



## The precipitation of “magnesium silicate” under geothermal stresses. Formation and characterization



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### ABSTRACT

Geology presents a well-defined family of minerals in the case of crystalline magnesium silicates. However, in industrial water processes deposits that contain both “Mg” and “Si” are usually referred to as “magnesium silicate” scales. In this paper we attempt to delineate the true nature of such Mg- and Si-containing precipitates formed under the severe stresses simulating geothermal-like conditions. The purpose of this work is to deliberately form precipitates in the presence of  $Mg^{2+}$  ions and soluble silica (silicic acid) and study these with a variety of analytical techniques, to reveal morphology, texture, structure and composition. Such precipitates are better described as “magnesium-containing amorphous silica”.

### 1. Introduction

Oxygen and silicon are the most abundant elements in Earth’s crust and mantle, and they form the strongly coordinating silicate species  $SiO_4^{4-}$  over a wide range of conditions. This species is even stable in silicate melts, and because more than 90% of the Earth’s crust is made of these two elements (more than 70% by weight), it is easy to understand why practically all crust and mantle minerals are composed of silicate tetrahedra with a wide variety of other elements incorporated in their structure. The composition of the nine rock forming minerals reveals that they all belong to the silicate group of minerals, whose basic building block is the  $SiO_4$  tetrahedron (Demadis, 2010).

The term “magnesium silicate” is widely recognized in the water treatment industry (Brooke, 1984). However, its definition differs from that in Geology. In contrast to the crystallographically well-defined metal silicate geological minerals (Earle, 2017), an inorganic deposit which forms in water systems and contains both “magnesium” and “silicon” is commonly called “magnesium silicate”. This may be quite misleading because the Mg:Si molar ratio is not stoichiometric and never corresponds to a true magnesium silicate mineral. In reality, these deposits are most likely amorphous silica with  $Mg^{2+}$  ions entrapped in its colloidal matrix and they bear little resemblance to their geological counterparts (Rashid et al., 2011). In more harsh environments, such as geothermal and oilfield applications, the effect of high temperature favors the formation of geologically-recognized magnesium silicates (Frenier and Ziauddin, 2008).

Over the past century geothermal energy is considered to be one of the most important, alternative solutions to issues regarding problems of energy, as it is looked upon as environmental friendly, renewable and recyclable (Rosen and Koohi-Fayegh, 2017). Geothermal systems represent once-throughput systems, which practically means that the water is discarded after a single use and it is not recirculated in the heating systems, in contrast to the cooling systems. Despite its benefits though, scale deposits, such as metal silicates and metal sulfides, are an issue of major importance (Pirajno, 1992).

In this paper the formation of inorganic precipitates is investigated in the presence of various concentrations of both  $Mg^{2+}$  and a water-soluble silicate source at pH values 7.0, 8.5, and 10.0. A wide variety of results are presented with the goal of shedding light on the nature of “magnesium silicate” precipitates that form under these conditions. Our results on the inhibitory effects of various scale inhibitors will be reported in the forthcoming Part 2.

### 2. Short literature overview

Magnesium silicate precipitates and deposits can cause problems in several water treatment applications from truck radiators to geothermal wells and plants (Demadis, 2003; Bott, 1990; Bott, 1995). The magnesium/silicate system is highly pH-dependent. Below pH 7 there is essentially no precipitation, because silica exists in an unreactive (towards  $Mg^{2+}$ ), non-ionized form. At pH above 9, magnesium silicate is very likely to form because silica forms reactive silicate ions.

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Fig. 1. Image of the high-throughput system that was used for the hydrothermal precipitation reactions.

Furthermore, the importance of temperature is highlighted in some reports, as precipitation begins at a lower pH if the temperature is sufficiently high (Demadis, 2010).

Magnesium silicate scaling has been a problem in some of the Icelandic district heating systems (Kristmannsdóttir et al., 1989). This kind of scaling was not encountered in heating systems utilizing geothermal water directly, but was observed by heating and de-aerating fresh water. The deposit was amorphous based on XRD experiments, therefore an argument was put forth that its structure resembled that of chrysotile (based on FT-IR data). It was also found that the Mg:Si ratio is close to 1 with small variations.

Magnesium silicate sepiolite was precipitated from sea water at low temperature (down to 25 °C), as the dissolved silica concentration was increased (Wollast et al., 1968). Increased temperature and high pH increased the rate of precipitation. The magnesium silicate talc formed easily in hydrothermal experiments. Several other magnesium silicates such as stevensite  $[(Ca_{0.5}, Na)_{0.33}(Mg, Fe^{+2})_3Si_4O_{10}(OH)_2 \cdot n(H_2O)]$ , saponite  $[Ca_{0.25}(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2 \cdot n(H_2O)]$  and chrysotile  $[Mg_3(Si_2O_5)(OH)_4]$  are known to be formed hydrothermally at relatively low temperatures. Heating of fresh water also initiated precipitation and it is well known that magnesium is one of the major components in “boilerstone”. The major factors controlling the degree of supersaturation are boiling temperature and pH, both dependent on the de-aeration process (Kent and Kastner, 1985).

