International Fertilizer Industry Association

IFA Technical Conference

New Orleans, Louisiana, USA
1-4 October 2000

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

Recovery of fluosilicic acid and fluoride bearing waters for the production of a mixture of silica and precipitated calcium fluoride usable for the production of cement

Michele Lavanga*, Sergio Di Lena*, Shane Sullivan** and Alan Ingram**
* Fluorid S.p.A, Italy, ** Svedala Ltd., Sweden

Fluorsid est une société de chimie, implantée en Italie, qui produit des dérivés du fluor, fluorure d'aluminium et cryolithe synthétique, pour l'industrie de l'aluminium.

Svedala est un constructeur multinational suédois de équipements pour l'industrie.

Bien que pas impliqué dans l'industrie d'engrais, Fluorsid participe à cette Conférence Technique en présentant un mémoire, parce qu'elle partage avec plusieurs sociétés du secteur le souci d'éliminer les eaux résiduelles contenant acide fluosilicique et fluorhydrique. Fluorsid a résolu ce problème par le biais d'une installation construite en coopération avec Svedala.

Comme les producteurs d'engrais le savent bien, l'elimination de l'acide fluosilicique est un problème écologique très important dans la fabrication de l'acide phosphorique et des engrais phosphorés.

Les fluorures, tels que le tetrafluorure de silicium et l'acide fluorhydrique, sont parmi les principales sources de pollution résultant de la production de l'acide phosphorique. Les roches de phospate contiennent de 2 à 4 pourcent de fluor. Une partie de ce fluor est précipitée avec le gypse, une autre partie est lixiviée avec l'acide phosphorique produit, et la partie restante est vaporisée dans le réacteur ou le vaporisateur. La répartition relative du fluor parmi ces trois formes dépend du type de la roche, de la configuration de l'installation et des conditions de fonctionnement.

Du réacteur et du vaporisateur, le fluor est libéré au début sous forme de fluorure d'hydrogène, mais en présence de la silice il réagit aisément au tetrafluorure de silicium de forme:

$$CaF_2 + 2H^+ \longrightarrow 2HF + Ca^{++}$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

Normalement on absorbe cette vapeur à travers un lavage è l'eau, pour former de l'acide fluosilicique:

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2$$

La quantité d'acide fluosilicique obtenue comme sous-produit dans la production d'acide phosphorique est normalement entre 20 et 40 kilogrammes (sous form de H_2SiF_6 100%) par tonne de P_2O_5 produit.

E-mail :* fluorsid@tin.it
** shane.sullivan@svedala.com
** alan.ingram@svedala.com

Actuellement, seule une petite partie de cet acide est utilisée. Dans la plupart des cas, l'effluent est simplement déchargé dans la mer ou dans des cours d'eau douce.

Il est, donc, évident que l'élimination de ces effluents est un problème d'environement de plus en plus grave pour les producteurs d'acide phosphorique. Selon la loi italienne, la concentration des ions F^- dans des décharges en mer ou en eau douce ne doit pas dépasser la valeur de 6 mg/litre.

Introduction

Fluorsid is a chemical company, based in Italy, which produces fluorine derivatives, namely aluminium fluoride and synthetic cryolite, for the aluminium industry.

Svedala is a Swedish multinational manufacturer of process equipment for industry.

The reason why Fluorsid, which is not involved in the fertilizer industry, is taking part in this Technical Conference by presenting a paper, is because it shares with many companies of this sector one identical problem: the elimination of waste waters containing fluosilicic acid and hydrofluoric acid. Fluorsid solved this problem with a plant built in cooperation with Svedala.

As fertilizer producers well know, the disposal of fluosilicic acid is a major environmental problem of phosphoric acid and phosphate fertilizer manufacture.

Fluorides, such as silicon tetrafluoride and hydrogen fluoride, are among the main polluting streams resulting from phosphoric acid production. Phosphate rocks contain 2 to 4 percent fluorine. Part of the fluorine from the rock is precipitated with the gypsum, another part is leached out with the phosphoric acid product, and the remaining portion is vaporized in the reactor or evaporator. The relative distribution of fluorine among these three forms depends on the type of the rock, the plant configuration and the operating conditions.

