Treatment of hydrogen sulfide enriched condensates by sulfuric acid

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ABSTRACT

The true issues of organizations are situated now in their capacity of facing industrial risks and unexpected events due to their activities. Hydrogen sulfide H_2S, is a highly toxic gas and a very aromatic chemical. This chemical species is especially produced by some industrial activities such as paper industries and oil refineries. The methods to eliminate them are burning treatment and stripping in a filling tower. The disadvantage of this treatment plant is the importance of corrosion of its metals by H_2S. The goal of our study is to bring alternatives in order to set up a new treatment process able to drain acid waters of condensates from the source. The tests of desulfurization by concentrated sulfuric acid combined to airing have generally given good results with a treatment yield that can reach 99%.
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INTRODUCTION

Bad smells are more and more considerate by industrialized countries. When we think about paper industry plants, oil refineries and water treatment plants we often link these activities to bad smell problems. This problematic, that used to be solved by simple means such as isolation of odor sources, is now taking a scale that can sometimes be negative for economic development of a whole activity. The aromatic components can be organic or inorganic. Among the most frequently encountered molecules, we have hydrogen sulfide. This chemical has a very bad smell and an extremely low detection level i.e. 0.01 ppm according to Le Cloirec (1991)[1]. In addition, hydrogen sulfide is highly toxic and corrosive[2].

Petroleum fragments contain impurities responsible of pollution and corrosion. These impurities are present in variable quantity and in different forms depending on the origin of crude oil, the most important polluting element is sulfur. The other impurities such as nitrogen and metals can be harmful. The sulfur content of crude oil fluctuates between 1.8% to 2.6% and tends to increase depending on the current market behavior. Condensate striping in the oil refinery process is the pre-treatment operation which happen before the recycling step and it goes to the desalinate unit or the STEP. This operation is necessary because condensates are very concentrated in NH_4 (+) and H_2S. This treatment allows eliminating some hydrogen sulfides and ammonia gas NH_3[3].

The oxidation of hydrogen sulfide is related to temperature, pH and ionic force. Moreover, oxidation rates are higher than in sea water than in air saturated wa-

tion concerns the sulfides that are initially present in acid condensates of the oil refinery, under the form of NH_4SH in couple with low concentrations of $(NH_4)_2S$ and NH_3. This oxidation is executable for concentration of S^{2-} from 30 to 300 mg/l. The oxidation speed is maximum between pH 7 and pH 8.5, it ensures the oxidation at the thiosulfate $S_2O_3^{2-}$ stage[7].

AIM OF SULFURES TREATMENT

After several problems concerning acid condensates that are very toxic and very smelly and that are linked to the activity of oil refineries, the decisions that have been taken in order to eliminate these effluents are evaporation-incineration treatment or striping by a filling tower. The main disadvantage of this treatment plant is the high corrosion of its metals by (H_2S).

