# IMPROVED METHODS FOR REMOVAL OF SILICATE DEPOSITS

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## ABSTRACT

The removal of silica scale deposits from process equipment represents a substantial challenge in chemical cleaning. Silicates form in a variety of systems as the result of their presence in natural water and in water treatment chemistry. The exact nature of the silicate in deposits depends on the type of cations present as well as temperature and flow rates when the silicate is deposited. Removing silicate deposits has depended on using fluorine based acids, such as HF, Ammonium bifluoride, and Fluoroboric acid. HF and related acids are very hazardous. In addition Fluoride ions form a number of insoluble salts that can limit the effectiveness of the acid in dissolving silicate scales. The paper describes the work of developing effective alternative chemistries and how scale composition variability makes multistage cleaning a necessity. The combination of chelation chemistry with caustic has been found to successfully dissolve a variety of silicate species and provide a safer more ecologically friendly alternative to HF

## INTRODUCTION

The formation of scale is a serious problem in industrial heat transfer. The scale forms an insulating layer on the heat transfer surface and reduces both the thermal conductivity of the system and the volumetric flow. Many different compounds can be found in scale but the class of compound of most interest in this study is silicates.

Mathematically, the effect of scale is described by the following equation:

$$Q_k/A = (T_1 - T_2)/(L_1/k_1 + L_2/k_2)$$

Where $Q_k/A$ is the Watt/area and $T_1$ is the inside Temperature, $T_2$ is the outside Temperature, $L_1$ is the wall thickness, $L_2$ is the scale thickness and $k_1$, and $k_2$ are the Thermal conductivity for the pipe and the scale.
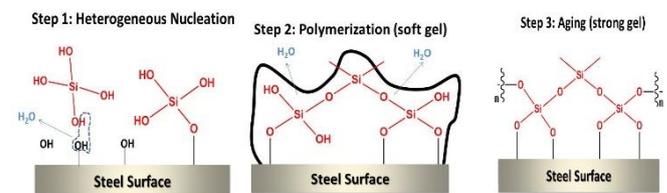
Table 1 Initial Parameters

| K1 | 54 w/m/°K | carbon Steel |
|---|---|---|
| L1 | pipewall | 4 mm |
| L2 | scale | .1 mm |

Table 2 : Heat transfer coefficients for various scales

| Q/A for various Scale types | | | | |
|---|---|---|---|---|
| | | $T_1-T_2$ (°C) | | |
| **Scale** | K2 | 20 | 40 | 100 |
| **None** | 0 | 270.00 | 540.00 | 1350 |
| **Glass** | 0.96 | 112.21 | 224.42 | 561.04 |
| **Silica** | 0.06 | 11.49 | 22.98 | 57.45 |
| **Clay** | 0.15 | 27.00 | 54.00 | 135.00 |
| **Calcium silicate** | 0.05 | 9.64 | 19.29 | 48.21 |
| **CaCO₃** | 2.4 | 172.80 | 345.60 | 864.00 |

As can be seen in the table the presence of a small amount of insulating scale can reduce the heat transfer by a factor of up to 28 times.

Silicate minerals tend to have very low conductivity relative to other deposits. This is partially due to the manner that silica forms deposits on surfaces.



Silica deposits on surfaces via heterogeneous nucleation steps, where silica monomer deposit on the surfaces, followed by a reaction with functional groups such as $OH^-$, $COO^-$, $NH^{4+}$ . After the surface is fully covered further deposition is then controlled by silica-silica interactions. The second step in silica scaling is controlled by a condensation process, where water molecules are expelled from the film. The gel in this stage is not fully polymerized and has low water content. With further ageing more water molecules are expelled from the film resulting in a dry condensed polymerized silica film. The process of silica condensation and polymerization involves complex chemistry that is not yet fully understood. Previous studies have revealed that the presence of inorganic cations such as $Ca^{2+}$, $Mg^{2+}$ $Fe^{2+}$ and

Na$^+$, have significant effect on the silica scaling kinetics and the resulting scale composition.

## SILICA SCALE DISSOLUTION

There are two generally accepted chemistries used for silica dissolution. The first, and the one most often used in chemical cleaning, is HF (hydrofluoric acid); either in the form of pure HF, or as fluoroboric acid, or created in situ by combining HCl with ammonium bifluoride (ABF). The second method is to react with strong alkali – NaOH or KOH. This is more typically used in industrial settings for the production of sodium or potassium silicates.

Hydrofluoric acid has its drawbacks. The first problem is the tremendous toxicity of the acid. HF is both strongly corrosive and a contact poison. It can be absorbed through the skin and eyes as well as by inhalation. HF can cause both serious burns as well as disruption of the nervous system that can lead to cardiac failure and death.
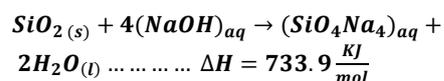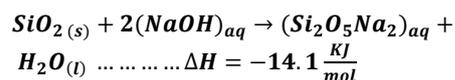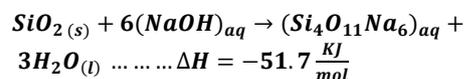
In addition to the extreme health hazards posed by HF it also reacts with the other cations present in the systems to be cleaned producing difficult to dissolve secondary precipitates. Table 3 shows the solubility of some of the salts resulting from the reactions of HF with common silicates. The risk of forming CaF$_2$ is particularly high as calcium carbonate is also often found in conjunction with silicate scales.

