

Study on Microstructure of Polysilicic acid in High Salinity

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Abstract. In a certain degree of mineralization, the polymerization of silicic acid with different silicon ion concentrations was observed by microscope in the alkaline sodium silicate solution. The polymerization of silicic acid is divided into following processes. It generates into silica nanoparticles firstly, then silica monomers polymerize and condensate into polysilicic acid by dehydration in alkaline condition, finally polysilicic acid dehydrates to silica scale. Therefore, it can be called a dehydration process. The structure and composition of silicic acid gel was investigated through FTIR, XRD, and TGA-DTA. The results show that silica scale is mainly amorphous silica composed of Si-O tetrahedron basically.

Introduction

The hydrogen and oxygen are the large amount of elements in crust. About 30% of silicate minerals in the earth, the fundamental problems are acquainting the structure and properties of silicates. Microscopic structure determines macroscopic properties, observing and studying the microstructure is the basis of understanding and explaining the macroscopic properties and phenomena. Scale formation in Oil Field is distributed into three stages, calcium carbonate scale, calcium carbonate scale with silicate scale, silicate scale. Now the study on calcium carbonate scale is quite comprehensive, while the study of silicate scale formation is few. The considerable complex process, not only solubility product theory, but also the polymerization properties determine it.

Lu Chen [1] et al considers that four Orthosilicic acid molecules gradually coalesce into tetra-silicic acid and finally produce particle of silica gel cubic octasilicic acid condensation polymer by cyclopolymerization. Silica gel clumps together in particles [2], they disperse in a medium to form sol, and it gelatinizes when the temperature changes or adding electrolyte, then generates biomaterial properties including dispersion medium within the entire volume, hence sol loses flow ability.

Silicic acid polymerization mainly emerge in monovalent anion and neutral molecule of silicic acid in alkaline or neutral medium; in strong acid solutions, polymerization process mainly exist in monovalent cations and neutral molecule of silicic acid by olation [3]. According to Professor Dai Anbang [4], full gelation curve should be "W", either acidic or alkaline sols are stable in acidic or alkaline environment because it possesses the same electric potential on the Surface of Silica GEL and the electrostatic repulsion. In the alkaline medium copolycondensation rate rapidly, it is contrary to what in the acid solution. In order to observe polymerization process faster, the experimental condition in this paper is alkaline as the Oilfield Production Fluid.

Peter A. Monson [5] et al presents an atomic lattice model for researching the polymerization of silicic acid in sol-gel. Their model is based on Si and O atoms occupying the sites of a

body-centered-cubic lattice, with all atoms arranged in SiO_4 tetrahedra. The model describes the assembly of polymerized silica structures starting from a solution of silicic acid in water at a given concentration and pH and captures the basic mechanism of silica polymerization.

Tingting Lu [6] investigates gel time concerned with pH value in a complicated silicic acid system, containing Al^{3+} , Mg^{2+} , Fe^{2+} , and Fe^{3+} . The study indicates that nonionic surfactant make the gel time increase from 11 to 312 h and is more suitable to control gel time than anionic surfactant.

Spinde [7] et al studies the influence of a number of N-containing macromolecules on the polycondensation of silicic acid to form amorphous silica by the combined use of ^{29}Si NMR spectroscopy and the silicomolybdate test. These polymeric additives comprise poly (allylamine hydrochloride) (PAH), the poly (aminoamide) dendrimer of generation 1 (PAMAM-1), poly (ethyleneimine) (PEI), and poly (vinylpyrrolidone) (PVP). It was found at pH 5.4 that all additives accelerate silicic acid polycondensation, except for PVP. At pH 7.0, polycondensation is much faster in the presence of PAMAM-1, PEI, and PAH. However, PVP significantly stabilizes mono- and disilicic acid.

Krumrine and Boyce [8] deem that the dielectric constant of solution containing organic compounds changes, and it has an influence on the rate of polymerization of silicic acid. The research concerning this is relatively little, thus continuing studying is needed. We add a series of organic compounds into the system, such as polymers, surface active agent (involving water soluble and oil soluble) to get gelation curve and morphology characteristics of polysilicate and explore how additional material can affect the process.

It is a two-stage oligomeric mechanism of silica monomers in the combination of silica sol and potassium sodium silicate. The colloidal particles dissolved firstly, and then the “active” silica in the silicates redeposited to make a distinct particle size distribution influenced by K^+ and Na^+ ions as well as by temperature [9].

