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A Study on Alkali Consumption Regularity in Minerals of Reservoirs During Alkali(NaOH)/Surfactant/Polymer Flooding in Daqing Oilfield

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Abstract

In the process of oil displacement of ASP (Alkali/Surfactant/Polymer) flooding , when Alkali interacts with the fluid and minerals of the reservoir, the alkali is subject to be consumed. The consumption regularity is the key factor affecting ASP ingredient, injection plan, scaling regularity for production wells and oil displacement effectiveness. Therefore to study the alkali consumption is of great significance in guiding ASP ingredient, injection project design, and the analysis for oil displacement mechanism. In this paper, aiming at the main components of minerals in the reservoir in Daqing Oilfield, the laboratory study on static alkali consumption for five kinds of minerals (kaolinite, grundite, chlorite, feldspar and quartz) in ASP system and single component NaOH solution are done respectively. The alkali consumption regularities for five kinds of minerals in ASP and single component NaOH solution are concluded.

The research indicates that the amount of alkali consumption for kaolinite, grundite, chlorite, feldspar and quartz is changing from larger to less accordingly, but is mainly caused by clay minerals; the average alkali consumption is 18.3% higher than that by matrix minerals. In single component NaOH solution, the alkali consumption styles of clay minerals and the matrix minerals take the chemical reaction as the lead, and the physical adsorption as the second. In ASP system solution, the alkali consumption style of clay minerals, takes the physical adsorption as the lead, and of matrix minerals takes the chemical reaction as the lead. In ASP solution, compared with single component solution, polymer and surfactant have the functions of restraint to alkali consumption in minerals of the reservoir, and the amount of alkali consumption decreases evidently.

Key words: Alkali; Surfactan; Polymer; ASPI; Oil displacement

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INTRODUCTION

In the process of oil displacement of ASP system, alkali in ASP system not only interacts with the fluids in the reservoir, but also interacts with the rock minerals definitely; therefore the consumption of Alkali is occurred. They are two kinds of consumption styles: One is chemical consumption when alkali interacts with the rock minerals. The other is alkali absorption on the surface of the rocks. The consumption regularity is the key factor affecting ASP ingredient, injection plan, scaling regularity for production wells and oil displacement effectiveness. Therefore to study the alkali consumption is of important significance in guiding ASP ingredient, injection project design, and the analysis for oil displacement mechanism. The initial report on ASP flooding was published in 1977[1], and from then on, a great number of researches have been performed by the scholars from different countries, and the researches involve ASP's chemical agent development, fluid rheology behavior, displacing mechanism, scaling mechanism and etc.[2-7]. But there are little systematic and profound reports concerning alkali consumption regularity and scale controlling measures in the process of strong Alkali (NaOH)/Surfactant/Polymer flooding [8-12]. In this paper, aiming at the main components of minerals in the reservoir in Daqing Oilfield, the laboratory study on static alkali consumption for five kinds of minerals (kaolinite, grundite, chlorite, feldspar and quartz) in ASP and single component NaOH solution are done respectively. The alkali consumption regularities for five kinds of minerals in ASP and single component NaOH solution are concluded and the comparison analysis is done as well.

1. ALKALI CONSUMPTION MECHANISMS OF MINERALS

When ASP is injected into the reservoirs, some of the alkali interacts with organic acid in the crude oil. In this process, surfactant is created, which is conductive to driving oil. The other alkali interacts with rock minerals and water in the formation. Deposit is created in the same process, which resulted in a great amount of consumption of alkali. They are two kinds of consumption styles. One is chemical alkali consumption when alkali interacts with the rock minerals. The other is alkali absorption on the surface of the rocks.

