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Viability study on two treatments for an industrial effluent containing sulphide and fluoride

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ABSTRACT

Most industrial effluents require treatment before dumping in order to comply with stricter environmental regulations. Nevertheless, each industrial process renders a peculiar effluent that can contain a great variety of toxic compounds. This study addresses the viability of two chemical treatments for reducing the content of sulphide and fluoride in a highly saline effluent. This effluent (flow rate of 30 m^3/h) was generated in the process for purifying the Waelz oxide after its recovery from electric arc furnace dust (EAF dust).

Regarding sulphide treatment, the controlled addition of hydrogen peroxide to the industrial saline effluent rendered an efficient removal of sulphide to concentrations lower than 1 mg/l in the final dumping wastewater. Furthermore, the process was easily controlled and monitored by on-line measurement of the effluent redox potential. The annually averaged reagent cost was 0.01 €/m^3 of treated effluent. No by-products requiring treatment are produced, although special care should be taken in the storage of this oxidant. Thus, the proposed sulphide treatment for this effluent is strongly recommended.

Regarding fluoride treatment, the high flow rate and high dried solid content (as high as 46 kg/m^3) invalidated any other technological alternatives to be studied but precipitation. Even in this case, the precipitation process by Ca^{2+} and Al^{3+} additions did not achieve an acceptable fluoride removal efficiency unless extremely large amounts of reagents were added. Thus, the annualized cost of chemicals was 4 €/m^3 for treated effluent and an additional disposal cost incurred of 3.6 €/m^3 for dried sludge. Furthermore, one of the major technical drawbacks is the generation of large amounts of sludge whose subsequent treatment and management would require extremely large facilities. Consequently, there is currently no viable treatment for ensuring saline industrial effluent attains the desired target value of 6 mg/l fluoride in the dumping wastewater.

1. Introduction

Steel production in electric arc furnaces (EAF) involves a significant generation of wastes as dust, amongst others. In the European Union, the steel industry produced about 700 000 tons of EAF dust in 2000 [1]. Zinc (and eventually lead) contained in this dust is the most valuable component and can be affordably recovered by the Waelz process. This process converts the EAF dust (with a high zinc concentration) into an impure zinc oxide, called Waelz oxide. After generation, a variety of chemicals are used to purify this oxide (namely sodium bicarbonate and sodium bisulphide). Regarding the final wastewater generated after all treatment steps, a highly saline effluent is obtained. In this saline aqueous matrix, toxic anions such as fluoride and sulphide should be removed if an available and affordable treatment is found.

Although all the effluents generated in this cleansing procedure are currently being treated before dumping, companies are forced to search for further treatments in order to comply with environmental protection targets and stricter environmental regulations.

Due to the risk of hydrogen sulphide gas generation under acidic conditions (pH value lower than 8), the sulphide content in industrial effluents needs to be controlled. This gaseous compound is unstable and toxic and has an unpleasant odour (like many sulphides). Besides, an air concentration higher than 140 mg/m^3 causes sickness and conjunctivitis. When the concentration is higher than 280 mg/m^3, it causes death. Thus, efficient processes are clearly required for eliminating sulphide from industrial waste streams.

Regarding sulphide treatments, aeration and chemical oxidation are commonly used. Oxidants for sulphide oxidation include

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chlorine, potassium permanganate and ozone, as well as hydrogen peroxide and biological oxidants [2]. As far as hydrogen peroxide is concerned, more than two million tons of this oxidant are used worldwide in multiple applications, and it is recognised as environmentally friendly because its by-products, water and oxygen, do not pose any toxicological risk [3]. However, the potential hazards associated with peroxide storage and use should be carefully considered.

Fluoride in drinking water at a concentration below 1.5 mg/l can be beneficial, but a high concentration is hazardous for human beings [4]. As far as aquatic systems are concerned, when the concentration was higher than 5 mg/l serious growth disorders were observed in *Artemia salina*. Fluoride-containing wastewater is generated mainly in semiconductor production facilities (a typical fluoride concentration ranging from 350 to 1000 mg/l), in photovoltaic energy manufacturing facilities (concentration ranging from 500 to 2000 mg/l) and in beryllium extraction plants (concentration higher than 1000 mg/l) [5,6]. Such high concentrations of fluoride obviously cannot be discharged without prior treatment.