From the reactor and the evaporator, fluorine is liberated initially in the form of hydrogen fluoride, but in the presence of silica it readily reacts to form silicon tetrafluoride :

$$CaF_2 + 2H^+ \longrightarrow 2HF + Ca^{++}$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

It is common practice to absorb this vapour by water scrubbing, to form fluosilicic acid:

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2$$

The quantity of fluosilicic acid obtained as a by-product in phosphoric acid production is normally in the range 20 to 40 Kg (as H_2SiF_6 100%) per ton of P_2O_5 produced.

At present, only a small portion of this acid is used. In most cases, the effluent is simply discharged to sea or to fresh water rivers.

It is, therefore, evident that the disposal of these effluents is an ever more serious environmental problem for phosphoric acid manufacturers. According to Italian law, the concentration of F^- ions in sea or fresh water discharges must be lower than 6 mg/liter.

Fluorsid's experience

Fluorsid has produced, since the early 1970's, hydrogen fluoride, aluminium fluoride and synthetic cryolite (sodium hexafluoroaluminate). These last two products are used by the aluminium industry. Fluorsid is one of the main producers in the world of aluminium fluoride and the largest producer of synthetic cryolite.

For the production of 60,000 tons per year of cryolite and aluminium fluoride, Fluorsid consumes about 90,000 tpy of acid grade fluorspar, which contains on average 1% SiO_2. During the first phase of the process, hydrofluoric acid is produced through the attack of fluorspar using sulphuric acid which takes place in rotary kilns at a temperature of 200°C. Silicon tetrafluoride, coming from the reaction between HF and SiO_2, then develops together with HF. The SiF_4 constitutes a pollutant in the gaseous stream and is separated downstream of the production process through absorption in water. Fluosilicic acid is thus obtained. Annually a total quantity of about 2,200 tons (basis H_2SiF_6 100%) is recovered:

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2$$

To this, we add hydrofluoric acid contained in the mother liquor of the cryolite production process as well as in fluorinated waters coming from wet scrubbers of other production processes.

The total stream is then conveyed to the water treatment plant where Fluorsid overall treats about 600,000 cubic meters per year of waste water containing about 3,000 tpy of fluorine (as F).

In the course of Fluorsid's activity of more than thirty years, to which the experience acquired by its technicians at other companies since the 1950s has to be added, various solutions have been put into operation aimed at the recovery of hydrofluoric acid in order to obtain fluorinated products. Also the literature is full of patents, studies, publications in this sense: Paul A. Smith, of Société Chimique Prayon-Rupel, has indicated in its presentation at the IFA meeting of Novgorod, in September 1999, nearly 400 bibliographical quotations on the recovery of fluorine from the effluent waters.

The various solutions undertaken by Fluorsid (or by its technicians prior to Fluorsid's existence) have been the following:

1. Production and sale of sodium fluosilicate. This was abandoned because the market is too limited.
2. Production and sale of sodium fluoride. Abandoned for the same reason as above.

3. Production and sale of aluminium fluoride. Abandoned because the resulting product has qualitative characteristics no longer suitable to be employed with the modern

technologies for aluminium production (it has in fact a bulk density of 0.6 Kg/dm^3 and cannot be fed into the electrolysis cells with the point feeder system).

4. Production and sale of synthetic cryolite. Abandoned for quality and cost problems.

5. Disposal of fluorinated muds coming from water treatment plant, after neutralization with calcium carbonate and calcium hydroxide.

This last solution was the most economic. However since the early 1990s this method of disposal has become impracticable due to new more restrictive rules and extremely high (60 US$/wet ton) disposal costs. Consequently, Fluorsid has been compelled to look for new solutions.

A careful market survey uncovered in the cement industry an interesting consumer of low concentration calcium fluoride. The cement plants, in fact, add fluorspar during the preparation of the raw cement mix both for obtaining a white cement and to adjust the mineralization of the available raw materials. The CaF_2 contents acceptable for this application are in the order of 40-50%.

Fluorsid's attention has been focused on developing a product of this kind. Through laboratory and a pilot plant research, Fluorsid has been able to optimize its own water treatment plant (containing hydrofluoric acid and fluosilicic acid) in order to obtain a synthetic compound whose chemical composition would be acceptable to the cement plants.