This paper makes a tentative study on silicic acid polymerization process with microscope. Some interesting phenomena and laws were found, silica scale formation is polymerization of silicate. It grew up together to yield a frame structure filled with water, afterwards the frame structure dehydrates gradually. The structure and composition of silica gel were analyzed through infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA-DTA), X ray diffraction spectroscopy (XRD).

Experimental

Chemicals and apparatuses. The following apparatuses were used in the experiments: biological microscope (XSZ-106, Ningbo), infrared spectrometric analyzer (Tensor27, Bruker), Thermo gravimetric/differential Thermal Analyzer (Japan), X-RAY Diffractometer (D/max-2200, Japan), Acidity meter (PHS-3C, Jiangsu), electronic balance (AL104, Mettler Toledo), Glass instrument air dryer (Lingke C, Henan). The chemicals (NaCl , Na_2SO_4 , NaHCO_3 , Na_2CO_3 , Na_2SiO_3 , NaOH , hydrochloric acid, analytically purity) were used as received.

The experimental method.

- (1) Preparation of mother liquor according to table 1.
- (2) Preparation of high concentration ($C_{\text{Si}^{4+}} = 3000 \text{ mg/L}$, $C_{\text{Si}^{4+}} = 2500 \text{ mg/L}$), medium concentration ($C_{\text{Si}^{4+}} = 2000 \text{ mg/L}$) of silicon system by dissolving a certain amount of sodium silicate in the mother liquor. The pH was adjusted to alkaline.
- (3) The prepared silicate solution was placed in a special cuvette.

- (4) Observe the silicate solution to get the formation and topography of silica scale after a certain time in room temperature by light microscope.

Table 1 The ion concentration of the mother liquor (mg/L)

CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	pH
2305.1	1078.3	1372.7	27.0	0	0	3075.6	10.4

Results and discussion

Framework of silicate gel formation process. Fig. 1 explains that the generation of silicic acid gel is the same as the formation process of polysilicic acid. Simple silicate ions and molecules were produced as soon as adding hydrochloric acid into sodium silicate solution. Original single molecule of silicic acid is soluble in water, nevertheless it is very unstable. It collided with each other to aggregate into polysilicate due to Brownian motion, polysilicate molecular dehydrated and condensated under alkaline conditions to build macromolecules of polymer silicate, and polysilicate is basically amorphous. It produced sol when the molecular size suited the size of colloidal particles. At this moment, the system is uniform, transparent, and had the general characteristics of colloids. As silicic acid polymerization degree increasing, its adsorption ability of water molecules became stronger. The internal mesh stent structure of polysilicic acid was filled with water. The micro-region outline was clear, flat and smooth. After a while, observed region gradually lost water from the external edge and formed floc. It dehydrated and gradually increased, the final white film-like precipitate was silica scale.

