

Additive-Driven Dissolution Enhancement of Colloidal Silica. 3. Fluorine-Containing Additives

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ABSTRACT: The effect of various fluorine-containing chemical additives on the dissolution of colloidal silica is systematically studied. These silica scale dissolvers are ammonium bifluoride ($\text{NH}_4\cdot\text{HF}_2$), ammonium fluoride (NH_4F), sodium tetrafluoroborate (NaBF_4), and disodium fluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$). The most effective dissolver was $\text{NH}_4\cdot\text{HF}_2$, which was extensively studied at the pH range 2–7. The highest dissolution efficiency was demonstrated in the pH range 2–4. The dissolution capability of $\text{Na}_2\text{PO}_3\text{F}$ was monitored not by the silicomolybdate method, but on the basis of a weight-loss approach. It showed substantial dissolution ability at pH's 7 and 9.

■ INTRODUCTION

In Parts 1 and 2 of this series entitled “Additive-Driven Dissolution Enhancement of Colloidal Silica”^{1,2} we outlined the significance of silica deposits in the water treatment industry. Briefly, silica deposits are generated either in bulk or on surfaces in silica-laden industrial waters.³ The chemistry of silica has been reviewed extensively,⁴ yet certain problems associated with specific applications still remain unsolved. Although mineral scale deposits⁵ (such as alkaline earth metal carbonates and sulfates) can be more-or-less satisfactorily mitigated, colloidal silica deposits remain an enigmatic challenge. This is principally due to the unique nature of silica deposits.⁶ Silica scales in industrial and process waters pose a number of challenges for the following reasons:

- Colloidal silica is an amorphous solid (in contrast to the well-known and recognized mineral scales).⁷
- Colloidal silica is a random, three-dimensional polymer formed by Si–O bonds.⁸
- Silica forms *not* by cation–anion association, but by polycondensation of silicic acid.⁹
- Silica deposits in real systems (e.g., heat exchange tube bundles) can undergo physicochemical transformations, such as Ostwald ripening.¹⁰
- Very commonly, silica is not a “pure” deposit; that is, it tends to form composite fouling either with other scales or by incorporation of metal ions.¹¹

The water treatment industry has been convinced that silica (or metal silicates¹²) deposits are undesirable complications and pose severe operational problems. Silica deposits can be mitigated either by preventive approaches or by therapeutic ones. Among the former are silica removal by ion-exchange methods¹³ and utilization of scale inhibitors.¹⁴ The latter include silica deposit removal either by mechanical¹⁵ (e.g., sandblasting) or chemical means (dissolution).¹⁶ Our present paper describes silica dissolution approaches by the use of fluorine-containing additives; specifically, ammonium bifluoride ($\text{NH}_4\cdot\text{HF}_2$), ammonium fluoride (NH_4F), sodium tetrafluoroborate (NaBF_4), and disodium fluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$). Some properties of these additives are given in Table 1. We

took the initiative to study these fluorine-containing additives in a systematic way to fill the gap in the literature on this issue. As will be discussed in the remaining part of the Introduction, the only dissolution additive mentioned in the literature for silica deposit descaling is ammonium bifluoride ($\text{NH}_4\cdot\text{HF}_2$), described mostly in the patent literature. Therefore, we would like to broaden the scope of the potential utilization of fluorine-containing additives with the objective that a broader choice of additive selection will be available to end-users.

Short Literature Review on Silica Dissolution by Fluorine-Containing Additives in Biological and Non-biological Silica Samples. The literature on silica deposit cleaning by F-containing additives is rather scarce. Herein, we will try to include as much information as possible. A review article contains a considerable amount of information.²⁰

Wet chemical etching of silicate glasses in aqueous HF solutions is a subject that has been studied over many years. The first report originates from the discovery of HF by Scheele in 1771.²¹ The specific property of HF-containing solutions to attack the glass is related to the presence in solution of the fluorine-containing species: F^- , HF, and HF_2^- . The dissolution mechanism—in particular, the role of the various fluorine-containing species—has been reviewed by Spierings.²² The HF_2^- ions are adsorbed on surface silanol groups; the HF molecules, on vicinal silanol groups; and H^+ ions, on surface bridging oxygens in siloxane units. Fluorine-containing adsorption complexes have been observed at hydrated SiO_2 surfaces in gaseous HF by infrared spectroscopy. These are transformed into surface groups such as =Si-F and =Si-O-SiF_3 . The adsorption of HF and HF_2^- increases the electronic density on the bridging oxygen in the siloxane unit. This in turn makes these oxygens more basic, so more H^+ ions are adsorbed, which leads to more siloxane bonds being broken per time unit, that is, a kind of catalytic effect. The rate-determining step is

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Table 1. Fluorine-Containing Chemical Additives Used in This Study

additive	IUPAC name	MW (g·mol ⁻¹)	synthesis	uses	ref
NH ₄ HF ₂	ammonium bifluoride	57.04	thermal decomposition of ammonium fluoride: 2NH ₄ F → NH ₃ + NH ₄ HF ₂	commonly used etchant for glasses and related silicates.	17
NH ₄ F	ammonium fluoride	37.037	passing ammonia gas into ice-cooled 40% hydrofluoric acid: NH ₃ + HF → NH ₄ F	used in the preparation of NH ₄ HF ₂ and for preserving wood, as a mothproofing agent, in printing and dyeing textiles, and as an antiseptic in breweries	17
NaBF ₄	sodium tetrafluoroborate	109.79	by neutralizing tetrafluoroboric acid with sodium carbonate or sodium hydroxide: Na ₂ CO ₃ + 2HBF ₄ → 2NaBF ₄ + H ₂ O + CO ₂	in organic chemistry for fluorination reactions and as a catalyst and for lab-scale preparation of boron trifluoride; also used in some fluxes for brazing for synthesis of ionic liquids, where BF ₄ ⁻ plays the role of the product's anion	18
Na ₂ PO ₃ F	disodium monofluorophosphate	143.95	prepared by hydrolysis of difluorophosphate ions with dilute sodium hydroxide: PO ₂ F ₂ ⁻ + 2NaOH → Na ₂ PO ₃ F + H ₂ O + F ⁻	ingredient in toothpastes; it is claimed to protect tooth enamel from attack by bacteria that cause dental caries (cavities)	19

then the breakage of the siloxane bond by the combined action of the adsorbed species.

Judge et al.²³ found that the etching rate depends on the concentration of HF molecules but does not depend on the concentration of the HF₂⁻ ion. This result showed that solutions with a pH of 7 and higher that contain essentially all fluorides in the deprotonated state exhibit essentially a zero rate of SiO₂ dissolution, which indicates that an HF₂⁻ or F⁻ ion in solution is quite benign and much less reactive than the HF molecule. Previous experimental studies showed that HF etching of SiO₂ films was enhanced by the addition of water. Consequently, H₂O may play a direct role in the etching mechanism itself.