The Fluorsid product has a residual humidity at 110°C of about 30%; the chemical composition is found within the following range:

CaF_2	50÷65%
SiO_2	9÷10%
$CaSO_4$	8÷10%
$CaCO_3$	3÷6%
Al_2O_3	2÷3%
Fe_2O_3	1÷2%
$MgCO_3$	1÷2%
L.O.I. (450 °C)	10% max.

Mg, Fe and certain heavy metals (Pb, Zn, Cu, Sn), are present at concentrations of a few parts per million, they come from the limestone or from the lime which is used for the neutralization of waste waters. The calcium sulphate originates from the neutralization of acid waste waters containing H_2SO_4.

Description of the Fluorsid Process

Figure 1 shows the flow-sheet of the treatment plant for fluoride waters and filtration of the resulting muds. It was designed and constructed by Fluorsid. It has been in operation in its present configuration for about 9 years. It treats presently a volume of water of about 100

m^3/h and is designed for a flow of 200 m^3/h. The capacity of the filtration plant can reach 150 tons per day of filtercake. Presently this plant is used to treat besides current production the accumulated muds from previous years when the market was not yet sufficiently developed. For the year 2000 it is forecast to sell about 35,000 tons of product tel quel.

The plant is composed of two sections: water treatment (of traditional type) and filtration.

Water Treatment Section

The process waters containing HF, H_2SiF_6 HCl and H_2SO_4 are made to react in rubber lined digestors R1 and R2 with limestone in pieces. The pH in this phase is maintained at a value of about 5. The neutralization is completed with a calcium hydroxide in reactors R3, R4 and R5. In tank R6 we treat also water with a low concentration of acids which come from the production plants.

The neutralization reactions are the following:

$$2HF + CaCO_3 \longrightarrow CaF_2 + CO_2 + H_2O$$

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + CO_2 + H_2O$$

$$H_2SiF_6 + CaCO_3 \longrightarrow CaSiF_6 + CO_2 + H_2O$$

$$2HCl + CaCO_3 \longrightarrow CaCl_2 + CO_2 + H_2O$$

$$Ca_2SiF_6 + 2Ca(OH)_2 \longrightarrow 3CaF_2 + SiO_2 + 2H_2O$$

The volume of reactors R3, R4 and R5 is 20 m^3. The residence time of the slurry in each reactor is about 25 minutes.

The neutralized slurry, after the addition of an anionic flocculating agent is sent to a clarifier. The thickened slurry is sent to a thickener where it reaches the optimum concentration for filtration (between 280 and 300 grams per liter).

The slurry pumps used are centrifugal, with the pump body lined in polyurethane. The rotors are made of Ni-hard cast iron and the mechanical seals are of a bellows type.

Filtration Section

Having resolved the neutralization problem, it remained to be resolved the problem of solid-liquid separation and the drying of the resulting mud to obtain a saleable product. Because the thermal drying of the resulting muds from the traditional low pressure filtration process presented very high costs due to the high residual filtercake moisture content, we oriented ourselves towards a system of filtration at high pressure which would directly yield a desirable product.

At this point the intervention of Svedala was crucial. They supplied Tube Press filters which work at 100 bar from which one obtains a solid filtercake in hard compact flakes with a thickness of 1-3 cms. These flakes can also be stored outside as they no longer absorb water and do not give rise to air borne dust.

The Svedala Tube Press is an automatic variable chamber cylindrical filterpress composed of an external casing, a flexible membrane and an internal candle which acts like a sieve over which is fitted the filter cloth (see Figure 2).

The filtration cycle takes place in five phases:

1. *Feeding*
   The thickened slurry is pumped at a pressure of 7 bar into the filter press between the filter cloth and the membrane. In this phase the first filtration of the slurry takes place and a filtercake is formed (pre-filtration)

2. *Washing* (not always necessary)
   In this phase water is pushed through the filtercake in order to remove soluble salts which are present.

3. *Compression of the Filtercake*
   This is obtained by introducing service water at 100 bar pressure which pushes the membrane against the filtercake which has been deposited on the filter cloth, creating a squeezing action. The filtrate drains through the cloth while the solids are held on the cloth and form the filtercake.

4. *Vacuum*
   The service water pulls the membrane back against the external casing leaving the filtercake compressed onto the candle body.

