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Economical comparison of Hydrofluoric Acid Production from Fluorosilicic Acid and Fluorspar

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Abstract

The fluorine content in the phosphate rock generates a toxic gas and subsequently neutralization costs to the phosphoric acid producers. The fluorine is typically scrubbed as fluorosilicic acid (FSA) and only small quantities of this FSA are commercially used (drinking water fluorination, metal cleaning etc.). Instead the FSA is neutralized or dumped. These expenses can be minimized by producing a high value product: anhydrous hydrofluoric acid (AHF). This paper compares the traditional and established process to make AHF from fluorspar, a mined ore, with the new process to make AHF from FSA. AHF is a widely used precursor for pharmaceuticals, herbicides, refrigerants, rechargeable lithium batteries and many more.

The comparison of these distinct processes is made in a methodical and standardized way and covers the economical and the ecological factors. As per today, only 3% of the global AHF production capacity is based on using FSA as a feedstock. This paper gives an overview of the different opportunities of the two processes.

Keywords: Fluorosilicic Acid, Hydrofluoric Acid, Environmental Protection, Process Economics, Fluorspar

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1. Introduction

The majority of the world’s anhydrous hydrofluoric acid (AHF) production plants uses acid grade fluorspar. Only a minor percentage uses the economically advantageous process with fluorosilicic acid (FSA) as a raw material.

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Process plants with fluorspar as raw material are in operation for several decades. The process is well established and the plants, independent of the technology provider, have a rotary kiln, off-gas and anhydrite handling and liquefaction/purification sections [1].

The idea of making AHF from FSA has been researched and patented during the last decades. Numerous patents and process designs have been published. Thus far, only one process has been built in industrial scale [2].

The process to make AHF from FSA offers phosphoric acid (PA) producers a way to manufacture a high value product from a waste stream. The process has many advantages including no or negligible raw material costs, re-useable sulphuric acid (SA) and independence of the international fluorspar market. The latter aspect is currently of growing importance as some countries have export limitations on fluorspar, causing price fluctuations. Despite these many advantages and increasing pressure due to stricter environmental regulations, PA producers are nonetheless hesitant to investigate this possibility.

This is mostly due to a lack of information on process economics and the safe production, handling and transportation of AHF. The process design is studied using qualitative and quantitative risk analysis [3]. Process safety can be ensured by integrating all identified safety relevant requirements in the plant design.

An exhaustive study comparing the fluorspar with the FSA process has not been carried out to date. This paper presents a comparison of the two processes based on standard methods for environmental impact studies and economical models. Potential customers will be able to judge feasibility based on investment and operation costs for both, the traditional fluorspar process and Buss ChemTech's FSA process.

Strategical decisions from AHF Producers such as independency of international fluorspar trading, securing the AHF supply, integrated production using AHF as intermediate, company internal standards and regulations are not covered within the scope of this paper.

Nomenclature

AHF	Anhydrous Hydrofluoric Acid
Anhydrite	$CaSO_4$
CAPEX	Capital Expenditure
Fluorspar	Ore (≥ 97 wt-% calcium fluoride, CaF_2)
FSA	Fluorosilicic Acid (H_2SiF_6)
Oleum	Fuming sulphuric acid
OPEX	Operational Expenditure
PA	Phosphoric Acid (H_3PO_4)
ROI	Return on investment
SA	Sulphuric Acid, H_2SO_4
Silica	SiO_2
STF	Silicon Tetrafluoride, SiF_4

2. Methodology

2.1. Methods Used

An economic evaluation of chemical process plants is based on numerous factors. In general, two important aspects for decision-makers are to be clarified in order to approve an investment. On the one hand, the economy (CAPEX and OPEX) of a process plant must be known. On the other hand, the ecological factors cannot be neglected. However, ecological factors such as a reduction of energy consumption (and consequently the carbon footprint) will be given more importance when they are directly linked with cost savings. Further, the ecological factors are strongly dependent on the location of a process plant, the company internal or local regulations and the sustainable operation.