**Table 3: Solubility in water at room Temperature HF Silicate reaction products**

| Reaction species | Solubility (g/100 ml.) |
|---|---|
| Ortho Silicic acid | 0.015 |
| Calcium Fluoride | 0.0016 |
| Sodium Fluorosilicate | 0.65 |
| Sodium Fluoroaluminate | Slightly |
| Potassium Fluorosilicate | 0.12 |
| Ammonium Fluorosilicate | 18.6 |
| Calcium Fluorosilicate | Slightly |
| Aluminum Fluoride | 0.595 |

With the exception of ammonium fluorosilicate, most of the resulting reaction products are only slightly soluble in water.

Alkaline dissolution is thought to be more effective than acidic dissolution but the reactions are complex and the mechanism is not clear.

$$SiO_{2\,(s)} + 6(NaOH)_{aq} \rightarrow (Si_4O_{11}Na_6)_{aq} + 3H_2O_{(l)} \ldots\ldots\ldots \Delta H = -51.7\frac{KJ}{mol}$$

$$SiO_{2\,(s)} + 2(NaOH)_{aq} \rightarrow (Si_2O_5Na_2)_{aq} + H_2O_{(l)} \ldots\ldots\ldots \Delta H = -14.1\frac{KJ}{mol}$$

$$SiO_{2\,(s)} + 4(NaOH)_{aq} \rightarrow (SiO_4Na_4)_{aq} + 2H_2O_{(l)} \ldots\ldots\ldots \Delta H = 733.9\frac{KJ}{mol}$$

Previous work on dissolution of silicates discussed that the silicon atom is buried below the surface so hydroxyl atoms won't react directly and the hydroxyl anion alone won't react with it. This is supported by reactions with anhydrous methanolic NaOH, where no water is present, having zero

rates of reaction. The concentration of NaOH is important; the rate increases as NaOH increases to a maximum of 15% at which point the amount of water present becomes a limiting reaction.

It is important to note for the purposes of this study that these kinetic results are for $SiO_2$ and not for the complex mixtures found in real industrial deposits.

**Experiments and Results**

To study silicates we first had to look at the range of silicate materials we had in our sample archive.

We chose five samples representing four different systems.

**Table 4: Sample source and description**

| Sample # | Source | Description |
|---|---|---|
| 1 | Silicates Storage tank – paper mill | Hard white solid |
| 2 | Silicates storage tank – silicate manufacturer | Hard white solid |
| 3 | Evaporator tube – SAGD horizontal evaporator | Brown and white flakes |
| 4 | Evaporator Walls – SAGD horizontal evaporator | Shiny brown blacks |
| 5 | Exchanger tube – pilot plant Mechanical vapour compression evaporator | Soft grey deposit |

Each sample was analyzed to determine its composition. The analysis was carried out as a combination of chemical extraction as well as XRD and XRF.

Table 5: Sample compositions

| | | Wt. % for sample # | | | | |
|---|---|---|---|---|---|---|
| Compound | Chemical Formula | 1 | 2 | 3 | 4 | 5 |
| Clinoptilolite | $Si_{14.52}Al_{3.48}$ | 3.3 | 7.4 | | | |
| Zeolite | $K_6Na_3(Al_9Si_{27})$ | 2.4 | 3.9 | | | |
| Kanemite | $Si_2NaO_8H_8$ | 77.2 | 68.7 | | | |
| Cristobalite | $SiO_2$ | | | 5.7 | | |
| Wairakite | $CaSi_4Al_2O$ | | | 53.1 | 19.4 | |
| Wairakite | $CaSi_4Al_2O_{14}H_4$ | | | 41.2 | | |
| Analcime | $Na_2Si_4Al_2O_{14}H$ | | | | 8.2 | |
| Phillipsite | $Na_2K_{.5}Al_{2.5}Si_{5.5}O_{21}H_2$ | | | | 24.6 | |
| Calcite | $CaCO_3$ | | | | | 18 |
| Mg Silicate | $Ca_{0.36}Na_{0.56}Mg_{0.81}(Mg_{0.73}Si_{0.27})Si_2O_6$ | | | | | 18 |
| Magnetite | $Fe_3O_4$ | | | | | 2 |
| Hydroxyapatite | $Ca_5(PO_4)_3(OH)$ | | | | | 2 |
| Amorphous | | 17 | 19.9 | 41.2 | 47.8 | 60 |

Chemical analysis showed all of the deposits to contain at least 40% Si.