1.1 Mechanism of Physical Absorption

Cation Na^+ in solution exchanges with H^+ and absorbs on the surface of the rocks, and alkali is consumed, the chemical equation is as follow:

$$\text{M-H} + Na^+ + OH^- \rightleftharpoons \text{M-Na} + H_2O$$

1.2 Mechanisms of Chemical Alkali Consumption

The minerals in the formation are composed of frame minerals and clay minerals. The frame minerals in Daqing oilfield are mainly quartz, feldspar and etc., and clay minerals are mainly grundite, kaolinite, chlorite, and etc. There are Ca^{2+} and Mg^{2+} in fluid in the formation, when the rock minerals interact with alkali, the main chemical reaction equations are as follows:

The chemical formula of the feldspar presents as $K[AlSi_3O_8]$+$Ca[Al_2Si_2O_8]$, and when the feldspar reacts with alkali, its chemical equation is:

$$K[AlSi_3O_8]+Ca[Al_2Si_2O_8]+9OH^- \rightleftharpoons Al(OH)_3\downarrow+K^++Ca^{2+}+SiO_3^{2-}$$

The chemical formula of the quartz is SiO_2, and the chemical equations between quartz and alkali are as the follows:

$$SiO_2+2OH^- \rightleftharpoons SiO_3^{2-}+H_2O$$

$$SiO_3^{2-}+H_2O \rightleftharpoons H_2SiO_4^{2-}$$

$$H_2SiO_4^{2-}+H_2O \rightleftharpoons SiO(OH)_3^- + OH^-$$

$$SiO(OH)_3^- +H_2O \rightleftharpoons SiO(OH)_4\downarrow+OH^-$$

$Al_2Si_2O_5(OH)_4$ is the chemical formula of kaolinite, and its chemical equations reacted with alkali are :

$$Al_2Si_2O_5(OH)_4+2OH^-+4H_2O \rightleftharpoons 2Al(OH)_3\downarrow+2H_3SiO_4^-$$

$$Al_2Si_2O_5(OH)_4+2OH^-+2Na^++4Si(OH)_4 \rightleftharpoons 2NaAlSi_3O_5+11H_2O$$

$$Al_2Si_2O_5(OH)_4+2OH^-+2Na^++2Si(OH)_4 \rightleftharpoons 2NaAlSi_2O_5{\bullet}H_2O+5H_2O$$

The chemical formula of grundite, chlorite, and montmorillonite are similar presented as $Al_2[Si_4O_{10}](OH)_2$.Crystal strata may form differently. When reacted with alkali, the chemical equations are:

$$Al_2[Si_4O_{10}](OH)_2+10H_2O \rightleftharpoons 2Al(OH)_3\downarrow+4Si(OH)_4\downarrow$$

$$Al_2[Si_4O_{10}](OH)_2+2Na^++2OH^-+2Si(OH)_4 \rightleftharpoons 2NaAlSi_3O_8+6H_2O$$

$$5Al_2[Si_4O_{10}](OH)_2+12Na^++2Al(OH)_3+12OH^-+10H_2O \rightleftharpoons 4Na_3Al_3Si_5O_{16}{\bullet}6H_2O$$

The silicic acid is unstable, and under alkali conditions, intro-molecular aggregation arises and poly-silicic acid, polysilicate and trimer silicic acid are formed:

$$Si(OH)_4+2OH^- \rightleftharpoons [Si(OH)_6]^{2-}$$

$$2[Si(OH)_6]^{2-} \rightleftharpoons [Si_2(OH)_{10}]^{2-}+2OH^-$$

$$[Si(OH)_6]^{2-}+[Si_2(OH)_{10}]^{2-} \rightleftharpoons [Si_3(OH)_{14}]^{2-}+2OH^-$$

2. LABORATORY RESEARCH OF ALKALI CONSUMPTION OF MINERALS

2.1 Test Introduction

The water used to prepare ASP system is injection water from Daqing oil field, the salinity is 4826.7mg/L. The mass percentage of surfactant and NaOH in ASP is 0.3%, and 1.2% respectively. The concentration of partially hydrolysis polyarylamide is 2000 mg/L, the molecular weight is 25 millions. The degree of hydrolysis is 25%.

Minerals of formation are prepared as quartz, feldspar, grundite, kaolinite, and chlorite separately, the purity of them is more than 95%. Acid proof plastic bottle, AAS-475 atomic absorption spectrum instrument, THZ-82 temperature constant bath oscillator, JY33-TGL-16 hi-speed centrifuge, JKY/SJ-4A PH test paper. The detailed testing methods and procedures are as follows:

(1) Get quartz, feldspar, grundite, kaolinite grinded to less than 120 mesh, dried to be standby.