Several methods have been proposed for removing fluoride from aqueous effluents, such as adsorption, electrocoagulation, ion-exchange and conventional chemical precipitation [6–9]. Toyoda and Taira [7] proposed a method to reduce fluoride concentration below 5 mg/l by modifying part of an existing conventional system.

The conventional method for the fluoride removal is based on the precipitation of fluoride as calcium fluoride (CaF_2) and on the subsequent addition of Al^{3+} salt resulting in the precipitation of $Al(OH)_3$. This latter addition reinforces the removal efficiency, because the residual fluoride in the solution is adsorbed by the $Al(OH)_3$ and the fluoride-adsorbing $Al(OH)_3$ thus settles on the bottom. Bearing in mind that the theoretical solubility of CaF_2 in water is 17 mg/l at 25 °C [8], CaF_2 plain precipitation can only reduce fluoride concentration to 10–20 mg/l in practice, due to other components in the wastewater to be treated. Al^{3+} salt addition is required to reduce fluoride concentrations below 10 mg/l, although additional drawbacks, such as high sludge generation, are expected. A further alternative is to pass the fluoride-containing wastewater through different adsorbents [10]. Nevertheless, to the best of our knowledge, none of those methods proposed has been applied to effluents with a high salt content. One of those saline effluents is generated in the industrial recovery of Zn (and Pb) from waste dust in steel production, and treatment alternatives such as ion-exchange or adsorption are wholly invalidated by the high salt content. Thus a specific treatment should be investigated.

Industrial and domestic liquid effluents frequently include a variety of organic and inorganic pollutants whose treatment requires a case by case study. An excellent example is the chemical oxidation with hydrogen peroxide for domestic wastewater treatment proposed by Ksibi [11]. In order to comply with stricter environmental regulations, companies have to search for new treatment technologies especially designed for each waste generated. These technologies need to be affordable and environmentally friendly.

The aim of the present work is to study the technical, economic and environmental viability of two possible treatments for the removal of sulphide and fluoride contained in a highly saline industrial effluent from an operating steel industry. The target concentrations to be achieved after treatment prior to discharge are 1 and 6 mg/l for sulphide and fluoride, respectively. These concentrations were demanded by the local government. The effluent is generated in the final cleansing process of the impure zinc oxide, called Waelz oxide, which is obtained from EAF dust.

2. Experimental

2.1. Preliminary characterization

The liquid effluent was chemically characterized as per standard methods [12]. The relevant ions and parameters were determined as pH, temperature, sulphate, chloride, carbonate, bicarbonate, sodium, potassium, sulphide and fluoride. The total solid content dried at 103–105 °C was quantified. The average flow rate of this liquid effluent was 30 m^3/h.

2.2. Sulphide treatment

Bearing in mind the chemical instability of sulphides, a comparative study of the sulphide content in water solutions over time was conducted in three systems: deionized water, real effluent sample and synthetic matrix containing the main salts of the industrial effluent. The synthetic matrix was generated by dissolving a variety of salts (anions and cations) in a concentration similar to the content in the real matrix; that is, KCl (36 g/l), Na_2SO_4 (4.3 g/l), Na_2CO_3 (4.1 g/l) and $NaHCO_3$ (8 g/l). The resulting pH value was 9.1, measured in a GLP 21 Crison pH-meter.

Certain doses of sulphides were added to the three systems so that the initial concentration was in the range 10–15 mg/l. The evolution of the sulphide concentration with time was measured by potentiometry in a 920A Crison analyzer, by previous calibration with three standard dissolutions and a stabilizing agent.

In order to achieve the relationship between sulphide content and redox potential in the effluent, certain dissolutions containing sulphide (from 0 to 10 mg/l) were prepared in the synthetic matrix and the redox potential was measured in a 920A Crison analyzer.

Chemical oxidation by using hydrogen peroxide as oxidant was proposed to remove sulphides from the liquid effluent. In order to assess the relationship between hydrogen peroxide content and redox potential in the effluent, certain dissolutions containing hydrogen peroxide (from 0 to 27 mg/l) in the synthetic matrix were prepared and the redox potential was measured as explained earlier.

Finally, a series of volumetric assays were carried out by adding hydrogen peroxide to several dissolutions containing different amounts of sulphide. The redox potential and the remaining sulphide content were measured along time in order to calculate the stoichiometric amount of oxidant required to react with the sulphide contained in the effluent.