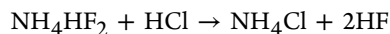
Unlike many physical properties, no linear relations are observed between the composition of the glass and its dissolution rate. The dissolution rate of a multicomponent silicate glass is found to be largely determined by two factors: the degree of linkage or connectivity of the silicate network and the concentration of SiO₂ in the glass. It is proposed that the dissolution of the glasses is preceded by the leaching of alkali and alkaline earth components present in the glass, followed by the subsequent dissolution of the leached layer. Probably fluorine species will diffuse into the leached layer to enhance the dissolution rate. Analysis of the activation energy data indicates that in some corrosive glasses, the leaching itself becomes rate-determining.

Demineralization of the siliceous spicules of sponges has already been described the 19th century²⁴ on the basis of the use of hydrofluoric acid. Kölliker was the first to describe the use of HF solution for the demineralization of *Hyalonema* spicules.²⁵ In 1888, Sollas reported on sponge spicule desilicification methods on the basis of not only HF but also on boiling solutions of KOH.²⁶ A HF-etching procedure developed for microscopic investigations of the structure of sponge siliceous spicules was described by Vosmaer and Wijsmann,²⁷ and this is still used today. A similar HF-based desilicification method was used by Schmidt in 1926 for a comparative study of organic and inorganic substances within the spicules of *Hyalonema* and *Monorhaphis* species.²⁸ HF dissolution of silica was used more recently to visualize the sponges' axial filaments but was satisfactory only for determining their gross morphology; unfortunately, it also had the drawback of partially masking the filament fine detail.²⁹ The removal of silica from the face of the block by soaking in HF circumvents some problems, but it results in the loss of the freed filaments, which are no longer supported by a surrounding matrix to hold them in the block.³⁰ In addition, cathepsin-like proteins called "silicateins" were isolated from siliceous spicules of *Tethya aurantia* by dissolving the silica in HF/NH₄F solutions;³¹ however, the fibrillar organic matrix was described for *Euplectella* sp. spicules that had been desilicated using HF gas rather than solution.³²

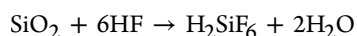
Even nowadays, HF-based techniques are still in use.³³ For the isolation of silica-associated proteins, diatom colonies (*Eucampia zodiacus*) were suspended in EDTA/SDS buffer. The resulting silica shells were then dissolved in anhydrous HF, followed by incubation at 0 °C for 30 min. In this way, all silica is dissolved.³⁴ A similar procedure was followed for the diatom *C. didymium*.³⁵ In several biosilica dissolution procedures, it is observed that HF degrades the organic matrix producing several unwanted processes, one of which is dephosphorylation. Therefore, NH₄F had to be used, which did not remove the

phosphate groups. Silaffins were extracted from the diatom *C. fusiformis* by ammonium fluoride extraction.³⁶

Ten years ago, W. W. Frenier published a book entitled "Technology for chemical cleaning of industrial equipment".³⁷ In there, it is stated that HF is usually generated by adding ammonium bifluoride to HCl:



The generated HF reacts with silica to form a more soluble fluorosilicic acid:



In 1978, Midkiff and Foyt reported that in Los Alamos National Laboratories (USA), several cooling towers suffered from severe silica scaling. Ammonium bifluoride (12% solution w/w) was able to effectively clean the deposits within a day.³⁸

Kline and Fogler studied the dissolution of various silicates (kaolinite, pyrophyllite, muscovite, talc, phlogopite, biotite, and Illite) by ammonium bifluoride in a slurry reactor.³⁹ They demonstrated that the measured dissolution rates were attributed entirely to attack by HF molecules, rather than by F^- or HF_2^- .

Mitra and Rimstidt performed batch reactor experiments in acidic fluoride solutions to measure the dissolution rate of quartz and amorphous silica.⁴⁰ Data fits produced rate laws whose interpretation indicated that the rate-determining step for silica dissolution in acidic fluoride solutions involves a coordinated attack of a Lewis acid on the bridging O atom and a Lewis base on the Si atom. This allows a redistribution of electrons from the Si–O bond to form an O–H group and a Si–FH group.

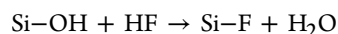
Kemmochi et al. have patented a method using HF to dissolve quartz to study the nondissolving impurities.⁴¹

Knotter used a method using a quartz crystal microbalance (QCM) to monitor the etch rate of vitreous silica by HF in situ and to establish the reactive species.⁴² At higher pH values (>1.5, relevant to the present study), the elimination of an OH^- group from the SiO_2 surface becomes the major reaction route. Once the OH^- group is eliminated, a HF_2^- molecule supplies a F^- ion. The $\text{p}K_a$ value of the deprotonation reaction increases as a result of the buildup of surface charge at $\text{pH} > 4$. Consequently, the Si–OH surface concentration and the etch rate are higher than expected from a simple acid/base equilibrium reaction. All subsequent reaction steps to remove the Si–F unit from the SiO_2 matrix are fast reaction steps (18–20 times as fast) involving HF_2^- addition reactions on $\text{F}_x\text{Si-O}$ bonds.

Pande et al. designed and fabricated an integrated wet etch and dry reactor system by studying various geometrical configurations using computational fluid dynamics simulations incorporating reaction kinetics from laboratory data and previously published information. The effect of various process parameters, such as HF concentration, flow rate, and flow velocity, on the etch rates and uniformity of thermally grown silicon dioxide and borophosphosilicate glass films was studied.⁴³

Verhaverbeke et al. proposed a new model for etching SiO_2 that takes into account the role of the dimer of hydrofluoric acid, $(\text{HF})_2$.⁴⁴ The composition of HF solutions was investigated as a function of total fluoride concentration and pH. On the basis of their results, two main etching species are present in HF solutions: namely, $(\text{HF})_2$ and HF_2^- .

Osseo-Asare proposed an alternative etching model that took into account the protonated $-\text{Si}-\text{OH}_2^+$ sites on the silica surface.⁴⁵ The absorption of the F^- ion results in the polarization of the underlying Si–O bonds when the following reaction takes place:



The subsequent detachment of the surface Si–F "complex" is effectively the dissolution event.

■ EXPERIMENTAL SECTION

Instruments. IR spectra were recorded on a FT-IR Perkin-Elmer FT 1760 in KBr discs. The measurements of soluble silicic acid were performed on a HACH 890 spectrophotometer from the Hach Co., Loveland, CO, USA. SEM images were collected on a scanning electron microscope, LEO VP-35 FEM.