(2) According to the proportion of 5g: 20mL, mix the dried powder of quartz, feldspar, grundite, kaolinite with NaOH solution whose mess concentration is 1.2%, or with ready prepared ASP solution respectively, put the mixture into the plastic alkali proof container whose volume is 50 mL, and got it sealed, after oscillating violently, put it into a thermotank with constant temperature 45°C, and conduct static soak test.

(3) Get it oscillated once a day, sampling on different fixing days (1, 5, 16, 30, 40 day), put the sample into oscillating tube, got it oscillated at the speed of 8000rpm for 20mins, take the clear liquid in the top of the tube, measure the concentration of NaOH, silicon ion and aluminium ion.

(4) Take phenothalin and metryl orange whose mess concentration is 0.5% as indicator, to titrate with diluted hydrochloric acid (0.04948 mol/L), according to equivalent law, apply the following equation to calculate the concentration of NaOH after chemical reaction, then to attain the consumption amount of alkali：

$$A_i = \frac{C_0 - C_i}{C_0} \times 100\%$$

In the equation: A_i is the alkali consumption percentage of each kind of mineral, %；C_0 is the initial concentration of NaOH, mg/L; C_i is the final concentration of NaOH after chemical reaction with each kind of mineral, mg/L.

(5) To measure the concentration of silicon ion and aluminium ion using AAS-475 atomic absorption spectrum instrument.

2.2 Test Results Analysis

2.2.1 Alkali Consumption Test for NaOH Reacting with Sigle Mineral

Fig 1 is the relation curve between static alkali consumption and time when kaolinite, grundite, chlorite, feldspar and quartz reacts with NaOH solution respectively. From the fig we can see, the longer the reaction time is, the larger the alkali consumption is, and in the initial time, the alkali consumption speed is faster; In addition, for different kind of mineral, it has a different alkali consumption speed, in the initial time, for kaolinite, it has the alkali consumption of 16.0%, for grundite, it has 15.6%, for chlorite, it has 11.6%, for feldspar, it has 7.2% and for quartz, it has 4.7%; When the reacting time is 40 days, for kaolinite, it has the alkali consumption of 38.9%, for grundite, it has 29.8%, for chlorite, it has 22.2%, for feldspar, it has 13.1% and for quartz, it has 10.9%, thus it can be seen that the order of alkali consumption for the minerals are: kaolinite, grundite, chlorite, feldspar and quartz, and the alkali consumption amount for clay minerals is 18.3% larger in average than frame minerals, it’s obvious that the alkali consumption in minerals is mainly caused by clay minerals.

