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Production of Hydrofluoric Acid from Hexafluorosilicic Acid: A Critical Review of Chemistry, Process Routes, Silica Control, and Industrial Feasibility

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Abstract

Hexafluorosilicic acid (H_2SiF_6), generated during fluoride capture in wet-process phosphoric acid production, represents a potential secondary feedstock for hydrogen fluoride (HF) manufacture. This critical review examines the reaction chemistry and phase behavior underpinning H_2SiF_6 conversion, evaluates thermal, sulfuric-acid-assisted, SiF_4-mediated, and indirect fluoride-salt routes, and assesses conditioning, silica management, HF finishing, materials compatibility, and industrial integration. An explicit evidence hierarchy separates descriptions of HF production from studies of supporting unit operations and alternative fluorine products. Across the routes examined, nominal fluorine recovery alone does not indicate industrial performance: multicomponent F–Si–H_2O equilibria, changing feed composition, silica formation and filtration, corrosion, and product-quality requirements govern achievable output and plant reliability. We propose elemental fluorine and silicon balances, route-comparison criteria, and a staged qualification framework without extrapolating unsupported laboratory results to commercial operating conditions. Development priorities include validated phase-equilibrium data, representative feed assays, quantified fluoride losses, integrated silica-control trials, and sustained pilot operation. Claims of economic or environmental advantage should remain conditional on product grade, complete system boundaries, and independently verifiable process performance.

Keywords: hexafluorosilicic acid; anhydrous hydrogen fluoride; fluorine recovery; silicon tetrafluoride; silica fouling; process integration

Highlights

- Direct HF production is differentiated from recovery of fluoride-containing coproducts.
- Silica formation and F–Si–H_2O equilibria dominate process operability and selectivity.
- Feed characterization and complete fluorine balances are indispensable for route comparison.
- Pilot evidence, purity, corrosion, and residue management govern industrial feasibility.

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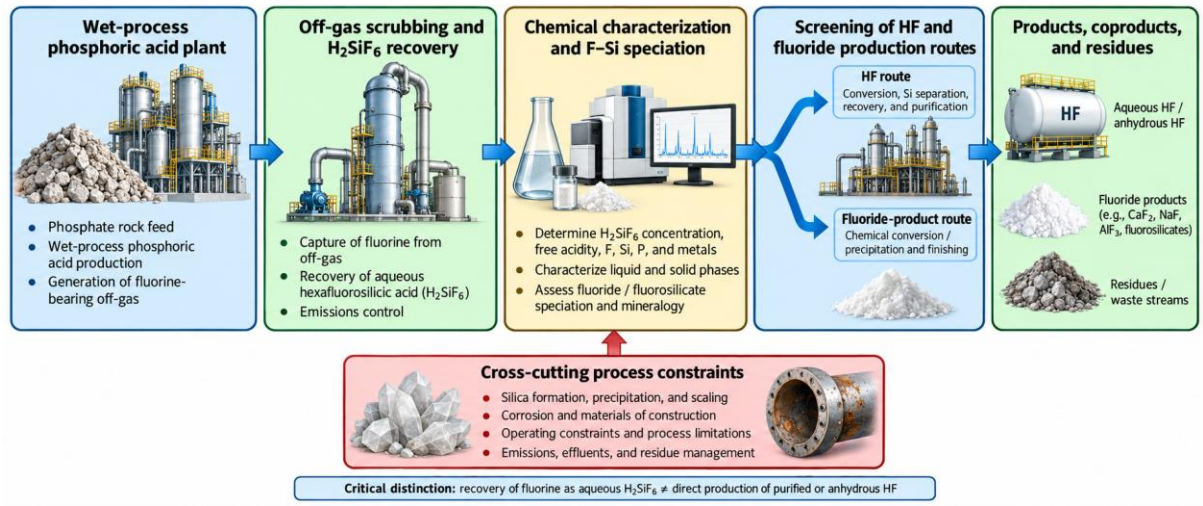
Graphical abstract



1. Introduction

Hydrogen fluoride (HF) is an essential intermediate in aluminum fluoride manufacture, fluorinated-chemical synthesis, fluoropolymer production, and selected metallurgical applications. Conventional HF production uses fluorspar and sulfuric acid. In contrast, wet-process phosphoric acid plants can recover fluoride-bearing gases into aqueous hexafluorosilicic acid (H_2SiF_6). The central engineering issue is therefore not the presence of recoverable fluorine, but the extent to which variable by-product liquors can support sustained manufacture of HF that satisfies a defined specification while controlling silicon transfer, corrosion, equipment availability, and environmental burdens (Dahlke et al., 2016; Dreveton, 2012; Dreveton, 2016; Gao et al., 2021; Gardiner, 2015; Joshi, 2022; Sicard et al., 2020; Will, 2016; Yang et al., 2024a).

Integrating with phosphate manufacturing creates an industrial-symbiosis opportunity but does not eliminate the need for concentration, impurity removal, silica separation, or HF purification. Figure 1 places fluoride capture within the phosphate process, Figure 2 maps competing conversion pathways, Figure 3 connects silicon chemistry to separation failures, and Figure 4 presents a staged qualification sequence. Table 1 distinguishes production objectives,

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Table 2 specifies feed-characterization requirements, Table 3 evaluates route-specific evidence, Table 4 identifies operating risks, and Table 5 defines decision gates. All five tables and four figures are conceptual syntheses rather than experimentally established rankings (Chen et al., 2024; Gelmboldt, 2023; Joshi, 2022; Li et al., 2025; Peng et al., 2021; Peng et al., 2022; Wang et al., 2020; Yang et al., 2024a).

Yang et al. (2024a) reviewed anhydrous HF production from fluorosilicic acid, including direct thermal conversion, sulfuric-acid-assisted decomposition, indirect fluoride pathways, and sustainability considerations. The present review is not the first review of those routes. Its distinct contribution is an author-developed, two-axis qualification of evidence relevance and maturity; explicit separation of total feed-fluorine recovery from H_2SiF_6 conversion and commercial HF output; coupled external-stream F/Si balances; quantitative silica aging, washing, and filtration requirements; materials and on-stream availability criteria; and product-specific, common-boundary TEA/LCA within the G1–G5 industrial qualification framework. These measures assess what evidence is needed to translate plausible chemistry into verified HF manufacture, rather than merely cataloging fluorine conversion pathways.