Reagents and Materials. All dissolution additives tested herein are from commercial sources and are used as received. Model colloidal silica is Aerosil 200 from Degussa (water content $\sim 1.5\%$, BET surface area $200 \pm 25 \text{ m}^2/\text{g}$). The choice of Aerosil 200 was based on its high surface area and absence (by powder X-ray diffractometry) of crystalline phases. The reagents needed for the silicomolybdate test were prepared as follows: (a) 10 g of ammonium molybdate were dissolved in 100 mL of water, and its pH was adjusted between 7 and 8 with NaOH to avoid precipitation of ammonium molybdate. This solution was kept in an airtight PET container in the refrigerator. (b) HCl 1 + 1 is prepared by mixing one volume 37% HCl with an equal volume of water. (c) Oxalic acid (8.75 g) was dissolved in 100 mL of water. All solutions were kept in PET containers (glass containers must be avoided to minimize SiO_2 dissolution and silicate leaching into the test solutions).

Preparation of Synthetic Silicon Dioxide (SSD). A quantity of $\text{NaSiO}_3 \cdot 5\text{H}_2\text{O}$ (5 g) was dissolved in 90 mL of nanopure water at ambient temperature. The pH of the solution was adjusted to 7.0 ± 0.1 by addition of 80% v/v HCl solution under vigorous stirring. At this point, a gel formed as the solution volume reached $\sim 100 \text{ mL}$. Within 10 min, stirring was not possible, and the reaction was stopped. The gel was then dried in the oven at 85°C overnight to yield a white solid. This was ground to a fine powder and then washed with copious amounts of nanopure water to remove byproduct NaCl and, finally, was dried again in the oven for 24 h. The water content was determined to be $\sim 1.5\text{--}2.0\%$ (by thermogravimetry) due to rapid surface adsorption of water. The BET surface area was measured to be $\sim 100 \pm 30 \text{ m}^2/\text{g}$.

Silica Dissolution Protocol. Glass containers must be avoided to minimize silica leach-out. A quantity of colloidal silica corresponding to 500 ppm as silica (for a 100 mL final solution volume, the calculated silica weight is 50 mg) is placed in a polyethylene container together with 80 mL of deionized water and a dosage of specific chemical additive (500–10 000 ppm, depending on the specific run). (We chose to calculate additive dosages based on parts per million rather than milligrams or millimoles to be consistent with the nomenclature used in the water treatment field.) Then, the solution pH is adjusted to the desirable value (see Results for details) with dilute NaOH or HCl solutions (depending on the individual run). Finally, solutions were diluted up to 100 mL and kept under continuous stirring for a total of 72 h. Soluble silica measurements on small samples withdrawn are made at 24, 48, and 72 h with the silicomolybdate spectrophotometric test.⁴⁶ After each measurement, pH is again checked, and in the case

of a pH shift from the target value, a readjustment is made. Such deviations were seldom. Dissolution experiments were also run at shorter times (8 h), and sampling was more frequent (every 1 h).

Quantification of Silica Dissolution by Weight Difference. In the case of $\text{Na}_2\text{PO}_3\text{F}$, we observed no significant silica dissolution on the basis of the silicomolybdate test (vide infra). Hence, we applied a different technique to study silica dissolution in the presence of $\text{Na}_2\text{PO}_3\text{F}$. A quantity of SSD silica corresponding to 500 ppm as silica (for 100 mL final solution volume, the calculated silica weight is 50 mg) is placed in a polyethylene container together with 80 mL of deionized water and a dosage of $\text{Na}_2\text{PO}_3\text{F}$ (500–5000 ppm, depending on the specific run). Then, the solution pH is adjusted to 7.0 or 9.0 by use of NaOH solution (10% v/v). The dissolution experiment was left under vigorous stirring for 24 h, after which the solution was filtered through a 0.2 μm membrane filter. The filter containing the undissolved silica was dried in an oven for 24 h, and weighed. By weight difference, the precise mass of undissolved silica was determined, and hence, the percent dissolution was calculated.

Interference Test. Every cleaning additive is tested for its interference with the silicomolybdate spectrophotometric test. A stock solution (500 ppm, expressed as parts per million of SiO_2) of soluble silica (prepared from commercial sodium silicate) is prepared by dissolving 4.4 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ in 2.5 L of nanopure water. The pH of the above solution was 11.50. To 100 mL of that solution, a dosage of the cleaning chemical is added (2500–10000 ppm). After appropriate dilutions are made, soluble silica is measured with the silicomolybdate spectrophotometric test. The results are compared to the expected value of 500 ppm. Results showed that ammonium bifluoride ($\text{NH}_4 \cdot \text{HF}_2$) above the dosage of 2000 ppm shows a slight interference with the silica quantification (false negative). $\text{Na}_2\text{PO}_3\text{F}$ strongly interfered; hence, an alternative dissolution method was employed (see above).

RESULTS

Aerosil 200 Silica Dissolution Results Using NaBF_4 .

These results are shown in Figure 1. They show that NaBF_4 is a

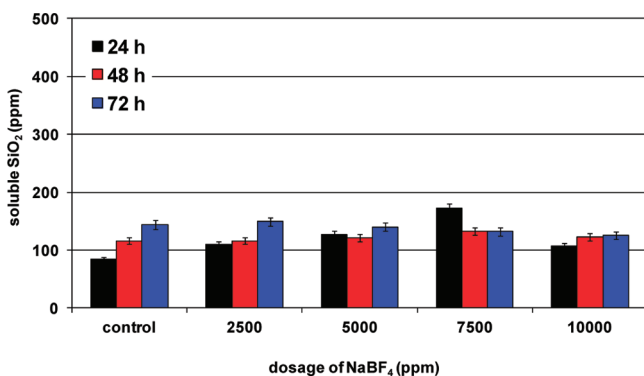


Figure 1. Dose–response graph of silica dissolution experiments for NaBF_4 .

poor dissolver of colloidal silica, since even at very high dosages (10 000 ppm), no dissolution enhancement is observed. Therefore, NaBF_4 was not studied further.

