

UDC 546.284'161-32

*V.O. Gelmboldt***FLUROSILICIC ACID: SECONDARY RAW MATERIAL AND REAGENT IN TECHNOLOGICAL PRACTICE AND PREPARATIVE SYNTHESIS (A REVIEW)****Odessa National Medical University, Odessa, Ukraine**

The present review systematizes and summarizes the results of research on utilization processes of fluorosilicic acid solutions as large-tonnage toxic by-products of phosphate fertilizers, phosphoric acid and elemental phosphorus production. Considering the marked decline in the world's fluor spar reserves, fluorosilicic acid is emerging as the main alternative source of fluoride for the chemical industry. The main ways of H_2SiF_6 processing are highlighted with obtaining of commercially demanded products: hexafluorosilicates of metals and ammonium, metal fluorides, anhydrous hydrogen fluoride, hydrochloric acid, amorphous silicon dioxide, aluminosilicates and titanosilicates catalysts, and enriched isotopes of silicon. Examples of H_2SiF_6 use as a main reagent for drinking water fluoridation municipal programs, in processes of surface modification and removal of trialkylsilyl protection in reactions of organic synthesis are also discussed. Known examples of H_2SiF_6 use as a raw material and reagent in industrial technologies and laboratory tests largely conform to principles of green chemistry.

Keywords: phosphate fertilizer, industrial waste, fluorosilicic acid, utilization, application.

DOI: 10.32434/0321-4095-2023-148-3-3-21

Introduction

Fluorine and its compounds have many uses in various fields of modern technology: from production technologies and disposal of spent nuclear fuel [1–3] to microelectronics [4–6] and pharmaceuticals [7–11]. At present, the main raw source of fluorine for chemical industry is calcium fluoride (fluor spar), with global resources estimated at 500 million tons [12,13]. Considering the current rates of use, the existing stocks of CaF_2 will be sufficient for further 100 years [14]. At the same time, the resources of fluorapatite $3Ca_3(PO_4)_2 \cdot CaF_2$ comprise 18 billion tons according to estimates of the United States Bureau of Mines [12]. Fluorapatite is used as a raw material for producing phosphate fertilizers, a large-tonnage by-product of which is fluorosilicic acid (FSA) [12–15]. Interest towards various aspects of FSA chemistry is connected with its possible use as the main alternative source of fluorine in various technological processes [12,14–17]. The USA industry is the largest producer of FSA, which forms during the processing of phosphates and apatites [12], but utilizes only about

1% of it. FSA itself has rather limited uses (fluoridation of drinking water, hardening of cement, wood preservation) [15] and is toxic ($LD_{50}=200$ mg/kg [18]). The use of FSA as a secondary chemical raw material is therefore economically and ecologically attractive to obtain various commercial products. During the last years, FSA is actively used as a reagent and raw material in preparative reactions of organic and inorganic synthesis [19,20], and in the production of mesoporous silicon dioxide [16,21,22] and aluminosilicate/titanosilicate catalysts and adsorbents [23–25]. The present review is the first attempt to analyze and to systemize known data, published mainly after 2010, relating to various aspects of FSA utilization in modern technological and laboratory practice.

Industrial sources of fluorosilicic acid

The FSA solutions can be obtained by interaction of silicon dioxide with diluted solutions of HF. However, in practice, the FSA production is integrated into technologies for processing phosphate raw materials to obtain phosphate fertilizers, phosphoric acid and elemental phosphorus [14,15].

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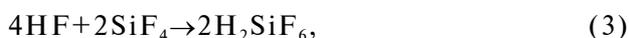
Fluorosilicic acid: secondary raw material and reagent in technological practice and preparative synthesis (a review)

Sources of raw material for mentioned productions are deposits of fluorapatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ and other fluorine-containing phosphate ores [26,27]. According to data [26], fluorine content in phosphate ores of various deposits varies within 2.0–4.9%, which corresponds to 1.29 billion tons of fluorspar or 630 million tons of fluorine according to estimations [12].

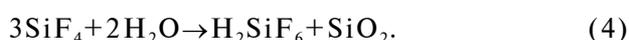
Fluorides are involved in chemical processing of phosphate raw materials [27] during production of simple superphosphate, phosphoric acid by the wet method, double superphosphate, and nitrophosphates; all processes resulting in the formation and emission of hydrogen fluoride and silicon tetrafluoride (reaction product (1) of HF with silica and silicates contained in raw material) into the gaseous phase:



Reaction gases containing HF and SiF_4 (with a predominance of the latter) undergo water absorption in scrubbers of various design with formation of 15–25% FSA solutions [28]. A high degree of absorption can be achieved by gas washing with a circulating solution of FSA. Processes in such absorptive systems are described by schemes [15]:



leading to the overall reaction:



The resulting solutions of commercial FSA usually contain a certain amount of dissolved SiO_2 . Concentrated FSA solutions (40–45%) can be obtained by distillation of more diluted solutions at room temperature and reduced pressure [15]. Overall about 39 tons of FSA could be obtained during processing of 1000 tons of phosphate raw material by the wet method [12].

It should be emphasized that processing of phosphate raw materials with formation of FSA does not remove 100% of fluorine from the commodity products as shown by the fluorides content of various phosphate fertilizers (Table 1).

According to Ramteke et al. [31], heat treatment of fertilizers at $140 \pm 5^\circ\text{C}$ could be a possible option for defluoridation in the case of simple superphosphate and diammonium phosphate. Heat treatment eliminates 57–89% and 53–93% of fluorides, respectively, thus reducing the risk of soil and water contamination by fluorides as a result of fertilizers application. However, the proposed scheme [31] of thermal defluoridation of fertilizers is a laboratory method which is hardly acceptable for large-scale industrial application. In this regard, improvement of existing technologies and development of new ones are still relevant for reducing fluorides levels in fertilizers produced via processing of phosphates.

Fluoridation of drinking water

The adoption of drinking water fluoridation as a method of caries prevention was first put into practice in the USA during the 1940s [32]. At present, municipal programs of drinking water fluoridation are implemented in about 40 countries. Water fluoridation schemes cover 100% of the population in Singapore and Hong Kong, 80% in Columbia, 75% in Israel, 73% in Ireland and 64% in the USA. About 400 million people are users of fluoridated water worldwide, including more than 200 million inhabitants of the USA [32]. Fluoridation of drinking water accounts for 11% of the total FSA industrial use [33]. Compared with other fluoridation agents (Na_2SiF_6 , NaF) [34], FSA is by far the most used one.

The use of FSA in water fluoridation programs is connected with the quick and quantitative hydrolysis of SiF_6^{2-} anion [34] according to schemes:



Table 1

Fluorides content of phosphate fertilizers

Sample	Average concentration of fluorides, %	References
Single superphosphate, India	0.42–1.16	[29]
Diammonium phosphate, India	0.14; 1.07	[29]
Ammonium nitrophosphate, India	1.33	[29]
Single superphosphate, New Zealand	1.08–1.84	[30]
Triple superphosphate, New Zealand	1.30–2.40	[30]
Monoammonium phosphate, New Zealand	1.60–2.20	[30]
Diammonium phosphate, New Zealand	1.20–3.00	[30]

The resulting fluoride-ions manifest the complex caries-prophylactic effect on the pathogenic microflora of oral cavity (bacteriostatic effect, inhibition of glycolytic enzymes), tooth enamel (transformation of hydroxyapatite into fluorapatite, remineralization of enamel) and dentine (occlusion of tubule dentine by CaF₂ deposition) [35]. Regardless of the periodic criticism of drinking water fluoridation because of toxicological effects of fluoride [36], WHO recommends this method as a key one in the set of measures for oral health improvement [35]. The economic aspects of FSA use for fluoridation of drinking water were discussed in works [37,38].

Production of hexafluorosilicates

Hexafluorosilicates of metals and ammonium have various applications [28,39,40] and occupy the first place among the products of FSA processing. Their production uses 40% of the total volume of utilized FSA [33].

Optimization of the processes to obtain Na₂SiF₆ and K₂SiF₆ using FSA solutions of various origins are discussed in works [41–44]. Ruixiang [41] reacted 10–12% FSA solutions and 25% sodium chloride solution at NaCl:FSA ratios of 1.067–0.898:



A decrease in the ratio of NaCl:FSA and velocity of reagents supply contributed to the increase in yield. Na₂SiF₆ crystals with better filterability were obtained at a ratio of 0.9. According to data [42], the use of 20% FSA solution (generated as by-product during production of phosphoric acid) in the process (7) requires the following optimal conditions: 25% excess of NaCl, reagents contact time of 40 min and temperature of 40°C. Under these conditions, the yield of Na₂SiF₆ is 94.26%. The use of NaOH as sedimentation reagent can increase yield up to 97.3%.

Solutions forming during hydrometallurgical processing of molybdenum concentrate were studied in publication [43]. These solutions contained fluorine acids H₂SiF₆ (0.32 mol/L), H₃AlF₆ (0.06 mol/L) and compounds of Fe(III) (0.046 mol/L). When using sodium carbonate (3 mol/L) as a precipitation reagent, almost total precipitation of the desired product Na₂SiF₆ is attained at pH 1.50 and 110% excess of Na₂CO₃. After separation of Na₂SiF₆, the remaining filtrate is used for precipitation of Na₃AlF₆ (synthetic cryolite) at pH > 1.50 and after increasing Na₂CO₃ excess, although the forming precipitate is contaminated by Na₃FeF₆:



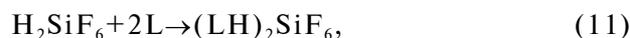
The purity of Na₂SiF₆ obtained according to scheme (8) is 99.5% and purification of Na₃AlF₆ from the admixture of iron(III) fluorocomplex can be done via extraction or fractional recrystallization.

Wang et al. [44] studied the conditions of utilization of fluorine from FSA solution (by-product in the production of nitrophosphate fertilizers; H₂SiF₆ 0.78%, HF 0.10%), using the following reaction:



Process (10) reaches completion in 1 hour at a temperature of 25°C. The efficiency of fluoride extraction is 70.22% at 400% of KNO₃ excess, while the maximal efficiency of 88.18% is achieved at 700% excess of KNO₃.

Solutions of 34% and 45% FSA were reacted with biologically active organic bases for the synthesis of ammonium hexafluorosilicates (AHFS) with composition (LH)₂SiF₆ (L=amino acids [45,46], derivatives of pyridine [47–50], aniline [51], pyrimidine [52]). These AHFS are of interest as active pharmaceutical ingredients of potential caries-prophylactic drugs:



The molar ratio of reagents comprised FSA:L=2:1, 1:1, 1:2 in the syntheses [45,46] and 3:1 in the syntheses [47–52]. The yields of AHFS were within 76–99% [48–51]. The use of FSA amounts in excess of stoichiometric ratio during the synthesis increases the yield in AHFS (11), (12). Thus, according to results of phases equilibrium study FSA provides a desalinating action in H₂SiF₆–L–H₂O systems [53,54], thus lowering the solubility of AHFS.

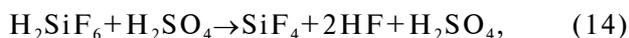
Production of metal fluorides and hydrogen fluoride

Aluminium trifluoride is the most important reactant in the process of electrolytic aluminium production [28,55]: 28% of utilized FSA is used to obtain AlF₃ [33]. The production technology of AlF₃ with the low bulk density (LBD) is based on the direct interaction of FSA with aluminium hydroxide (the so-called first-generation «wet-process» [56]):



Process (13) is multi-stage; it is accompanied

by high fluoride losses and requires the use of highly purified FSA. The reaction by-product amorphous silicon dioxide (13) can be purified from fluorine compounds and used as a filler of rubber mixtures and urethane elastomers [57]. More progressive is a «dry process» of AlF_3 production of the high bulk density (HBD) of second generation (Buss Chemtech AG, Switzerland) [56,58], based on decomposition of FSA under the action of concentrated sulphuric acid with formation of anhydrous HF [59]:



The «dry» technology is preferable from ecological and economical points of view and does not require high purity FSA. The main weakness of this technology is a significant expense of 75% H_2SO_4 – 30 t per 1 t of anhydrous HF. According to estimations performed by Dreveton [59], processing of FSA with obtaining of AlF_3 is economically more viable compared to the use of «dry» technology only for production of anhydrous HF.

At present, the third-generation technology for the production of HBD AlF_3 and anhydrous HF is at the stage of industrial implementation [56]. It is based on production and further acid decomposition of Na_2SiF_6 :



As in a case of «dry» technology, it undergoes stages (15)–(17). The third-generation process favourably differs from the «dry» method by significantly less water and sulfuric acid consumption.

Sodium fluoride and calcium difluoride belong to the number of commercially demanded products of FSA utilization [15,28]. They are obtained by interaction of FSA with the corresponding hydroxides:

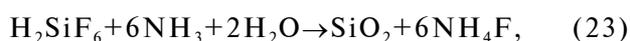


According to data [60], optimal conditions for obtaining high purity NaF (96–97%) based on 13.5% FSA are molar ratio $\text{NaOH}:\text{H}_2\text{SiF}_6=8.4-7.0:1$, temperature of 70–90°C, reaction time of 20–30 min, washing the precipitate of NaF on filter with 6–8% with NaOH or Na_2CO_3 solution at 30–50°C.

