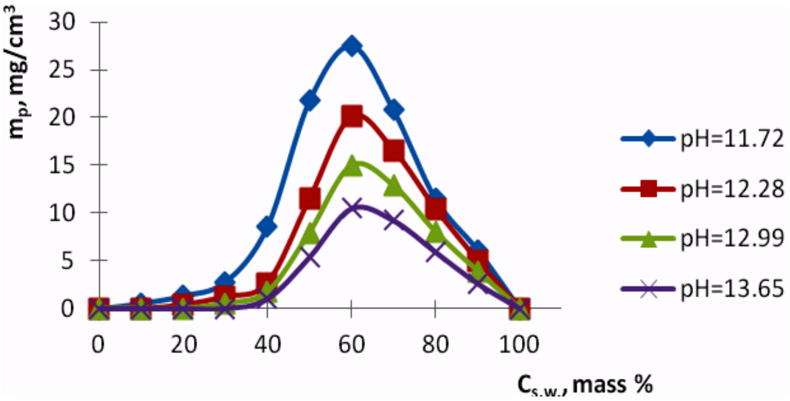

Fig. 1. Dependence the amount of formed precipitate m_p from the salt water content $C_{s.w.}$ in a solution at different pH values

Table 1

Precipitation when dilution silicate mixture (initial pH=11.72) with salt water

№	Salt water content	pH	Mass of a precipitate, mg/cm^3	Relative concentration of SiO_2 in the supernatant liquid
1	0	11,72	-	1,000
2	10	11,68	0,55	0,864
3	20	11,45	1,35	0,720
4	30	11,36	2,80	0,587
5	40	11,26	8,58	0,444
6	50	11,08	21,74	0,309
7	60	10,90	27,54	0,171
8	70	10,35	20,78	0,031
9	80	9,45	11,49	-
10	90	8,66	6,14	-
11	100	7,90	-	-

Influence of a pH value of an initial silicate-alkali mixture on the formed precipitate amount

The use of silicate-alkaline mixtures on the deposits of the Black Sea continental shelf requires studying the effect of salt water on the behavior of these mixtures.

Alkali-silicate mixtures with initial pH values 11.72; 12.28; 12.99; 13.65 were prepared for the study of pH value influence of initial mixtures on an amount of formed precipitate. Silicate concentration in mixtures was the same and equal to 6 mass % for the correct comparison of experimental data.

Necessary pH value of solution was obtained by addition alkali (NaOH) to the mixture. Earlier obtained silicate-alkali mixtures were mixed with salt water analogue in different ratio (salt water was added in amounts from 10 to 90 %). Following results were obtained in experiments (fig. 1-2, table 1-4).

In order to study the effect of the pH value of the initial mixtures diluted in various amounts by the analogue of sea water on the process of sedimentation and, in particular, on the amount of the precipitate formed, initial alkaline silicate compositions with initial pH of solutions = 11.72; 12.28; 12.99 and 13.65. For the correctness of the data compared, the concentration of silicate in the compositions was the same and was 6% by weight.

The necessary pH of the solutions was achieved by adding alkali (NaOH) to the composition. Pre-prepared solutions of the silicate-alkaline composition were mixed with an analogue of sea water in different proportions (sea water was added in amounts of 10 ... 90%). As a result of the experiments, the following results were obtained (Figs 1-2, Table 1-4).

The study of a sedimentation process showed that intensity of this process consistently decreases with increase of pH value of the initial silicate-alkali mixture from pH = 11.72 to pH =13.65. The formed precipitate amount was equal to 10.1 g/dm^3 at pH=13.65 and a content of salt water analogue 60 %. It is in 2.7 times less, than at pH = 11.72 and at the same content of salt water. The maximum precipitate amount was formed when the salt water content have been 60 % for all researched pH values.