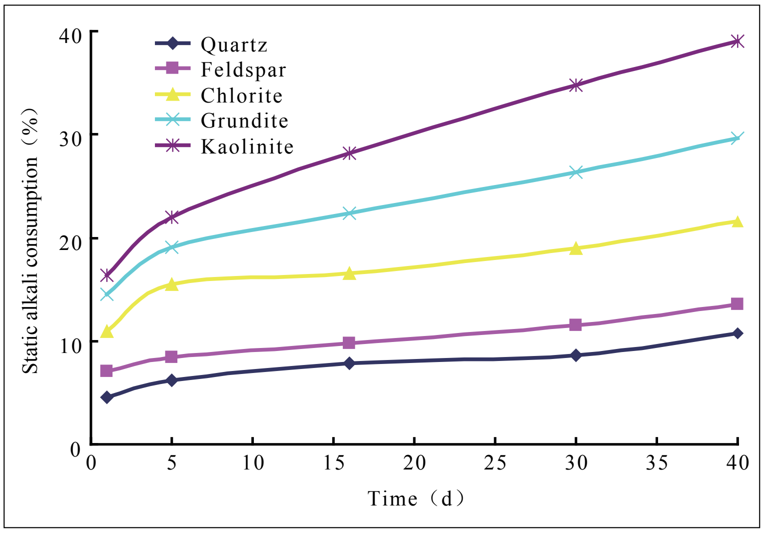

Figure 1
The Relation of Static Alkali Consumption Versus Time in NaOH Solution

The total amount of alkali consumed by minerals includes physical absorption and chemical reaction consumption. In order to make clear the alkali consumption proportion on the total for each of process mentioned above, the concentration of silicon ion and aluminum ion in the NaOH solution after reaction is traced and measured, the result is shown in Fig 2 and 3. From Fig 2 and 3 we can see that for each kind of mineral, the longer the reaction time with the NaOH solution is, the larger the concentration of silicon ion is increased gradually, and the increments are all large. The order of the concentration of silicon ion consumed from large to little is listed as: grundite, kaolinite, chlorite, feldspar and quartz; But only for grundite, the increment of concentration of aluminum ion is measured large, for other minerals, it's measured less. After reaction for minerals with NaOH solution, the order of the concentration of silicon ion consumed from large to little is listed as: grundite, kaolinite, chlorite, feldspar and quartz; The order of the concentration of aluminum ion consumed from large to little is listed as: grundite, kaolinite, chlorite, feldspar. The concentration of silicon ion and aluminum ion after reaction for frame minerals with NaOH solution is lower than that for clay minerals with NaOH solution. It is illustrated that the amount of alkali consumed by clay minerals is larger than frame minerals.

According to the concentration of silicon ion and aluminum ion after reaction for all kinds of minerals with NaOH solution, using the chemical reaction equation for AL_2O_3, SiO_2 reacting with NaOH respectively, the amount of alkali consumption and physical absorption for each kind of minerals reacting with NaOH can be calculated. In table 1, the total amount of alkali consumption, chemical reaction alkali consumption and physical absorption caused by all kinds of minerals reacting with NaOH solution are tabulated after 40 days reaction time. From table1 we can see that, after reactions for kaolinite with NaOH, the amount of chemical alkali consumption take the percentage of 79.5% of the total, for grundite, chlorite, feldspar and quartz, it is of 80.9%, 79.4% and 75.8% accordingly. It's given the fact that, after reaction for all kinds of minerals with NaOH solution, the chemical alkali consumption is the main style, the physical absorption take the second place.

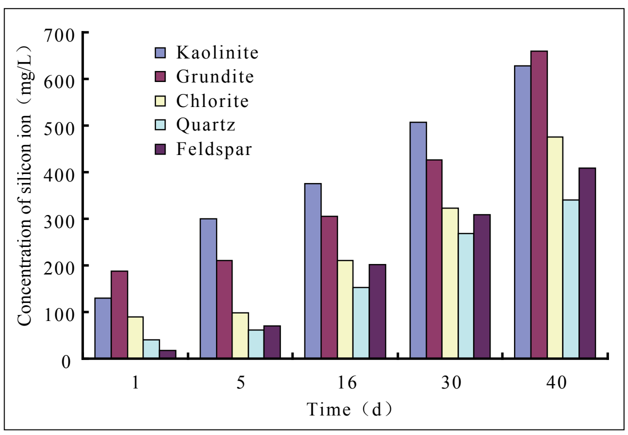

Figure 2
The Relation of the Concentration of Silicon Ion Versus Time in NaOH Solution

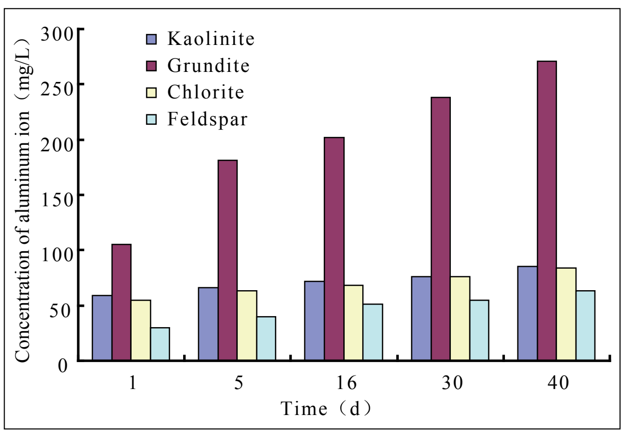

Figure 3
The Relation of the Concentration of Aluminum Ion Versus Time in NaOH Solution

Table 1
The Percentage of Chemical Alkali Consumption and Physical Absorption (in NaOH Solution)