Previous works [61–63] present results of optimization of fluorine extraction conditions in the form of CaF_2 from the FSA solutions, which model fluorine-containing technological solutions [61,62] or are real technological solutions in processes of quartz etching by hydrogen fluoride acid [63]. According to ref. [61], the percentage conversion of fluoride from FSA (mixture 0.90 M H_2SiF_6 and 1.28 M HF) into CaF_2 increased from 25% to 100% when the Ca/Si ratio in the process (26) was raised from 1.12 to 3.91. However, the target product was contaminated by SiO_2 . Treatment of the CaF_2 precipitate by a solution of NaOH at temperature 45–70°C during 10 minutes led to a product purity of about 90%. Publication [61] recommends a two stage process to consistently precipitate insoluble salts of CaF_2 and $\text{Ca}_3(\text{PO}_4)_3$ by neutralizing a mixture of H_2SiF_6 and H_3PO_4 acids, using $\text{Ca}(\text{OH})_2$. A high degree of separation was achieved in a narrow range of pH 3.6–3.9. In this range, the efficiency of fluorides and phosphates extraction was 93.2–95.1% and 8.3–9.8%, respectively. According to data [63], the solid-phase neutralization of sewage waters of high-purity quartz production, containing 22–24% of FSA, by treatment with calcium oxide at temperature 50°C permits to obtain the granulated product with a content of $\text{CaF}_2 \geq 65\%$, which corresponds to metallurgical grade.

Preparation of amorphous silicon dioxide

Various ways of FSA hydrolysis were proposed to obtain mesoporous silicon dioxide – amorphous SiO_2 with the pore size 2–50 Å [64], based on the interaction of FSA with ammonia solutions [65–67], sodium carbonate [16] and sodium silicate [21,22,68]. Interactions in studied systems are described by the following general schemes:



Addition of surface-active substances (SAS) (cetyltrimethylammonium bromide (CTAB) [65], long-chain ethers of polyethylene oxide [21,22,66]) into the reactive mixtures of $\text{H}_2\text{SiF}_6-\text{NH}_4\text{OH}$ or $\text{H}_2\text{SiF}_6-\text{Na}_2\text{SiO}_3$ allows obtaining mesoporous silica

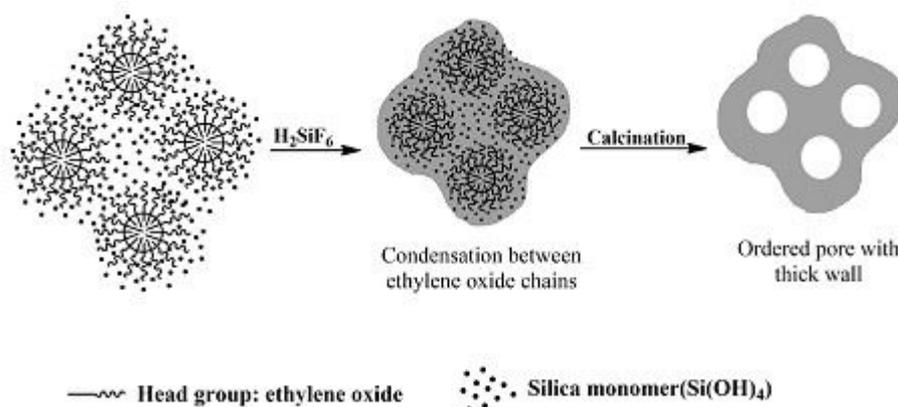


Fig. 1. Schematics of mesoporous silica formation via cationic and nonionic surfactant templating. Reprinted from [22] (Copyright (2019) Springer Nature, under a Creative Commons Attribution 4.0 International License)

dioxide of regular structure with pore size 31.2 Å [65], 4.1–4.6 Å [66], 2.5–3.1 Å [21], 2.4–3.1 Å [22] depending on surfactant type (Fig. 1).

Obtained samples of mesoporous SiO₂ can be used as filler for rubbers [68] or catalyst carriers [22]. In particular, Park et al. [22] demonstrated that a catalytic system obtained via impregnation of industrial catalyst Rh(5)/Al₂O₃ at the surface of mesoporous SiO₂ was more efficient than an industrial catalyst in the oxidative conversion of methane with hydrogen production (>90% and >80%, respectively).

In search of new effective catalysts for the synthesis of butadiene-1,3 (BD) from bioethanol and acetaldehyde, the work [69] carried out synthesis of Ta₂O₅-containing samples of ordered mesoporous silicon dioxide (OMS), obtained by using H₂SiF₆ as a source of SiO₂. The study of catalytic activity of synthesized compounds indicates better conversion and selectivity towards BD for the majority of Ta-OMS catalysts compared with two commercial Ta₂O₅/SiO₂ catalysts (Merck, Aldrich).

According to ref. [70], hydrothermal synthesis in H₂SiF₆-Si(OC₂H₅)₄-CTAB-NH₄OH solutions in the presence of ethyl acetate led to specimens of mesoporous silica dioxide with pore size 2.5–4.0 Å, characterized by high thermal and relative hydrothermal stability. These specimens of mesoporous SiO₂ were used for the creation of effectively regenerating sorbents based on iron oxide Fe₂O₃ for removal of H₂S from gaseous mixtures.

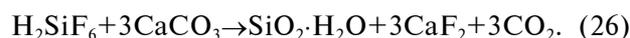
Elineema et al. [71] reported an almost quantitative processing of 34% FSA into high-quality nanoporous SiO₂ according to scheme (24). According to ref. [71], the conversion of FSA to SiO₂ following (24) leads to a product with higher purity (99.3%) compared to the commonly used technology based on the reaction of Na₂SiO₃ with

sulfuric acid (99.1%).

The pore sizes in SiO₂ specimens obtained according to reaction (24) depend on process temperature and were 123.8 Å (25°C), 194.9 Å (40°C), 222.2 Å (60°C). These materials were characterized by high thermal stability and could be used as adsorbents, fillers for polymeric materials, pharmaceutical supplements, cleaning and polishing components of toothpastes.

A procedure for the use of 13% FSA according to scheme (23) was proposed in the work [72], including subsequent use of the reaction product (amorphous nanodimensional SiO₂) as reinforcing material for rubber compounds (RC). Amorphous SiO₂, premodified by the action of p-tolytriethoxysilane and bis-(γ-triethoxypropyl)-tetrasulfide, was introduced into composition of uncured RC. The obtained composites containing 4% SiO₂ had better mechanical properties and higher thermal stability compared to the parent RC.

Zorya and Krot [73] developed the following scheme to obtain marketable products (amorphous SiO₂ and calcium difluoride) using 6–8% FSA solutions:



The purity of obtained CaF₂ (92–95%) and SiO₂ after the procedure of additional purification (total content of impurities ≤ 1·10⁻³%) satisfies the requirements for raw materials used in metallurgy and quartz glass production.

Obtaining of aluminosilicate and titanosilicate catalysts

Aluminosilicates are a group of natural and synthetic compounds of porous structure that are widely used in modern technological practice and

actively studied as heterogeneous catalysts in petrochemical synthesis and ecological catalysis [74–77]. The so-called zeolites (molecular sieves, MS) are of particular interest. They are crystalline aluminosilicates whose three-dimensional structure consists in tetrahedral fragments of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ interlinked at the apexes into carcasses and with a Si:Al ratio larger than 1 [74].

Apparently, Jeong et al. [65] were the first who used FSA as a source of silicon dioxide for hydrothermal synthesis of mesoporous MS (MMS) by interaction in solutions H_2SiF_6 – $\text{Al}(\text{NO}_3)_3$ –CTAB– NH_4OH . The obtained samples of Si–Al–MMS with pore size of 30.0–34.7 Å had high specific surface area values (801–827 m^2/g). In a series of publications [78–80], a simple synthesis method of MMS in mild conditions, based on hydrolysis reaction of H_2SiF_6 in a NH_4OH medium in the presence of a surface active component, CTAB [65], was used to obtain different Si–Al–MMS with specific surface areas of 807–820 m^2/g [78], 811–971 m^2/g [79] and 981 m^2/g [80]. The adsorption and catalytic properties of these Si–Al–MMS made them effective as adsorbents of CO_2 and water vapour [78] as well as carriers of bimetallic Pt/Pd-catalysts for naphthalene hydrogenation [79] and aromatic component of petroleum cracking [80].

In publication [24], the proposed method of MMS synthesis [65] was modified by substituting CTAB with $[(\text{C}_3\text{H}_7)_4\text{N}]\text{Br}$ and $\text{Al}(\text{NO}_3)_3$ with $\text{Al}(\text{OH})_3$ while maintaining the general concept of hydrothermal synthesis. Increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and reaction time led to transformation of the resulting crystalline phase from the orthorhombic to monoclinic. The reaction product, zeolite ZSM-5, demonstrates catalytic activity in transalkylation reactions and disproportionation of toluene and 1,2,4-trimethylbenzene. Stability of ZSM-5 catalytic characteristics was observed in the specified reactions.

The first examples of obtaining mesoporous Ti-containing analogues of aluminosilicates Si–Ti–MMS in reactions of hydrothermal synthesis based on FSA were published in works [65,81]. According to data [81], products of the interaction in solutions of H_2SiF_6 – $\text{Ti}(\text{OC}_3\text{H}_7)_4$ –CTAB– NH_4OH are crystalline samples of Si–Ti–MMS with the pore size of 31.0–31.4 Å and specific surface area of 882–911 m^2/g . It was noted [81] that incorporation of Ti into Si–MMS composition reduces the corresponding specific surface area and pore volume compared to pure silicon analogue Si–MMS. Experimental results for the catalytic activity of synthesized Si–Ti–MMS in the oxidation reaction of 2,6-*di*-tertbutylphenol (2,6-DTBP) and epoxidation of cyclohexene (CH) under

the action of H_2O_2 showed that catalytic conversion for 2,6-DTBP and CH increases linearly with the growth of Ti content in Si–Ti–MMS structure within the limits of 1–4 mol.%.

In publication [82], samples of Si–Ti–MMS synthesized with the use of procedure [65,81] were studied in the reaction of oxidative desulfurization (ODS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). According to data [82], catalytic activity of Si–Ti–MMS in reaction with 4,6-DMDBT increases with Ti content up to a maximum at 5% w/w Ti and then substantially decreases at 10% (w/w) Ti content. Compared with other Ti-containing catalysts, Si–Ti–MMS manifests higher catalytic activity in ODS reactions with participation of DBT and 4,6-DMDBT.

According to data [23], hydrothermal synthesis in the system H_2SiF_6 – $\text{Ti}[(\text{OCH}(\text{CH}_3)_2)_4]$ –CTAB– NH_4OH – H_2O_2 led to obtaining Si–Ti–MCM-41, a Ti-containing analog of known mesoporous material MCM-41 [83,84]. It was established that the product of reaction at molar ratios Si/Ti 60 and CTAB/Si 0.81 and synthesis temperature 343 K had a specific surface area of 1040 m^2/g and demonstrated a high catalytic activity in the epoxidation reaction of cyclohexene by *tert*-butyl hydroperoxide (TBHP).

Production of hydrochloric acid

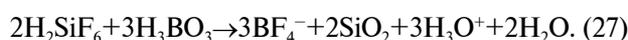
Among commercially viable products of FSA solutions utilization can be also included hydrochloric acid (HCl), one of the most important industrial chemical agents [85]. In work [86], it was shown the possibility of processing 25% industrial FSA, a by-product of phosphoric acid production, to obtain concentrated solutions of HCl (30–33%). At the basis of the proposed scheme there is an exchange reaction (7) between H_2SiF_6 and technical NaCl (90%). The reaction products, 18% aqueous solution of hydrochloric acid HCl and precipitate of sodium hexafluorosilicate Na_2SiF_6 , were separated by filtration using a membrane pump. The precipitate was washed with water, dried at 100°C and underwent further processing resulting in 6–7% NaOH solutions with yield of 70–80% and a mixture of calcium fluoride and silicon dioxide, a potential raw material for cement industry [87]. In its turn, azeotropic distillation of the HCl solution in the presence of sulphuric acid at an optimal volume ratio $V_{\text{HCl}}/V_{\text{H}_2\text{SO}_4}=1.33$ led to the production of a 30.9% HCl solution with the yield of about 60%.

Surface modification

It is well known that numerous technologies of surface modification basically attempt to provide new properties and functions to a particular material, while

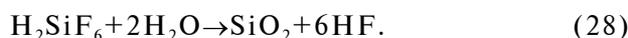
maintaining its initial bulk properties [88]. In the modern arsenal of surface modification methods, an important role is played by chemical treatment of the surface and processes of liquid phase deposition (LPD) in which FSA solutions were successfully used.

The method of deposition from the liquid phase (LPD) in $\text{H}_2\text{SiF}_6\text{-H}_3\text{BO}_3$ solutions is used for coating thin films of amorphous SiO_2 on various substrata such as glass [89], polymer material ARTON [90], silicon plates of n-type and glass [91]. The interaction in solutions could be described by the following scheme:



Process (27) is carried out under mild conditions at temperatures of 50°C [89], 40°C [90], and 40–60°C [91]. Moreover, SiO_2 films are chemically stable, possess high dielectric and mechanical characteristics and are promising candidates as dielectric materials in microelectronics [89,91] and reflective coatings [90].

Whitsitt and Barron [92] have applied coatings of SiO_2 films on single-walled carbon nanotubes (SWCNTs) using hydrolysis in a $\text{SWCNTs-H}_2\text{SiF}_6$ system at 30°C in the presence of SAS – dodecyl(trimethyl ammonium) bromide (1%) and sodium dodecyl sulfate (1%):



The film thickness was controlled by reaction time and selected SAS. According to ref. [92], sensor devices are a possible area of application for materials based on SWCNTs-SiO_2 .