5. *Discharge*
   The candle is lowered and air is blown into the internal of the candle which expands the filter cloth and allows the filtercake to fall on to a belt located below (see Figure 3).

The Fluorsid plant is composed of eight tube presses in parallel, of 3 meters height. The filtering surface of each press is 3.47 m2. The filtration cycles of the different filters is opportunely timed to give a continuity to the process.

Operating Costs

At Fluorsid the operation of the plants for water treatment and mud filtration is controlled by a single operator per shift and is carried out on a continuous 24 hour basis. Maintenance is carried out for 8 hours a day, 5 days a week, by one mechanical and one helper.

For what concerns other costs, we give below, indicatively only, some data on the Fluorsid plant:

Power Installed	110	KW
Lime and Limestone	Stoichiometric	
Water	240	m^3/day
Flocculant	65	Kg/day
Spare parts and consumables	75,000	US$/year

Applicability of the process to the fertilizer industry

In order to verify the applicability of the process to the fertilizer industry, filtration tests were carried out, both in a laboratory and on industrial plants, of slurry originating from the neutralization of only fluosilicic acid. In a laboratory slurry was filtered coming from the neutralization of H_2SiF_6 at 15%. Similarly in the industrial plant slurry was filtered coming from the neutralization of about 1% of H_2SiF_6, after suitable treatment with flocculant, clarification and successive thickening. In both cases, the filtration at 100 bar yielded a good filtercake which presented itself as a hard crust, compact and manageable having the following composition (referred to a dry basis contained humidity 33%):

CaF_2	70%
SiO_2	17%
$CaCO_3$	6%
Al_2O_3	2%
Fe_2O_3	1%
L.O.I. (450 °C)	4%

As one can observe, such a product is of a quality superior to that which is presently obtained by Fluorsid in that it does not contain sulphates and has a higher level of CaF_2. With these characteristics, the product is suitable for usage not only in the cement industry but also in the iron and steel industry.

Based on the laboratory and industrial tests mentioned above, Fluorsid believes its process can be successfully applied to the fluorinated muds resulting from the processing of phosphate rock. The fertilizer industry can expect to have a similar result as regards process and product as the Fluorsid's plant, which was set up 9 years ago with a limited investment and that has operated since with a discreet economic margin.

Furthermore, we also think that this type of process is particularly suitable to be used by the fertilizer industry. In fact, the type of process (neutralizing, filtration, etc.) is part of the basic inorganic chemical culture normally present in the fertilizer sector. Moreover, the process does not foresee drying operations and does not give rise to gaseous emissions. The product does not create problems for storage and can be easily handled by a front-end loader. The market is well defined and consists of a few large customers who don't require a particularly difficult marketing effort.

Estimate of the Necessary Investment

With respect to the Fluorsid plant, the flowsheet of which is given in Figure 1, a plant for the treatment of fluosilicic acid deriving from the production of phosphoric acid results much more simplified. The foreseen plant requires only a single neutralization with lime which can be carried out at a higher slurry temperature which also favours filterability. Moreover, settling and thickening are not required since the slurry is sufficiently dense to obtain the best results from the filters. A layout of the simplified plant is given in Figure 4.

For a plant of 4,000 tons per month of solids tel quel, corresponding to 1,200 tons per month of 100% H_2SiF_6 (obtainable from a plant of 400-500,000 tpy of P_2O_5), the investment can be estimated to be in the order of 2 million US$, broken down as follows:

	US$ x 1,000
Tube Press Filters with valves (8 filters)	*750*
Equipment and Apparatus (tanks, pumps, belts, etc.)	*300*
Carpentry, Piping and Mechanical Erection	*200*
Electrical Plant and Instrumentation	*200*
Civil Works (including warehouse for 5,000 T)	*550*
Total	***2,000***

Naturally, the number of filters depends on the filtering capacity desired. If one considers an indicative selling price of 50 US$/t delivered to the customer, the time to recover the investment can be estimated in 2-3 years.

<u>Conclusions</u>

For about 9 years Fluorsid has operated a plant for the neutralization of fluoridated water and, thanks to a filter plant supplied by Svedala, it has transformed the muds obtained from the water treatment plant into a commercial product which has been successfully sold to the cement industry.