Aerosil 200 Silica Dissolution Results Using Ammonium Fluoride (NH_4F). In Figure 2, we present dissolution data for NH_4F at pH 10. For a level of 2500 ppm NH_4F ,

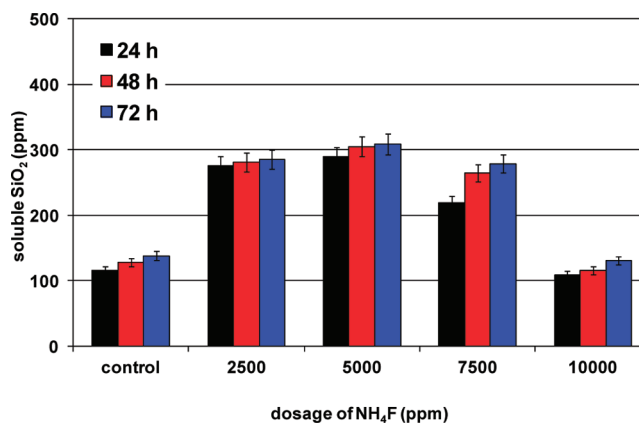


Figure 2. Dose–response graph of silica dissolution experiments for NH_4F .

solubilized silica reaches 276 ppm following a steady (but small increase) to 281 and 285 ppm after 48 and 72 h, respectively. The same trend is observed for a 5000 ppm NH_4F dosage, but the solubilized silica reaches 309 ppm after 72 h. A NH_4F dosage increase above 5000 ppm seems to be detrimental to dissolution, but this is probably due to the fact that at such high NH_4F concentrations, there is severe interference with the silicomolybdate test.

Aerosil 200 Silica Dissolution Results Using Ammonium Bifluoride ($\text{NH}_4 \cdot \text{HF}_2$). Ammonium bifluoride is used commercially for silica deposit removal. Herein, we undertook a systematic study that involved two critical variables: additive dosage and pH. On the basis of the results noted for NH_4F and the interference with the quantification method, we decided to limit the $\text{NH}_4 \cdot \text{HF}_2$ dosage to the region 500–2500 ppm. The $\text{NH}_4 \cdot \text{HF}_2$ concentrations tested were 500, 1000, 1500, 2000, and 2500 ppm. The pH range studied was from 2.0 to 7.0. For higher than 7 pH regions, we found that $\text{NH}_4 \cdot \text{HF}_2$ is not effective (data not shown). All the results are presented in Figure 3.

On the basis of the graphs of Figure 3, a clear trend is observed. The dissolution efficiency of $\text{NH}_4 \cdot \text{HF}_2$ is higher at lower pH regions. Therefore, the best results are obtained at pH = 2. Even the low dosage of 500 ppm $\text{NH}_4 \cdot \text{HF}_2$ solubilizes 215 ppm of silica after 24 h of dissolution. At pH = 2, an additive dosage increase induces higher dissolution. This is true for a dosage up to 2000 ppm of $\text{NH}_4 \cdot \text{HF}_2$. At 2500 ppm, there seems to be a slight decrease of solubilized silica measured, and this may be due to interference with the silicomolybdate test. The concentration of choice for $\text{NH}_4 \cdot \text{HF}_2$ is 2000 ppm because after 72 h, it achieves virtually quantitative dissolution of silica (473 ppm, ~ 95%).

The above results strongly suggest a dramatic pH dependence of silica dissolution by $\text{NH}_4 \cdot \text{HF}_2$. This is clearly demonstrated in Figure 4, where dissolved silica levels are plotted vs pH (for 2000 ppm $\text{NH}_4 \cdot \text{HF}_2$).

Aerosil 200 and Laboratory-Synthesized SSD Silica Dissolution Results Using Sodium Fluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$). $\text{Na}_2\text{PO}_3\text{F}$ was tested as an Aerosil 200 silica dissolver according to the procedure described above (and using the silicomolybdate test for soluble silica quantification) in the pH range 2–9. No dissolution higher than the control was observed at any of the mentioned pH values. An interference test showed that $\text{Na}_2\text{PO}_3\text{F}$ severely interferes with the silicomolybdate test; hence, an alternative method was

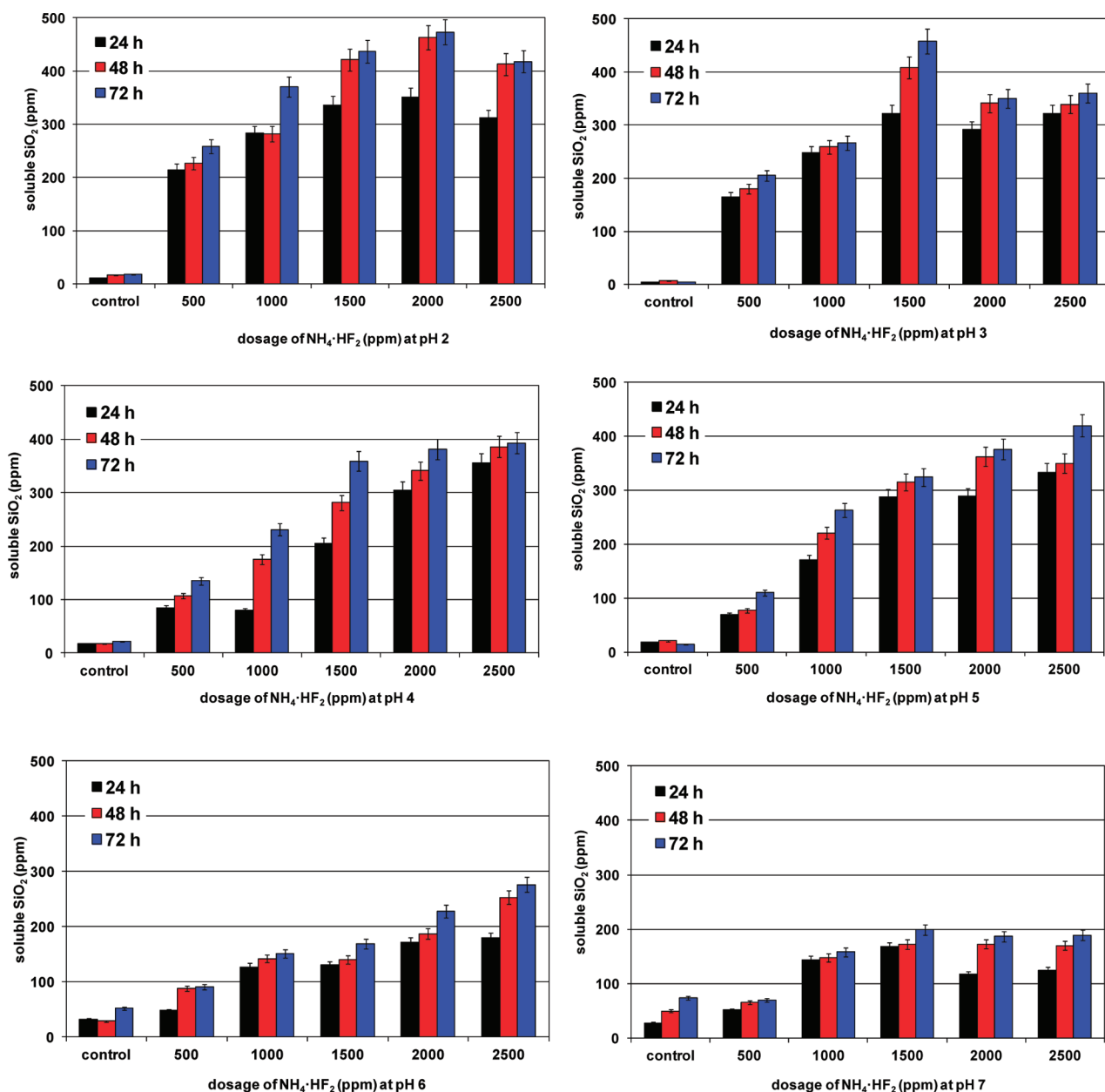


Figure 3. Dose–response graphs of silica dissolution experiments for NH_4^+HF_2 in the pH regime 2–7.