In works [93,94], the LPD process with the use of FSA was applied for coating a SiO_2 film on silica balls, organized into a tightly packed monolayer of hexagonally ordered particles, to obtain a nanostructured surface. A solution of 35% FSA enriched with silica served as reagent for the following reactions [93]:

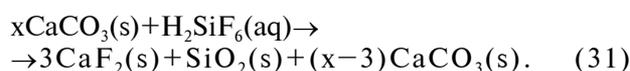


HF formed according to (30) causes etching of silica spheres with reduction of their sizes. It is expected that materials based on silica surface modified by LPD method could be used as substrates to influence biological systems, such as cells and bacteria [93].

Thin films based on SiO_2 are extensively used

in electronics technologies owing to their high electric insulation properties [95]. Thus, a simple and effective LPD method, based on hydrolysis of FSA solutions additionally saturated by SiO_2 with subsequent annealing at 700–900°C, was used for application of SiO_2 passivation films on the surface of n-type silicon solar cells (scheme (28), 50°C) [96,97] and p-type polycrystalline silicon (scheme (27), 40°C) [98] of large size (156 mm×156 mm). The obtained films showed high quality and provided 19.06% [96], 19.5% [97] efficiency and high antireflection characteristics [98] of solar elements of big sized silicon plates. In review [99], a comparative analysis of various methods of deposition of SiO_2 films on silicon surfaces of solar cells (thermal annealing, plasma-enhanced chemical vapour deposition, ozone-based oxidation, LPD) allowed identifying LPD method as low-cost, simple, realized at low temperatures and with a high rate of SiO_2 precipitation.

Calcium carbonate, a material widely used as sorbent in desulfurization processes of waste gases [100,101] and as filler in paper production [102], is an example of surface modification, described in work [103]. The known disadvantages of CaCO_3 are its low acid resistance and surface resistance, which stimulate the development of technologies of surface modification of calcium carbonate. The objects of study in ref. [103] were samples of CaCO_3 with 98.7% purity, an average particles size of 2.7 μm and a relative density of 2.69. The modifying agent was 20% FSA with molar ratios $\text{H}_2\text{SiF}_6\text{:CaCO}_3=0.05, 0.1,$ and 0.2. Interaction at the surface of CaCO_3 is described by the following scheme:



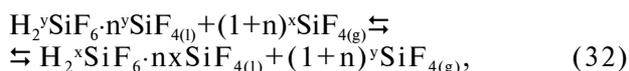
The reaction products (31), amorphous SiO_2 and calcium fluoride, precipitated onto the entire surface of CaCO_3 in the form of a thin film. The results of solubility determination of CaCO_3 samples in sulfuric acid with pH 4.0 before and after surface modification point to higher acid resistance of modified specimens.

Separation of silicon isotopes

The natural abundances of the three stable isotopes of silicon ^{28}Si , ^{29}Si and ^{30}Si are 92.21, 4.70 and 3.09%, respectively [104]. The enriched silicon isotopes are used in geochemistry [105], astrophysics [106], in experiments to determine the Avogadro constant [107].

Among methods of separation of silicon isotopes for large-scale production (dozens of kg per year), the most promising are the processes based on

chemical exchange reactions and centrifugation of gases [108]. The results from studies of chemical exchange reaction in the «gas–liquid» system were presented in the patent [109]:



in which compound with the composition $\text{H}_2^y\text{SiF}_6 \cdot n^y\text{SiF}_4$ is a product of saturation of FSA by silicon tetrafluoride and is a so-called high-silica fluorosilicic acid. In process (32), an isotope exchange occurs between the water solution containing $\text{H}_2\text{SiF}_6 \cdot n\text{SiF}_4$ component (where $n \geq 0$) and the gas containing SiF_4 . The exchange is accompanied by enrichment of lighter isotope of ^{28}Si in the liquid phase and of heavier isotopes of ^{29}Si and ^{30}Si in the gaseous phase.

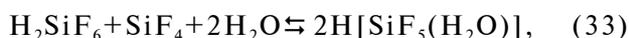
According to data [109], the highest value of separation factor α for ^{28}Si , which is possible to achieve in the system (32), is 1.021 (Table 2).

Table 2

Separation factors α of ^{28}Si at 293 K using aqueous saturated high-silica fluorosilicic acid solution as the raw materials

Aqueous saturated high-silica fluorosilicic acid solution		Separation factor α of ^{28}Si
$\text{H}_2\text{SiF}_6 \cdot n\text{SiF}_4$ (wt.%)	Free HF (wt.%)	
56.14	1.53	1.021
56.69	3.97	1.019
56.91	6.59	1.016

At the same time, chemical exchange in the system in which FSA solution of azeotropic composition (36%, 10% free HF) undergoes distillation at 116.3°C, appeared to be a more efficient method of silicon isotope separation. The calculated value of the separation factor α for ^{28}Si for distillate was 1.022. In the context of the patent discussion [109], it should be noticed that the composition of one of the equilibrium members (32), high-silica fluorosilicic acid $\text{H}_2\text{SiF}_6 \cdot \text{SiF}_4$, obtained by saturation of FSA of stoichiometric composition H_2SiF_6 by silicon tetrafluoride, is more correctly described by the formula $\text{H}[\text{SiF}_5(\text{H}_2\text{O})]$:



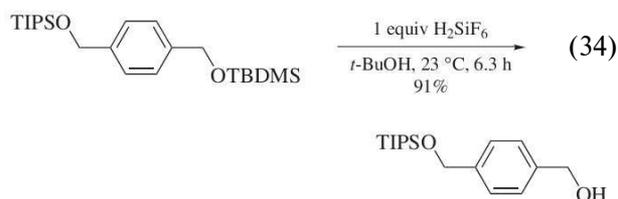
which is confirmed by numerous spectral and structural observations [110,111]. The same comment applies to schemes (29) and (30) given above.

Desilylation reactions

As noted in ref. [112], FSA is one of the best

reagents to break Si–O bonds. Unlike hydrofluoric acid, which is often used in desilylation reactions, FSA possesses greater selectivity and can be used in stoichiometric and even catalytic amounts under mild conditions of synthesis. The first examples of FSA use for deprotection of trialkylsilyl ethers in alcohols were published in the 1990s. Pilcher et al. [113,114] used solutions of FSA 31% in organic solvents to break the Si–O bonds in trialkylsilyl ethers – *tert*-butyldimethylsilyl (TBDMS) and triisopropylsilyl ethers (TIPS).

As is seen from scheme (34), FSA has specific characteristics to remove differentially the protection of the ether TBDMS while retaining the TIPS fragment [113]:



It was shown [114] that the solvent nature is an important factor influencing desilylation. After a series of experiments, the system of solvents 90:10 MeCN/*t*-butanol was considered optimal in terms of selectivity ratio, reaction rate and FSA concentration.

The effectiveness of FSA in the process of desilylation of trimethylsilylacetylenes, products of Sonogashira reaction, was demonstrated in publications [19,115,116] and dissertation [117]. The desilylation process led to nonsymmetrical acetylenes and five-membered heterocycles – 1-benzyl-4-aryl-1H-1,2,3-triazoles, 2-(aryl)benzofurans [115], and also exocyclic allenic cyclobutanes [116]. During the study of the synthetic possibilities of FSA in the Sonogashira reaction, it was stated that the amount of FSA in the reaction system can be reduced from 1.5 to 0.5 equivalents without any negative influence on the degree of conversion or prolongation of the reaction time (Fig. 2).

Thus, the acid properties of FSA do not influence its activity in the desilylation process [117]. The procedure of trialkylsilyl protection removal by FSA action is often used at different stages of the synthesis of natural bioactive compounds, their derivatives and metabolites – epothilone A [118], polyanthellin A [119], calcitriol, 5-*epi*-hexacyclinol, desoxohexacyclinol [120–122], and tambjamine alkaloids [123].

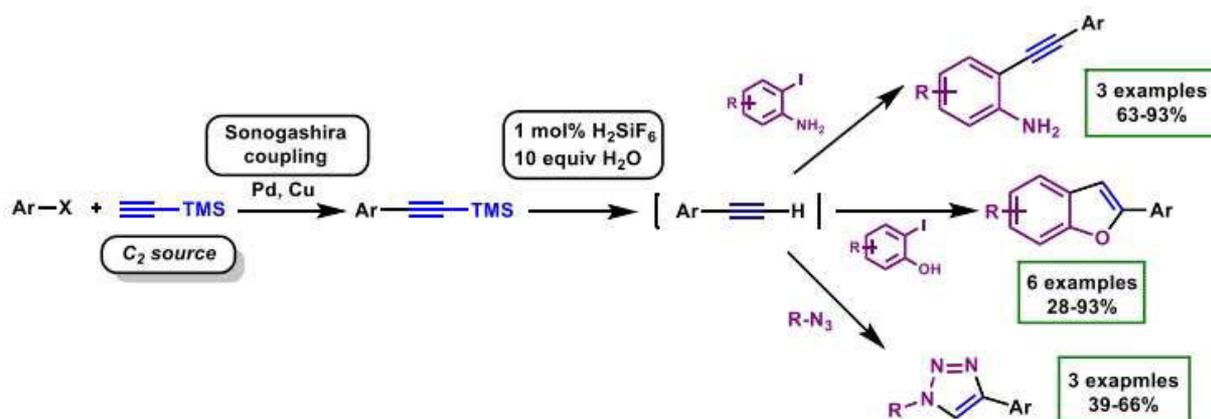


Fig. 2. Compound types synthesized using catalytic amount of H_2SiF_6 [117]

Conclusions

The present review allows identifying some general tendencies from the results of original publications appeared during the last 10–15 years in various fields of FSA applied use. First, developers' attention persists toward the improvement of multi-tonnage processes using FSA to obtain the basic products of fluoride technologies (aluminium trifluoride, hydrogen fluoride, calcium difluoride, sodium hexafluoridosilicate, sodium fluoride). The production technology of HBD AlF_3 and anhydrous HF of third generation [58,124], developed by Buss ChemTech AG (Switzerland), is an important achievement in this field. This technology ensures a high purity of target products while reducing reagents consumption, including water, and increasing compliance with environmental protection requirements. According to estimations [124], the implementation of this technology will allow to produce more than 200,000 tons of anhydrous hydrogen fluoride by 2023. At the same time, there is a sharp increase of published work in the field of relatively low-tonnage, low-energy sophisticated technologies using FSA as a raw material. One of the most important developments in this direction is the synthesis of new aluminosilicates and related metal silicate catalysts with an ordered mesoporous structure that show high conversion and selectivity in reactions of disproportionation, oxidation and desulfurization of organic substrates. It has been repeatedly emphasized [16,24,65,78,82], that the use of industrial solutions of FSA (a toxic by-product of phosphate fertilizers production) as a raw material for synthesis of new catalytic agents is very promising from the economical, ecological and social point of view. The present review also summarized and discussed the results of studies using FSA as a raw material for obtaining of amorphous silicon dioxide,

hydrochloric acid, separation of silicon isotopes and reagent for fluoridation of drinking water and removal of trialkylsilyl protection. It is possible to predict the emergence of new fields of FSA use, in particular for the synthesis of pharmaceutical substances with high anticaries and hyposensitive activity [48,50,52,125,126]. In conclusion it is important to remind the evident success of studies using FSA as a raw material and reagent in various processes, whose development could be further fostered by economic factors [59,67,127], requirements for environmental protection [13,17,23,29–31,67,68,70,86,128], increase in utilization quality of products [70,71,109,129,130], the need to minimize wastes, consumables and solvents [56,86,87,112,131,132] as well as energy expenditure [21,22,65–67,71,72,78–82,89–91,96,97,113–116]. All these factors clearly correspond to known general principles of «green chemistry» [133] and follow the modern trends of development of laboratory and technological practice.

Acknowledgements

The author is deeply indebted to the brave soldiers of the Armed Forces of Ukraine that made possible the writing of this article. The author thanks Dr. Davide A.L. Vignati (Université de Lorraine and CNRS, France) for helpful discussion and assistance during the preparation of the manuscript for publication.

REFERENCES

1. Morel B., Duperret B. Uranium and fluorine cycles in the nuclear industry // *J. Fluorine Chem.* – 2009. – Vol.130. – P.7-10.
2. Borgard J.M., Herbelet F., Gwinner B. Recycling hydrofluoric acid in the nuclear industry: The over azeotropic flash process (OVAF) // *J. Fluorine Chem.* – 2016. – Vol.185. –

P.17-23.

3. *Behavior* and distribution of nuclides in the fluoride volatility process of uranium containing molten salt fuel / Sun L., Niu Y., Hu C., Wang X., Zhao Z., Chen J., Cai X., Fu H., Dou Q., Li Q. // *J. Fluorine Chem.* – 2022. – Vol.261-262. – Art. No. 110016.

4. *Cardinaud C.* Fluorine-based plasmas: main features and application in micro- and nanotechnology and in surface treatment // *Comp. Rend. Chim.* – 2018. – Vol.21. – P.723-739.

5. *Ober C.K., Kafer F., Deng J.* Review of essential use of fluorochemicals in lithographic patterning and semiconductor processing // *J. Micro/Nanopattern. Mater. Metrol.* – 2022. – Vol.21. – Art. No. 010901.

6. *Recent* advances in fluorinated graphene from synthesis to applications: critical review on functional chemistry and structural engineering / Chen X., Fan K., Liu Y., Liu X., Wang X. // *Adv. Mater.* – 2022. – Vol.34. – Art. No. 2101665.

7. *O'Hagan D.* Fluorine in health care: organofluorine containing blockbuster drugs // *J. Fluorine Chem.* – 2010. – Vol.131. – P.1071-1081.

8. *Next* generation organofluorine containing blockbuster drugs / Han J., Remete A.M., Dobson L.S., Kiss L., Izawa K., Moriwaki H., Soloshonok V.A., O'Hagan D. // *J. Fluorine Chem.* – 2020. – Vol.239. – Art. No. 109639.