Tests effected both in the laboratory as well as on industrial scale have shown that a solution of this nature can also be applied to resolve the problem of fluosilicic acid generated by plants for the production of phosphoric acid.

The investment necessary is very limited as is the cost of operation. The management of the plant and sale of the product obtained do not require a particular effort by the fertilizer producers nor oblige them to enter into new, different sectors of the chemical industry only to resolve a problem which is environmental in nature. The sale of the product covers entirely operating costs and depreciation. Depending on the geographical location of the customers with respect to the producer, a small profit can also result.

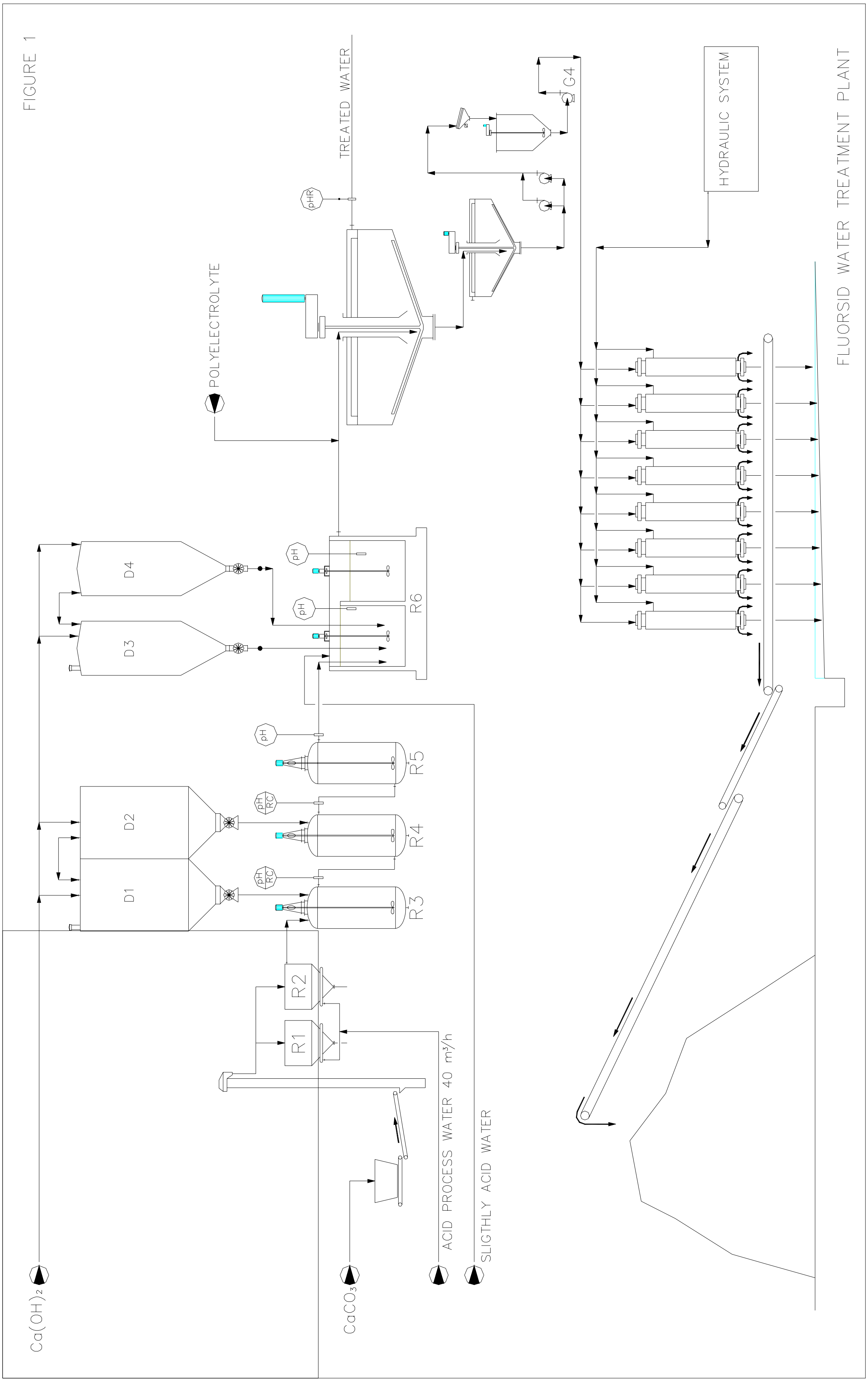
TREATED WATER
pHR
POLYELECTROLYTE
G4
HYDRAULIC SYSTEM
FLUORSID WATER TREATMENT PLANT
D4
D3
D2
D1
pH
R6
R5
pH RC
R4
R3
R2
R1
Ca(OH)₂
CaCO₃
ACID PROCESS WATER 40 m³/h
SLIGTHLY ACID WATER