A comparison of two fundamentally different processes to manufacture the identical product must be based on relative numbers for consumption of raw materials, utilities, electricity and man power. For processes, annual industrial AHF production capacities of 53’000 t/a (fluorspar) and 20’000 t/a (FSA), respectively, were used to determine the characteristic numbers.

The ecological factor based on carbon footprint can be assessed according to the methods given in the greenhouse gas protocol [4]. In case of the comparison of two process plants, a project-specific procedure is applied.

The economic aspects to conclude the comparison of chemical production plants are done with a static approach for the calculations of the investments [5], [7]. Final result of the evaluation are the return on investment (ROI) and the payback period. The detailed calculation has been performed according to the methods in [7]. Within the scope of this paper, the results are presented as a shortened summary.

2.2. Application of the Methods

To determine the required numbers for an economic and ecologic comparison of the processes to manufacture AHF from fluorspar and FSA, both must be characterized with an approach based on the laws for the conservation of heat and mass (heat and mass balance), refined with consumption figures of operating industrial scale plants. Within a process plant, this defines all process streams and requirements for heating and cooling, combustion and electricity. When performing a mass balance, firstly, the boundary of the system is to be defined. Secondly, the resulting equations are solved analytically or by iterative methods. The result of a mass and heat balance gives characteristic numbers related to the amount of product. These are

- Raw material consumption
- Effluents, off-gases and by-products
- Utility consumption (steam, cooling water, fuel gas…)
- Electricity demand

To link these technical numbers to an operational cost calculation, prices for

- Raw materials (including transportation)
- Products (selling price)
- Utilities (costs per ton of steam, cooling water, fuel gas…)
  must be considered.

The carbon footprint of the processes is calculated according to the IPCC Guidelines [6]. For the calculation of the carbon footprint, the approach for stationary combustion was chosen due to the assumption that all emissions and required electrical power for utilities are based on the combustion of natural gas. The energy consumption was taken from operating industrial scale plant data, engineered by Buss ChemTech and not from literature. The equivalent of CO_2 per kWh for natural gas is defined as 667 g/kWh [8].

We have chosen the system boundaries such that secondary energy like steam, is only included as a direct combustion of natural gas. However in these processes, mostly steam is taken from sulphuric acid plants located on site or in close vicinity. Therefore, the carbon footprint for a steam boiler will exaggerate the numbers. For comparability reasons and simplification, the sulphuric acid plant was not included in the system boundaries for both processes.

2.3. General Assumptions and Definitions

To compare the processes, the plant capacities for this paper have been set to 30’000mtpy AHF. The investment and the total production costs have been estimated for these capacities.

The plant will be designed, constructed and erected within 3 years, the fixed capital investment is assumed with 15% in the first, 35% in the second and 50% in the third year. The startup costs are due in the first production year.

The investment costs are estimated based on Western European equipment prices, construction and installation rates.

The production costs include direct costs such as raw materials, utilities, labor, maintenance and consumables and indirect cost as administrative expense, depreciation, interest.

The plant capacity considered is 50% for the first, 75% for the second and 100% of the name plate capacity for the third and the consequent production years.

The depreciation calculation is considering a linear depreciation over ten years and the annual inflation is assumed with 2%.

An income tax of 35% per annum has been applied on the profit.

The price assumption for raw materials and products in table 1 and the operating labor costs in table 2 have been used in the calculation.

Table 1: Price Assumptions for Raw Materials and Products

	Fluorspar Process	FSA Process	Unit
Fluorspar [9] (basis FOB China)	260	-	USD/t
Sulphuric Acid	60	0 *1)	USD/t
Fluorosilicic Acid	-	0 *2)	USD/t
AHF [10] (basis EXW China)	1150	1150	USD/t
Anhydrite	9	-	USD/t

*1) Sulphuric acid is not consumed in the FSA process and will be returned to the PA plant.