2.3. Fluoride treatment

The fluoride was removed from the effluent by adding Ca^{2+} ion (from a calcium chloride solution) to the original effluent. Five different doses of Ca^{2+} (1000, 1500, 2000, 2500 and 3000 mg/l) were added to 100 ml of the real sample and the remaining fluoride concentration was measured by potentiometry in a 920A Crison analyzer. The final pH value after treatment was also measured as explained before.

In order to achieve the most efficient fluoride removal, Al^{3+} ions (from an aqueous dissolution of aluminium and potassium sulphate) were added to the effluent after the addition of 1000 and 2500 mg/l of Ca^{2+}. The Al^{3+} doses were 50, 125, 250 and 300 mg/l.

The settleable solid (sludge) amount generated after the addition of 1000 mg/l Ca^{2+} and variable amounts of Al^{3+} was measured in Imhoff cones after settlement times of 10 min and 24 h. The total solid (sludge) amount was determined by filtration, drying at 103–105 °C and final weighing.

Table 1
Annual chemical characterization of the effluent as far as major ions are concerned [14].

Parameter	Average	Maximum	Minimum
pH	9.1	9.3	8.8
Temperature (°C)	30.8	39.0	24.0
Sulphate (g/l)	2.8	3.7	1.7
Chloride (g/l)	17.1	25.3	11.8
Carbonate/bicarbonate (g/l)	6.5	8.0	5.0
Sodium (g/l)	12	10	14
Potassium (g/l)	10	12	8
Sulphide (mg/l)	10	22	0
Fluoride (mg/l)	58	65	40

3. Results and discussion

3.1. General characterization

As far as the major ions are concerned, the annually averaged chemical composition of the liquid effluent to be treated is shown in Table 1. The major anions are chloride, carbonate/bicarbonate and sulphate, with an average value of 17.1, 6.5 and 2.8 g/l, respectively. This highly saline composition (average dried solid content of 46 g/l) provided the effluent with a specific complex matrix nature that is clearly different from other published studies [5]. The target toxic anions to be removed reached maximum annual values of 22 mg/l sulphide and 65 mg/l fluoride in the industrial effluent.

3.2. Sulphide treatment

The sulphide content in the original effluent (real sample) steadily decreased along time before any treatment was carried out (Fig. 1). Thus, the sulphide content was half the initial amount (14 mg/l) after 1 h left standing with shaking. This "dynamic" saline effluent, with a continuously changing content of sulphide with time, was unsuitable for any laboratory treatment study. Hence, a synthetic sample (synthetic matrix) with the major compounds was prepared and, subsequent to the addition of a controlled amount of sulphide, the natural degradation of sulphide in this matrix did not occur during the first 90 min (Fig. 1). Other additional assays with the synthetic sample were carried out with different amounts of sulphides and this anion stability was proven to be stable. Thus, the synthetic matrix was used for subsequent experimentation.

Although the sulphide undergoes natural degradation (Fig. 1), the "left to stand" option was not considered for industrial implementation because the high effluent flow of 30 m^3/h would require a long residence time in the industrial pipe system or a huge standing tank before dumping.

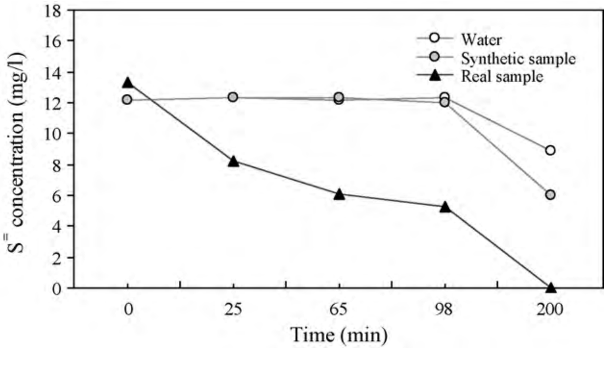

Fig. 1. Stability study of the sulphide in a real sample, synthetic sample and deionized water.

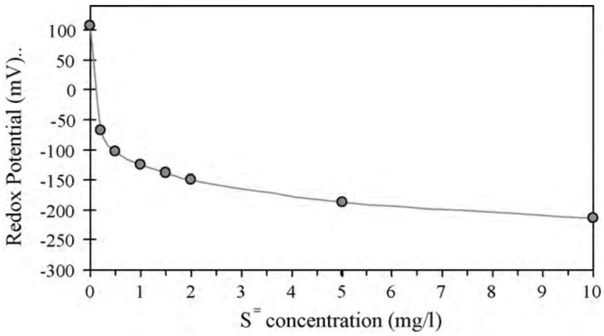

Fig. 2. Evolution of redox potential value with sulphide content.