FIGURE 1

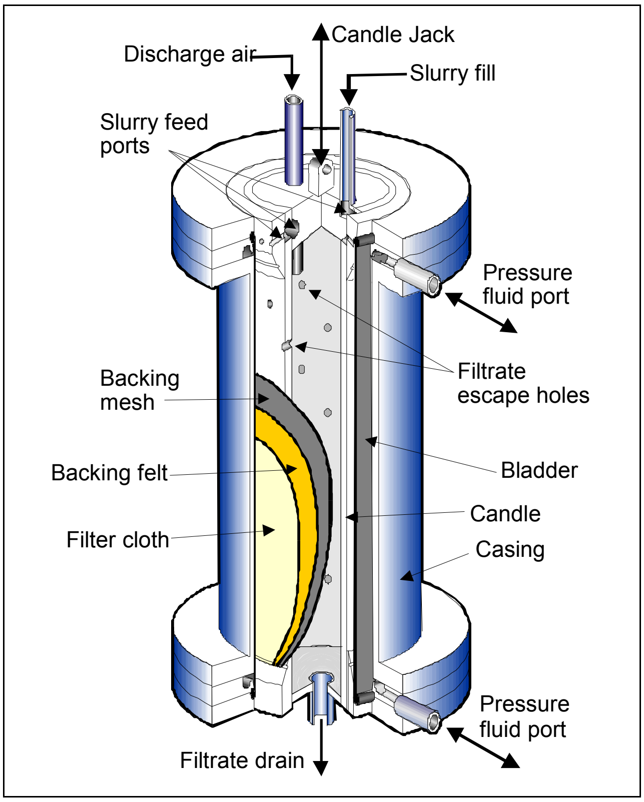

Figure 2: Cross sectional view of a Svedala Tube Press

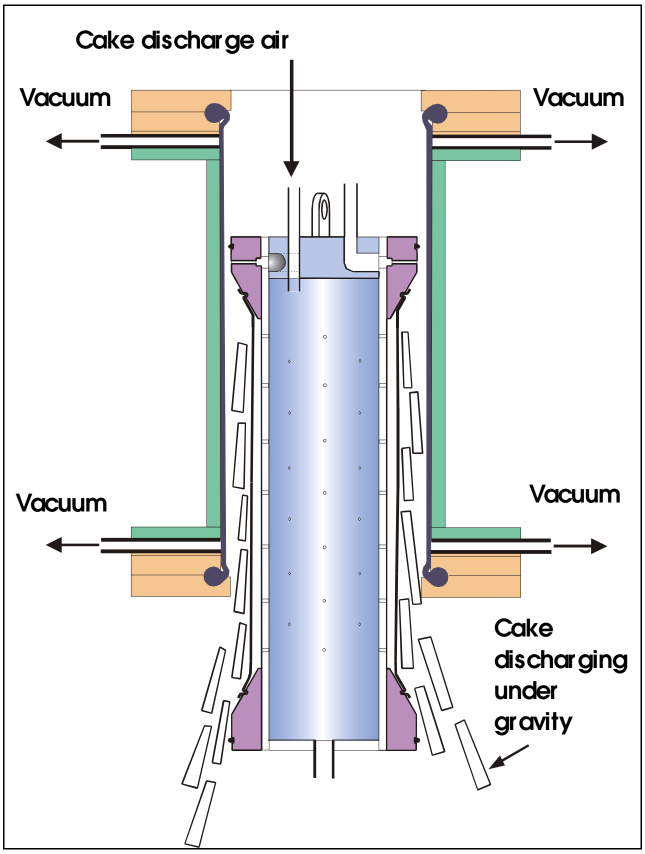

Figure 3: Discharge stage