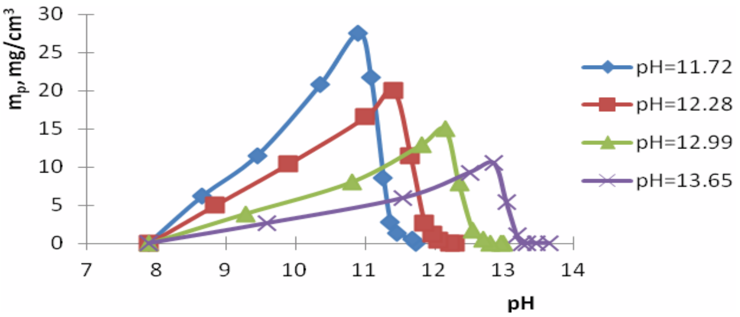

Fig. 2. Dependence of the precipitation process m_p from the pH value of silicate mixtures diluted with salt water

Table 2

Precipitation when dilution silicate mixture (initial pH=12.28) with salt water

№	Salt water content	pH	Mass of a precipitate, mg/cm^3	Relative concentration of SiO_2 in the supernatant liquid
1	0	12,28	-	1,000
2	10	12,22	-	0,869
3	20	12,05	0,39	0,741
4	30	11,97	1,23	0,612
5	40	11,85	2,66	0,471
6	50	11,65	11,44	0,341
7	60	11,40	20,07	0,211
8	70	11,00	16,56	0,081
9	80	9,90	10,42	-
10	90	8,85	5,01	-
11	100	7,90	-	-

Table 3

Precipitation when dilution silicate mixture (initial pH=12.99) with salt water

№	Salt water content	pH	Mass of a precipitate, mg/cm^3	Relative concentration of SiO_2 in the above precipitate liquid
1	0	12,99	-	1,000
2	10	12,95	-	0,879
3	20	12,79	-	0,752
4	30	12,69	0,52	0,629
5	40	12,55	1,75	0,501
6	50	12,35	7,95	0,378
7	60	12,15	14,99	0,251
8	70	11,81	12,87	0,130
9	80	10,81	8,01	-
10	90	9,29	3,89	-
11	100	7,90	-	-

Table 4

Precipitation when dilution silicate mixture (initial pH=13.65) with salt water

№	Salt water content	pH	Mass of a precipitate, mg/cm^3	Relative concentration of SiO_2 in the supernatant liquid
1	0	13,65	-	1,000
2	10	13,45	-	0,899
3	20	13,33	-	0,764
4	30	13,25	-	0,646
5	40	13,18	1,01	0,525
6	50	13,03	5,37	0,403
7	60	12,85	10,49	0,280
8	70	12,50	9,23	0,162
9	80	11,55	5,92	0,041
10	90	9,60	2,62	-
11	100	7,90	-	-

6. Discussion of results

The influence of a dilution on the mixture's pH value

pH values of the obtained silicate-alkali solutions after dilution with salt water were determined depending on the salt water content in these solutions. Initial pH values of mixtures were 11.72; 12.28; 12.99; 13.65. The amount of salt water in a mixture varied from 0 to 100%.

Following results have been obtained during investigation. pH value of the obtained solution didn't change greatly when the salt water content varied from 10 to 50 % comparatively with initial solution (fig. 3). It is connected probably with high buffer capacity of silicate mixtures. A sharp decrease of solution's pH value took place with increase of salt water content to 50 %. Increase of solution ionic power caused neutralization of silicate-alkali solution. The revealed regularity was preserved for all the studied solutions (with different initial pH values).

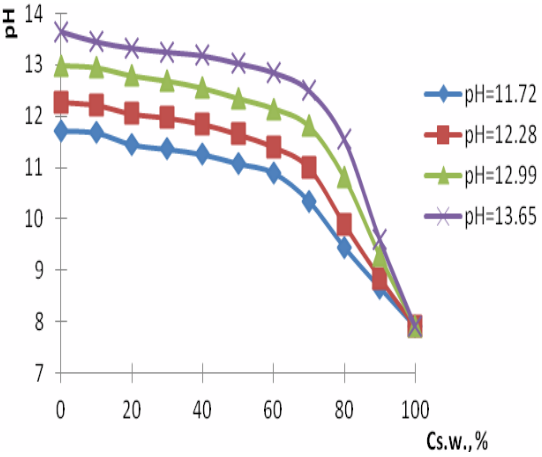

Fig. 3. Dependence of silicate-alkali mixture *pH* value on salt water content $C_{s.w.}$

Influence of a dilution on the residual concentration of silicate in a solution

Silicate concentration in the supernatant liquid (filtrate) has been calculated for the determination of the minimal silicate concentration necessary for gel formation when mixing silicate mixtures with salt water. Silicate concentration has been determined in mixtures with initial pH values (11.72; 12.28; 12.99; 13.65) and salt water content from 0 to 100 % (fig. 4).