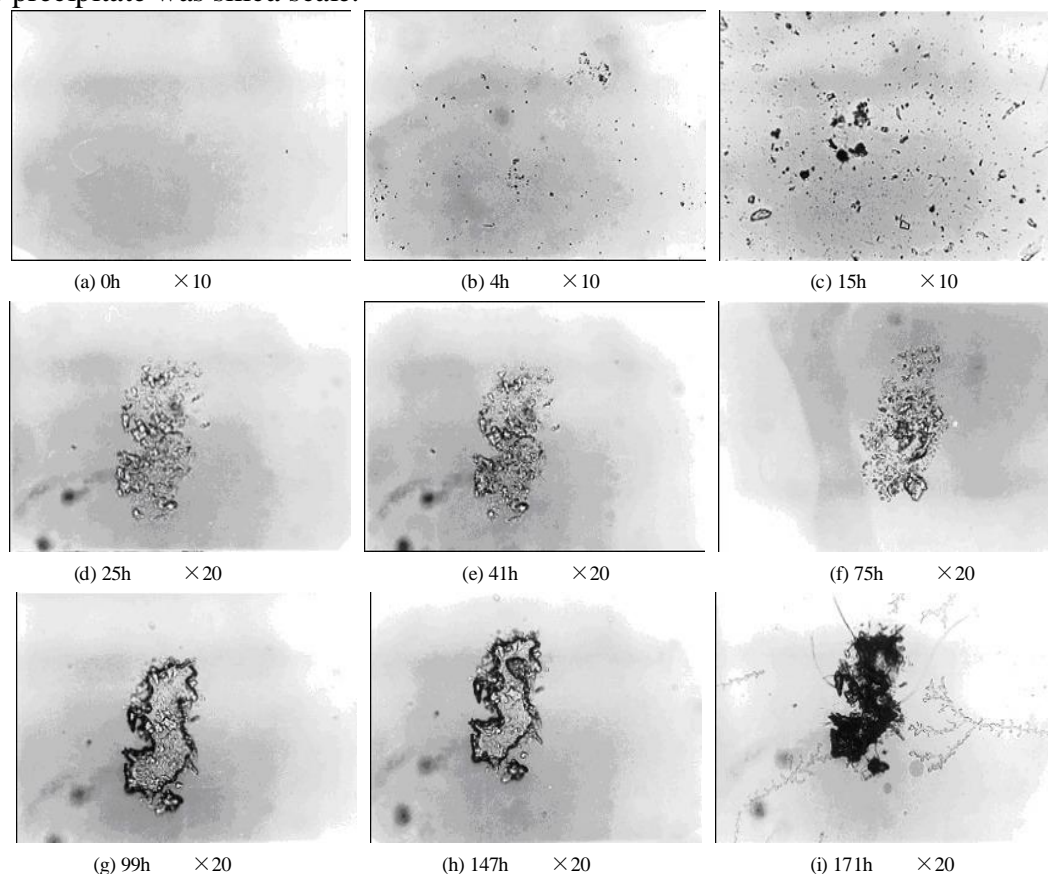


Fig. 1 Microscopic pictures of silicic acid polymerization process ($C_{\text{Si}^{4+}}=2000\text{ppm}$)

Silicate gel skeleton structure. Fig. 2 describes that a strong tetrahedron antisymmetric stretching vibration absorption peak exists in 1014.8 cm^{-1} and a strong absorption band. A strong tetrahedron bending vibration absorption peak arises in 468 cm^{-1} . A weak tetrahedron symmetric stretching vibration absorption peak emerges in 690 cm^{-1} . These show that the network skeleton of polysilicic acid is composed of Si-O tetrahedron basically.

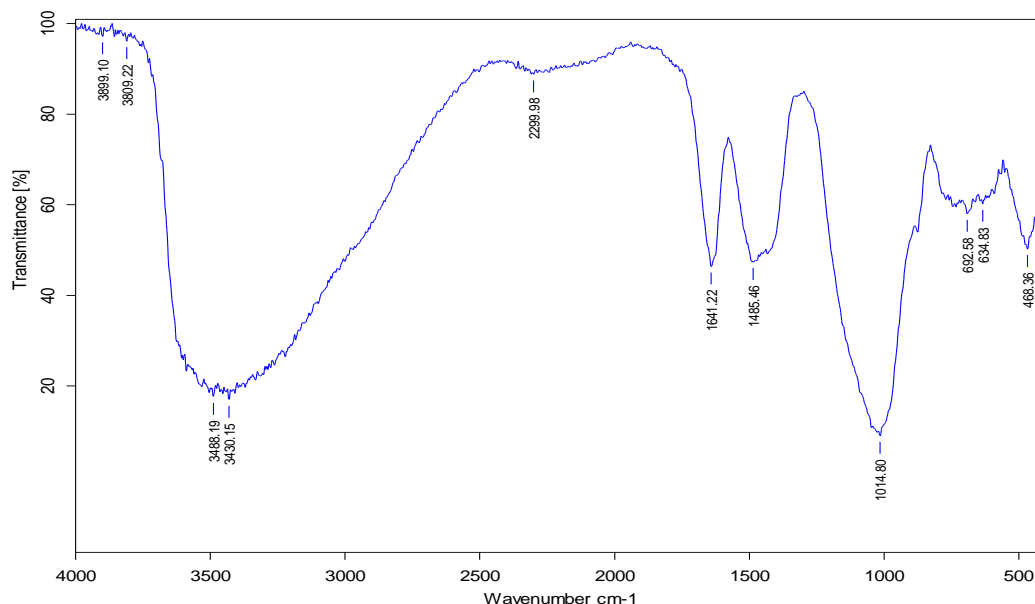


Fig. 2 IR spectra of silica gel

The composition of silica gel. Fig. 3 shows that the adsorbent water of silica gel is removed and about 14.9% of the weight is lost at $150\text{ }^{\circ}\text{C}$. Between $400\text{ }^{\circ}\text{C}$ ~ $500\text{ }^{\circ}\text{C}$, silicon alcohol is dehydrated and the weight loss is 11.7%. It is considered to be the change of particle surface properties until this temperature. It is vitrification transfer point (TG) at $800\text{ }^{\circ}\text{C}$.