9. *Applications* of fluorine in medicinal chemistry / Gillis E.P., Eastman K.J., Hill M.D., Donnelly D.J., Meanwell N.A. // *J. Med. Chem.* – 2015. – Vol.58. – P.8315-8359.

10. *Metabolic* and pharmaceutical aspects of fluorinated compounds / Johnson B.M., Shu Y.-Z., Zhuo X., Meanwell N.A. // *J. Med. Chem.* – 2020. – Vol.63. – P.6315-6386.

11. *Chemical* aspects of human and environmental overload with fluorine / Han J., Kiss L., Mei H., Remete A.M., Ponikvar-Svet M., Sedgwick D.M., Roman R., Fustero S., Moriwaki H., Soloshonok V.A. // *Chem. Rev.* – 2021. – Vol.121. – P.4678-4742.

12. *Villalba G., Ayres R.U., Schroder H.* Accounting for fluorine: production, use, and loss // *J. Ind. Ecology.* – 2007. – Vol.11. – P.85-101.

13. *Fuge R.* Fluorine in the environment, a review of its sources and geochemistry // *Appl. Geochem.* – 2019. – Vol.100. – P.393-406.

14. *Harsanyi A., Sandford G.* Organofluorine chemistry: applications, sources and sustainability // *Green Chem.* – 2015. – Vol.17. – P.2081-2086.

15. *Meshri D.T.* The modern inorganic fluorochemical industry // *J. Fluorine Chem.* – 1986. – Vol.33. – P.195-226.

16. *Recovery* of high surface area mesoporous silica from waste hexafluorosilicic acid (H_2SiF_6) of fertilizer industry / Sarawade P.B., Kim J.-K., Hilonga A., Kim H.T. // *J. Hazard. Mater.* – 2010. – Vol.173. – P.576-580.

17. *Joshi A.N.* A review of processes for separation and utilization of fluorine from phosphoric acid and phosphate fertilizers // *Chem. Pap.* – 2022. – Vol.76. – P.6033-6045.

18. *Karen E., Haneke M.S., Bonnie L.* Sodium hexafluorosilicate [CASRN 16893-85-9] and fluorosilicic acid [CASRN 16961-83-4] // Review of toxicological literature. – 2001. – P.1-26.

19. *Hexafluorosilicic* acid as a novel reagent for the desilylation of silylacetylenes: Application in sequential Sonogashira coupling and click reaction / Sinai A., Meszaros A., Balogh A., Zwillinger M., Novak Z. // *Synthesis.* – 2017. – Vol.49. – P.2374-2388.

20. *Synthesis*, crystal structure, and magnetic properties of a new vanadium fluoride hydrate $V_2F_6 \cdot 4H_2O$ / Nakhil S., Weber D., Irran E., Lerch M., Schwarz B., Ehrenberg H. // *Z. Kristallogr.* – 2013. – Vol.228. – P.347-350.

21. *Kim J., Park K.W., Kwon O.Y.* Preparation of mesoporous silica by the rapid gelation of Na_2SiO_3 and H_2SiF_6 in aqueous surfactant solution // *Micropor. Mesopor. Mater.* – 2019. – Vol.285. – P.137-141.

22. *Preparation* of mesoporous silica by nonionic surfactant micelle-templated gelation of Na_2SiO_3 and H_2SiF_6 and application as a catalyst carrier for the partial oxidation of CH_4 / Park K.W., Kim J.Y., Seo H.J., Kwon O.Y. // *Sci. Rep.* – 2019. – Vol.9. – Art. No. 13360.

23. *Synthesis* of titanium containing MCM-41 from industrial hexafluorosilicic acid as epoxidation catalyst / Liu T., Jin F., Wang X., Fan Y., Yuan M. // *Catal. Today.* – 2017. – Vol.297. – P.316-323.

24. *Synthesis* of ZSM-5 with the silica source from industrial hexafluorosilicic acid as transalkylation catalyst / Jin F., Wang X., Liu T., Wu Y., Xiao L., Yuan M., Fan Y. // *Chinese J. Chem. Eng.* – 2017. – Vol.25. – P.1303-1313.

25. *Effective* removal of fluorine ions in phosphoric acid by silicate molecular sieve synthesized by hexafluorosilicic acid / Zhang J., Tian C., Xu Y., Chen J., Xiao L., Wu G. // *Sep. Purif. Technol.* – 2023. – Vol.305. – Art. No. 122395.

26. *Salas B.V., Wiener M.S., Martinez J.R.S.* Phosphoric acid industry: problems and solutions // *Phosphoric acid industry.* Wiener M.S., Valdez B., ed. – InTechOpen, 2017. – P.83-99.

27. *Leikam D.F., Achorn F.P.* Phosphate fertilizers: production, characteristics, and technologies // *Phosphorus: agriculture and the environment.* Agronomy monograph no. 46. Sims T., Sharpley A.N., ed. – American Society of Agronomy, Inc., 2005. – P.23-50.

28. *Fluorine* compounds, inorganic / Aigueperse J., Mollard P., Devilliers D., Chemla M., Faron R., Romano R., Cuer J.P. // *Ullmann's encyclopedia of industrial chemistry.* – Weinheim: Wiley, 2012. – P.428-429.

29. *tudy* of fluoride content in some commercial phosphate fertilizer / Ramteke L.P., Sahayam A.C., Ghosh A., Rambabu U., Reddy M.R.P., Popat K.M., Rebary B., Kubavat D., Marathe K.V., Ghosh P.K. // *J. Fluorine Chem.* – 2018. – Vol.210. – P.149-155.

30. *Fluoride:* a review of its fate, bioavailability, and risks of fluorosis in grazed pasture systems in New Zealand / Cronin S.J., Manoharan V., Hedley M.J., Loganathan P. // *N. Z. J.*

Agric. Res. – 2000. – Vol.43. – P.295-321.

31. *Removal* of fluoride contaminant in phosphate fertilizers through solid state thermal treatment / Ramteke L.P., Sarode D.D., Marathe Y.S., Ghosh P.K. // *J. Fluorine Chem.* – 2021. – Vol.241. – Art. No. 109693.

32. *Mullen J.* History of water fluoridation // *British Dental J.* – 2005. – Vol.199. – P.1-4.

33. *Will R.K.* The benefits of isolating & utilizing fluorine from phosphate operations // *Proc. Eng.* – 2016. – Vol.138. – P.267-272.

34. *Urbansky E.T.* Fate of fluorosilicate drinking water additives // *Chem. Rev.* – 2002. – Vol.102. – P.2837-2854.

35. *Ullah R., Zafar M.S.* Oral and dental delivery of fluoride: a review // *Fluoride.* – 2015. – Vol.48. – P.195-204.

36. *Peckham S., Awofeso N.* Water fluoridation: a critical review of the physiological effects of ingested fluoride as a public health intervention // *Sci. World J.* – 2014. – Vol.2014. – Art. No. 293019.

37. *Comparison* of hydrofluorosilicic acid and pharmaceutical sodium fluoride as fluoridating agents – a cost-benefit analysis / Hirzy J.W., Carton R.J., Bonanni C.D., Montanero C.M., Nagle M.F. // *Environ. Sci. Policy.* – 2013. – Vol.29. – P.81-86.

38. *Belotti L., Frazao P.* Intervening factors in the costs of fluoridation in water supply systems: a case study in seven population sizes // *Eng. Sanit. Ambient.* – 2021. – Vol.26. – P.785-791.

39. *Gelmboldt V.O., Kravtsov V.Ch., Fonari M.S.* Ammonium hexafluoridosilicates: Synthesis, structures, properties, applications // *J. Fluorine Chem.* – 2019. – Vol.221. – P.91-102.

40. *Ouasri A., Rhandour A.* Structural, vibrational, thermal, phase transitions, and properties review of alkylammonium, alkylenediammonium, and aminoacid hexafluorosilicate salts // *Russ. J. Coord. Chem.* – 2021. – Vol.47. – P.502-517.

41. *Ruixiang Z.* Process optimization in batch crystallization of sodium fluosilicate // *Cryst. Res. Technol.* – 2005. – Vol.40. – P.243-247.

42. *Batiha M.M., Al-Harabsheh M.* The effect of reaction conditions on the precipitation of sodium hexafluorosilicate produced from waste hexafluorosilicic acid // *Pol. J. Chem. Tech.* – 2011. – Vol.13. – P.23-28.

43. *Precipitation* of sodium silicofluoride (Na_2SiF_6) and cryolite (Na_3AlF_6) from HF/HCl leach liquors of alumino-silicates / Kumar M., Nani B.M., Mankhand T.R., Pandey B.D. // *Hydrometallurgy.* – 2010. – Vol.104. – P.304-307.

44. *Removal* of fluoride from the acid digestion liquor in production process of nitrophosphate fertilizer / Wang H., Li R., Fan C., Feng J., Jiang S., Han Z. // *J. Fluorine Chem.* – 2015. – Vol.180. – P.122-129.

45. *Ghazaryan V.V., Fleck M., Petrosyan A.M.* Salts of amino acids with hexafluorosilicate anion // *J. Cryst. Growth.* – 2013. – Vol.362. – P.162-166.

46. *Fleck M., Ghazaryan V.V., Petrosyan A.M.* Amino acid hexafluorosilicates – an overview // *Z. Kristallogr.* – 2013. – Vol.228. – P.240-249.

47. *Preparation*, structure and properties of pyridinium/bipyridinium hexafluorosilicates / Gelmboldt V.O., Ganin Ed.V., Botoshansky M.M., Anisimov V.Yu., Prodan O.V., Kravtsov V.Ch., Fonari M.S. // *J. Fluorine Chem.* – 2014. – Vol.160. – P.57-63.

48. Synthesis, crystal structures, properties and caries prevention efficiency of 2-, 3-, 4-carboxymethylpyridinium hexafluorosilicates / Gelmboldt V.O., Anisimov V.Yu., Shyshkin I.O., Fonari M.S., Kravtsov V.Ch. // *J. Fluorine Chem.* – 2018. – Vol.205. – P.15-21.

49. *Bis(3-hydroxymethylpyridinium)* hexafluorosilicate monohydrate as a new potential anticaries agent: Synthesis, crystal structure and pharmacological properties / Gelmboldt V.O., Shyshkin I.O., Anisimov V.Yu., Fonari M.S., Kravtsov V.Ch. // *J. Fluorine Chem.* – 2020. – Vol.235. – Art. No. 109547.

50. *Bis(2-, 3-, 4-carboxyethylpyridinium)* hexafluorosilicates as potential caries prophylactic agents / Gelmboldt V.O., Lytvynchuk I.V., Shyshkin I.O., Khromagina L.N., Kravtsov V.Ch., Fonari M.S. // *Arch. Pharm.* – 2022. – Vol.355. – Art. No. e2200074.

51. *Lytvynchuk I.V., Hritsyuk A.G., Gelmboldt V.O.* Synthesis, structure and some properties of 2-, 3-, 4-aminophenylacetic acids hexafluorosilicates // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2022. – No. 5. – P.63-68.

52. *Synthesis*, structure and anticaries activity of 2-amino-4,6-dihydroxypyrimidinium hexafluorosilicate / Gelmboldt V.O., Anisimov V.Yu., Shyshkin I.O., Fonari M.S., Kravtsov V.Ch. // *Pharm. Chem. J.* – 2018. – Vol.52. – P.606-610.

53. *The solubility* of urea, thiocarbamide and acetamide in solutions of hexafluorosilicic acid / Beremzhanov B.A., Nurakhmetov N.N., Tashenov A., Suyundikova F.O. // *Zhurn. Neorg. Khim.* – 1987. – Vol.32. – P.256-259.

54. *Gelmboldt V.O., Koroeva L.V., Domasevich K.V.* Phase equilibria in the fluorosilicic acid – *o*-phenylenediamine – water system at 25 °C: The crystal structure of *o*-phenylenediammonium hexafluorosilicate // *Russ. J. Inorg. Chem.* – 2006. – Vol.51. – P.1653-1658.

55. *Lindsay S.J.* Aluminium fluoride – a users guide // *Essential Readings in Light Metals.* Bearn G., Dupuis M., Tarcy G., ed. – Cham: Springer, 2016. – P.608-609.

56. *Drevetov A.* Manufacture of aluminium fluoride of high density and anhydrous hydrofluoric acid from fluosilicic acid // *Proc. Eng.* – 2012. – Vol.46. – P.255-265.

57. *Krysztafkiwicz A., Rager B., Maik M.* Silica recovery from waste obtained in hydrofluoric acid and aluminum fluoride production from fluosilicic acid // *J. Hazard. Mater.* – 1996. – Vol.48. – P.31-49.

58. *Pashkevich D.S., Mamaev A.V.* Production of hydrogen fluoride by processing fluorine-containing wastes and by-products of modern industries // *WIT Trans. Ecol. Environ.* – 2019. – Vol.231. – P.111-123.