This study aims to bring additional solutions in order to set up a treatment process able to drain acid waters from the sources and acting at the origin of the pollution, in order to maximize the reduction of sulfide concentration in these acid waters before their transportation to the waste water treatment plant. Indeed, a
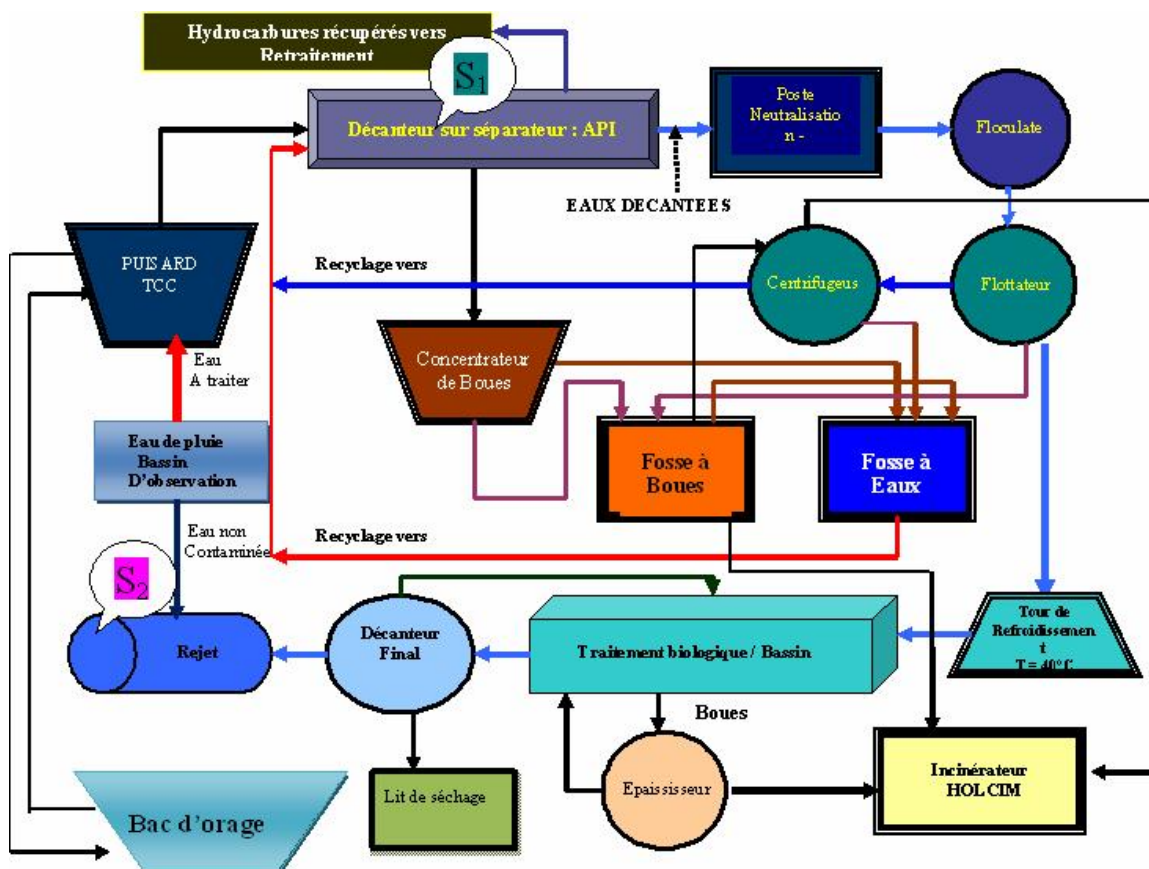

Figure 1 : Striping unit in an oil refinery

ter[4]. In well ventilated water, hydrogen sulfide is oxidized into sulfates or elementary sulfur by naturally present biological systems[5].

Sulfides can also chemically react with dissolved oxygen, but in this case we think that it is a slow and complex process which generates several kinds of products including thiosulfate, sulfite and sulfate[6]. Oxida-

Figure 2 : Scheme of the STEP: Waste water treatment.plant of the oil refinery of Sidi Kacem (Morocco). (x 8 pcn)

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H_2S concentration superior to 1mg/l is very problematic at the level of the biological ventilated pool of the STEP: it may cause the intoxication of microorganisms that are useful for the degradation of organic pollutants of this pool. (Figure 2)

MATERIALS AND METHODS

The samples of condensates that were studied have been analyzed before and after treatment in order to check the efficiency of the studied technology. This one has been carried out at the laboratory in an open bucher at atmospheric pressure, placed in the bottom of compressed air supplier. Without the catalyst, the reaction is slow but it would involve production of polysulfide of which the oxidation is fast. Sulfur is less electronegative than oxygen, so only alkaline sulfides and alkaline earth metals and other transition metals would be ionic. The determination of hydrogen sulfide is realized by iodometric method following the Rodier's method[8]: It is a simple volumetric titration of sulfides by iodine with presence of starch. By using the material of the laboratory of quality assessment and environment of the oil refinery, we decided to study several methods to process acid condensates and among them the one using oxidation by sulfuric acid, with and/or without airing. Initial conditions of all the experiments are stable i.e.:

Temperature and pH of the samples (250 ml) are respectively in average of 27°C and 8.4. The iodine normality is 0.456 N and the initial hydrogen sulfide concentration in the samples is 1185.60 mg/l. Finally, each experimental value represents the average of three tests.