The analysis applies three evidence categories. Category A covers reports directly concerned with HF production from H_2SiF_6; Category B covers characterization, conditioning, conversion, and separation studies that may support an HF process; and Category C covers alternative fluoride products or analogous applications. The categories describe relevance, not commercial maturity. Recovery of CaF_2, NaF, AlF_3, or silica must not be reported as an HF yield. Accordingly, we compare routes by target product, actual experimental configuration, assay and mass-balance completeness, and operating duration rather than headline conversion percentages.

Table 1. Comparison of fluorine production and recovery pathways

Pathway	Target product	Main advantage	Dominant constraint
$CaF_2 + H_2SO_4$	HF	Mature reference technology	Fluorspar and acid supply; energy

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Pathway	Target product	Main advantage	Dominant constraint
H_2SiF_6 direct conversion	HF	Secondary fluorine feed	SiF_4/H_2O separation and silica
$H_2SiF_6 \rightarrow$ salts	CaF_2, NaF, NH_4F, AlF_3	Broader products and integration	Further reaction required for HF
SiF_4 intermediate	HF or fluoride derivatives	Selective gas-phase integration	Hydrolysis, absorption, recycle

Note. Qualitative comparison synthesized from cited literature; no comparative plant-scale cost values are asserted.

Table 1 demonstrates why "fluorine recovery" is not a common functional endpoint. Producing fluoride salts and producing specified HF require different reaction, purification, and residue-management boundaries. Comparing their nominal fluoride recoveries alone would obscure these differences (Albustami et al., 2014; Chen et al., 2021; Dahlke et al., 2016; Dreveton, 2012; Dreveton, 2014; Gelmboldt, 2023; Lv et al., 2024; Tran et al., 2022).

2. Review Methodology, Scope, and Evidence Qualification

2.1 Literature discovery and selection

This structured critical narrative review covers literature published from 2000 to 2026, prioritizing recent contributions while retaining older foundational chemistry and industrial evidence. Searches and targeted citation chaining addressed "hexafluorosilicic acid" OR "fluosilicic acid" OR "H_2SiF_6" in combination with "hydrogen fluoride" OR "anhydrous HF" OR "SiF_4"; additional combinations addressed pyrolysis, sulfuric-acid decomposition, aqueous speciation, phase equilibria, silica precipitation, filtration, corrosion, product purification, phosphoric-acid integration, TEA, and LCA. Because the original platform-by-platform search log, screening decisions, language filters, and final search execution date were not documented, the search cannot be represented as reproducible or exhaustive. No unverified search database or date is claimed. Reference-list citation chaining supplemented topical retrieval. Records were evaluated by relevance to the specified HF product boundary, and repeated bibliographic entries were excluded where identifiable. The compiled bibliography contains 86 distinct

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entries, as counted in the submitted reference list. This work is a structured critical review and does not claim PRISMA compliance or systematic-review status.

2.2 Evidence grading and interpretive boundaries

The author-developed A/B/C scheme evaluates evidence relevance, not commercial maturity: A denotes a study or industrial description directly addressing HF production; B denotes potentially integrable conditioning, conversion, or separation operations; and C denotes contextual or analogous fluoride valorization. A separate evidence-maturity dimension identifies conceptual, laboratory, pilot, industrial-description, or independently validated industrial evidence. Thus, an A-class concept is not commercially validated, and a well-established fluoride-salt operation does not constitute A-class evidence of saleable HF. Assessment also records feed speciation and representativeness, product assay, measurement limits, F/Si balance closure, operational duration, independently reported performance, and uncertainty (Dahlke et al., 2016; Dreveton, 2012; Gelmboldt, 2023; Yang et al., 2024a).

A reproducible evidence database should record the verified authors, title, year, DOI, feed origin, experimental conditions, analytical methods, test duration, impurity profile, product specification, and elemental mass-balance basis for each study. This information is particularly important when process descriptions are used to infer industrial applicability; a nominal recovery value without a defined measurement boundary is not a transferable design parameter.

Reports without original product analyses, closed elemental balances, or sustained operating records are interpreted as evidence of possibility rather than validated performance. In particular, industrial existence claims reported by developers are distinguished from independently measured multi-year plant availability, yields, purity, and material losses. A record-by-record verification of all bibliographic metadata and DOI landing pages is outstanding; citations therefore remain provisional pending the documented editorial audit. This limitation is disclosed instead of representing unperformed verification as complete.

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3. Formation, Recovery, and Characterization of H_2SiF_6

3.1 Fluorine deportment in phosphate-acid operations

During wet-process phosphoric acid manufacture, fluorine partitions among phosphatic solids, process acid, condensates, and off-gases. Scrubbing can absorb HF- and SiF_4-containing gases to produce fluorosilicic acid solutions, although liquor composition depends on phosphate-rock mineralogy, process conditions, capture efficiency, and recycle practices. Studies of phosphate upgrading, fluoride volatilization, stripping, and selective precipitation help establish where recovery may be integrated, but they do not independently demonstrate net HF production (Ai et al., 2024; Chen et al., 2024; He et al., 2024; He et al., 2023a; He et al., 2023b; He et al., 2023c; He et al., 2023d; Joshi, 2022; Li et al., 2025; Matta et al., 2017; Peng et al., 2021; Peng et al., 2022; Wang et al., 2020; Yao et al., 2025; Zuo et al., 2019).

Figure 1 maps key fluoride-bearing streams, gas scrubbing, and characterization interfaces in a wet-process phosphoric acid complex. It neither assumes all captured fluoride converts to H_2SiF_6 nor specifies achievable downstream HF concentration.