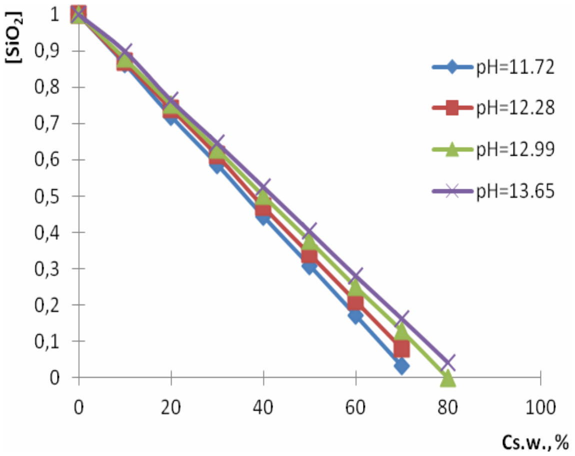

Fig. 4. Dependence of SO_2 relative concentrati on *[SO_2]* in supernatant liquid from salt water content $C_{s.w.}$ in silicate-alkali solution

Analysis of experimental date showed, that the amount of silicate in the supernatant liquid increase for all ratios of silicate and salt water with increase of initial mixture pH value. Besides the salt water content in a mixture increases with increase of pH for obtaining equal silicate concentration in the supernatant liquid. Dilution of the initial mixture by 50 % salt water caused the value of silicate residue concentration in a solution from 0.3 to 0.4 from the initial one for pH = 11.72, …, 13.65. It was also found, that gel formation (for a mixture with initial pH = 11.72) occurred at residual concentration of silicate in a solution 0.25 – 0.3 from initial one. Thus, it was determined, that minimal concentration of silicate in the solution can be 1.5 – 2 mass %.

7. Conclusions

Performed investigations on the study the presipitation process under static conditions allow to conclude:

– precipitation process proceeds most intensively when silicate ratio in a mixture with salt water is 40 – 60 %;

– the precipitate amount consistently decreases with increase of the initial mixture pH value when mixing with salt water;

– necessary residue concentration of silicate in the solution for gel formation is 1.5 – 2 mass %;

– salt water content in the mixture over 50 % causes the most significant change pH values of mixtures.

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О.С. Тітова[1], Н.В. Столярова[2], З.В. Грушак[3], Т.В. Кравчук[4]

Вивчення особливостей процесу осадоутворення силікатно-лужної композиції в присутності морської води

Національний авіаційний університет, проспект Космонавта Комарова, 1, Київ, 03680, Україна
E-mails: [1]kafedra_hht@ukr.net; [2]kafedra_hht@ukr.net; [3]kafedra_hht@ukr.net; [4]kafedra_hht@ukr.net

Мета: Метою цієї статті є дослідження процесу осадоутворення при розведенні розчину силікату морською водою. Проаналізіровано зміну процесу осадоутворення зі збільшенням pH вихідного розчину силікатно-лужної композиції. **Методи дослідження:** Для визначення відносної концентрації силікату в надосадовій рідині використовувалися методи прямого і зворотного титрування; pH-метрія – для контролю за зміною pH силікатно-лужних композицій в процесі експерименту. **Результати:** найбільш інтенсивно процес осадоутворення відбувається при співвідношенні силікату в морській воді в суміші 40 ÷ 60; зі збільшенням pH вихідної композиції кількість осаду при змішуванні з морською водою послідовно зменшується; для утворення гелю достатньо, щоб залишкова концентрація силікату в розчині становила 1,5–2 % мас; найбільш значні зміни pH композицій відбувається при вмісті в суміші морської води понад 50 %. **Обговорення:** З метою визначення мінімальної концентрації силікату, необхідною для утворення гелю при змішуванні силікатних композицій з морською водою, необхідно визначати концентрацію силікату в надосадовій рідині (фільтраті). Було встановлено, що кількість силікату в надосадовій рідині збільшується для всіх співвідношень силікату і морської води зі збільшенням pH вихідної композиції, причому для досягнення однакової концентрації силікату в надосадовій рідині зі збільшенням pH збільшується частка морської води в суміші. Виявлено, що утворення гелю (для композиції з вихідним значенням pH = 11,72) відбувалося при залишковій концентрації силікату в розчині 0,25-0,3 від вихідної. Таким чином, було встановлено, що мінімальна концентрація силікату в розчині може становити 1,5-2,0% мас.