*2) FSA is considered as free of charge, on the other hand the obsolete neutralization costs for the FSA are not considered.

Table 2: Price Assumption for Operating Labor Costs

	Fluorspar	Fluorosilicic Acid	Unit
Number of operators per shift	6	6	-
Shifts per day	3	3	-
Operator rate	50	50	USD/h

The price assumption in table 3 have been applied and may vary depending on the location of the plant:

Table 3: Price Assumptions for Utilities

	Default costs	Unit
Instrument air	0.05	USD/m^3
Electricity	0.061	USD/kWh
Fuel – Natural Gas	3.00	USD/GJ
Refrigeration	15.00	USD/GJ
Steam, saturated	12.00	USD/t
Cooling Water	0.02	USD/m^3
Demineralised Process Water	1.15	USD/m^3
Waste Water Treatment	0.53	USD/m^3

3. Results

3.1. AHF from Fluorspar

3.1.1. Heat and Mass Balance

AHF from fluorspar is manufactured by intensive mixing of sulphuric acid, oleum and fluorspar in a prereactor. The mixture is reacted in a rotary, indirectly fired kiln. HF as product and anhydrite ($CaSO_4$) as by-product are coming as gaseous and solid streams from the kiln. The crude HF gas is purified and liquefied before going to storage or to further downstream processes. The off-gas from liquefaction and the HF generation are treated in a series of scrubbers before being released to atmosphere. The main raw material (fluorspar) must be available in exactly defined boundaries for particle size distribution and impurities. This is to ensure a reaction that leads to a sufficient yield and a non-violent reaction. In case of too small particles, the reaction is violent, leads to dust formation and consequently problems in operation. Too high impurity levels are responsible for higher acid consumption and increased corrosion rates. Impurities as arsenic or P_2O_5 can be reduced with additional process steps. This comparison is made with a high quality fluorspar without these hazardous impurities.

In Figure 1, the boundary for the process to manufacture AHF from fluorspar is shown. For simplification reasons, only the main process flows and the main source of energy are shown. Utilities are summarized in tabular form.

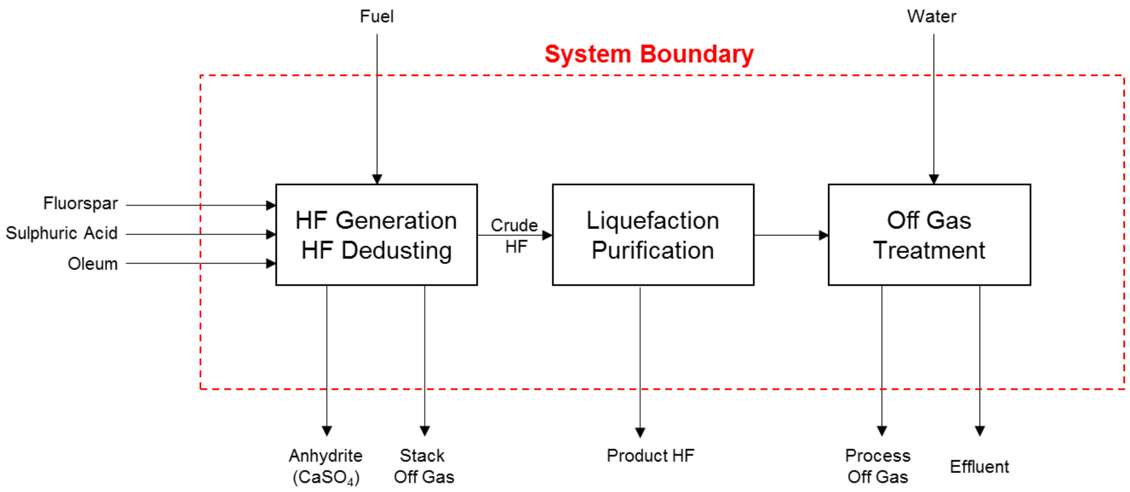

Fig. 1. System boundary and main process flows for the process to manufacture AHF from fluorspar

Results of the heat and mass balance are summarized in table 4. All numbers are related to one ton of produced AHF.