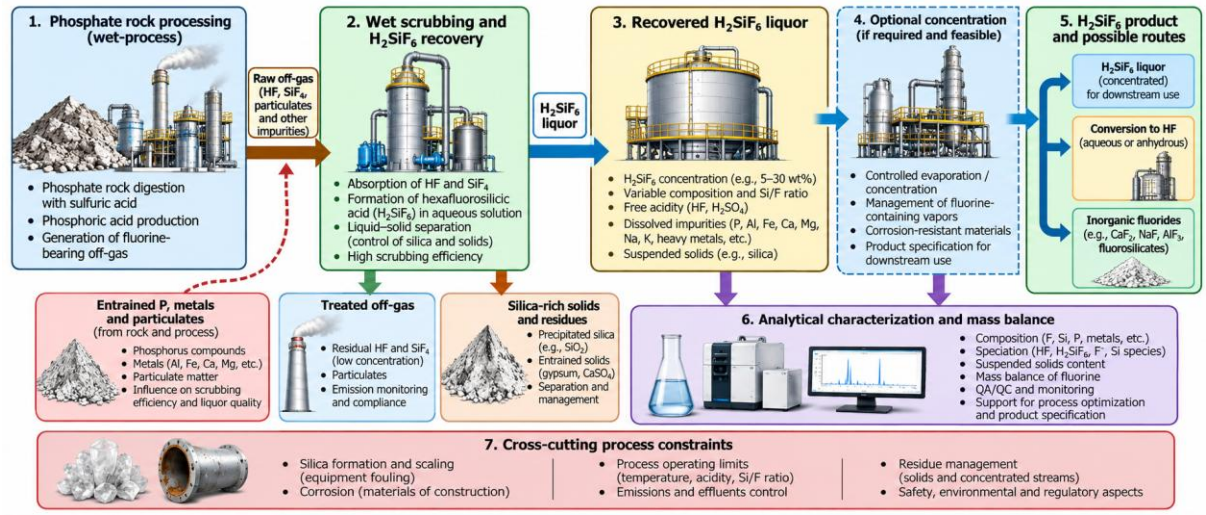

Figure 1. Formation and characterization of phosphate-derived fluorosilicic acid in a wet-process off-gas system.
Note. Original conceptual synthesis informed by Joshi (2022), Peng et al. (2022), and Li et al. (2025); not traced or adapted from any individual source.

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As Figure 1 makes clear, an emissions-control scrubber and an HF feed-preparation system serve related but distinct objectives. Liquors produced under changing plant conditions may require clarification, concentration, and compositional control. Any integration assessment must include its effects on the existing phosphoric acid plant and must not treat recovered fluorine as environmentally or economically burden-free.

3.2 Analytical requirements and feed variability

The HF/H_2SiF_6 ratio, total and free fluoride, silicon speciation, water, phosphorus, sulfate, and suspended silica determine which recovery route is chemically plausible. Potentiometric titration, ion chromatography, and matrix-adjusted titrimetric approaches provide complementary information but are not always interchangeable because bound and unbound fluoride respond differently to analytical conditions (Acker et al., 2007; El Guendouzi et al., 2015; Henßge et al., 2007; Henßge et al., 2006; Kounbach et al., 2022; Kounbach et al., 2023; Tran et al., 2025; Weinreich et al., 2007).

Table 2 provides a minimum analytical framework to distinguish true feed variation from changes induced by storage, dilution, hydrolysis, solids aging, and sample preparation.

Table 2. Minimum feed-characterization matrix for HF-from-H_2SiF_6 route screening

Measurement	Purpose	Critical analytical precaution
Total F; free F/HF	F inventory and speciation	Separate soluble and particulate fractions
Total Si; dissolved Si	Si/F stoichiometry and scaling potential	Control hydrolysis during dilution
H_2SiF_6; water; acidity	Route and concentration suitability	Temperature- and matrix-matched method
P, sulfate, Al, Fe, Ca, Mg, Na	HF purity and precipitate formation	Traceable multielement QA/QC
Suspended solids, PSD, rheology	Clarification and filter design	Preserve aged and fresh sample states

Note. PSD = particle size distribution; QA/QC = quality assurance/quality control. Original synthesis based on the analytical literature cited in the text.

Table 2 highlights that an apparent single “acid grade” is insufficient for process design. Analysis should differentiate dissolved equilibrium composition from metastable material,

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using replicate samples from multiple plant operating regimes (Cheng et al., 2026; El Guendouzi et al., 2015; Kounbach et al., 2022; Kounbach et al., 2023; Li et al., 2024; Tran et al., 2025).

4. Chemical Speciation, Equilibria, and Thermodynamic Constraints

4.1 Coupled fluorine–silicon chemistry

Two atom-balanced expressions help organize the chemistry: $H_2SiF_6 \rightleftharpoons 2\ HF + SiF_4$ and $H_2SiF_6 + 2\ H_2O \rightleftharpoons 6\ HF + SiO_2(s)$. Neither expression, by itself, predicts equilibrium conversion, recoverable HF, or the performance of a practical flowsheet. Aqueous complexation, proton and water activities, HF and SiF_4 volatility, hydrolysis, silica polymerization, and reabsorption couple reaction and separation behavior. Concentrating a fluorosilicic solution alters both phase partitioning and the risks of silica formation (El Guendouzi et al., 2015; Gelmboldt, 2023; Hu et al., 2026; Kim et al., 2002; Kounbach et al., 2022; Long et al., 2020; Pan et al., 2023; Yang et al., 2024a).

The six fluorine atoms appearing in the idealized hydrolysis reaction represent a stoichiometric inventory, not six experimentally recovered equivalents of saleable HF. Fluorine can remain in mother liquor, silica cake, wash liquor, recycle, purge, and off-gas treatment streams; silicon may remain dissolved, deposit as scale, enter filter cake, or leave as volatile species. Route comparisons must therefore distinguish reaction extent, gross captured HF, and net on-specification HF product.

4.2 Phase behavior and route sensitivity

Concentration shifts the partial pressures and activities of HF, water, and volatile silicon species, increasing the propensity for deposition as chemistry and temperature change. Fluoride-solubility and fluoride-salt crystallization studies are relevant to indirect routes but do not alone supply reliable vapor–liquid-equilibrium data for the multicomponent HF–SiF_4–

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H_2SiF_6–H_2O system (El Guendouzi et al., 2015; Hu et al., 2026; Long et al., 2020; Ndiaye et al., 2022; Pan et al., 2023; Tomaszewska, 2000; Wang et al., 2024; Yang et al., 2024a).