RESULTS

Treatment of [H_2S] by concentrated H_2SO_4

The TABLE 1 and the figure 3, allow to see the evolution of hydrogen sulfide in function of pH with another strong acid; the sulfuric acid (10^{-2}M). The treatment of H_2S is important with H_2SO_4. Indeed, at pH 8, we obtain H_2SO_4, the following % of abatement of H_2S: 15%. The same thing for pH 5.5, these percentages are around 73%. With a pH of 2.5, the treatment is almost total, it reaches 94%.

TABLE 1 : Treatment yield of [H_2S] in function of pH, controlled by concentrated H_2SO_4.

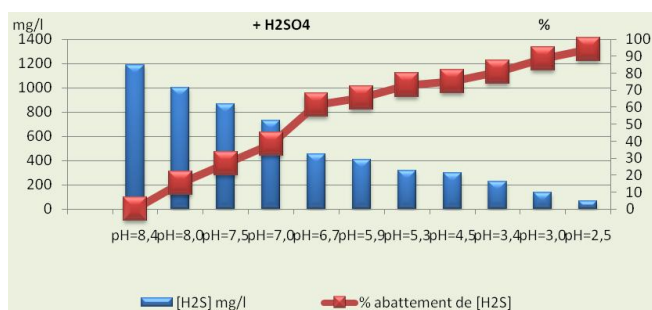| Adding of (H2SO4)	[H_2S] mg/l	Abatement % of [H_2S]
pH = 8,4	1185,60	0
pH = 8,0	1003,20	15,38
pH = 7,5	866,40	26,92
pH = 7,0	729,60	38,46
pH = 6,7	456,00	61,53
pH = 5,9	410,40	65,38
pH = 5,3	319,20	73,07
pH = 4,5	296,40	75,00
pH = 3,4	228,00	80,76
pH = 3,0	136,80	88,46
pH = 2,5	68,40	94,23

Figure 3 : Evolution of [H2S] in function of pH (concentrated + H2SO4).

Treatment of [H_2S] by airing and by concentrated H2SO$_4$

By using this time concentrated acetic acid (10^{-2}M) and we follow the evolution of the concentration of sulfides in function of pH, by soaking the solution of air oxygen during 30 minutes, the figure 4 and the TABLE 2 show these results. We note that airing has once again an important role on the improvement of the desulfurization. It is almost total at pH 2.5.
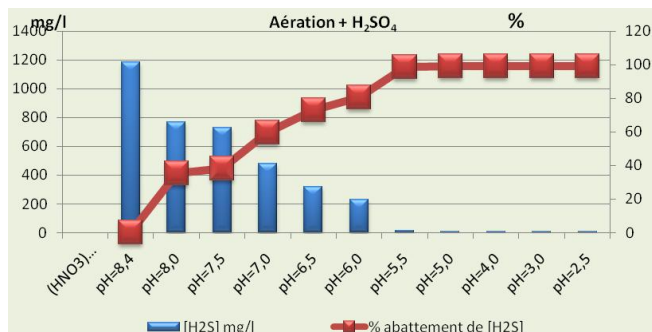

Figure 4 : Evolution of [H_2S] in function of airing and pH (concentrated+ H2SO4).

TABLE 2 : Treatment yield of [H₂S] in function of airing and pH, controlled by concentrated H₂SO₄.