The on-line control of the sulphide content in the effluent prior to dumping can be performed by measuring the redox potential in the waste liquid. Nevertheless, a relationship between potential value and sulphide content in the saline sample was required. In this study, redox values in the range from −125 to 100 mV were found to be indicative of a sulphide content lower than 1 mg/l (Fig. 2).

Hydrogen peroxide (H_2O_2) is one of the most used oxidants in industrial processes [3] and it was selected as reactive agent to remove sulphide from the industrial effluent. Before proceeding with the experiments for calculating the stoichiometric amount required, the redox potential of the saline sample was measured in the absence of sulphides but in the presence of different H_2O_2 concentrations (Fig. 3). As a result, it was concluded that a redox value higher than 110 mV was indicative of the presence of H_2O_2 in the sample. Nevertheless, when the H_2O_2 content in the sample was higher than 5 mg/l, the redox response was not case sensitive.

The redox potential value was used for two purposes, namely, to measure the content of sulphide in the effluent prior to oxidant addition and to measure the disappearance of both sulphide and hydrogen peroxide after treatment (absence of peroxide hydrogen in excess).

The products of the reaction between sulphides and H_2O_2 depend on the pH value of the dissolution. When the pH is basic, two reactions have been proposed [11,13]:

$$HS^- + 4H_2O_2 \leftrightarrow SO_4{}^{2-} + 4H_2O + H^+ \qquad (1)$$

$$S^{2-} + 4H_2O_2 \leftrightarrow SO_4{}^{2-} + 4H_2O \qquad (2)$$

A further proposal is the reaction between sulphides and hydrogen peroxide that gives way to a decrease in pH according to the following reaction:

$$S^{2-} + H_2O_2 \leftrightarrow S^0\downarrow + 2OH^- \qquad (3)$$

Different amounts of hydrogen peroxide were added to the effluent containing 20 mg/l of sulphide, and the redox potential and

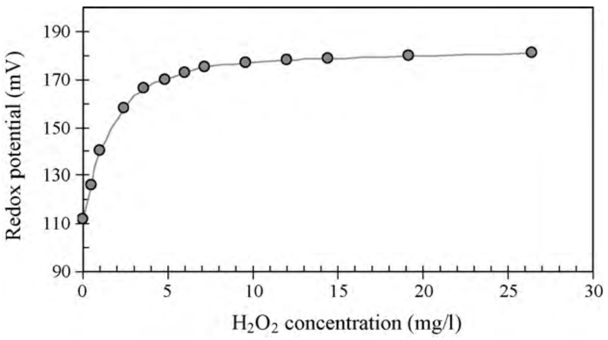

Fig. 3. Evolution of the redox potential with hydrogen peroxide content.

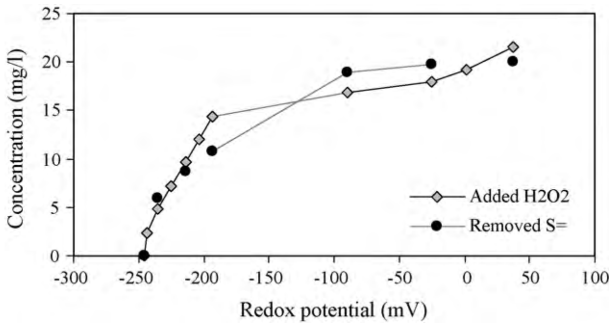

Fig. 4. Relationship between the hydrogen peroxide amount added to the sample and the consequent amount of sulphide removed.

the remaining sulphide content were measured after each addition. Fig. 4 shows the removed sulphide content and the corresponding amounts of H_2O_2 added. Given that the molecular weight of sulphide and hydrogen peroxide is 32 and 34, respectively, the stoichiometric ratio was found to be 1:1 and (3) the most probable reaction.

As a conclusion, the controlled addition of a “clean” oxidant, such as hydrogen peroxide, to an industrial saline effluent rendered the removal of sulphide content to concentrations lower than 1 mg/l in the dumping liquid waste. Furthermore, the process is rapid and can be easily controlled by on-line measurement of the effluent redox potential before and after oxidant addition.