Thermodynamic models should therefore report their parameter basis, domain of calibration, activity-coefficient approach, gas–liquid assumptions, and metastable silica treatment. A process simulation without verified phase speciation should be interpreted as a sensitivity exercise, not as evidence of achievable commercial purity.

For a defined process boundary, the overall fraction of external-feed fluorine recovered in saleable HF is $R_{F,HF}$ (%) = 100 × $m_{F,on\text{-}spec\ HF}$ / $\Sigma m_{F,external\ inputs}$. Every fluorine-bearing external feed or reagent is counted; internal recycle is excluded from the denominator to prevent double counting. The chemical conversion $X_{H_2SiF_6}$ must be determined independently from a validated H_2SiF_6 species balance where that species can be quantified. Gross HF capture $R_{HF,gross}$ refers to HF captured upstream of finishing and is not equivalent to $R_{F,HF}$. Product F is assigned only to HF that demonstrably meets the stated commercial specification. This distinction is especially necessary when the initial liquor contains free HF in addition to H_2SiF_6.

Elemental closure should be calculated as C_F (%) = 100 × ($\Sigma m_{F,external\ outputs}$ + $\Delta m_{F,inventory}$)/$\Sigma m_{F,external\ inputs}$ and C_{Si} (%) = 100 × ($\Sigma m_{Si,external\ outputs}$ + $\Delta m_{Si,inventory}$)/$\Sigma m_{Si,external\ inputs}$, with accumulation positive when retained within the boundary. At steady state, net inventory accumulation approaches zero. External outputs include product, silica cake, wash liquors, mother liquor and purge, wastewater, vent-treatment products, and alternate fluoride products. Silicon accounting additionally includes volatile SiF_4, dissolved Si, product contamination, and measurable scale or equipment deposits. Unmeasured accumulation must be treated as an uncertainty rather than hidden in a nominally closed balance. Measurement uncertainties and the time interval should accompany both closure factors.

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5. Production Pathways: Direct, Indirect, and Hybrid

5.1 Benchmark fluorspar process

The conventional benchmark is $CaF_2 + H_2SO_4 \rightarrow 2\ HF + CaSO_4$. Because the benchmark relies on a different feedstock and separation train, comparisons based only on feed price or reactor severity are misleading. Equivalent assessments must include acid supply, reagent regeneration, concentration and drying, product purification, solids handling, utilities, emissions control, transport, and the purity specification imposed on saleable HF (Dreveton, 2014; Dreveton, 2016; Gao et al., 2021; Huang et al., 2022; Will, 2016).

5.2 Thermal decomposition and SiF_4-mediated conversion

Thermal and SiF_4-mediated routes attempt to partition fluorine into a recoverable HF stream while separating silicon-containing species. Although the published descriptions establish chemical and process possibilities, they should not be interpreted as evidence of sustained anhydrous-HF production without corroborating operational data. Hydrolysis of SiF_4 can generate hydrated silica and increase aqueous separation duties, shifting rather than eliminating the process bottleneck. Route validation therefore requires feed and product assays, captured volatile fluorine, silicon balances, energy use, and uninterrupted operating duration (Dahlke et al., 2016; Dreveton, 2012; Dreveton, 2014; Gelmboldt, 2023; Yang et al., 2024a; Zhang, 2023).

5.3 Sulfuric-acid-assisted and fluoride-salt intermediates

Acid-assisted routes change liquid speciation and water removal; indirect conversions produce CaF_2, NaF, NH_4F, or AlF_3 as intermediates or alternative products. In those pathways, fluorine recovery can be high without any net HF output. The necessary extra unit operations, reagent consumption, and purification steps must be included in route comparisons (Abburi et al., 2025; Albustami et al., 2014; Chen et al., 2021; Deng et al., 2025; Elineema et al., 2013; Hu et al., 2026; Jiang et al., 2021; Jiang et al., 2025; Kim et al., 2007; Long et al., 2020; Lv et

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al., 2024; Ma et al., 2024; Morita et al., 2018; Toure et al., 2012; Tran et al., 2022; Wang et al., 2026; Wang et al., 2024; Wang et al., 2025; Xu et al., 2014; Ya et al., 2019; Yu et al., 2000).

5.4 Concentration, membranes, and intensification

Membrane distillation and solvent-extraction studies can support feed conditioning, while bipolar electrodialysis and selective membranes can split fluoride-containing streams and manage silicon. Microwaves, reactive crystallization, fluidized-bed decomposition, and other intensification concepts warrant attention when they improve separation and operability; they should not be labeled commercial HF processes merely because the individual operations have been experimentally demonstrated (Epshtein et al., 2020; He et al., 2023a; Hogen et al., 2024; Jin et al., 2017; Li et al., 2024; Liu et al., 2017; Lou et al., 2024; Ouedraogo et al., 2023; Qiu et al., 2022; Qiu et al., 2025a; Qiu et al., 2025b; Quedi et al., 2024; Ramteke et al., 2021; Tomaszewska, 2000; Vacca et al., 2020; Yang et al., 2024b; Yang et al., 2025; Zhang et al., 2023; Zhang et al., 2026; Zhao et al., 2022).

Figure 2 distinguishes pathways intended to yield HF from routes that recover alternative fluorine products. The complete downstream purification, recycle, and residue treatment required for a specified HF product must be included when comparing these options.