Co-precipitation of magnesium hydroxide,  $Mg(OH)_2$ , and colloidal silica has also been observed (Dubin, 1991; Meier and Dubin, 1987; Dubin et al., 1985). One scenario proposes that formation of  $Mg(OH)_2$  occurs first, and  $Mg(OH)_2$  subsequently reacts with monomeric silicate and/or polymeric silica to form magnesium silicate (Smith, 1993).  $Ca^{2+}$  and  $Mg^{2+}$  salts were found to catalyze the silica autocondensation process (Sheikholeslami and Tan, 1999). Higher concentrations of total hardness lead to a faster drop in dissolved silica in solution. In batch runs,  $Mg^{2+}$  was found to affect silica concentrations more than that of  $Ca^{2+}$ . For example, runs with a given hardness level but with lower ratios of Ca:Mg caused a faster decline in dissolved silica concentration.

Magnesium silicate is a “true” compound according to Young, (1993). According to their report, a fairly consistent amorphous precipitate was obtained. The stoichiometric Si:Mg ratio was found to be 1:1. This ratio was maintained regardless of the Si:Mg molar ratio in the working solution (1:2 or 2:1) and the precipitation temperature (RT or 75 °C).

It was also reported by MacKenzie et al. that temperature has a greater influence upon the deposition than any of the variables. It was reported that a hydroxylated magnesium silicate forms in sea-water in which the  $SiO_2$  concentration exceeds 26 ppm at pH 8.1 and clay minerals are found (kaolinite, glauconite and montmorillonite) (MacKenzie et al., 1967).

Demir et al. studied precipitates formed in an autoclave from a combination of chloride salts of metal cations ( $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Fe^{2+}$ )

and silicic acid and carbonate ions (Çelik et al., 2017). Analyses revealed that the morphology of the deposits formed mainly comprised clusters of nanoscale particles that had a spherical geometry. The results of studies by XRD, EPR, and XPS have shown that the precipitates contained both crystalline and amorphous regions. The crystalline region was identified as magnetite ( $Fe_3O_4$ ) and salts of sodium, calcium, and magnesium. The amorphous portion was identified as a silicate structure modified by sodium, iron, and calcium.

### 3. Experimental section

#### 3.1. Instrumentation

ATR-IR spectra were collected on a Thermo-Electron NICOLET 6700 FTIR optical spectrometer. Determinations of soluble silicic acid (molybdate-reactive silica) were carried out using a HACH 1900 spectrophotometer from the Hach Co., Loveland, CO, USA. SEM images were collected on a scanning electron microscope LEO VP-35 FEM.

Hydrothermal reactions under autogenous pressure were carried out using a parallel synthesis procedure in an autoclave block made of aluminum which contains 36 reaction chambers in a  $6 \times 6$  array. Teflon reactors have an inner diameter of 19 mm and a depth of 18 mm, with a total volume of about 5 mL. A thin sheet of Teflon covers the reaction vessels, which are then sealed inside a specially designed aluminum autoclave. The set-up is shown in Fig. 1.

#### 3.2. Reagents and materials

All chemicals were from commercial sources. Sodium silicate  $Na_2SiO_3 \cdot 5H_2O$ , ammonium molybdate  $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ , and oxalic acid ( $H_2C_2O_4 \cdot 2H_2O$ ) were from EM Science (Merck). Sodium hydroxide (NaOH) was from Merck, hydrochloric acid 37% was from Riedel de Haen. Magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ) was from Riedel de Haen. Ethylenediamine tetraacetic acid (EDTA, tetrasodium salt) and Eriochrome Black T were from Alfa Aesar. All reagents were used as received from suppliers. Acrodisc filters (0.45  $\mu m$ ) were from the Pall-Gelman Corporation. In-house, deionized (DI) water with an electrical conductivity 0.05  $\mu S/cm$  was used for all experiments. This water was tested for soluble silica and magnesium ions and was found to contain negligible amounts.

#### 3.3. Solution preparation

The sodium silicate stock solution (solution A) used in all experiments was prepared by dissolving 4.080 g of  $Na_2SiO_3 \cdot 5H_2O$  in 2 L DI water. The mixture is stirred for at least a day to ensure complete dissolution. This stock solution contains 500 ppm “Si” (8.33 mM), expressed as “ppm  $SiO_2$ ”. A 1% w/v (10,000 ppm in  $Mg^{2+}$ ) solution (solution B) was prepared by dissolving 8.360 g of  $MgCl_2 \cdot 6H_2O$  in 100 mL

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