3.3. Cost estimation of the sulphide treatment process

The only chemical required for the treatment of sulphide is hydrogen peroxide. Considering an annual effluent flow to be treated of 263 000 m^3 and an average sulphide content of 10 mg/l, H_2O_2 consumption depends on the available commercial solution concentration (ranging from 20% to 60%, w/w). The most commonly used (and recommended) H_2O_2 solutions are the ones containing 35% and 50% (w/w). Assuming an average solution (with a weight composition between 20% and 50%) and a price of €400 per ton of oxidant solution, an average amount of 6000 l is expected to be consumed. Consequently, the reagent cost per year is €2720, which means a cost of 0.01 €/m^3 of treated effluent.

The industrial equipment required for the on-line addition of hydrogen peroxide to the industrial effluent prior to dumping is a stainless steel tank with a capacity of around 30 m^3, two redox electrodes (one to measure the sulphide content prior to oxidant addition and the other one to check the absence of hydrogen peroxide in excess after reaction) and one feed pump. The piping, installation and safety systems and ancillaries depend on the location of the equipment. The hazards associated with the handling of hydrogen peroxide should be carefully considered (decomposition leading to vapour release or pressure burst if venting is inadequate and possible loss of containment leading to fire and environmental and health hazards).

The industrial viability of the treatment proposed was assessed by fulfilling the technical (equipment required and process efficiency), economic (reagent annual cost and other initial investments) and environmental (no dangerous by-product generation) requirements.

3.4. Fluoride treatment

Bearing in mind that the aim of the fluoride treatment was to reach a final fluoride concentration lower than 6 mg/l in the dumped effluent, the first attempt was to add different Ca^{2+} amounts ranging from 1000 to 3000 mg/l to the industrial effluent. Table 2 shows the concentration of fluoride remaining after Ca^{2+} addition. Although the pH value considerably decreased from 9.1 to 6.5, the lowest fluoride concentration obtained was 18.4 mg/l after adding a high amount of calcium salt (equivalent to 3000 mg/l Ca^{2+}) to the saline effluent. The solid precipitate generated in the liquid sample settled quickly.

The following experimental step consisted in previously adding Ca^{2+} ions and the subsequent addition of different amounts of Al^{3+} ions in order to reduce the remaining fluoride concentration below the target level. As shown in Table 3, the remaining fluoride concentration was below 6 mg/l only when an addition of 2500 mg/l Ca^{2+} and 250 mg/l Al^{3+} was carried out. Nevertheless, two important drawbacks are to be considered. First, the ions (corresponding salt) doses to be added to the saline effluent were very high, which would be very expensive. The second drawback and the crucial one was that the addition of Al^{3+} ions generated a highly voluminous precipitate (solid sludge). This sludge volume was much higher than the one obtained when only Ca^{2+} ions were added. In fact, the higher the Al^{3+} dose was, the more voluminous the sludge generated.

Consequently, the next step was to quantify the amount of the voluminous solid (sludge) generated. Thus, the settleable solid content and the total dried solid content were determined. Bearing in mind that the amount of 2500 mg/l Ca^{2+} to be added to the saline effluent was extremely high, lower doses (1000 mg/l Ca^{2+}) with different Al^{3+} amounts were selected for the subsequent study.

The settleable solid content (measured after 10 min) ranged from 46 to 850 ml/l for the different doses when the removed fluoride content ranged from 45% to 88% (Table 4). Furthermore, the settleable solid content in the original effluent was negligible (lower than 0.5 ml/l).

The lowest amount of the remaining fluoride (6.8 mg/l) was attained with the highest Al^{3+} addition, which rendered the highest settleable solid content (850 ml/l after 10 min and 270 ml/l after 24 h). The dried solid content generated (precipitate amount)

Table 2
Fluoride concentrations remaining after Ca^{2+} additions.

Test no.	0	1	2	3	4	5
Added Ca^{2+} (mg/l)	0	1000	1500	2000	2500	3000
Remaining F^- (mg/l)	58.0	37.5	28.6	23.7	19.3	18.4
pH after treatment	9.1	8.6	7.8	7.0	6.7	6.5

Table 3
Fluoride concentrations remaining after Ca^{2+} and Al^{3+} additions.

Test no.	0	1	1A	1B	2	2A	2B	2C
Added Ca^{2+} (mg/l)	0	1000	1000	1000	2500	2500	2500	2500
Added Al^{3+} (mg/l)	0	0	250	300	0	50	125	250
Remaining F^- (mg/l)	58.2	37.5	7.8	6.8	23.7	13.3	10.2	5.3
pH after treatment	9.1	8.6	7.5	7.5	6.7	6.8	6.8	7.0

Table 4

Sludge generation after effluent treatment with 1000 mg/l Ca^{2+} and variable amounts of Al^{3+} for an initial fluoride concentration of 58.0 mg/l.