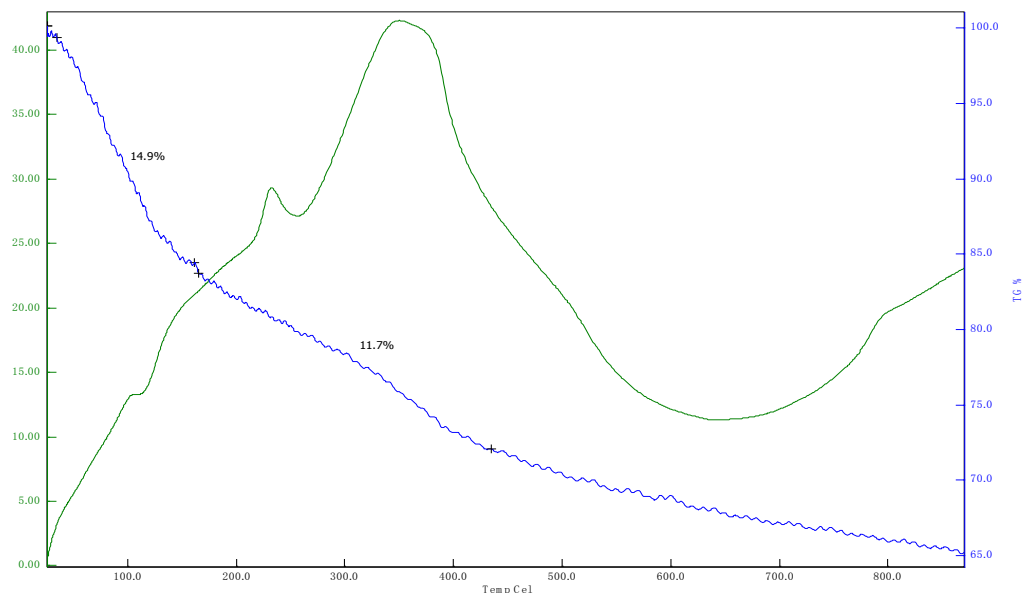


Fig. 3 DTA and TG of silica gel

The crystalline of silica gel. Fig. 4 indicates that silica gel has an untypical symmetrical distribution amorphous peaks and crystalline peak in other angle. Silica gel is between crystal and amorphous.

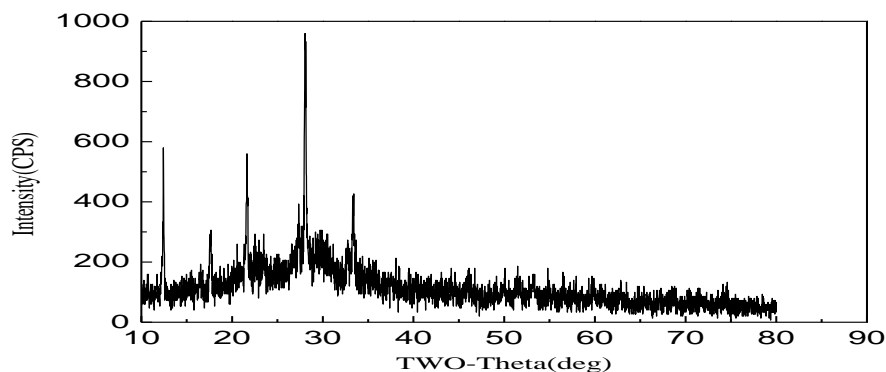
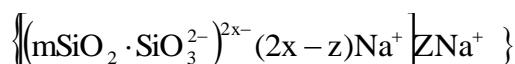


Fig. 4 X-ray diffraction spectrum of silica gel

Conclusions

- (1) Single silicate molecule polymerized and condensated into polysilicic acid in alkaline condition and polysilicic acid dehydrated to silica scale.
- (2) FTIR shows that the skeleton structure of silicate gel is composed of Si-O tetrahedron basically; XRD indicates that silica gel is between crystal and amorphous. Thus silica scale is mainly amorphous silica.
- (3) In alkaline silicate solution, colloid structure is as following:



Negatively charged colloid particles is surrounded by hydrated sodion, $\text{SiO}_2 / \text{Na}_2\text{O}$ ratio increases when the concentration of silicon in the solution increases, that means sodion around the colloidal particles will decrease. Therefore it is easy to condensate into macromolecular oxygen-silicon polymers between hydroxyl on the surface of colloid.

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