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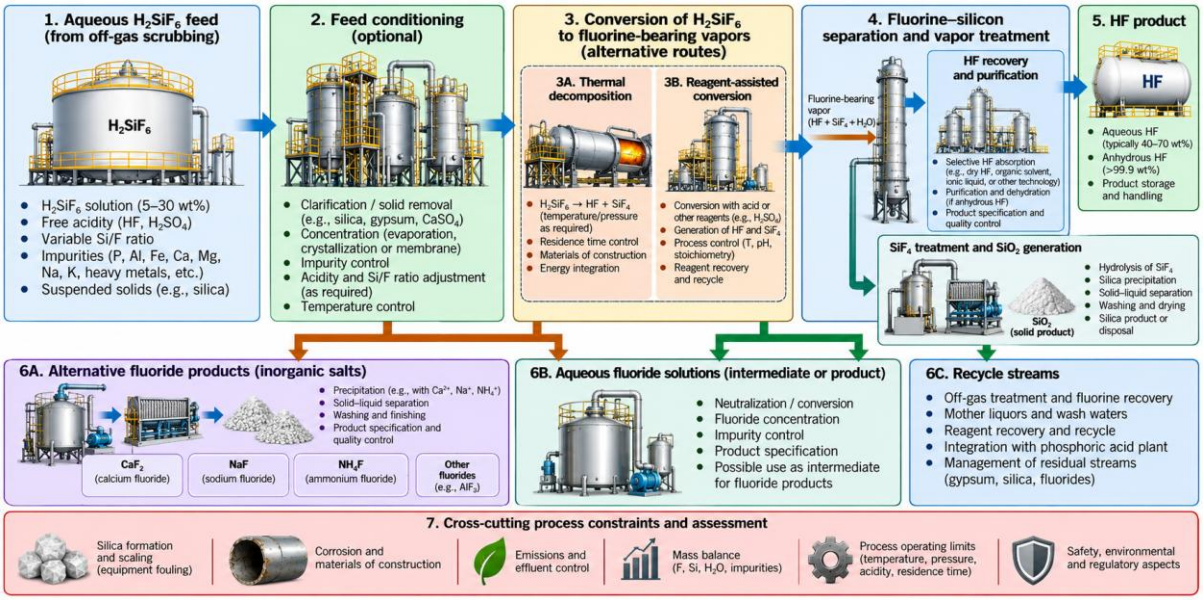

Figure 2. Conceptual conversion alternatives and associated separations for producing HF or competing fluoride products.
Note. Original process schematic developed from an evidence synthesis of Dahlke et al. (2016), Dreveton (2012, 2014), and Yang et al. (2024a).

As shown in Figure 2, the scheme is a conceptual route map rather than a validated plant flowsheet. Classify a pathway as HF manufacture only if its material balance terminates in a defined, saleable HF product; recovering a fluoride salt serves a different industrial objective.

Table 3 distinguishes a route's chemical feasibility from the evidentiary strength of its HF output and its main operating limit.

Table 3. Critical comparison of direct and indirect pathways

Route family	Relevant evidence	Key advantage	Verification need	Maturity / independence of evidence
Thermal / SiF_4-linked HF	Direct process descriptions (A)	Potential HF manufacturing	HF purity, Si balance, run duration	Process reports; independently audited long-term data not established
Acid-assisted HF	Process concepts (A/B)	Alternative separation leverage	Acid recycle and equipment duty	Concepts or limited studies; scale must be specified

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Route family	Relevant evidence	Key advantage	Verification need	Maturity / independence of evidence
AlF_3, NaF, CaF_2 via H_2SiF_6	Chemical/experimental (B)	Fluoride products and valorization	Do not report as net HF	Typically lab or production evidence for salts, not saleable HF
Membrane / extractive conditioning	Separation studies (B)	Potential feed upgrading	Membrane life and impurity transfer	Supporting experiments; equipment longevity must be demonstrated
Other intensified steps	Analogous studies (B/C)	Potential modularity	Linked HF demonstration	Conceptual or lab operations; integrated HF demonstration needed

Note. Evidence codes: A = HF-specific; B = integrable operation; C = contextual/analogous. Comparative entries are qualitative and not technology-readiness ratings.

As indicated by Table 3, any economic ranking derived from an incomplete flowsheet will systematically understate the utility, filtration, maintenance, and finishing costs of the most challenging route (Dahlke et al., 2016; Dreveton, 2014; Hogen et al., 2024; Joshi, 2022; Qiu et al., 2022; Tomaszewska, 2000; Yang et al., 2024a).

6. Silica Formation, Scaling, and Solid–Liquid Separation

6.1 Formation mechanism and aging

Hydrolysis-derived silicon may pass through dissolved species, oligomers, colloids, and gel networks before forming separable solids or adherent deposits. Aging changes aggregate size, compressibility, filter resistance, fluoride retention, and the tendency toward equipment fouling. Acid composition, temperature, residence time, agitation, and impurity concentrations determine the trajectory of these transformations. Laboratory production of silica as a useful coproduct does not, on its own, establish reliable continuous filtration of HF-containing process liquor (Abburi et al., 2025; Bayat et al., 2002; Bayat et al., 2005; Elineema et al., 2013; Jin et al., 2017; Kim et al., 2007; Liu et al., 2017; Sarawade et al., 2010; Vacca et al., 2020; Xu et al., 2014; Yu et al., 2000; Zhang et al., 2026; Zhao et al., 2022).

Figure 3 traces the progression from solution speciation and supersaturation to particle evolution, deposition, filtration limitation, and interruption of continuous operation.

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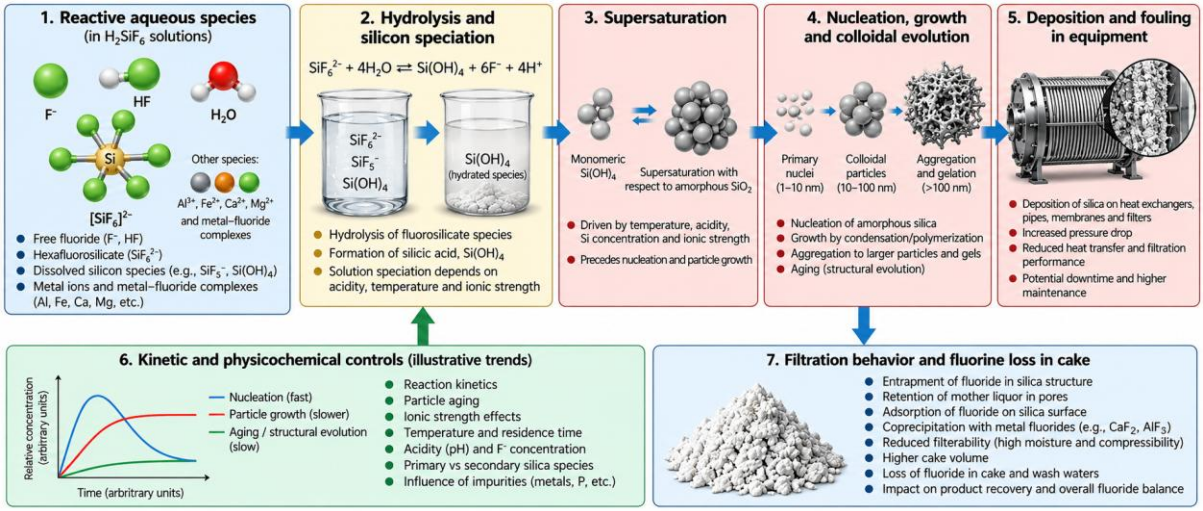

Figure 3. Mechanistic links between silicon hydrolysis, colloidal silica formation, separation behavior, and process interruption.
Note. Original conceptual schematic informed by Bayat et al. (2002, 2005) and related silica-valorization studies; no numerical kinetics implied.