Adding of (H2SO4) with Airing	[H₂S] mg/l	Abatement % of [H₂S]
pH=8,4	1185,60	0
pH=8,0	852,72	28,07
pH=7,5	814,04	31,33
pH=7,0	597,70	49,58
pH=6,7	401,00	66,17
pH=5,9	260,50	78,02
pH=5,3	83,50	92,95
pH=4,5	40,70	96,56
pH=3,4	25,50	97,84
pH=3,0	10,50	99,11
pH=2,5	8,50	99,28

DISCUSSION

The pH of the sample is always between 8.8 to 9.4; to justify it, we have:

$NH_4OH + H_2S = NH4SH + H2O$

$NH_4SH + NH_4OH = (NH4)2S + H2O$
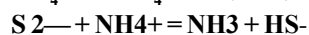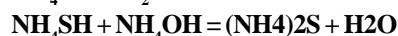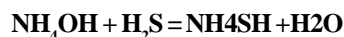
$S\ 2— + NH4+ = NH3 + HS-$
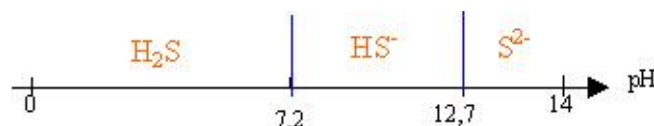
With pKa HS /S 2— = 13.1 and pKa NH4+ /NH3 = 9.1

Figure 5 : Influence of pH on the equilibrium of H2S and its dissolved forms, source:[9].

At the equilibrium, we have:

$Kr = ([NH3] * [HS-])*([H3O+]) / ([S\ 2—] * [NH4+])* ([H3O+])QQ$

$Kr = (1/10-13.1)*(10-9.1)$

Kr = 10-4 : So the solution is total and the quantity of acid and its conjugated base are equals, so: pH = pKa = 9.1.

This explains the alkalinity of our solution.

Oxidation of H2S by H2SO4

The increasing of the desulfurization capacity of the acid waters solution that we have observed in the results of the TABLES 1, 2 and the figures 3, 4 is function of the initial concentration which was around 1185.60 mg/l, is actually due to the oxidation degree of sulfur in presence of a oxidizing agent of a strong profile such as

H2SO4 (10 -2M). In fact, we can have in these conditions of pH and temperature the following forms in solution: figures 6 and 7.

The most probable reaction is :

$H_2SO_4 + 3H_2S \rightarrow 4S + 4H_2O$
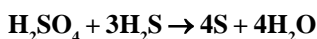
Indeed:

Through oxidation, we can switch from dihydrogen sulfide, H2S, to sulfur, S, then to sulfate, SO42-. They are oxidation forms of sulfur, presented on the potential-pH diagram of sulfur and its by-products. We can obtain SO3²⁻ by sulfur oxidation, thanks to dioxygen, O₂: dry redox reaction. We switch from SO_2 to $SO_3{}^{2-}$ only by changing the pH of the aqueous solution of sulfur dioxide SO_2. The thiosulfate anion, S2O32- is unstable in an acid milieu and it break down itself, particularly in colloidal sulfur, S.

The Frost diagrams in acid and alkaline milieu for the sulfur system are (in volts)
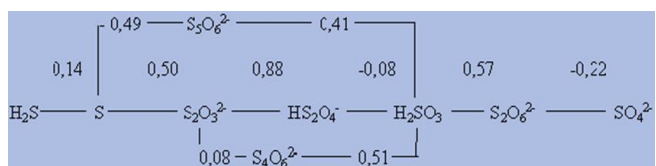
At pH = 0

Figure 6 : Frost diagrams in acid milieu at pH = 0 for the sulfur system (in volts)
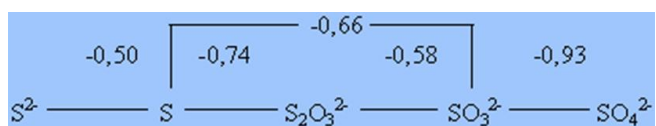
At pH = 14

Figure 7 : Frost diagrams in alkaline milieu at pH = 14 for the sulfur system (in volts)

We say that the thiosulfate ion dismute itself, because it appears in two different couples, as a reducing agent in one couple and as an oxidizing agent in the other couple.