	Previously added Ca^{2+}: 1000 mg/l			
	Subsequently added Al^{3+} amounts			
	50 mg/l	100 mg/l	200 mg/l	300 mg/l
Remaining F^- concentration (mg/l)	32.0	23.8	12.0	6.8
Removed F^- (%)	45	59	79	88
Settleable solid content after 10 min (ml/l)	46	132	330	850
Settleable solid content after 24 h (ml/l)	22	60	144	270
Dried solid content (g/l)	2.52	2.75	3.26	3.71

was also high ranging from 2.52 to 4.02 g/l, which implied an extremely high amount of sludge to be filtered, dried and conveniently dumped.

3.5. *Cost estimation of the fluoride treatment process*

In order to asses the cost of chemicals for the fluoride treatment, two commercial solutions containing Ca^{2+} and Al^{3+} were selected: a commercial solution of $CaCl_2$ at 35% (w/w) and a commercial solution of $Al_2(SO_4)_3$ at 18% (w/w). Regarding an annual effluent flow to be treated of 263 000 m^3 and an average fluoride content of 58.0 mg/l, 8 kg of $CaCl_2$ solution and 10 kg of $Al_2(SO_4)_3$ solution would be required for treating 1 m^3 of effluent. This additional dose would imply an annually averaged reagent cost of around one million euros, which means a cost of 4 €/m^3 of treated effluent.

Apart from the excessive reagent cost, another drawback for this treatment is the enormous amount of precipitate generated—about 947 tons per year (which needs to be suitably disposed of) and the installation of large equipment (such as large decantation tanks and two large tanks for reagent storage).

4. Conclusions

Two chemical treatment processes to be applied to an industrial saline effluent were studied. The flow rate of the effluent to be treated was 30 m^3/h, the average dried solid content was 46 kg/m^3 and the toxic anions to be removed were sulphide and fluoride with an average concentration of 10 and 58 mg/l, respectively.

The industrial viability of sulphide treatment with hydrogen peroxide was determined as follows:

Technically: The proposed treatment with hydrogen sulphide was able to efficiently reduce the sulphide content in the effluent below the target concentration (1 mg/l). The equipment and ancillaries required are very common in industrial processes. Nevertheless, special care should be taken with hydrogen peroxide storage due to its possible exothermic decomposition.

Economically: The equipment investment depends on the material selected for H_2O_2 storage (stainless steel or HDPE) and on its location (piping, pumps). The yearly reagent cost is €2 720 or 0.01 €/m^3 of treated effluent. No by-products to be treated or dumped are produced and consequently no extra dumping costs are to be considered.

Environmentally: Hydrogen peroxide is considered to be a clean oxidant, as its decomposition products are H_2O and O_2. The reaction between sulphide and H_2O_2 produces elemental sulphur, which is considered to be less toxic than sulphide. Subsequent to the treatment, no risk of H_2S generation is to be considered, although the pH value decreases.

As a conclusion, sulphide treatment is strongly recommended.

The industrial viability of fluoride treatment for its industrial implementation was determined as follows:

Technically: The proposed treatment with Ca^{2+} and Al^{3+} additions did not render a high fluoride removal efficiency (for a target value below 6 mg/l) unless extremely large amounts of reagents were added. Apart from the high reagent consumption, the major technical drawback is the generation of large amounts of sludge (947 tons per year) whose subsequent treatment and management would require extremely large facilities.

Economically: Given the large facilities required, the investment cost is incalculable. The annual cost of chemicals is over 1 million euros, which means a cost of 4 €/m^3 of treated effluent. Regarding sludge costs, an additional disposal cost would be incurred of 3.6 €/m^3 of dried sludge.

Environmentally: The yearly generation of tons and tons of sludge that would require drying and the associated energy consumption, transportation and proper disposal is not environmentally affordable when the sole objective is to reduce fluoride concentration from 58 to 6 mg/l. Furthermore, the sludge did not contain valuable compounds to be recovered.

To conclude, there is currently no viable treatment to be applied to the highly saline industrial effluent in order to reduce fluoride concentration from 58 mg/l to below 6 mg/l. And, consequently, there is currently no viable treatment system to be installed in the operating steel industry.

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