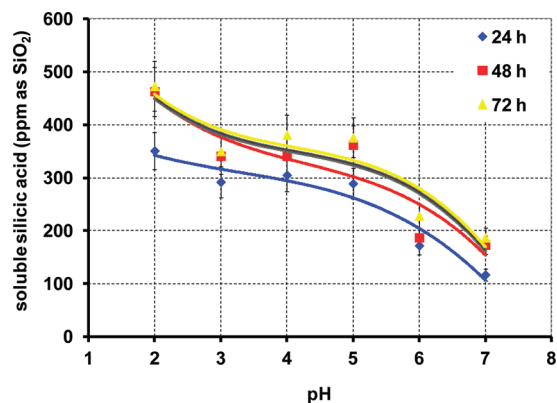


Figure 4. pH dependence of silica dissolution experiments for NH_4^+HF_2 (2000 ppm).

employed to study its silica dissolution efficiency. This was based on the weight difference of a SSD silica sample before and after dissolution. Aerosil 200 was avoided in this case because the very small particle size could lead to small particle loss during the filtration process. Two pH values (7.0 and 9.0) and additive dosages 500, 1000, 2500, and 5000 were tested. The results are shown in Figures 5 and 6. On the basis of these results, it appears that $\text{Na}_2\text{PO}_3\text{F}$ very effectively reduces the mass of the initial silica scale. Even at fairly low concentrations (500 ppm), it achieves silica dissolution $\sim 70\%$ at pH 7 and $\sim 80\%$ at pH 9. Enhanced silica dissolution at higher pH regions is expected.^{1,2} Finally, there is a small but discernible dosage dependence dissolution effect.

The methodology used suffers from the drawback that silica particles smaller than the filter pores may be lost during the filtration procedure, and thus, give a “false” positive. At this point, we cannot exclude this possibility. The rigorous stirring employed during the dissolution experiments may break larger

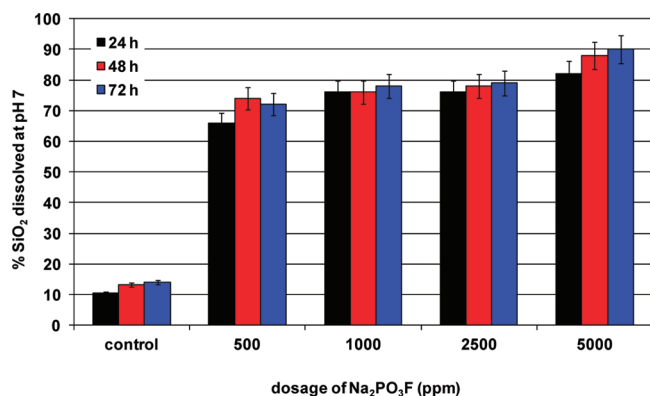


Figure 5. Dose–response graph of silica dissolution experiments for $\text{Na}_2\text{PO}_3\text{F}$ at pH 7.

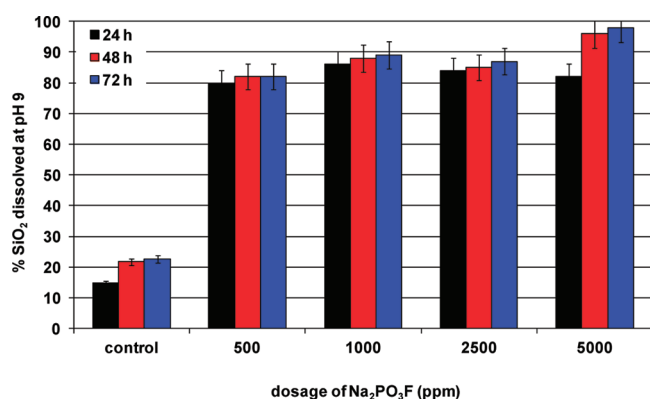


Figure 6. Dose–response graph of silica dissolution experiments for $\text{Na}_2\text{PO}_3\text{F}$ at pH 9.

silica aggregates into smaller (<200 nm) ones, and these, in turn, might escape the solid isolation. However, since all results are compared to the “control”, it is clear that stirring alone is not sufficient to disaggregate the silica particles. We propose that the additive $\text{Na}_2\text{PO}_3\text{F}$ may contribute to aggregate breakage and generation of nanometer-scale silica particles.

Study of Silica Dissolution by Scanning Electron Microscopy (SEM). The morphology of the silica particles that underwent the dissolution process in the presence of $\text{NH}_4\cdot\text{HF}_2$ and $\text{Na}_2\text{PO}_3\text{F}$ was evaluated by SEM, and the results can be compared with those from authentic samples of Aerosil 200 and SSD (after dissolution). For comparison/consistency reasons, we are dealing with silica samples that were collected after 24 h at pH 7. The images are presented in Figures 7–9. In Figure 7, we present SEM images of (undissolved) silica particles that were subjected to a dissolution experiment without any additives (“control”) at pH 7, for 24 h. No dramatic differences were noted (in comparison with silica particles not exposed to dissolution), neither in particle size nor in particle morphology. This was stated in our previous paper.²

Silica particles that were exposed to solutions containing $\text{NH}_4\cdot\text{HF}_2$ (2000 ppm dosage, at pH 7 for 24 h) were studied by SEM. The images are presented in Figure 8. For the Aerosil 200 silica particles (Figure 8, two upper images), there are no notable differences in morphology when viewed in high magnification. However, the upper left image in Figure 8 shows that the undissolved silica particles form continuous films in comparison with those that have undergone a dissolution process in the absence of $\text{NH}_4\cdot\text{HF}_2$ (Figure 7, upper left image), where the continuous film appears “rougher”. Similar observations can be put forth for the SSD silica particles exposed to $\text{NH}_4\cdot\text{HF}_2$, under the same conditions (Figure 8, two lower images). Again, the silica particles exhibit severe