59. Drevetov A. Economic aspects of utilizing fluosilicic acid as raw material for the manufacture of hydrofluoric acid and aluminium fluoride // *Proc. Eng.* – 2014. – Vol.83. – P.279-285.
60. Shayakhmetov D.I., Mustafin A.G., Sharipov T.V. Recycling fluorosilicic acid to produce sodium fluoride // *Bashkir Chem. J.* – 2013. – Vol.20. – P.12-15.
61. Gouider M., Feki M., Sayadi S. Separative recovery with lime of phosphate and fluoride from an acidic effluent containing H_3PO_4 , HF and/or H_2SiF_6 // *J. Hazard. Mater.* – 2009. – Vol.170. – P.962-968.
62. Morita M., Granata G., Tokoro C. Recovery of calcium fluoride from highly contaminated fluoric/hexafluorosilicic acid wastewater // *Mater. Trans.* – 2017. – Vol.59. – P.290-296.
63. Kol'tsov V.Yu. Neutralization and purification of acidic waste waters containing hydrofluorosilicic acid // *Glass Ceram.* – 2014. – Vol.70. – P.387-390.
64. McCusker L.B., Liebau F., Engelhardt G. Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts // *Micropor. Mesopor. Mater.* – 2003. – Vol.58. – P.3-13.
65. Preparation of silica-based mesoporous materials from fluorosilicon compounds: Gelation of H_2SiF_6 in ammonia surfactant solution / Jeong S.Y., Suh J.K., Lee J.M., Kwon O.Y. // *J. Colloid. Interface Sci.* – 1997. – Vol.192. – P.156-161.
66. Kwon O.Y., Kim S., Choi S.W. Synthesis of mesoporous molecular sieves. Hydrolysis of H_2SiF_6 by a non-ionic polyethyleneoxide surfactant template // *Micropor. Mesopor. Mater.* – 1999. – Vol.27. – P.255-259.
67. Nanosilica extracted from hexafluorosilicic acid of waste fertilizer as reinforcement material for natural rubber: Preparation and mechanical characteristics / Nguyen V.H., Vu C.M., Choi H.J., Kien B.X. // *Materials.* – 2019. – Vol.12. – Art. No. 2707.
68. Two-step rapid synthesis of mesoporous silica for green tire / Hilonga A., Kim J.K., Sarawade P.B., Quang D.V., Shao G.N., Elineema G., Kim H.T. // *Korean J. Chem. Eng.* – 2012. – Vol.29. – P.1643-1646.
69. Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported ordered mesoporous silica catalysts / Chae H.-J., Kim T.-W., Moon Y.-K., Kim H.-K., Jeong K.-E., Kim C.-U., Jeong S.-Y. // *Appl. Catal. B Environ.* – 2014. – Vol.150-151. – P.596-604.
70. Hexafluorosilicic acid (FSA): from hazardous waste to precious resource in obtaining high value-added mesostructured silica / Vacca M.A., Cara C., Mameli V., Sanna Angotzi M., Scorciapino M.A., Cutrufello M.G., Musinu A., Tyrpekl V., Pala L., Cannas C. // *ACS Sustainable Chem. Eng.* – 2020. – Vol.8. – P.14286-14300.
71. Quantitative recovery of high purity nanoporous silica from waste products of the phosphate fertilizer industry / Elineema G., Kim J.K., Hilonga A., Shao G.N., Kim Y.N., Quang D.V., Sarawade P.B., Kim H.T. // *J. Ind. Eng. Chem.* – 2013. – Vol.19. – P.63-67.
72. Bach Q.V., Vu C.M., Vu H.T. Effects of co-silanized silica on the mechanical properties and thermal characteristics of natural rubber/styrene-butadiene rubber blend // *Silicon.* – 2020. – Vol.12. – P.1799-1809.
73. Zorya L., Krot V. Method of high-purity silica production from hexafluorosilicic acid // *React. Kinet. Catal. Lett.* – 1993. – Vol.50. – P.349-354.
74. Heterogeneous catalysis in zeolites, mesoporous silica, and metal-organic frameworks / Liang J., Liang Z., Zou R., Zhao Y. // *Adv. Mater.* – 2017. – Vol.29. – Art. No. 1701139.
75. Primo A., Garcia H. Zeolites as catalysts in oil refining // *Chem. Soc. Rev.* – 2014. – Vol.43. – P.7548-7561.
76. Environmental catalysis: present and future / Rodriguez-Padron D., Puente-Santiago A.R., Balu A.M., Munoz-Batista M.J., Luquea R. // *ChemCatChem* – 2019. – Vol.11. – P.18-38.
77. CO_2 towards fuels: A review of catalytic conversion of carbon dioxide to hydrocarbons / Garba M., Usman M., Khan S., Shehzad F., Galadima A., Ehsan M.F., Ghanem A.S., Humayun M. // *J. Env. Chem. Eng.* – 2021. – Vol.9. – Art. No. 104756.
78. Adsorption on Ti- and Al-containing mesoporous materials prepared from fluorosilicon / Jeong S.-Y., Jin H., Lee J.-M., Yim D.-J. // *Micropor. Mesopor. Mat.* – 2001. – Vol.44-45. – P.717-723.
79. Jeong S.-Y. Hydrogenation of aromatics on Pt/Pd bimetallic catalyst supported by Al-containing mesoporous silica // *Stud. Surf. Sci. Catal.* – 2003. – Vol.146. – P.717-720.
80. Jeong K.-E., Jeong S.-Y. Aromatic reduction of residue oil of naphtha cracking over bimetallic Pt–Pd catalysts supported on mesoporous molecular sieve // *Res. Chem. Intermed.* – 2008. – Vol.34. – P.693-701.
81. Ahn W.-S., Kim N.-K., Jeong S.-Y. Synthesis, characterization, and catalytic properties of Ti-containing mesoporous molecular sieves prepared using a fluorosilicon compound // *Catal. Today.* – 2001. – Vol.68. – P.83-88.
82. Oxidation of refractory sulfur compounds over Ti-containing mesoporous molecular sieves prepared by using a fluorosilicon compound / Jeong K.-E., Cho C.-S., Chae H.-J., Kim C.-U., Jeong S.-Y. // *J. Nanosci. Nanotechnol.* – 2010. – Vol.10. – P.3547-3550.
83. Recent advances on the preparation and catalytic applications of metal complexes supported-mesoporous silica MCM-41 (review) / Habeche F., Hachemaoui M., Mokhtar A., Chikh K., Benali F., Mekki A., Zaoui F., Cherifi Z., Boukoussa B. // *J. Inorg. Organomet. Polym. Mater.* – 2020. – Vol.30. – P.4245-4268.
84. Functional mesoporous silica nanomaterials for catalysis and environmental applications / Singh B., Na J., Konarova M., Wakihara T., Yamauchi Y., Salomon C., Gawande M.B. // *Bull. Chem. Soc. Jpn.* – 2020. – Vol.93. – P.1459-1496.
85. Austin S., Glowacki A. Hydrochloric acid // *Ullmann's encyclopedia of industrial chemistry.* – Weinheim: Wiley, 2012. – Vol.18. – P.191-205.

86. Recovery and valorization of fluosilicic acid from phosphoric acid plant for the production of concentrated hydrochloric acid / Toure A.O., Sambe F.M., Koita D., Diop C.M.G. // *J. Soc. Ouest-Afr. Chim.* – 2013. – Vol.036. – P.21-25.
87. Processes for working-up an aqueous fluosilicic acid solution / Toure A.O., Sambe F.M., Koita D., Diop C.M.G., Sock O. // *S. Afr. J. Sci.* – 2012. – Vol.108. – P.108-113.
88. Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites – a review / Kango S., Kalia S., Celli A., Njuguna J., Habibi Y., Kumar R. // *Prog. Polym. Sci.* – 2013. – Vol.38. – P.1232-1261.
89. Wang L., Yu S., Cho J. Properties of liquid-phase deposited silica films for low-k dielectric applications // *J. Am. Ceram. Soc.* – 2009. – Vol.92. – P.2388-2391.
90. Huang C.J., Shih W.C. Optimization of pretreatment for liquid-phase deposition of SiO₂ on ARTON plastic substrate // *J. Electron. Mater.* – 2003. – Vol.32. – P.478-482.
91. Microstructure developments of F-doped SiO₂ thin films prepared by liquid phase deposition / Yu S., Lee J.S., Nozaki S., Cho J. // *Thin Solid Films.* – 2012. – Vol.520. – P.1718-1723.
92. Whitsitt E.A., Barron A.R. Silica coated single walled carbon nanotubes // *Nano Lett.* – 2003. – Vol.3. – P.775-778.
93. Yoon S.Y., Choi S.-E., Lee J.S. Liquid phase deposition of silica on the hexagonally close-packed monolayer of silica spheres // *J. Nanomater.* – 2013. – Art. No. 510524.
94. Yoon S.Y., Park Y.-S., Lee J.S. Local liquid phase deposition of silicon dioxide on hexagonally close-packed silica beads // *Langmuir.* – 2015. – Vol.31. – P.249-253.
95. Preparation methods and application of silicon oxide films / Wang G., Yang H., Liang J., Chen Q. // *Proceedings of the 2014 International Conference on Mechatronics, Electronic, Industrial and Control Engineering (MEIC 2014).* – Shenyang, China: Atlantis Press, 2014. – P.479-483.
96. SiO₂ passivation layer grown by liquid phase deposition for n-type bifacial silicon solar cells / Chen Y.L., Lu G.L., Zhong S.H., Shen W.Z. // *International Symposium on Materials Application and Engineering 2016 (SMAE 2016).* – Chiang Mai, Thailand: Curran Associates, Inc., 2016. – P.981-987.
97. SiO₂ passivation layer grown by liquid phase deposition for silicon solar cell application / Chen Y., Zhong S., Tan M., Shen W. // *Front. Energy.* – 2017. – Vol.11. – P.52-59.
98. He J., Ke Y. Microstructure developments and anti-reflection properties of SiO₂ films by liquid-phase deposition // *Mater. Sci. Semicond. Proc.* – 2017. – Vol.63. – P.153-160.
99. Sui M., Chu Y., Zhang R. A review of technologies for high efficiency silicon solar cells // *J. Phys. Conf. Series.* – 2021. – Vol.1907. – Art. No. 012026.
100. Dragan S., Ozunu A. Characterization of calcium carbonates used in wet flue gas desulphurization processes // *Cent. Eur. J. Chem.* – 2012. – Vol.10. – P.1556-1564.
101. Reactivity of calcium carbonate prepared from flue gas desulfurization gypsum / Jurisova J., Danielik V., Fellner P., Kralik M., Foltinovic T. // *Acta Chim. Slov.* – 2019. – Vol.12. – P.14-21.
102. Development of deformable calcium carbonate for high filler paper / Kang D.S., Han J.S., Choi J.S., Seo Y.B. // *ACS Omega.* – 2020. – Vol.5. – P.15202-15209.
103. Kim D.S., Lee C.K. Surface modification of precipitated calcium carbonate using aqueous fluosilicic acid // *Appl. Surf. Sci.* – 2002. – Vol.202. – P.15-23.
104. Andre L., Cardinal D. Silicon isotopes // *Encyclopedia of astrobiology.* – Berlin, Heidelberg: Springer, 2011. – P.1511-1514.
105. Silicon isotope geochemistry: fractionation linked to silicon complexations and its geological applications / Wang W., Wei H.-Z., Jiang S.-Y., Liu X., Lei F., Lin Y.-B., Zhao Y. // *Molecules.* – 2019. – Vol.24. – Art. No. 1415.
106. Naturally occurring ³²Si and low-background silicon dark matter detectors / Orrell J.L., Arnquist I.J., Bliss M., Bunker R., Finch Z.S. // *Astropart. Phys.* – 2018. – Vol.99. – P.9-20.
107. Molar-mass measurement of a ²⁸Si-enriched silicon crystal for determination of the Avogadro constant / Narukawa T., Hioki A., Kuramoto N., Fujii K. // *Metrologia.* – 2014. – Vol.5. – P.161-168.
108. Wang C., Bai P., Guo X. Advances in separation methods for large-scale production of silicon isotopes // *J. Radioanal. Nucl. Chem.* – 2015. – Vol.304. – P.989-999.
109. Waki M., Miyamoto K. Isotope enrichment method. – Stella Chemifa Corporation. Patent U.S. 7943107, 2009.
110. Gelmboldt V.O., Ganin E.V., Fonari M.S. Supramolecular compounds of fluorocomplexes of p-elements with crown and azacrown ethers: synthesis, transformations and crystal structures // *J. Fluorine Chem.* – 2012. – Vol.135. – P.15-24.
111. Gelmboldt V.O. To the properties of fluorosilicic acid: evolution of views on the state in aqueous solutions (overview) // *Russ. J. Inorg. Chem.* – 2018. – Vol.63. – P.1746-1751.
112. Pilcher A.S., DeShong P. Fluorosilicic acid // *Encyclopedia of reagents for organic synthesis.* – Wiley, 2001.
113. Selective deprotection of trialkylsilyl ethers using fluorosilicic acid / Pilcher A.S., Hill D.K., Shimshock S.J., Waltermire R.E., DeShong P. // *J. Org. Chem.* – 1992. – Vol.57. – P.2492-2495.
114. Pilcher A.S., DeShong P. Improved protocols for the selective deprotection of trialkylsilyl ethers using fluorosilicic acid // *J. Org. Chem.* – 1993. – Vol.58. – P.5130-5134.
115. Catalytic activation of trimethylsilylacetylenes: a one-pot route to unsymmetrical acetylenes and heterocycles / Lasanyi D., Meszaros A., Novak Z., Tolnai G.L. // *J. Org. Chem.* – 2018. – Vol.83. – P.8281-8291.
116. Lasanyi D., Tolnai G.L. Copper-catalyzed ring opening of [1.1.1]propellane with alkynes: Synthesis of exocyclic allenic cyclobutanes // *Org. Lett.* – 2019. – Vol.21. – P.10057-10062.
117. Meszaros A. Design and application of fluorinated reagents: PhD Theses. – Budapest: Eotvos Loránd University, 2019. – 160 p.