The dismutation reaction of the thiosulfate ion in acid milieu is a slow transformation. The couples are $S_2O_3{}^{2-}/ S$ et $SO_2/SO_3{}^{2-}$
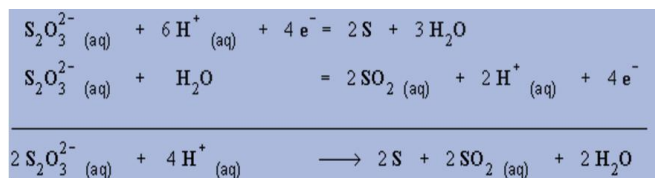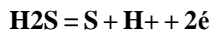

Figure 8 : The equation of the dismutation reaction of the thiosulfate ion

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We have the halve reactions:

H2S = S + H+ + 2é

SO2 + 2H2O = SO42- +4H+ + 2é

H2SO4 + H2S → SO2 + S + 2H2O (A)

We have noticed that water was not clear in the bucher at the pH=4 zone; the sulfur (a solid), in suspension is water-insoluble, that is why the water is cloudy. The formed sulfur dioxide and the hydrogen sulfide not transformed yet are mixed in aqueous solution. The sulfur is formed in suspension. The chemical equation that represents the reaction between the two gases in aqueous solution is:

2x (H2S = S + H+ + 2é)

SO2 + 4H+ + 4é = S + 2H2O

SO2 (aq) + 2H2S (aq) → 3S(s) + 2H2O(l) (B)
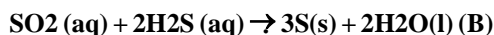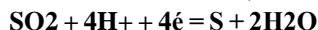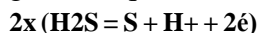
The sulfur atom in H_2S has an oxidation number of -2. This number becomes 0 when the atom S is in the solid sulfur. H atoms (hydrogen) do not change their oxidation number. So the hydrogen sulfide has been oxidized. The sulfur atom in SO_2 has an oxidation number of +4. This number becomes zero when the S atom is in the solid sulfur.

O atoms (oxygen) do not change their oxidation number. The sulfur dioxide molecules have earned electrons so they have been reduced when the two gases mixed each other in aqueous solution.

H2SO4 + 3H2S → 4S + 4H2O (A) + (B)

The airing benefits to desulfurization with H2SO4 adding to H2S.

Our results comply with those of Hui Wang et al, (2003)[10]. Their thermodynamic analysis of the possible reactions between hydrogen sulfide and concentrated sulfuric acid show that only two reactions occurs during the experiments at 1 atm and between 0°C and 150°C.

H2S + H2SO4 = S + SO2 + 2H2O

2H2S + SO2 = 3S + 2H2O
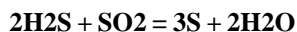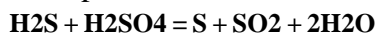
As a conclusion, Sublette, et al, (1994)[11], have shown that in the case of hydrogen sulfide treatment, the sulfates concentration in the solution at a acceptable level for biodegradation, i.e. under 810 mg/l. Thus, with a very strong oxidizing agent; such as (H2SO4 + K2Cr2O7) we can also have:

3 H_2S + 13 H_2SO_4 + 4 $K_2Cr_2O_7$ = 4 K_2SO_4 + 4 $Cr_2(SO_4)_3$ + 16 H_2O
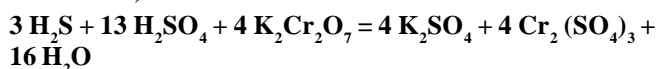
CONCLUSION

The use of acid waters from oil refineries conden-sates is limited by the presence of sulfur components inside them. The results of this study demonstrate that the use of a strong oxidation combined with air oxygen airing allows a complete oxidation of sulfides which are then present under the form of non-aromatic and less toxic chemical species than H_2S. These processes have also the advantage of allowing the improvement of the recycling potential of clean condensates by eliminating their smells and their toxicities or their transport. The recycling process of clean condensates or their transport to a waste water treatment plant or to a natural drip tray allows cumulating environment protection and energy savings.

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