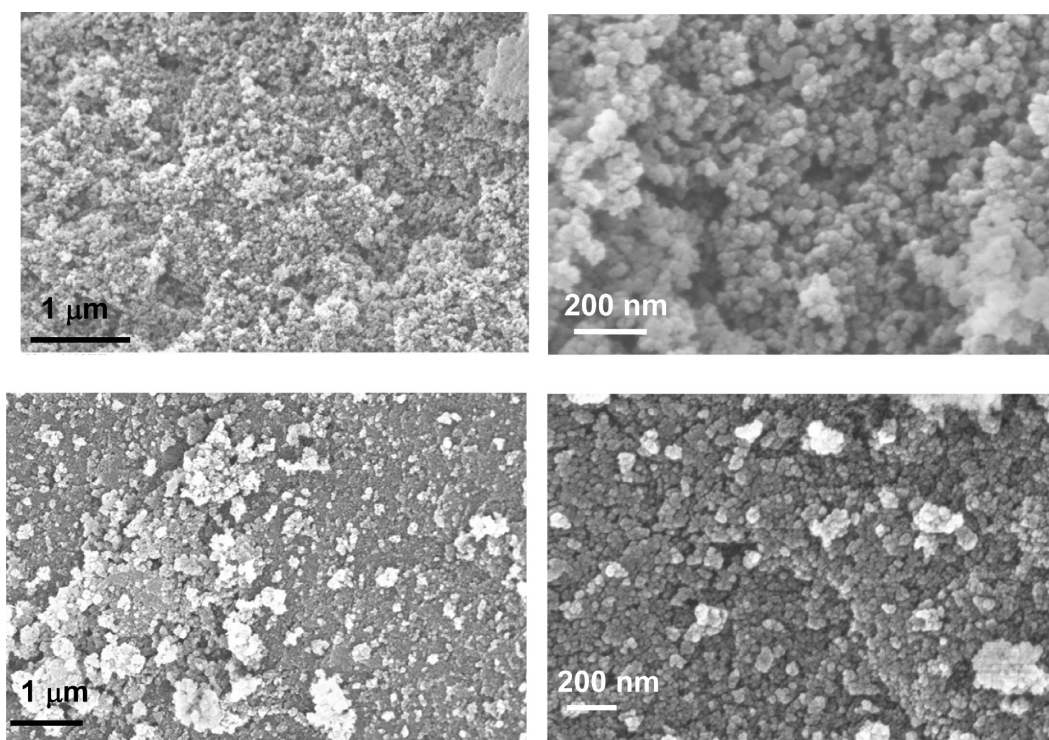


Figure 7. SEM images of silica particles after dissolution at pH 7 for 24 h from Aerosil 200 (two upper images) and synthetic SSD silica (two lower images) in the absence of any additives.

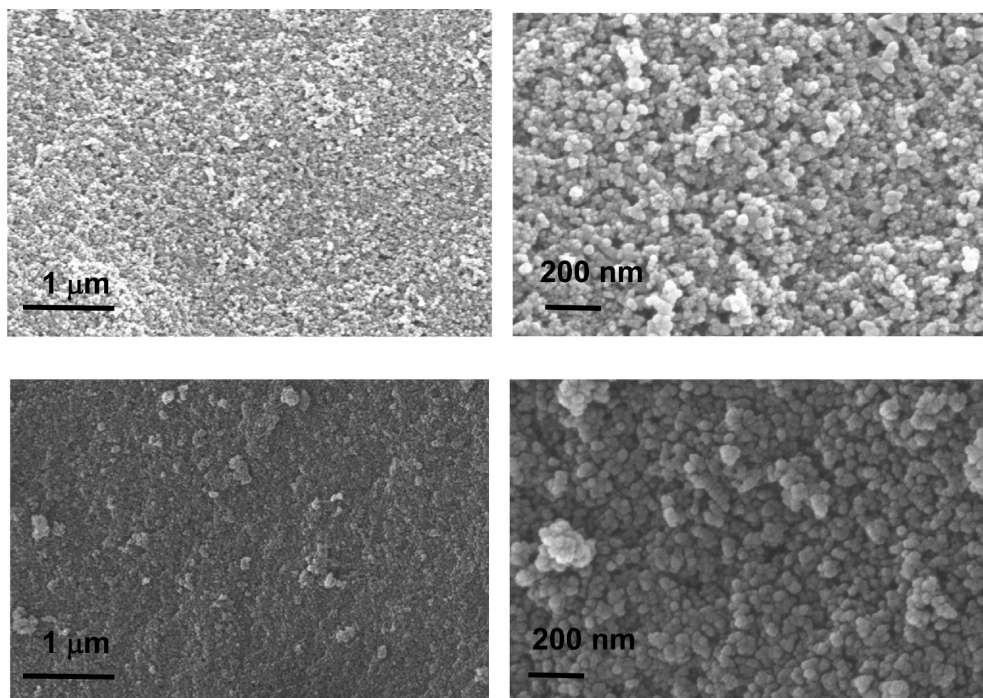


Figure 8. SEM images of silica particles after dissolution in the presence of 2000 ppm NH_4HF_2 at pH 7 for 24 h from Aerosil 200 (two upper images) and synthetic SSD silica (two lower images).

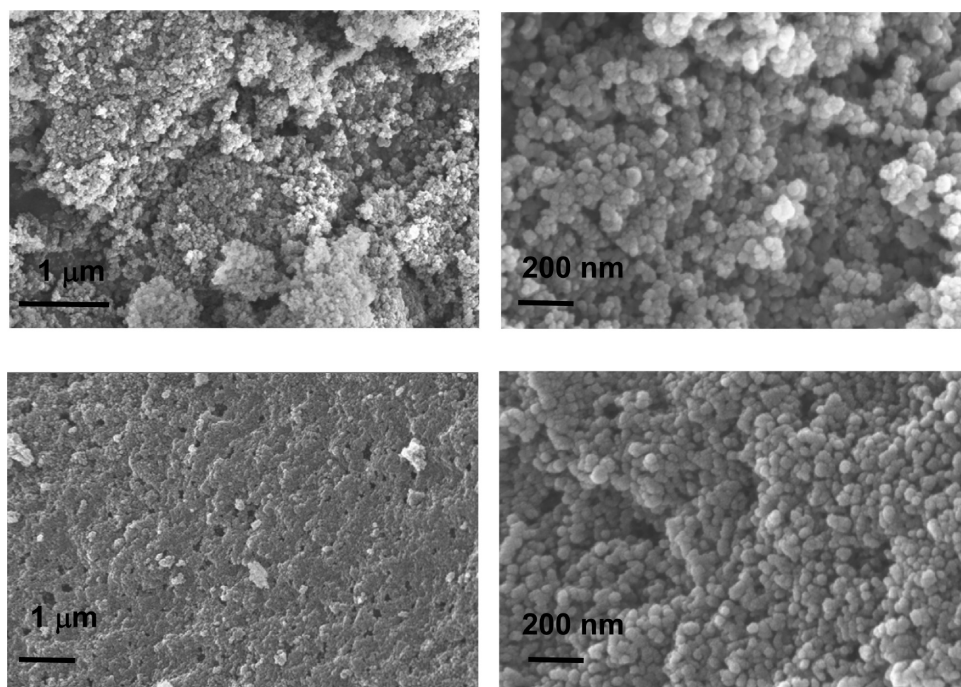


Figure 9. SEM images of silica particles after dissolution in the presence of 2000 ppm $\text{Na}_2\text{PO}_3\text{F}$ at pH 7 for 24 h from Aerosil 200 (two upper images) and synthetic SSD silica (two lower images).