118. Total synthesis of epothilone A / Hindupur R.M., Panicker B., Valluria M., Avery M.A. // *Tetrahedron Lett.* – 2001. – Vol.42. – P.7341-7344.
119. Campbell M.J., Johnson J.S. Enantioselective synthesis of (+)-Polyanthellin A via cyclopropane–aldehyde (3+2)-annulation // *Synthesis.* – 2010. – P.2841-2852.
120. La Clair J.J. Total syntheses of hexacyclinol, 5-epi-hexacyclinol, and desoxohexacyclinol unveil an antimalarial prodrug motif // *Angew. Chem. Int. Ed.* – 2006. – Vol.45. – P.2769-2773.
121. Calcitriol derivatives with two different side chains at C-20. V. Potent inhibitors of mammary carcinogenesis and inducers of leukemia differentiation / Maehr H., Lee H.J., Perry B., Suh N., Uskokovic M.R. // *J. Med. Chem.* – 2009. – Vol.52. – P.5505-5519.
122. Calcitriol derivatives with two different side-chains at C-20. Part 4: Further chain modifications that alter VDR-dependent monocytic differentiation potency in human leukemia cells / Garay E., Jankowski P., Lizano P., Marczak S., Maehr H., Adorini L., Uskokovic M.R., Studzinski G.P. // *Bioorg. Med. Chem.* – 2007. – Vol.15. – P.4444-4455.
123. Pinkerton D.M. Total syntheses of the tambjamine alkaloids and certain epoxyquinol-type natural products: PhD Thesis. – Canberra: Australian National University, 2010. – 215 p.
124. Dahlke T., Sen E. Converting fluorosilicic acid into value-added hydrogen fluoride // *Fertil. Int.* – 2021. – Vol.504. – P.1-3.
125. Politz A.R., Scott L., Montz H. Ammonium hexafluorosilicate: a prospective alternative to silver diamine fluoride: undergraduate research scholars program at Texas A&M University, 2020. Available from: <https://hdl.handle.net/1969.1/189278>.
126. Comparative morphology of dentinal tubules occlusion at the use of different desensitizing agents in experiment / Brsikyan N.A., Andriasyan L.H., Badalyan G.R., Harutyunyan A.V., Petrosyan A.M., Ghazaryan V.V. // *New Armenian Med. J.* – 2012. – Vol.6. – P.52-55.
127. Dahlke T., Ruffinera O., Dincer B. Economical comparison of hydrofluoric acid production from fluorosilicic acid and fluorspar // *Proc. Eng.* – 2017. – P.1-9.
128. Zero-liquid discharge treatment of wastewater from a fertilizer factory / Zueva S.B., Ferella F., Taglieri G., Michelis I. De, Pugacheva I., Veglio F. // *Sustainability.* – 2020. – Vol.12. – Art. No. 397.
129. The prospective approach for the reduction of fluoride ions mobility in industrial waste by creating products of commercial value / Rudelis V., Dambrauskas T., Grineviciene A., Baltakys K. // *Sustainability.* – 2019. – Vol.11. – Art. No. 634.
130. Beneficial use of a by-product from the phosphate fertilizer industry in tropical soils: effects on soil properties and maize and soybean growth / Valle L.A.R., Rodrigues S.L., Ramos S.J., Pereira H.S., Amaral D.C., Siqueira J.O., Guilherme L.R.G. // *J. Clean Prod.* – 2016. – Vol.112. – P.113-120.
131. Olejarczyk M., Rykowska I., Urbaniak W. Management of solid waste containing fluoride – a review // *Materials.* – 2022. – Vol.15. – Art. No. 3461.
132. Phosphoric acid production by attacking phosphate rock with recycled hexafluorosilicic acid / Matta S., Stephan K., Stephan J., Lteif R., Goutaudier C., Saab J. // *Int. J. Miner. Process.* – 2017. – Vol.161. – P.21-27.
133. Anastas P.T., Warner J.C. Green chemistry: theory and practice. – Oxford, New York: Oxford University Press, 1998. – 135 p.

Received 08.03.2023

КРЕМНІЙФТОРОВОДНЕВА КИСЛОТА: ВТОРИННА СИРОВИНА ТА РЕАГЕНТ У ТЕХНОЛОГІЧНІЙ ПРАКТИЦІ ТА ПРЕПАРАТИВНОМУ СИНТЕЗІ (ОГЛЯД)

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У даному огляді систематизовано і узагальнено результати досліджень процесів утилізації розчинів фторокремнієвої кислоти як великотоннажних токсичних побічних продуктів виробництва фосфорних добрив, фосфорної кислоти та елементного фосфору. Враховуючи значне скорочення світових запасів плавикового шпату, фторокремнієва кислота стає основним альтернативним джерелом фтору для хімічної промисловості. Висвітлено основні шляхи переробки H_2SiF_6 з одержанням промислово затребуваних продуктів: гексафторидосилкатів металів і амонію, фторидів металів, безводного фтористого водню, соляної кислоти, аморфного діоксиду кремнію, алюмосилікатних і титаносилікатних каталізаторів, збагачених ізотопів кремнію. Також обговорюються приклади використання H_2SiF_6 як головного реагенту для муніципальних програм фторування питної води, у процесах модифікації поверхні та зняття триалкілсилильного захисту в реакціях органічного синтезу. Відомі приклади використання H_2SiF_6 як сировини і реагенту в промислових технологіях і лабораторних дослідженнях значною мірою відповідають принципам «зеленої хімії».

Ключові слова: фосфорні добрива, промислові відходи, фторокремнієва кислота, утилізація, використання.

FLUROSILICIC ACID: SECONDARY RAW MATERIAL AND REAGENT IN TECHNOLOGICAL PRACTICE AND PREPARATIVE SYNTHESIS (A REVIEW)

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The present review systematizes and summarizes the results of research on utilization processes of fluorosilicic acid solutions as large-tonnage toxic by-products of phosphate fertilizers, phosphoric acid and elemental phosphorus production. Considering the marked decline in the world's fluorspar reserves, fluorosilicic acid is emerging as the main alternative source of fluoride for the chemical industry. The main ways of H_2SiF_6 processing are highlighted with obtaining of commercially demanded products: hexafluoridosilicates of metals and ammonium, metal fluorides, anhydrous hydrogen fluoride, hydrochloric acid, amorphous silicon dioxide, aluminosilicates

and titanosilicates catalysts, and enriched isotopes of silicon. Examples of H_2SiF_6 use as a main reagent for drinking water fluoridation municipal programs, in processes of surface modification and removal of trialkylsilyl protection in reactions of organic synthesis are also discussed. Known examples of H_2SiF_6 use as a raw material and reagent in industrial technologies and laboratory tests largely conform to principles of green chemistry.

Keywords: phosphate fertilizer; industrial waste; fluorosilicic acid; utilization; application.

REFERENCES

1. Morel B, Duperret B. Uranium and fluorine cycles in the nuclear industry. *J Fluorine Chem.* 2009; 130: 7-10. doi: 10.1016/j.jfluchem.2008.05.022.
2. Borgard JM, Herbelet F, Gwinner B. Recycling hydrofluoric acid in the nuclear industry: the over azeotropic flash process (OVAF). *J Fluorine Chem.* 2016; 185: 17-23. doi: 10.1016/j.jfluchem.2016.03.001.
3. Sun L, Niu Y, Hu C, Wang X, Zhao Z, Chen J, et al. Behavior and distribution of nuclides in the fluoride volatility process of uranium containing molten salt fuel. *J Fluorine Chem.* 2022; 261-262: 110016. doi: 10.1016/j.jfluchem.2022.110016.
4. Cardinaud C. Fluorine-based plasmas: main features and application in micro- and nanotechnology and in surface treatment. *Comp Rend Chim.* 2018; 21: 723-739. doi: 10.1016/j.crci.2018.01.009.
5. Ober CK, Kafer F, Deng J. Review of essential use of fluorochemicals in lithographic patterning and semiconductor processing. *J Micro/Nanopattern Mater Metrol.* 2022; 21: 010901. doi: 10.1117/1.JMM.21.1.010901.
6. Chen X, Fan K, Liu Y, Liu X, Wang X. Recent advances in fluorinated graphene from synthesis to applications: critical review on functional chemistry and structural engineering. *Adv Mater.* 2022; 34: 2101665. doi: 10.1002/adma.2101665.
7. O'Hagan D. Fluorine in health care: organofluorine containing blockbuster drugs. *J Fluorine Chem.* 2010; 131: 1071-1081. doi: 10.1016/j.jfluchem.2010.03.003.
8. Han J, Remete AM, Dobson LS, Kiss L, Izawa K, Moriawaki H, et al. Next generation organofluorine containing blockbuster drugs. *J Fluorine Chem.* 2020; 239: 109639. doi: 10.1016/j.jfluchem.2020.109639.
9. Gillis EP, Eastman KJ, Hill MD, Donnelly DJ, Meanwell NA. Applications of fluorine in medicinal chemistry. *J Med Chem.* 2015; 58: 8315-8359. doi: 10.1021/acs.jmedchem.5b00258.
10. Johnson BM, Shu YZ, Zhuo X, Meanwell NA. Metabolic and pharmaceutical aspects of fluorinated compounds. *J Med Chem.* 2020; 63: 6315-6386. doi: 10.1021/acs.jmedchem.9b01877.
11. Han J, Kiss L, Mei H, Remete AM, Ponikvar-Svet M, Sedgwick DM, et al. Chemical aspects of human and environmental overload with fluorine. *Chem Rev.* 2021; 121: 4678-4742. doi: 10.1021/acs.chemrev.0c01263.
12. Villalba G., Ayres RU, Schroder H. Accounting for fluorine: production, use, and loss. *J Ind Ecology.* 2007; 11: 85-101. doi: 10.1162/jiec.2007.1075.
13. Fuge R. Fluorine in the environment, a review of its sources and geochemistry. *Appl Geochem.* 2019; 100: 393-406. doi: 10.1016/j.apgeochem.2018.12.016.
14. Harsanyi A, Sandford G. Organofluorine chemistry: applications, sources and sustainability. *Green Chem.* 2015; 17: 2081-2086. doi: 10.1039/C4GC02166E.
15. Meshri DT. The modern inorganic fluorochemical industry. *J Fluorine Chem.* 1986; 33: 195-226. doi: 10.1016/S0022-1139(00)85278-1.
16. Sarawade PB, Kim JK, Hilonga A, Kim HT. Recovery of high surface area mesoporous silica from waste hexafluorosilicic acid (H_2SiF_6) of fertilizer industry. *J Hazard Mater.* 2010; 173: 576-580. doi: 10.1016/j.jhazmat.2009.08.125.
17. Joshi AN. A review of processes for separation and utilization of fluorine from phosphoric acid and phosphate fertilizers. *Chem Pap.* 2022; 76: 6033-6045. doi: 10.1007/s11696-022-02323-9.
18. Karen E, Haneke MS, Bonnie L. *Sodium hexafluorosilicate [CASRN 16893-85-9] and fluorosilicic acid [CASRN 16961-83-4]*. Review of toxicological literature. 2001; 1-26.
19. Sinai A, Meszaros A, Balogh A, Zwillinger M, Novak Z. Hexafluorosilicic acid as a novel reagent for the desilylation of silylacetylenes: application in sequential Sonogashira coupling and click reaction. *Synthesis.* 2017; 49: 2374-2388. doi: 10.1055/s-0036-1588981.
20. Nakhil S, Weber D, Irran E, Lerch M, Schwarz B, Ehrenberg H. Synthesis, crystal structure, and magnetic properties of a new vanadium fluoride hydrate $V_2F_6 \cdot 4H_2O$. *Z Kristallogr.* 2013; 228: 347-350. doi: 10.1524/zkri.2013.1664.
21. Kim J, Park KW, Kwon OY. Preparation of mesoporous silica by the rapid gelation of Na_2SiO_3 and H_2SiF_6 in aqueous surfactant solution. *Micropor Mesopor Mater.* 2019; 285: 137-141. doi: 10.1016/j.micromeso.2019.05.008.
22. Park KW, Kim JY, Seo HJ, Kwon OY. Preparation of mesoporous silica by nonionic surfactant micelle-templated gelation of Na_2SiO_3 and H_2SiF_6 and application as a catalyst carrier for the partial oxidation of CH_4 . *Sci Rep.* 2019; 9: 13360. doi: 10.1038/s41598-019-50053-y.
23. Liu T, Jin F, Wang X, Fan Y, Yuan M. Synthesis of titanium containing MCM-41 from industrial hexafluorosilicic acid as epoxidation catalyst. *Catal Today.* 2017; 297: 316-323. doi: 10.1016/j.cattod.2017.03.011.
24. Jin F, Wang X, Liu T, Wu Y, Xiao L, Yuan M, et al. Synthesis of ZSM-5 with the silica source from industrial hexafluorosilicic acid as transalkylation catalyst. *Chinese J Chem Eng.* 2017; 25: 1303-1313. doi: 10.1016/j.cjche.2016.11.004.
25. Zhang J, Tian C, Xu Y, Chen J, Xiao L, Wu G. Effective removal of fluorine ions in phosphoric acid by silicate molecular sieve synthesized by hexafluorosilicic acid. *Sep Purif Technol.* 2023; 305: 122395. doi: 10.1016/j.seppur.2022.122395.
26. Salas BV, Wiener MS, Martinez JRS. Phosphoric acid industry: problems and solutions. In: Wiener MS, Valdez B, editors. *Phosphoric acid industry*. InTechOpen; 2017: 83-99. doi: 10.5772/intechopen.7003.