Mineral Type	Total Amount Alkali Consumption (%)	The Percentage of Chemical Alkali Consumption in the Total (%)	The Percentage of Physical Absorption in the Total (%)
Kaolinite	38.9	79.5	20.5
Grundite	29.8	90.6	9.4
Chlorite	22.2	80.9	19.1
Feldspar	13.1	79.4	20.6
Quartz	10.9	75.8	24.2

2.2.2 The Alkali Consumption Test for ASP System Reacting with Single Mineral

Fig 4 is the relation curve between static alkali consumption versus time when kaolinite, grundite, chlorite, feldspar and quartz reacts with ASP system respectively. From the fig 4 we can see, the alkali consumption regularity for all kinds of mineral reacting with ASP system has the same trend basically with that when reacting with NaOH solution. That is the longer the reaction time is, the larger the alkali consumption is, and in the initial time, the alkali consumption speed is faster, but by comparison with NaOH solution, the alkali consumption is lower, the alkali consumed from large to little by grundite, kaolinite, chlorite, feldspar and quartz is 26.9%, 22.5%, 19.4%, 6.8% and 9.0% respectively, dropped 30.8%, 24.5%, 12.6%, 48.1% and 17.4% respectively. This indicates that the alkali consumption has been restrained effectively by the presence of polymer and surfactant in ASP system. After reacted with ASP system, the order of alkali consumption caused by the minerals is: kaolinite, grundite, chlorite, quartz and feldspar. It's obvious that the alkali consumption in minerals is mainly caused by clay minerals, but for ASP system, the alkali consumed by quartz is larger than that by feldspar.

The variations of concentration of silicon ion and aluminum ion in ASP system after reaction are shown in Fig 5 and 6. From Fig 5 and 6 we can see that for each kind of mineral, by comparison with NaOH solution, both the concentration of silicon ion and aluminum ion in ASP system have been dropped,the dropping value of silicon ion is bigger than aluminum ion. This indicates that the chemical reaction alkali consumption has been restrained by the presence of polymer and surfactant in ASP system. After reacted with ASP system for each kind of minerals, the order of concentration of silicon ion in the ASP system from large to little is: kaolinite, grundite, feldspar, chlorite, and quartz, for the concentration of aluminum ion, the order from large to little is: grundite, chlorite, kaolinite and feldspar.

In table 2, the total amount of alkali consumption, chemical reaction alkali consumption and physical absorption caused by all kinds of minerals reacting with ASP system are tabulated after 40 days reaction time. From table 2 we can see that, after reaction for kaolinite with ASP system, the amount of chemical alkali consumption take the percentage of 32.5% of the total, for grundite, chlorite, feldspar and quartz, it is of 43.6%, 44.8%, 60.0% and 62.2% accordingly. By contrast with the reaction with NaOH, the alkali consumption dropped 59.1%, 51.9%, 44.6%, 24.4% and 17.9% respectively. It's given the fact that, to some extent, the chemical reaction alkali consumption has been dropped by the presence of polymer and surfactant in ASP system. But the dropping range of chemical reaction alkali consumption caused by clay minerals is larger than frame minerals, thereby, for clay minerals, the alkali absorption in ASP system is the main style. For matrix minerals, the chemical reaction alkali consumption in ASP system is the main style.

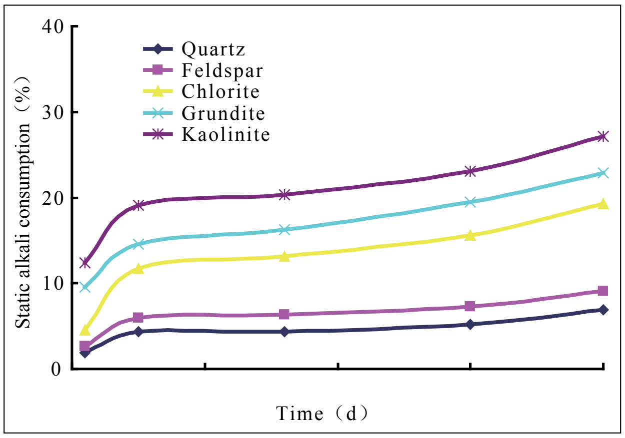

Figure 4
The Relation Curve Between Static Alkali Consumption Versus Time in ASP System