aggregation and form continuous films (lower left image), although the films appear “rougher” than those for Aerosil 200 silica. Under higher magnification (lower right image), the tendency for aggregation is further revealed. It is worth noting that upon closer examination of the aggregated particles, it becomes apparent that they are composed of even much smaller elementary particles of <50 nm size.

In Figure 9 SEM images are presented of silica particles (Aerosil 200, upper two images and SSD silica, lower two

images) that have been exposed to solutions containing 2000 ppm $\text{Na}_2\text{PO}_3\text{F}$ at pH 7.0 for 24 h. Again, similar spherical particle morphologies are observed with severe aggregation. In the case of SSD silica (lower two images), there is a much more pronounced tendency for aggregation (lower two images) in comparison with Aerosil 200 silica (upper two images).

Study of Silica Dissolution by Electron Dispersive Spectrometry (EDS). All studied dissolution additives contain fluorine; therefore, the undissolved silica precipitates were also

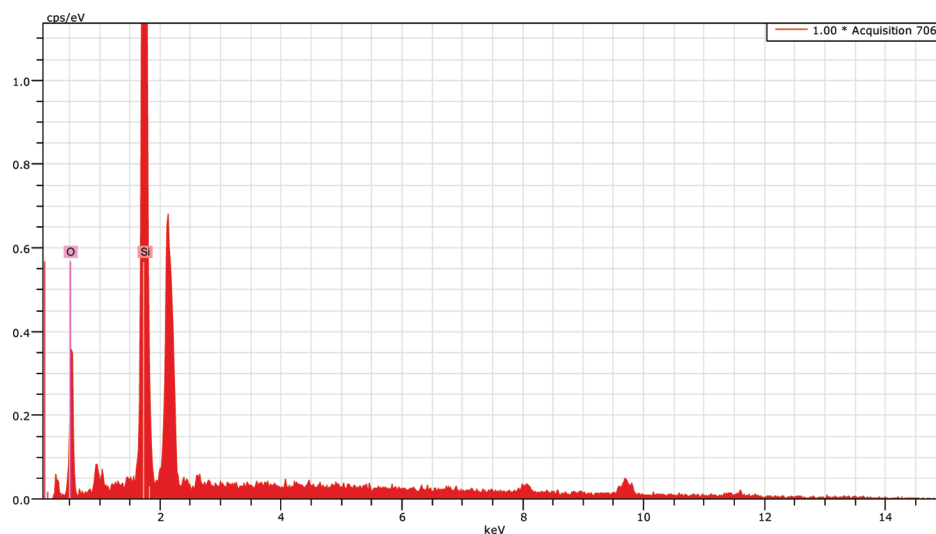


Figure 10. EDS of Aerosil 200 particles after exposure to an aqueous solution containing no additives at pH 7, after 24 h.

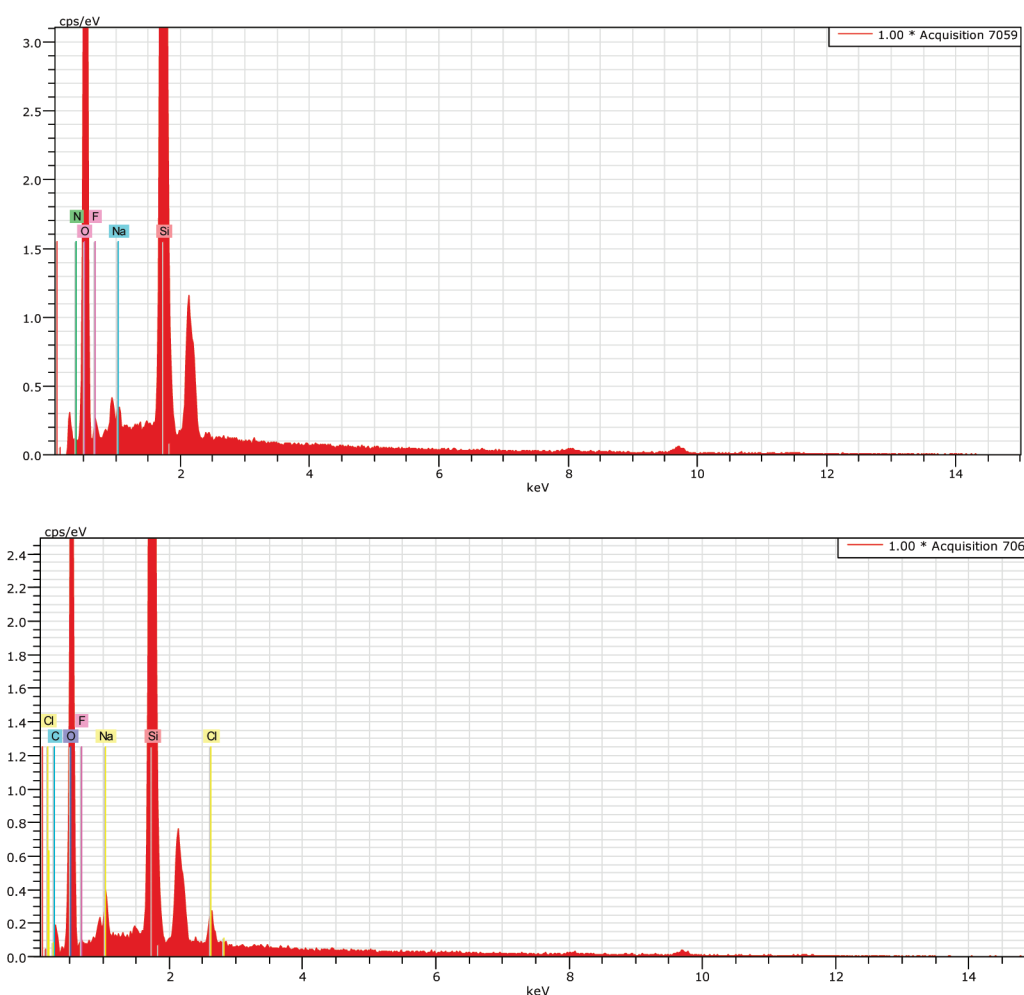


Figure 11. EDS of Aerosil 200 (upper) and SSD particles after exposure to an aqueous solution containing 2000 ppm $\text{NH}_4\cdot\text{HF}_2$ at pH 7, after 24 h.

studied by EDS to map the elements present on the surface of the particles. All silica solids studied by EDS were first thoroughly rinsed with deionized water. Figure 10 reveals that silica particles at pH 7 after 24 h of dissolution contain exclusively Si and O, as expected.