Table 4: Summary of the mass and heat balance results per metric ton of AHF produced from fluorspar

		Unit
Electrical Energy	220	kWh
Combustion Gas	1329	kWh
Steam	224	kWh
Cooling Tower Water	4	kWh
Chilled Water	250	kWh
Sulphuric Acid	2.45	t
Fluorspar	2.15	t
Water	0.8	t
Anhydrite	3.6	t
Liquid Effluent	0.85	t

The carbon footprint for the process has been calculated to 1’353 kg CO_2 equivalent for one metric ton of AHF produced. This number is the sum of the CO_2 equivalent of each utility (electrical energy, combustion gas, steam and cooling tower and chilled water).

3.1.2. Economic Evaluation

The economic evaluation for the fluorspar process (over the first 10 years) shows the results summarized in table 5.

Table 5: Economical evaluation of the process AHF from Fluorspar after 10 years

Fixed capital investment	-52.9	mio USD
Total capital investment	-59.7	mio USD
Total gross profit	-39.6	mio USD
Total net profit	-39.6	mio USD
Total operating cash flow	13.3	mio USD
Payback period	39	years

3.2. AHF from FSA

3.2.1. Heat and Mass Balance

AHF from FSA is manufactured by mixing concentrated FSA with sulphuric acid. The sulphuric acid acts as a sort of catalyst (not like its classical definition) and splits the FSA into HF and SiF_4 (Silicon Tetrafluoride, STF). The STF is separated from HF and is fed to the concentration plant, where the weak FSA is contacted in counter-current flow with the STF and is concentrated up to values close to the theoretically achievable maximum concentration. In the final stage of the concentration plant, silica crystallizes in acidic conditions and is filtered off. Silica can partially be reused in the PA plant.

In Figure 2, the boundary for the process to manufacture HF from FSA is shown. The same assumptions for the main process flows and energy sources are made.

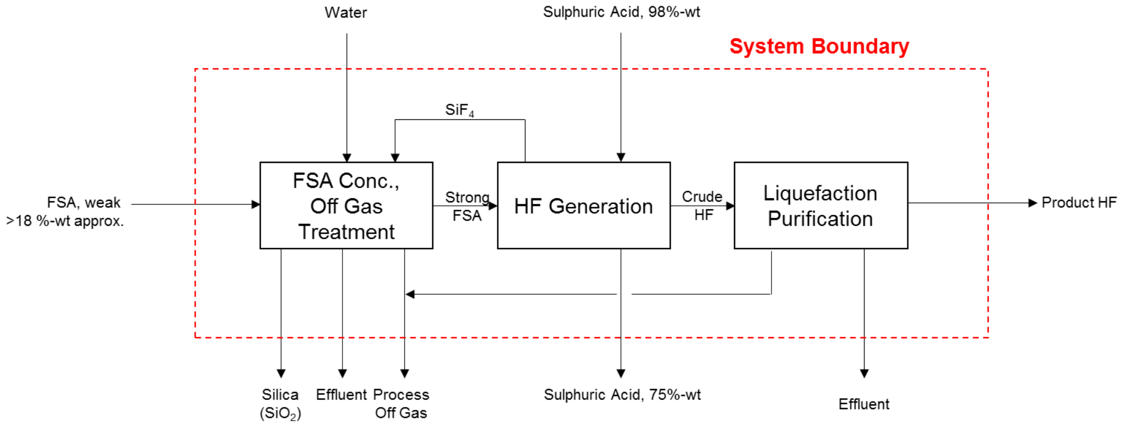

Fig. 2. System boundary and main process flows for the process to manufacture AHF from FSA

Similar to section 3.1.1, the results of the heat and mass balance are summarized as follows in table 6.