The process implications shown in Figure 3 extend beyond the fraction of silicon precipitated. Cake moisture, fluoride entrainment, wash-water requirements, gel rheology, pressure-drop growth, and product losses can determine whether silica removal is technically sustainable.

6.2 Process metrics for meaningful comparison

Useful normalized metrics include kilograms of dry silica per tonne of recovered HF, filter-cake moisture and fluoride loading, fluorine wash efficiency, filtration flux at specified differential pressure, pressure-drop evolution, cleaning frequency, and silicon breakthrough into HF purification. These indicators should be measured over representative residence times and repeated operating cycles, not inferred from an isolated filtration test (Aldaco et al., 2006; Bayat et al., 2002; Bayat et al., 2005; Kim et al., 2002; Morita et al., 2018; Sarawade et al., 2010; Wang et al., 2026).

For silica management, dry-cake fluoride loading is L_F,cake = m_F,cake/m_dry cake (kg F/kg dry cake), and fluoride washing efficiency is η_F,wash (%) = 100 × (m_F,cake before

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wash − m_F,cake after wash)/m_F,cake before wash; wash-liquor fluorine must appear in the overall balance. Record filtration flux at stated differential pressure and temperature, cake specific resistance where measurable, dry-cake production per tonne of on-spec HF, cake moisture, wash-water-to-dry-solids ratio, filtrate turbidity, soluble and particulate silicon breakthrough, cycle duration, pressure-drop development, reversible and irreversible fouling, and cake-compressibility or rheological observations. Silicon precipitation alone is not a successful separation when gelation, colloid breakthrough, fluoride retention, or scaling prevent continuous operation.

The engineering assessment also requires a coupled silicon–fluorine wash balance, since removal of hydrated silica can shift fluorine into cake liquid or wash streams. A high dry-solids recovery without low fluoride retention can increase reagent consumption and downstream waste-treatment burdens.

7. HF Finishing, Materials Selection, and Operating Safety

7.1 Product-purity framework

Commercial aqueous HF and anhydrous HF are distinct products and must not be grouped under an undefined “HF recovery” claim. A reported product specification should include water and relevant silicon, sulfur, phosphorus, particulate, and metallic contaminants. Depending on the route, gas cleaning, absorption, fractionation, drying, and polishing may be integral parts of the core process rather than discretionary finishing stages (Acker et al., 2007; Dahlke et al., 2016; Dreveton, 2012; El Guendouzi et al., 2015; Henßge et al., 2007; Henßge et al., 2006; Kounbach et al., 2022; Weinreich et al., 2007; Yang et al., 2024a).

For either aqueous HF or AHF, report numerical product specification and measured HF mass fraction together with water, silicon, sulfur, phosphorus, relevant metals, and particulate limits. Identify sampling basis, analytical methods, measurement uncertainty, and

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detection or quantification limits. A claim of "high-purity HF" without an explicit grade and assay is not a reproducible process-performance claim.

7.2 Corrosion and materials compatibility

Materials selection must address actual chemical exposure throughout normal operation, shutdown, startup, and upset conditions. HF and water content, temperature, dissolved impurities, oxygen, suspended solids, erosion, and transient dilution can alter corrosion mechanisms and equipment integrity. Consider PTFE-lined construction, PVDF, graphite, and selected nickel alloys only after service-specific verification of chemical compatibility, pressure and temperature limits, permeation, abrasion, thermal cycling, and maintenance needs. Generic "HF-resistant" classifications cannot substitute for materials qualification.

Plant-specific process safety qualification must include process-hazard analysis, equipment containment, HF/SiF_4 detection and alarm strategy, vent and scrubber contingency capacity, startup and shutdown exposure scenarios, credible loss-of-containment events, and emergency-response arrangements. These are evidence and governance requirements; materials cannot be qualified solely by generalized corrosion-resistance tables. Pilot material testing should document chemical composition, operating temperature, wet/dry transients, erosion by solids, and corrosion observations or coupons as appropriate.

Table 4 organizes the operating risks that must be mitigated before extended pilot operation.

Table 4. Integrated operability and materials-risk register

Failure mode	Potential consequence	Minimum validation
Silica nucleation and gelling	Fouling and shutdown	Aging/filtration at plant conditions
HF/SiF_4 carryover	Out-of-spec product	Impurity mass balance and gas analysis
Wet/dry transient corrosion	Loss of containment	Corrosion coupons and material qualification

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Failure mode	Potential consequence	Minimum validation
Solids entrainment	Erosion, blockage, yield loss	PSD, hydraulic tests, wash studies
Recycle impurity buildup	Drift and higher purge	Steady-state recycle sensitivity

Note. Original engineering risk framework; actual protection measures require plant-specific hazard studies and applicable safety standards.

Table 4 shows why chemistry, equipment, and operability tests must be coupled. A stable flask-scale fluoride conversion can coexist with unacceptable pilot-scale fouling, corrosion, or product instability.

8. Environmental Integration and Alternative Fluoride Valorization

8.1 Recovery and residue accounting

Reusing fluorine from phosphate facilities may avoid waste discharge and potentially displace primary feed production. However, the net outcome depends on energy consumption, neutralization reagent demand, process vents, silica residues, wastewater, and the fate of both fluorine and silicon. A life-cycle comparison should be performed on the same functional unit of specified HF output and should not credit avoided fluorine disposal twice (Epshtein et al., 2020; Fuge, 2019; Gouider et al., 2009; Hogen et al., 2024; Lou et al., 2024; Peng et al., 2021; Peng et al., 2022; Quedi et al., 2024; Ramteke et al., 2021; Tran et al., 2022; Wang et al., 2020; Will, 2016; Yang et al., 2026).