Figure 11 shows EDS of Aerosil 200 (upper) and SSD silica (lower) that have been exposed to solutions containing 2000 ppm $\text{NH}_4\cdot\text{HF}_2$ for 24 h at pH 7. Both show the presence of F, indicating that there are Si–F moieties on the surface of the particles.

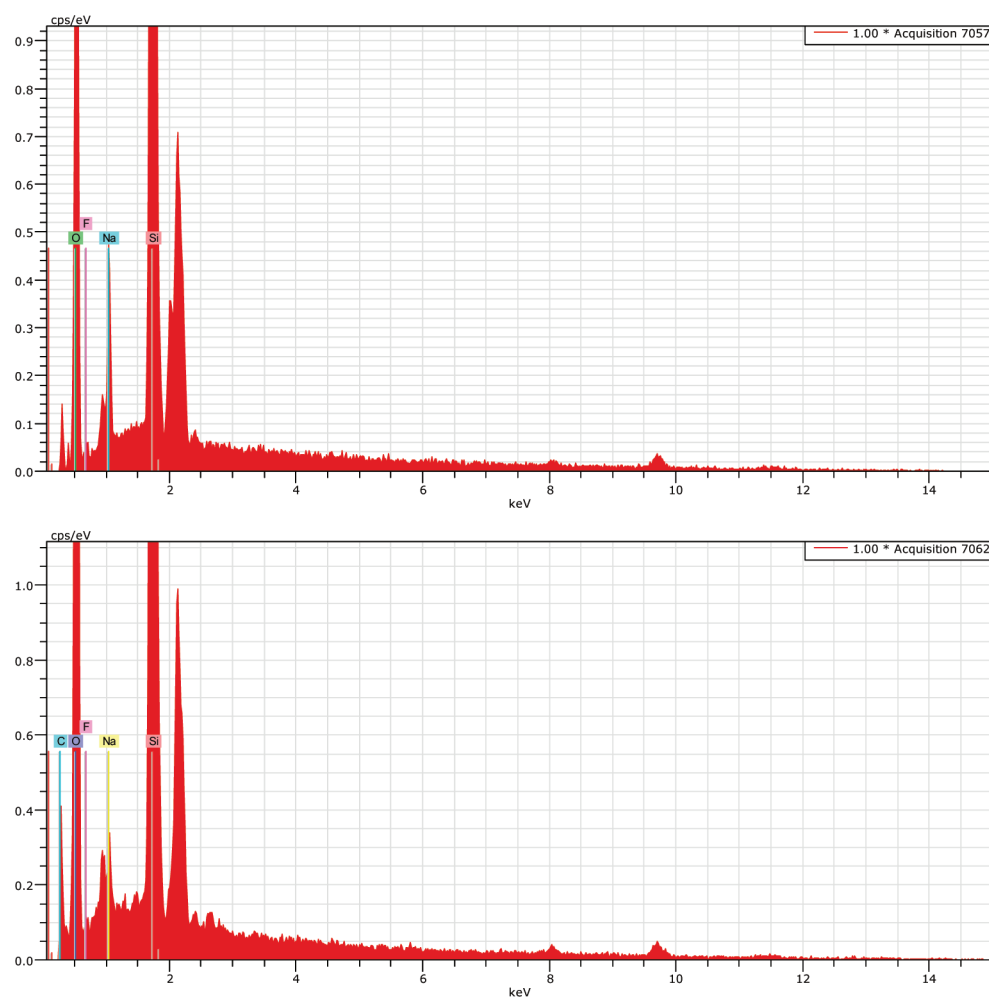
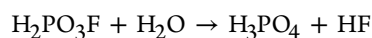
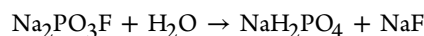


Figure 12. EDS of Aerosil 200 (upper) and SSD particles after exposure to an aqueous solution containing 2000 ppm $\text{Na}_2\text{PO}_3\text{F}$ at pH 7 after 24 h.

Figure 12 shows EDS of Aerosil 200 (upper) and SSD silica (lower) that have been exposed to solutions containing 2000 ppm $\text{Na}_2\text{PO}_3\text{F}$ for 24 h at pH 7. Here, it is interesting to note the presence of F. This event, at first glance, seems rather peculiar because the presence of P should be expected at a ratio of 1:1 with F, at ~ 2 KeV. Hence, the possibility of decomposition of $\text{Na}_2\text{PO}_3\text{F}$ needs to be invoked. There is a literature report that fluorophosphoric acid can decompose in aqueous solutions to phosphoric acid and hydrofluoric acid, according to the reaction:⁴⁷



Therefore, at pH 7, a similar reaction can be envisioned, as follows:



Hence, it is reasonable to envision F^- being the true dissolver additive. At pH 7, F^- is the dominant species, since the $\text{p}K_a$ of hydrofluoric acid is 3.17.⁴⁸ As seen in Figure 2, NH_4F is an effective silica dissolver; therefore, the dissolution activity could be, at least partially, attributed to the presence of F^- .

CONCLUSIONS

The principal findings of this work are summarized as follows: (1) A number of F-containing additives (ammonium bifluoride, NH_4HF_2 ; ammonium fluoride, NH_4F ; sodium tetrafluoroborate,

NaBF_4 ; and disodium fluorophosphate, $\text{Na}_2\text{PO}_3\text{F}$) were tested as potential silica scale dissolvers. They all showed variable dissolution efficiency, except NaBF_4 , which was totally inactive. (b) The most effective dissolver was ammonium bifluoride, NH_4HF_2 , which was extensively studied at the pH range 2–7. The highest dissolution efficiency was demonstrated in the pH range 2–4. (c) The dissolution capability of disodium fluorophosphate, $\text{Na}_2\text{PO}_3\text{F}$, was monitored not by the silicomolybdate method, but on the basis of a weight-loss approach. It showed substantial dissolution ability at pHs 7 and 9.

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Notes

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