27. Leikam DF, Achorn FP. Phosphate fertilizers: production, characteristics, and technologies. In: Sims T, Sharpley AN, editors. *Phosphorus: agriculture and the environment. Agronomy monograph No 46*. American Society of Agronomy, Inc; 2005: 23-50. doi: 10.2134/agronmonogr46.c2.
28. Aigueperse J, Mollard P, Devilliers D, Chemla M, Faron R, Romano R, et al. Fluorine compounds, inorganic. In: *Ullmann's Encyclopedia of industrial chemistry*. Weinheim: Wiley; 2012. 428-429. doi: 10.1002/14356007.a11_307.
29. Ramteke LP, Sahayam AC, Ghosh A, Rambabu U, Reddy MRP, Popat KM, et al. Study of fluoride content in some commercial phosphate fertilizer. *J Fluorine Chem*. 2018; 210: 149-155. doi: 10.1016/j.jfluchem.2018.03.018.
30. Cronin SJ, Manoharan V, Hedley MJ, Loganathan P. Fluoride: a review of its fate, bioavailability, and risks of fluorosis in grazed pasture systems in New Zealand. *NZ J Agric Res*. 2000; 43: 295-321. doi: 10.1080/00288233.2000.9513430.
31. Ramteke LP, Sarode DD, Marathe YS, Ghosh PK. Removal of fluoride contaminant in phosphate fertilizers through solid state thermal treatment. *J Fluorine Chem*. 2021; 241: 109693. doi: 10.1016/j.jfluchem.2020.109693.
32. Mullen J. History of water fluoridation. *British Dental J*. 2005; 199: 1-4. doi: 10.1038/sj.bdj.4812863.
33. Will RK. The benefits of isolating & utilizing fluorine from phosphate operations. *Proc Eng*. 2016; 138: 267-272. doi: 10.1016/j.proeng.2016.02.084.
34. Urbansky ET. Fate of fluorosilicate drinking water additives. *Chem Rev*. 2002; 102: 2837-2854. doi: 10.1021/cr020403c.
35. Ullah R, Zafar MS. Oral and dental delivery of fluoride: a review. *Fluoride*. 2015; 48: 195-204.
36. Peckham S, Awofeso N. Water fluoridation: a critical review of the physiological effects of ingested fluoride as a public health intervention. *Sci World J*. 2014; 293019. doi: 10.1155/2014/293019.
37. Hirzy JW, Carton RJ, Bonanni CD, Montanero CM, Nagle MF. Comparison of hydrofluorosilicic acid and pharmaceutical sodium fluoride as fluoridating agents – a cost-benefit analysis. *Environ Sci Policy*. 2013; 29: 81-86. doi: 10.1016/j.envsci.2013.01.007.
38. Belotti L, Frazao P. Intervening factors in the costs of fluoridation in water supply systems: a case study in seven population sizes. *Eng Sanit Ambient*. 2021; 26: 785-791. doi: 10.1590/S1413-415220200045.
39. Gelmboldt VO, Kravtsov VC, Fonari MS. Ammonium hexafluoridosilicates: synthesis, structures, properties, applications. *J Fluorine Chem*. 2019; 221: 91-102. doi: 10.1016/j.jfluchem.2019.04.005.
40. Ouasri A, Rhandour A. Structural, vibrational, thermal, phase transitions, and properties review of alkylammonium, alkylendiammonium, and aminoacid hexafluorosilicate salts. *Russ J Coord Chem*. 2021; 47: 502-517. doi: 10.1134/S1070328421070046.
41. Ruixiang Z. Process optimization in batch crystallization of sodium fluosilicate. *Cryst Res Technol*. 2005; 40: 243-247. doi: 10.1002/crat.200410332.
42. Batiha MM, Al-Harashsheh M. The effect of reaction conditions on the precipitation of sodium hexafluorosilicate produced from waste hexafluorosilicic acid. *Pol J Chem Tech*. 2011; 13: 23-28. doi: 10.2478/v10026-011-0019-4.
43. Kumar M, Nani BM, Mankhand TR, Pandey BD. Precipitation of sodium silicofluoride (Na_2SiF_6) and cryolite (Na_3AlF_6) from HF/HCl leach liquors of aluminosilicates. *Hydrometallurgy*. 2010; 104: 304-307. doi: 10.1016/j.hydromet.2010.05.014.
44. Wang H, Li R, Fan C, Feng J, Jiang S, Han Z. Removal of fluoride from the acid digestion liquor in production process of nitrophosphate fertilizer. *J Fluorine Chem*. 2015; 180: 122-129. doi: 10.1016/j.jfluchem.2015.09.009.
45. Ghazaryan VV, Fleck M, Petrosyan AM. Salts of amino acids with hexafluorosilicate anion. *J Cryst Growth*. 2013; 362: 162-166. doi: 10.1016/j.jcrysgro.2011.11.017.
46. Fleck M, Ghazaryan VV, Petrosyan AM. Amino acid hexafluorosilicates – an overview. *Z Kristallogr*. 2013; 228: 240-249. doi: 10.1524/zkri.2013.1604.
47. Gelmboldt VO, Ganin EdV, Botoshansky MM, Anisimov VYu, Prodan OV, Kravtsov VCh, et al. Preparation, structure and properties of pyridinium/bipyridinium hexafluorosilicates. *J Fluorine Chem*. 2014; 160: 57-63. doi: 10.1016/j.jfluchem.2014.01.014.
48. Gelmboldt VO, Anisimov VYu, Shyshkin IO, Fonari MS, Kravtsov VCh. Synthesis, crystal structures, properties and caries prevention efficiency of 2-, 3-, 4-carboxymethylpyridinium hexafluorosilicates. *J Fluorine Chem*. 2018; 205: 15-21. doi: 10.1016/j.jfluchem.2017.11.004.
49. Gelmboldt VO, Shyshkin IO, Anisimov VYu, Fonari MS, Kravtsov VCh. Bis(3-hydroxymethylpyridinium) hexafluorosilicate monohydrate as a new potential anticaries agent: Synthesis, crystal structure and pharmacological properties. *J Fluorine Chem*. 2020; 235: 109547. doi: 10.1016/j.jfluchem.2020.109547.
50. Gelmboldt VO, Lytvynchuk IV, Shyshkin IO, Khromagina LN, Kravtsov VCh, Fonari MS. Bis(2-, 3-, 4-carboxyethylpyridinium) hexafluorosilicates as potential caries prophylactic agents. *Arch Pharm*. 2022; 355: e2200074. doi: 10.1002/ardp.202200074.
51. Lytvynchuk IV, Hritsiuk AH, Gelmboldt VO. Synthesis, structure and some properties of 2-, 3-, 4-aminophenylacetic acids hexafluorosilicates. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2022; (5): 63-68. doi: 10.32434/0321-4095-2022-144-5-63-68.
52. Gelmboldt VO, Anisimov VYu, Shyshkin IO, Fonari MS, Kravtsov VCh. Synthesis, structure and anticaries activity of 2-amino-4,6-dihydroxypyrimidinium hexafluorosilicate. *Pharm Chem J*. 2018; 52: 606-610. doi: 10.1007/s11094-018-1868-4.

53. Beremzhanov BA, Nurakhmetov NN, Tashenov A, Suyundikova FO. The solubility of urea, thiocarbamide and acetamide in solutions of hexafluorosilicic acid. *Zhurn Neorg Khim.* 1987; 32: 256-259. (in Russian).
54. Gelmboldt VO, Koroeva LV, Domasevich KV. Phase equilibria in the fluorosilicic acid – o-phenylenediamine – water system at 25 °C: the crystal structure of o-phenylenediammonium hexafluorosilicate. *Russ J Inorg Chem.* 2006; 51: 1653-1658. doi: 10.1134/S0036023606100226.
55. Lindsay SJ. Aluminium fluoride – a users guide. In: Bearne G, Dupuis M, Tarcy G, editors. Essential readings in light metals. Cham: Springer; 2016. p. 608-609. doi: 10.1007/978-3-319-48156-2_90.
56. Dreveton A. Manufacture of aluminium fluoride of high density and anhydrous hydrofluoric acid from fluosilicic acid. *Proc Eng.* 2012; 46: 255-265. doi: 10.1016/j.proeng.2012.09.471.
57. Krysztafkiewicz A, Rager B, Maik M. Silica recovery from waste obtained in hydrofluoric acid and aluminum fluoride production from fluosilicic acid. *J Hazard Mater.* 1996; 48: 31-49. doi: 10.1016/0304-3894(95)00126-3.
58. Pashkevich DS, Mamaev AV. Production of hydrogen fluoride by processing fluorine-containing wastes and by-products of modern industries. *WIT Trans Ecology Environ.* 2019; 231: 111-123. doi: 10.2495/WM180111.
59. Dreveton A. Economic aspects of utilizing fluosilicic acid as raw material for the manufacture of hydrofluoric acid and aluminium fluoride. *Proc Eng.* 2014; 83: 279-285. doi: 10.1016/j.proeng.2014.09.006.
60. Shayakhmetov DI, Mustafin AG, Sharipov TV. Recycling fluorosilicic acid to produce sodium fluoride. *Bashkir Chem J.* 2013; 20: 12-15.
61. Gouider M, Feki M, Sayadi S. Separative recovery with lime of phosphate and fluoride from an acidic effluent containing H₃PO₄, HF and/or H₂SiF₆. *J Hazard Mater.* 2009; 170: 962-968. doi: 10.1016/j.jhazmat.2009.05.067.
62. Morita M, Granata G, Tokoro C. Recovery of calcium fluoride from highly contaminated fluoric/hexafluorosilicic acid wastewater. *Mater Trans.* 2017; 59: 290-296. doi: 10.2320/matertrans.M-M2017850.
63. Kol'tsov VYu. Neutralization and purification of acidic waste waters containing hydrofluorosilicic acid. *Glass Ceram.* 2014; 70: 387-390. doi: 10.1007/s10717-014-9586-1.
64. McCusker LB, Liebau F, Engelhardt G. Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts. *Micropor Mesopor Mater.* 2003; 58: 3-13. doi: 10.1016/S1387-1811(02)00545-0.
65. Jeong SY, Suh JK, Lee JM, Kwon OY. Preparation of silica-based mesoporous materials from fluorosilicon compounds: gelation of H₂SiF₆ in ammonia surfactant solution. *J Colloid Interface Sci.* 1997; 192: 156-161. doi: 10.1006/jcis.1997.4974.
66. Kwon OY, Kim S, Choi SW. Synthesis of mesoporous molecular sieves. Hydrolysis of H₂SiF₆ by a non-ionic polyethyleneoxide surfactant template. *Micropor Mesopor Mater.* 1999; 27: 255-259. doi: 10.1016/S1387-1811(98)00259-5.
67. Nguyen VH., Vu C.M, Choi HJ, Kien BX. Nanosilica extracted from hexafluorosilicic acid of waste fertilizer as reinforcement material for natural rubber: preparation and mechanical characteristics. *Materials.* 2019; 12: 2707. doi: 10.3390/ma12172707.
68. Hilonga A, Kim JK, Sarawade PB, Quang DV, Shao GN, Elineema G, et al. Two-step rapid synthesis of mesoporous silica for green tire. *Korean J Chem Eng.* 2012; 29: 1643-1646. doi: 10.1007/s11814-012-0053-9.
69. Chae HJ, Kim TW, Moon YK, Kim HK, Jeong KE, Kim CU, et al. Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported ordered mesoporous silica catalysts. *Appl Catal B Environ.* 2014; 150-151: 596-604. doi: 10.1016/j.apcatb.2013.12.023.
70. Vacca MA, Cara C, Mamei V, Sanna Angotzi M, Scoriapino MA, Cutrufello MG, et al. Hexafluorosilicic acid (FSA): from hazardous waste to precious resource in obtaining high value-added mesostructured silica. *ACS Sustainable Chem Eng.* 2020; 8: 14286-14300. doi: 10.1021/acssuschemeng.0c03218.
71. Elineema G, Kim JK, Hilonga A, Shao GN, Kim YN, Quang DV, et al. Quantitative recovery of high purity nanoporous silica from waste products of the phosphate fertilizer industry. *J Ind Eng Chem.* 2013; 19: 63-67. doi: 10.1016/j.jiec.2012.07.001.
72. Bach QV, Vu CM, Vu HT. Effects of co-silanized silica on the mechanical properties and thermal characteristics of natural rubber/styrene-butadiene rubber blend. *Silicon.* 2020; 12: 1799-1809. doi: 10.1007/s12633-019-00281-8.
73. Zorya L, Krot V. Method of high-purity silica production from hexafluorosilicic acid. *React Kinet Catal Lett.* 1993; 50: 349-354. doi: 10.1007/BF02062235.
74. Liang J, Liang Z, Zou R, Zhao Y. Heterogeneous catalysis in zeolites, mesoporous silica, and metal-organic frameworks. *Adv Mater.* 2017; 29: 1701139. doi: 10.1002/adma.201701139.
75. Primo A, Garcia H. Zeolites as catalysts in oil refining. *Chem Soc Rev.* 2014; 43: 7548-7561. doi: 10.1039/C3CS60394F.
76. Rodriguez-Padron D, Puente-Santiago AR, Balu AM, Munoz-Batista MJ, Luquea R. Environmental catalysis: present and future. *ChemCatChem.* 2019; 11: 18-38. doi: 10.1002/cctc.201801248.
77. Garba M, Usman M, Khan S, Shehzad F, Galadima A, Ehsan MF, et al. CO₂ towards fuels: a review of catalytic conversion of carbon dioxide to hydrocarbons. *J Environ Chem Eng.* 2021; 9: 104756. doi: 10.1016/j.jece.2020.104756.
78. Jeong SY, Jin H, Lee JM, Yim DJ. Adsorption on Ti- and Al-containing mesoporous materials prepared from fluorosilicon. *Micropor Mesopor Mater.* 2001; 44-45: 717-723. doi: 10.1016/S1387-1811(01)00253-0.