Because by-product H_2SiF_6 does not intrinsically carry a zero upstream burden, the LCA should report allocation sensitivity, including a justified burden-free-waste scenario, relevant mass or economic allocation, and an avoided-disposal credit stated separately. Coproduct displacement and waste-avoidance credits must not be counted twice. Any claimed silica or fluoride coproduct benefit requires demonstrated quality, recoverable volume, destination, displacement logic, and market sensitivity.

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8.2 Markets for coproducts

Alternative outlets for H_2SiF_6 include CaF_2, AlF_3, cryolite, sodium fluoride, engineered silica, and certain construction-chemistry applications. Their relevance is as competing utilization strategies or upstream suppliers, not proof of HF manufacturing. Material specifications, local demand, logistics, and residue liability must be matched to the chosen route (Abburi et al., 2025; Albustami et al., 2014; Chen et al., 2021; Deng et al., 2025; Elineema et al., 2013; Gardiner, 2015; Gelmboldt, 2023; Jiang et al., 2021; Jiang et al., 2025; Jin et al., 2017; Kim et al., 2007; Liu et al., 2017; Lv et al., 2024; Ma et al., 2024; Morita et al., 2018; Sarawade et al., 2010; Sicard et al., 2020; Vacca et al., 2020; Wang et al., 2026; Wang et al., 2024; Wang et al., 2025; Ya et al., 2019; Yang et al., 2022; Yu et al., 2000; Zhang et al., 2023; Zhang et al., 2026; Zhao et al., 2022).

9. Industrial Evidence, Process Scale-Up, and Techno-Economics

9.1 Interpreting published industrial claims

Available industrial descriptions and techno-economic studies justify examining H_2SiF_6 conversion, but their conclusions are difficult to compare without consistent boundaries. Differences in acid concentration, plant integration, impurity burden, target HF grade, capacity utilization, cost year, and utility accounting can reverse an apparent ranking. Evidence for industrial readiness is strongest when supported by sustained operations, measured product assays, maintenance records, equipment-scale observations, and reconciled fluorine and silicon balances (Dahlke et al., 2016; Dreveton, 2012; Dreveton, 2014; Dreveton, 2016; Gelmboldt, 2023; Hogen et al., 2024; Li et al., 2025; Tomaszewska, 2000; Will, 2016; Yang et al., 2024a; Zhang, 2023).

Dahlke et al. (2016) provide valuable process-developer descriptions of pilot and commercial implementation, establishing evidence of industrial deployment. Such reporting should not be confused with an independently audited, multi-year dataset covering feed

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variability, saleable product yield, operating availability, maintenance, silicon carryover, and waste streams. Maturity is therefore recorded independently from relevance, and whole-plant TRL is not assigned from component-scale or descriptive evidence alone.

9.2 Economic sensitivity and boundaries

An economically meaningful comparison should adopt one functional unit—one tonne of on-specification saleable HF—and report the tonnes of H_2SiF_6 solution and contained fluorine required per tonne of product. Feed availability, preconcentration, utilities, corrosion-resistant equipment, silica washing and disposal, downstream purification, turnaround frequency, process utilization, and credible coproduct revenues should all enter the assessment. Economic sensitivity should vary uncertain inputs rather than present a single deterministic advantage. The available evidence does not substantiate an unconditional claim that secondary-feed HF is less costly than fluorspar-based production (Dreveton, 2014; Hogen et al., 2024; Joshi, 2022; Li et al., 2025; Matta et al., 2017; Tomaszewska, 2000; Will, 2016).

On-stream availability should be reported as A (%) = 100 × t_on-stream/t_scheduled, with the scheduled basis disclosed. Together with throughput and product grade, report run length between cleaning, cleaning downtime, irreversible capacity loss, filter-media replacement, corrosion-related maintenance, and unplanned shutdowns. Evaluate recycle through an impurity component balance: at quasi-steady state, total external impurity input must equal impurity discharge in product, purges, residues, and emissions; otherwise, quantify accumulation and required purge. Comparable TEA must include conditioning, concentration, reagents, utilities, filtration and silica management, corrosion-resistant equipment, purification, effluent treatment, maintenance, downtime, and utilization. The consistent functional unit is one tonne of saleable on-specification HF, with site, market, and coproduct sensitivity analyses.

A useful maturity discussion is limited to specific operations with demonstrable validation. For example, a published process description is not sufficient for assigning a whole-

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plant TRL; only documented operating scale, duration, integration, and product conformity can support a defensible maturity classification.

10. Critical Synthesis: What Limits Adoption?

The principal barrier to industrial adoption is the interaction among feed variability, coupled HF–SiF_4–water equilibria, silica formation and separation, and corrosive HF finishing. Improving fluoride release in one operation can increase water-removal demand, silica deposition, contaminant carryover, or fluorine retention in residues elsewhere in the flowsheet. An isolated conversion maximum may therefore correspond to poor net HF yield or limited availability in continuous service (Bayat et al., 2002; Bayat et al., 2005; Dahlke et al., 2016; Dreveton, 2012; Dreveton, 2014; El Guendouzi et al., 2015; Gelmboldt, 2023; Joshi, 2022; Tomaszewska, 2000; Yang et al., 2024a).

This coupled perspective changes the order of development decisions. Feed characterization and elemental accounting should precede nominal process ranking; bench tests should examine HF grade alongside silica separability; and integrated pilot operation should demonstrate recycle stability, maintainability, and availability. Recovering CaF_2 or AlF_3 remains commercially relevant, but those routes require a separate product and market assessment.

Figure 4 converts these requirements into sequential evidence gates, while Table 5 specifies minimum decision criteria for distinguishing a defensible HF manufacturing scheme from an unqualified chemical concept.