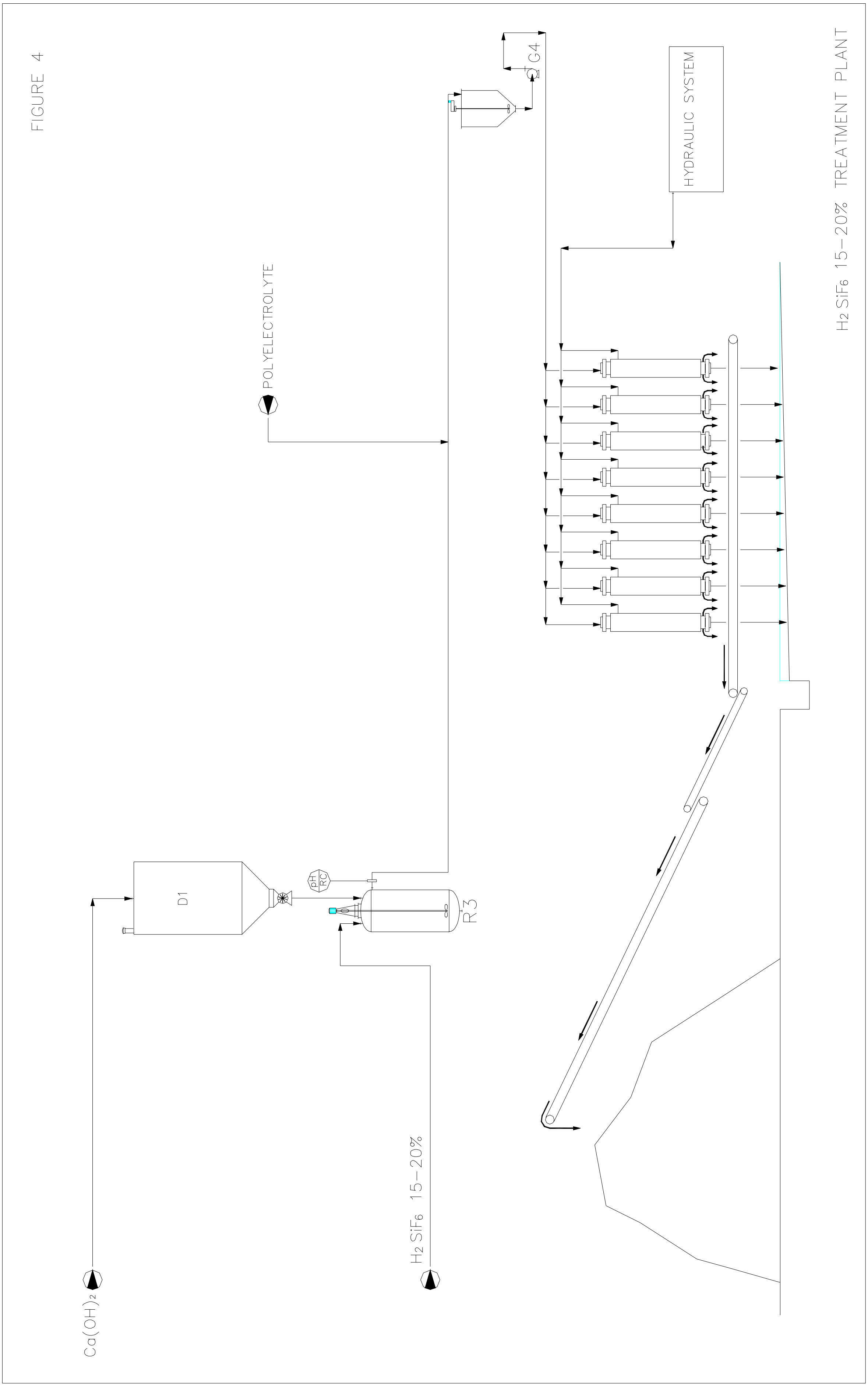
H2 SiF6 15–20% TREATMENT PLANT
HYDRAULIC SYSTEM
G4
POLYELECTROLYTE
pH RC
D1
R3
Ca(OH)2
H2 SiF6 15–20%

FIGURE 4