79. Jeong SY. Hydrogenation of aromatics on Pt/Pd bimetallic catalyst supported by Al-containing mesoporous silica. *Stud Surface Sci Catal.* 2003; 146: 717-720. doi: 10.1016/S0167-2991(03)80484-6.
80. Jeong KE, Jeong SY. Aromatic reduction of residue oil of naphtha cracking over bimetallic Pt–Pd catalysts supported on mesoporous molecular sieve. *Res Chem Intermed.* 2008; 34: 693-701. doi: 10.1007/BF03036927.
81. Ahn WS, Kim NK, Jeong SY. Synthesis, characterization, and catalytic properties of Ti-containing mesoporous molecular sieves prepared using a fluorosilicon compound. *Catal Today.* 2001; 68: 83-88. doi: 10.1016/S0920-5861(01)00294-2.
82. Jeong KE, Cho CS, Chae HJ, Kim CU, Jeong SY. Oxidation of refractory sulfur compounds over Ti-containing mesoporous molecular sieves prepared by using a fluorosilicon compound. *J Nanosci Nanotechnol.* 2010; 10: 3547-3550. doi: 10.1166/jnn.2010.2315.
83. Habeche F, Hachemaoui M, Mokhtar A, Chikh K, Benali F, Mekki A, et al. Recent advances on the preparation and catalytic applications of metal complexes supported-mesoporous silica MCM-41 (Review). *J Inorg Organomet Polym Mater.* 2020; 30: 4245-4268. doi: 10.1007/s10904-020-01689-1.
84. Singh B, Na J, Konarova M, Wakihara T, Yamauchi Y, Salomon C, et al. Functional mesoporous silica nanomaterials for catalysis and environmental applications. *Bull Chem Soc Jpn.* 2020; 93: 1459-1496. doi: 10.1246/bcsj.20200136.
85. Austin S, Glowacki A. Hydrochloric Acid. In: *Ullmanns' Encyclopedia of industrial chemistry. Vol 18.* Weinheim: Wiley; 2012. p. 191-205. doi: 10.1002/14356007.a13_283.
86. Toure AO, Sambe FM, Koita D, Diop CMG. Recovery and valorization of fluosilicic acid from phosphoric acid plant for the production of concentrated hydrochloric acid. *J Soc Ouest-Afr Chim.* 2013; 036: 21-25.
87. Toure AO, Sambe FM, Koita D, Diop CMG, Sock O. Processes for working-up an aqueous fluosilicic acid solution. *S Afr J Sci.* 2012; 108: 108-113. doi: 10.4102/sajs.v108i11/12.919.
88. Kango S, Kalia S, Celli A, Njuguna J, Habibi Y, Kumar R. Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites – a review. *Prog Polym Sci.* 2013; 38: 1232-1261. doi: 10.1016/j.progpolymsci.2013.02.003.
89. Wang L, Yu S, Cho J. Properties of liquid-phase deposited silica films for low-k dielectric applications. *J Am Ceram Soc.* 2009; 92: 2388-2391. doi: 10.1111/j.1551-2916.2009.03186.x.
90. Huang CJ, Shih WC. Optimization of pretreatment for liquid-phase deposition of SiO₂ on ARTON plastic substrate. *J Electron Mater.* 2003; 32: 478-482. doi: 10.1007/s11664-003-0129-8.
91. Yu S, Lee JS, Nozaki S, Cho J. Microstructure developments of F-doped SiO₂ thin films prepared by liquid phase deposition. *Thin Solid Films.* 2012; 520: 1718-1723. doi: 10.1016/j.tsf.2011.08.039.
92. Whitsitt EA, Barron AR. Silica coated single walled carbon nanotubes. *Nano Lett.* 2003; 3: 775-778. doi: 10.1021/nl034186m.
93. Yoon SY, Choi SE, Lee JS. Liquid phase deposition of silica on the hexagonally close-packed monolayer of silica spheres. *J Nanomater.* 2013; 510524. doi: 10.1155/2013/510524.
94. Yoon SY, Park YS, Lee JS. Local liquid phase deposition of silicon dioxide on hexagonally close-packed silica beads. *Langmuir.* 2015; 31: 249-253. doi: 10.1021/la5041536.
95. Wang G, Yang H, Liang J, Chen Q. Preparation methods and application of silicon oxide films. In: Liu Chang, Chang Guiran, Luo Zhen, editors. Proceedings of the 2014 International Conference on Mechatronics, Electronic, Industrial and Control Engineering (MEIC 2014); November 15-17, 2014, Shenyang, China; 2014. p. 479-483. doi: 10.2991/meic-14.2014.108.
96. Chen YL, Lu GL, Zhong SH, Shen WZ. SiO₂ passivation layer grown by liquid phase deposition for n-type bifacial silicon solar cells. In: Mohammad Jawaid, El-Refaie Kenawy, editors. *International Symposium on Materials Application and Engineering 2016 (SMAE 2016).* 20-21 August 2016, Chiang Mai, Thailand; 2016. p. 981-987. doi: 10.1051/mateconf/20166704008.
97. Chen Y, Zhong S, Tan M, Shen W. SiO₂ passivation layer grown by liquid phase deposition for silicon solar cell application. *Front Energy.* 2017; 11: 52-59. doi: 10.1007/s11708-016-0429-3.
98. He J, Ke Y. Microstructure developments and anti-reflection properties of SiO₂ films by liquid-phase deposition. *Mater Sci Semicond Proc.* 2017; 63: 153-160. doi: 10.1016/j.msssp.2017.02.008.
99. Sui M, Chu Y, Zhang R. A review of technologies for high efficiency silicon solar cells. *J Phys Conf Ser.* 2021; 1907: 012026. doi: 10.1088/1742-6596/1907/1/012026.
100. Dragan S, Ozunu A. Characterization of calcium carbonates used in wet flue gas desulfurization processes. *Cent Eur J Chem.* 2012; 10: 1556-1564. doi: 10.2478/s11532-012-0068-4.
101. Jurisova J, Danielik V, Fellner P, Kralik M, Foltinovic T. Reactivity of calcium carbonate prepared from flue gas desulfurization gypsum. *Acta Chim Slov.* 2019; 12: 14-21. doi: 10.2478/acs-2019-0003.
102. Kang DS., Han JS, Choi JS, Seo YB. Development of deformable calcium carbonate for high filler paper. *ACS Omega.* 2020; 5: 15202-15209. doi: 10.1021/acsomega.0c01179.
103. Kim DS, Lee CK. Surface modification of precipitated calcium carbonate using aqueous fluosilicic acid. *Appl Surf Sci.* 2002; 202: 15-23. doi: 10.1016/S0169-4332(02)00534-2.
104. Andre L, Cardinal D. Silicon isotopes. In: Gargaud M, editor-in-chief. *Encyclopedia of Astrobiology. Vol. 3.* Berlin, Heidelberg: Springer; 2011. p. 1511-1514.
105. Wang W, Wei HZ, Jiang SY, Liu X, Lei F, Lin YB, et al. Silicon isotope geochemistry: fractionation linked to silicon complexations and its geological applications. *Molecules.* 2019; 24: 1415. doi: 10.3390/molecules24071415.
106. Orrell JL, Arnquist IJ, Bliss M, Bunker R, Finch ZS. Naturally occurring ³²Si and low-background silicon dark matter detectors. *Astropart Phys.* 2018; 99: 9-20. doi: 10.1016/j.astropartphys.2018.02.005.

107. Narukawa T, Hioki A, Kuramoto N, Fujii K. Molar-mass measurement of a ^{28}Si -enriched silicon crystal for determination of the Avogadro constant. *Metrologia*. 2014; 5: 161-168. doi: 10.1088/0026-1394/51/3/161.
108. Wang C, Bai P, Guo X. Advances in separation methods for large-scale production of silicon isotopes. *J Radioanal Nucl Chem*. 2015; 304: 989-999. doi: 10.1007/s10967-015-3950-7.
109. Waki M, Miyamoto K, inventors; Stella Chemifa Corporation, assignee. *Isotope enrichment method*. Patent U.S. 7943107. 2009 May 28.
110. Gelmboldt VO, Ganin EdV, Fonari MS. Supramolecular compounds of fluorocomplexes of p-elements with crown and azacrown ethers: Synthesis, transformations and crystal structures. *J Fluorine Chem*. 2012; 135: 15-24. doi: 10.1016/j.jfluchem.2011.12.014.
111. Gelmboldt VO. To the properties of fluorosilicic acid: evolution of views on the state in aqueous solutions (overview). *Russ J Inorg Chem*. 2018; 63: 1746-1751. doi: 10.1134/S003602361813003X.
112. Pilcher AS, DeShong P. Fluorosilicic acid. In: *Encyclopedia of reagents for organic synthesis*. Wiley, 2001. doi: 10.1002/047084289X.rf013.
113. Pilcher AS, Hill DK, Shimshock SJ, Waltermire RE, DeShong P. Selective deprotection of trialkylsilyl ethers using fluorosilicic acid. *J Org Chem*. 1992; 57: 2492-2495. doi: 10.1021/jo00034a057.
114. Pilcher AS, DeShong P. Improved protocols for the selective deprotection of trialkylsilyl ethers using fluorosilicic acid. *J Org Chem*. 1993; 58: 5130-5134. doi: 10.1021/jo00071a023.
115. Lasanyi D, Meszaros A, Novak Z, Tolnai GL. Catalytic activation of trimethylsilylacetylenes: a one-pot route to unsymmetrical acetylenes and heterocycles. *J Org Chem*. 2018; 83: 8281-8291. doi: 10.1021/acs.joc.8b00998.
116. Lasanyi D, Tolnai GL. Copper-catalyzed ring opening of [1.1.1]propellane with alkynes: synthesis of exocyclic allenic cyclobutanes. *Org Lett*. 2019; 21: 10057-10062. doi: 10.1021/acs.orglett.9b03999.
117. Meszaros A. *Design and application of fluorinated reagents*. [PhD theses]. Budapest (Hungary): Eotvos Lorand University; 2019. 160 p.
118. Hindupur RM, Panicker B, Valluria M, Avery MA. Total synthesis of epothilone A. *Tetrahedron Lett*. 2001; 42: 7341-7344. doi: 10.1021/ol006104w.
119. Campbell MJ, Johnson JS. Enantioselective synthesis of (+)-polyanthellin A via cyclopropane-aldehyde (3+2)-annulation. *Synthesis*. 2010; 2841-2852. doi: 10.1055/s-0030-1258151.
120. La Clair JJ. Total syntheses of hexacyclinol, 5-epi-hexacyclinol, and desoxohexacyclinol unveil an antimalarial prodrug motif. *Angew Chem Int Ed*. 2006; 45: 2769-2773. doi: 10.1002/anie.200504033.
121. Maehr H, Lee HJ, Perry B, Suh N, Uskokovic MR. Calcitriol derivatives with two different side chains at C-20. V. Potent inhibitors of mammary carcinogenesis and inducers of leukemia differentiation. *J Med Chem*. 2009; 52: 5505-5519. doi: 10.1021/jm900780q.
122. Garay E, Jankowski P, Lizano P, Marczak S, Maehr H, Adorini L, et al. Calcitriol derivatives with two different side-chains at C-20. Part 4: Further chain modifications that alter VDR-dependent monocytic differentiation potency in human leukemia cells. *Bioorg Med Chem*. 2007; 15: 4444-4455. doi: 10.1021/jm900780q.
123. Pinkerton DM. *Total syntheses of the tambjamine alkaloids and certain epoxyquinol-type natural products*. [PhD thesis]. Canberra (Australia): Australian National University; 2010. 215 p.
124. Dahlke T, Sen E. Converting fluorosilicic acid into value-added hydrogen fluoride. *Fertil Int*. 2021; 504: 1-3.
125. Politz AR, Scott L, Montz H. *Ammonium hexafluorosilicate: a prospective alternative to silver diamine fluoride* [Internet]: Undergraduate research scholars program at Texas A&M University, 2020. Available from: <https://hdl.handle.net/1969.1/189278>.
126. Brsikyan NA, Andriasyan LH, Badalyan GR, Harutyunyan AV, Petrosyan AM, Ghazaryan VV. Comparative morphology of dentinal tubules occlusion at the use of different desensitizing agents in experiment. *New Armenian Med J*. 2012; 6: 52-55.
127. Dahlke T, Ruffiner O, Dincer B. Economical comparison of hydrofluoric acid production from fluorosilicic acid and fluorspar. *Proc Eng*. 2017; 1-9.
128. Zueva SB, Ferella F, Taglieri G, Michelis ID, Pugacheva I, Veglio F. Zero-liquid discharge treatment of wastewater from a fertilizer factory. *Sustainability*. 2020; 12: 397. doi: 10.3390/su12010397.
129. Rudelis V, Dambrauskas T, Grineviciene A, Baltakys K. The prospective approach for the reduction of fluoride ions mobility in industrial waste by creating products of commercial value. *Sustainability*. 2019; 11: 634. doi: 10.3390/su11030634.
130. Valle LAR, Rodrigues SL, Ramos SJ, Pereira HS, Amaral DC, Siqueira JO, et al. Beneficial use of a by-product from the phosphate fertilizer industry in tropical soils: effects on soil properties and maize and soybean growth. *J Clean Prod*. 2016; 112: 113-120. doi: 10.1016/j.jclepro.2015.07.037.
131. Olejarczyk M, Rykowska I, Urbaniak W. Management of solid waste containing fluoride – a review. *Materials*. 2022; 15: 3461. doi: 10.3390/ma15103461.
132. Matta S, Stephan K, Stephan J, Lteif R, Goutaudier C, Saab J. Phosphoric acid production by attacking phosphate rock with recycled hexafluorosilicic acid. *Int J Miner Process*. 2017; 161: 21-27. doi: 10.1016/j.minpro.2017.02.008.
133. Anastas PT, Warner JC. *Green chemistry: theory and practice*. Oxford, New York: Oxford University Press; 1998. 135 p.