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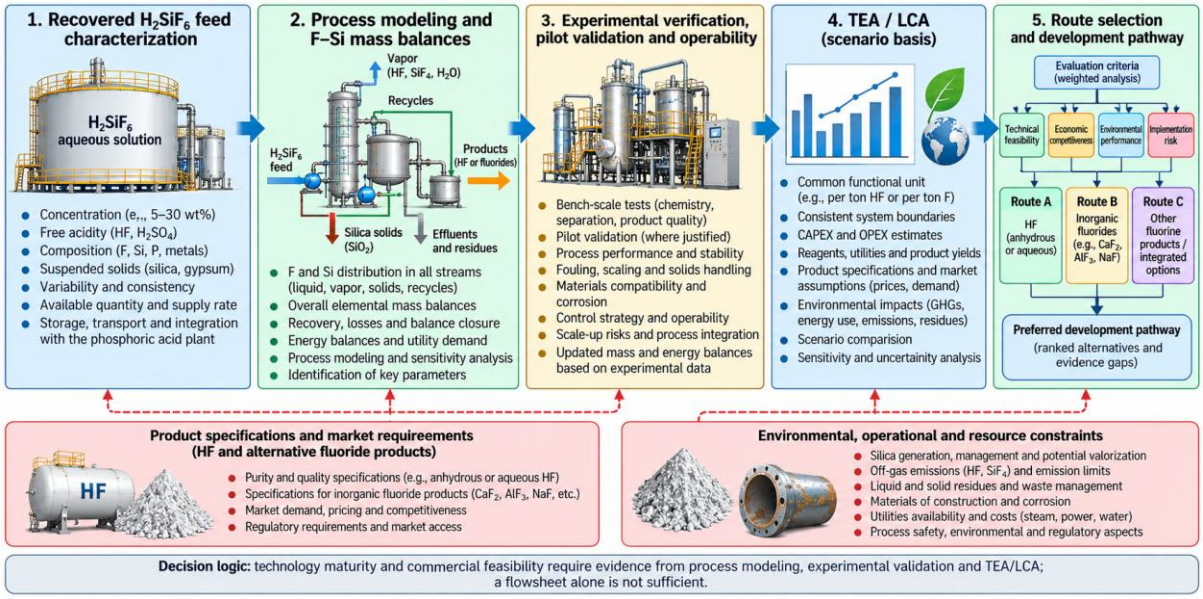

Figure 4. Stage-gated decision framework for evaluating H_2SiF_6-to-HF routes under industrial constraints.
Note. Original conceptual framework integrating chemistry, mass balances, operability, techno-economics, and product qualification.

Figure 4 emphasizes that technical selection should be revisited as material balances and pilot evidence improve. No route should be favored solely because H_2SiF_6 is a low-cost by-product.

Table 5. Recommended evidence package for comparative qualification of an HF production route

Gate	Minimum evidence	Decision metric
G1 Feed	Multiperiod characterization	F/Si composition variability
G2 Chemistry	Equilibria and impurity speciation	Independent F and Si closure
G3 Separations	Silica filterability and HF purity	Yield at target grade
G4 Operability	Continuous integrated pilot test	Uptime, cleaning, corrosion
G5 Sustainability/TEA	Common-boundary cost and inventory	Risk-adjusted cost per tonne HF

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Note. Original proposal; quantitative acceptance limits must be selected from product specifications and project requirements.

Table 5 provides an empirical basis for technology claims. In particular, a single high yield measured on a controlled synthetic feed is insufficient to qualify a plant handling real scrubber liquor.

11. Knowledge Gaps and Prioritized Research Agenda

11.1 Equilibrium, speciation, and transport data

A first priority is reproducible phase and speciation information for realistic H_2SiF_6–HF–SiF_4–H_2O–impurity compositions, validated over pressure, temperature, and concentration ranges relevant to equipment design. This includes the kinetics and hysteresis of silica precipitation, and the dependence of fluoride retention on ionic strength and solid aging (El Guendouzi et al., 2015; Hu et al., 2026; Kounbach et al., 2022; Long et al., 2020; Ndiaye et al., 2022; Pan et al., 2023; Tomaszewska, 2000; Yang et al., 2024a).

11.2 Integrated, auditable pilot evidence

Pilot campaigns should employ industrial H_2SiF_6 feed from multiple operating periods and report all major material outputs, including gas vent, condensate, product HF, silica cake, wash liquor, wastewater, and recycle purge. Comparative testing requires at least a common product grade and a measured on-stream factor. Standardized impurity analyses, corrosion monitoring, and filter performance would make published results substantially more transferable (Bayat et al., 2002; Bayat et al., 2005; Dahlke et al., 2016; Dreveton, 2014; Hogen et al., 2024; Joshi, 2022; Li et al., 2025; Tran et al., 2025).

Proposed pilot qualification should report measured inlet and outlet mass flows, element-resolved balances, acceptable product specifications, comparative impurity assays, silica filtration performance, corrosion observations, operational interruptions, and the

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disposition of fluoride-bearing residues. Where feed variability spans plant operating modes, uncertainty limits must accompany averaged data.

11.3 Transparent process selection

Future assessments should report uncertainty bands, product-specific market assumptions, and the impact of upstream phosphate-plant integration. Emerging membranes and intensified reactor concepts deserve investment primarily when they demonstrate continuous separation and maintainable units at scale, not only chemically attractive laboratory products (He et al., 2023a; Qiu et al., 2022; Qiu et al., 2025a; Qiu et al., 2025b; Tomaszewska, 2000; Yang et al., 2024b; Yang et al., 2025).

12. Conclusions

Hexafluorosilicic acid is a potentially valuable secondary fluorine resource, but fluorine content alone does not establish viable production of specification-grade hydrogen fluoride. The decisive challenges are coupled fluorine–silicon–water chemistry, representative feed preparation, silica formation and removal, corrosion, recycle control, and HF finishing. Direct HF manufacture must be distinguished from fluoride-salt and silica valorization, and all comparisons must apply consistent product specifications and complete fluorine and silicon balances. The most valuable next steps are verified phase-equilibrium measurements, representative industrial feed characterization, integrated silica and fluoride-loss studies, extended continuous pilot demonstrations, and comparable economic and environmental assessments. Without this evidence, assertions of general cost superiority, commercial readiness, or environmental benefit remain premature. This review provides a transparent framework for selecting the measurements and qualification tests needed to reduce these uncertainties.

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