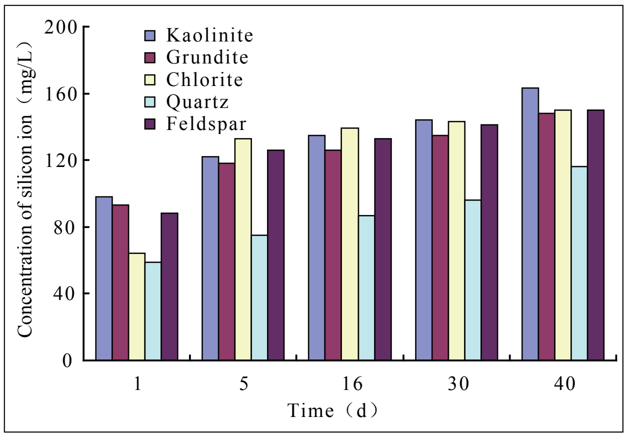

Figure 5
The Relation of the Concentration of Silicon Ion Versus Time in ASP System

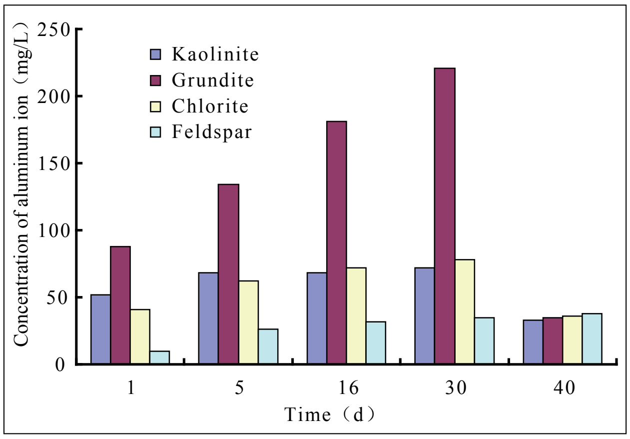

Figure 6
The Relation of the Concentration of Aluminum Ion Versus Time in ASP System

Table 2
The Percentage of Chemical Alkali Consumption and Physical Absorption (in ASP System)

Mineral Type	Total Amount Alkali Consumption（%）	The Percentage of Chemical Alkali Consumption in the Total（%）	The Percentage of Physical Absorption in the Total（%）
kaolinite	26.9	32.5	67.5
grundite	22.5	43.6	56.4
chlorite	19.4	44.8	55.2
feldspar	6.8	60.0	40.0
quartz	9.0	62.2	37.8

CONCLUSIONS

(1) The order of alkali consumption for 5 kinds of the minerals is: kaolinite, grundite, chlorite, feldspar and quartz, and the amount of alkali consumption is mainly caused by clay minerals, the alkali consumption amount for clay minerals is 18.3% larger in average than matrix minerals.

(2) When kaolinite, grundite, chlorite, feldspar and quartz reacts with NaOH solution respectively, the amount of chemical alkali consumption take the percentage of 79.5%, 90.6%, 80.9%, 79.4% and 75.8% of the total. It's given the fact that, after reaction for all kinds of minerals with NaOH solution, the chemical alkali consumption is the main style, the physical absorption take the second place.

(3) The alkali consumption regularity for all kinds of mineral reacting with ASP system, has the same trend basically with that of reacting with NaON solution, but the alkali consumption is lower, the alkali consumed from large to little by grundite, kaolinite, chlorite, feldspar and quartz is 26.9%, 22.5%, 19.4%, 6.8% and 9.0% respectively, this indicates that polymer and surfactant in ASP system have effective restrain functions to the alkali consumption.

(4) When kaolinite, grundite, chlorite, feldspar and quartz reacts with ASP system, the amount of chemical alkali consumption take the percentage are 32.5%, 43.6%, 44.8%, 60.0% and 62.2% of the total respectively, It's given the fact that for clay minerals, the main alkali consumption style in ASP system is the physical absorption; but for matrix minerals, the main alkali consumption style is the chemical reaction.

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