Ключові слова: величина pH; гелеутворення; концентрація; осадоутворення; силікатно-лужна композиція; фільтрат

О.С. Титова[1], **Н.В. Столярова**[2], **З.В. Грушак**[3], **Т.В. Кравчук**[4]

Изучение особенностей процесса осадкообразования силикатно-щелочной композиции в присутствии морской воды

Национальный авиационный университет, проспект Космонавта Комарова, 1, Киев, 03680, Украина
E-mails: [1]kafedra_hht@ukr.net; [2]kafedra_hht@ukr.net; [3]kafedra_hht@ukr.net; [4]kafedra_hht@ukr.net

Цель: Целью этой статьи является исследование процесса осадкообразования при разбавлении раствора силиката морской водой. Проанализировано изменение процесса осадкообразования с увеличением pH исходного раствора силикатно-щелочной композиции. **Методы исследования:** Для определения относительной концентрации силиката в надосадочной жидкости использовались методы прямого и обратного титрования; pH-метрия – для контроля за изменением pH силикатно-щелочных композиций в процессе эксперимента. **Результаты:** наиболее интенсивно процесс осадкообразования происходит при соотношении силиката в морской воде в смеси 40 ÷ 60; с увеличением pH исходной композиции количество осадка при смешивании с морской водой последовательно уменьшается; для образования геля достаточно, чтобы остаточная концентрация силиката в растворе составляла 1,5–2 % масс; наиболее значительные изменения pH композиций происходит при содержании в смеси морской воды свыше 50%. **Обсуждение:** С целью определения минимальной концентрации силиката, необходимой для образования геля при смешивании силикатных композиций с морской водой, необходимо определять концентрацию силиката в надосадочной жидкости (фильтрате). Было установлено, что количество силиката в надосадочной жидкости увеличивается для всех соотношений силиката и морской воды с увеличением pH исходной композиции, причем для достижения одинаковой концентрации силиката в надосадочной жидкости с увеличением pH увеличивается доля морской воды в смеси. Обнаружено, что образование геля (для композиции с исходным значением pH = 11,72) происходило при остаточной концентрации силиката в растворе 0,25–0,3 от исходной. Таким образом, было установлено, что минимальная концентрация силиката в растворе может составлять 1,5–2,0 % масс.

Ключевые слова: величина pH; гелеобразование; концентрация; осадкообразование; силикатно-щелочная композиция; фильтрат

Olga Titova (1953). Candidate of chemical sciences. Associate Professor.
Department of Chemistry and Chemical Technology, the Educational and Research Institute of Environmental Safety, National Aviation University.
Education: Kyiv State University named by T.G. Shevchenko, Kyiv, Ukraine (1977).
Research area: chemistry.
Publications: 37.
E-mail: kafedra_hht@ukr.net

Natalia Stoliarova (1958). Assistant Professor.
Department of Chemistry and Chemical Technology, the Educational and Research Institute of Environmental Safety, National Aviation University.
Education: Kyiv Institute of Civil Aviation, Kyiv, Ukraine (1987).

Research area: chemistry.
Publications: 25.
E-mail: kafedra_hht@ukr.net

Zoia Hrushak (1975). Junior lecturer.
Department of Chemistry and Chemical Technology, the Educational and Research Institute of Environmental Safety, National Aviation University.
Education: Kyiv International University of Civil Aviation, Kyiv, Ukraine (1999).
Research area: chemistry.
Publications: 14.
E-mail: kafedra_hht@ukr.net

Tetiana Kravchuk (1986). Junior lecturer.
Department of Chemistry and Chemical Technology, the Educational and Research Institute of Environmental Safety, National Aviation University.
Education: National Aviation University, Kyiv, Ukraine, (2009).
Research area: chemical thermodynamics and thermochemistry.
Publications: 5.
E-mail: kafedra_hht@ukr.net