Table 6: Summary of the mass and heat balance results per metric ton of AHF produced for from FSA

		Unit
Electrical Energy	235	kWh
Steam	3785	kWh
Cooling Tower Water	94	kWh
Chilled Water	557	kWh
Sulphuric Acid	0	t
Water	2.6	t
Silica	1.5	t
Liquid Effluent	1.0	t

The carbon footprint of this process was estimated to 3’115 kg CO_2 equivalents per metric ton of AHF produced.

3.2.2. Economic Evaluation

In table 7, the main parameters for the FSA process are listed (as a total over a period of 10 years).

Table 7: Economical evaluation of the process AHF from FSA

Fixed capital investment	-60.1	mio USD
Total capital investment	-67.0	mio USD
Total gross profit	142.3	mio USD
Total net profit	92.0	mio USD
Total operating cash flow	152.2	mio USD
Return on investment, average	13.7	% per annum
Payback period	4	years

4. Discussion

This discussion must be read under the precondition that the above made economical evaluations are made with the assumption listed in section 2.3 above and is a snap-shot at the time of this paper.

The AHF market price is having a volatility influenced by several factors. About 97% of the global AHF quantity is produced with the fluorspar process. With a consumption of approx. 2.2 metric ton fluorspar per metric ton AHF the fluorspar price is substantial factor and contributes around 75% (USD 260/t fluorspar corresponds to USD 575/t AHF) of the raw material costs. Figure 3 shows the price development over the last years [11]. Sulphuric acid, a widely used commodity and the other raw material, is available to stable prices and can be considered as constant. The economical evaluation of the fluorspar process results in a payback period of around 39 years what is beyond an acceptable return on investment. Figure 4 shows that the payback period of the investment as a function of the fluorspar price. With the current AHF market price, the investment into a brown field AHF plant be worthwhile with a fluorspar price in the range of USD 150-170.

AHF producers using the FSA process are converting a scrubbed waste gas from the PA plant into a valuable product. The PA plant operators have to scrub the STF, in order to neutralize the FSA to fulfill the environmental regulations. Attaching the FSA process to a PA plant makes on one hand this neutralization step obsolete and results in cost savings. On the other hand a part of the FSA can be sold for water fluorination or other applications and generates an income. Compared to the fluorspar process, the sulphuric acid in the FSA process is not consumed and is returned diluted to the PA plant. In the view of these aspects the costs for the FSA and the sulphuric acid have been defined as free of charge in the economical evaluations.

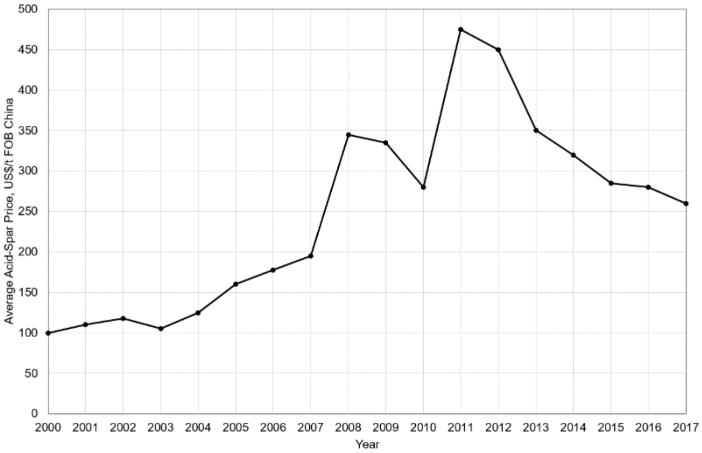

Fig. 3. Development of the prices per ton of fluorspar between 2000 and 2017 [11]

The total capital investment to build a plant using the FSA process is roughly 10% higher. This is mostly due to different material of construction for certain equipment and two additional stripping sections. These two strippers are the reason why the operating costs are twice as high as for the fluorspar process. As this AHF plant is connected to a PA complex, the steam will be generated in the integrated SA plant, means at low price. For comparability reasons in both economical evaluations the same steam price has been considered. Nevertheless the calculated payback period with 4 years is very attractive compared to the almost 40 for the fluorspar process. The negligible costs for the raw materials are contributing to the profit. Even with 50% name plate capacity in the first and 75% in the second year, the plant will generate a net profit during the second year.