Our first study was with our existing chemistry which was 10% sodium hydroxide with 5% DPTA. This was compared with 15% sodium Hydroxide. The samples used in this and subsequent development rounds were Samples 1 and 2. This was because we did not have sufficient evaporator samples to do development work and Samples 1 and 2 were in large amounts and nearly identical in composition. The results of the first test was only 30% of the sample dissolved in the 10% NaOH and 40% in the 15% in 48 hours at 70°C

The next round of tests were performed under the same static conditions of 70°C and 48 hours of contact time and 15% NaOH.

Table 6: Chelating agents

| Blend # | Chelant (5%) | % Dissolved |
|---|---|---|
| 1 | N-{2-[Bis(carboxymethyl)amino]ethyl}-N-(2-hydroxyethyl)glycine | 66 |
| 2 | Isoserine-N,N-diaceticacid trisodium salt | 62 |
| 3 | Poly phosphonate | 60 |
| 4 | Tetrasodium EDTA | 57 |
| 5 | Trisodium salt of methylglycinediacetic acid | 52 |
| 6 | Poly phosphonate | 46 |
| 7 | Na5DPTA | 36 |
| 8 | Sodium Glucoheptonate | 33 |
| 9 | Tetrasodium Glutamate Diacetate | 32 |
| 10 | Di sodium EDTA | 9 |
| 11 | Trisodium HEDTA | 8 |
| 12 | Pentasodium DPTA | 6 |

While the results were encouraging we decided to try to see if we could improve the amount of solids dissolved.

Table7: effect of polycarboxylate on overall performance

| Chelant | polycarboxylate A wt% Disolved | polycarboxylate B wt% Disolved | polycarboxylate C wt% Disolved |
|---|---|---|---|
| N-{2-[Bis(carboxymethyl)amino]ethyl}-N-(2-hydroxyethyl)glycine | 43 | 7 | 18 |
| Isoserine-N,N-diaceticacid trisodium salt | 31 | 88 | 62 |
| Poly phosphonate | 22 | 85 | 11 |
| Tetrasodium EDTA | 10 | 8 | 24 |
| Trisodium salt of methylglycinediacetic acid | 22 | 82 | 7 |
| Poly phosphonate | - | - | - |

As can be seen in the table combinations of the chelating agents with the poly carboxylates gave a substantial improvement in the amount of silicate dissolved, at least in a couple combinations.

Based on the study of the simpler silicate mixes we settled on the use of Polycarboxylate B and then tested that against a variety of chelants on samples 3, 4 and 5.

The initial tests with the solutions that worked well in the simpler samples showed them to be ineffective on the oilfield scale.

Table 8: effect of surfactant addition

| Solution | % dissolved No surfactant | % dissolved 0.2% surfactant |
|---|---|---|
| Glucoheptonate (5%) PC (10%) | 12 | 61 |
| Versene HEDTA (5%) PC (10%) | 0 | 66 |
| DTPA (5%) PC (10%) | 0 | 72 |
| MDGA (5%) PC (10%) | 0 | 58 |

As can be seen in the table the addition of a surfactant substantially improved the dissolution of the oilfield scale.

We settled on a blend of Polymer B and MDGA (exp-S1) and tested the effect of chelant concentration on the dissolution of the scale

Table 9: test of concentration effect

| EXP-S1 (wt. %) | NaOH | % Dissolved |
|---|---|---|
| 0 | 15% | 30 |
| 3 | 15% | 88 |
| 5 | 15% | 93 |
| 7 | 15% | 95 |
| 10 | 15% | 80 |
| 15 | 15% | 85 |

Increased polymer/chelant shows a maximum at around 7% of the combined solution, with a fall off beyond that.

Scale dissolution for these complex deposits could further be improved by using a multistage process of first dissolving the scale with a strong acid (HCl or methane sulfonic) then dissolving with a combination of caustic chelants and surfactants.

## DISCUSSION

We theorize that the addition of the chelating agents prevents the secondary reactions of the divalent cations with OH- at the reaction surface allowing the OH$^-$ to react with the silicate backbone of the deposit.

Several important questions remain unanswered.

What influence does the molecular weight of the poly carbonate have on the chelate performance? We know that the polycarboxylates have molecular weights where A<B<C So there is no direct correlation of the weight to effectiveness.

Why does the reaction efficiency decrease with increasing combined chelant/polycarboxylate after reaching maxima? It may have to do with reaching a maximum in the activity of the solution but in a solution with 15% NaOH as a base, small changes in the chelate concentration should not influence the ionic strength of the solution significantly.

In complex scales taken from oilfield systems the reaction rate appears to be limited by the secondary precipitates present. Layers of iron oxide slow or stop the reaction – so is it possible to use chelant - reducing agent combinations to permit the simultaneous dissolving of the silicate and the oxides?

## CONCLUSIONS
This work shows conclusively that concentrated NaOH solutions can be combined with chelating agents to dissolve complex silicate deposits.

Systems containing more than silicates require additional treatments specific to the secondary deposits. This is true even for HF dissolution and often ignored.

Safety and environmental hazards can be substantially improved by moving away from HF.

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