On the technical side of the comparison, the fluorspar process uses a large amount of fuel to heat the rotary kiln. Looking at the ecological aspects, here made by comparing the CO_2 equivalents, the FSA process theoretically emits almost three times more CO_2 than the fluorspar process. It has to be mentioned that usually, both processes will have an independent steam supply at low or no cost. If this is considered, then the equivalent is reduced to 1’203kg for fluorspar and 591kg CO_2 for FSA process, respectively. The change in favor of the FSA process can be explained with the major contributing factor of CO_2, by the burner to heat the rotary kiln of the fluorspar process.

5. Conclusion

As lined out in section 4, based on current fluorspar and AHF prices, the investment in a new AHF plant from fluorspar, only based on the return on investment and payback period figures is not attractive. This is applicable to AHF plants in North America, Europe or Japan where the investment and operating costs are high. It has even been observed that a few already depreciated AHF plants have been shut down in these countries in the last years. Others have been dismantled and moved to the vicinity of fluorspar mines.

Nevertheless a couple of AHF plants are still in operation in these countries. Based on the economic evaluation in this paper, it is assumed that these AHF plants are operating at the breakeven point or even with annual losses. However, AHF is an intermediate product used for production of downstream products, mainly for fluorocarbons and aluminium fluoride. To keep the AHF production from fluorspar upright has mainly strategical reasons for these companies as:

- Companies own a fluorspar mine and do not procure the raw material to world market prices
- The AHF production is subsidized with the revenues from other downstream products

- Producing AHF is a strategic decision to be independent from the world market or even from a direct competitor for sourcing AHF

Having a chemical production complex for AHF and downstream products will reduce the operation costs by using the common infrastructure, utilities, logistics and general administration. Nevertheless it is expected that the pressure on these producers will increase in the near future. The main reason is the constant high consumption of fluorspar in combination with the decreasing reported fluorspar reserves, which results in higher prices. In addition to this shortage the available fluorspar is containing impurities as arsenic or P_2O_5 and the existing plants must be extended by additional removal sections.

AHF plants using the FSA process are neither affected by a shortage of raw materials, the fluorine is in the phosphate rock nor dependent on price fluctuations, FSA can be considered as a waste. With the current PA production capacity, approximately 3.4 Mio tons FSA per annum (calculated as 100 wt-%) could be recovered and used as raw material. Therefore potential new AHF plants using the FSA process are located either directly at the PA complex or in the close vicinity. This results in the following benefits:

- The sulphuric acid and the FSA are readily available
- Sulphuric acid is used to split the FSA molecule only and is returned diluted to the PA complex, only minor changes in the PA unit necessary
- The sulphuric acid unit generates the required steam at no or low costs
- Neutralization of the FSA is obsolete

Both economical evaluations are made for standalone plants. As outlined above in section 3.2.2 table 7, the calculated payback period for the FSA process is 4 years. If the plant is linked directly to an existing PA plant, the investment and operating costs can even be reduced significantly by sharing the common infrastructure and utilities.

The environmental legislations are being tightened worldwide and PA producers are forced to reduce their fluorine emissions. As the scrubbed FSA is in most cases neutralized or disposed to sea or ponds, an AHF plant using the FSA process will reduce the neutralization costs and the same time the operating costs of the PA plant.

As implication of this economical comparison, an investment in a AHF plant using fluorspar as raw material is only worthwhile if strategic considerations are the driving force or fluorspar from an own mine is processed.

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