CLEANING TREATMENT IMPROVEMENT OF THE "SPENT" CAUSTIC FROM THE REFINERIES

O.G.Cvetkovic[1], S.D. Nikolic-Mandic[1,2], M.B. Simic[3], D. Manojlovic[1,2], S. Hadzi-Peric[4]

[1]Centre of Chemistry-IChTM, Njegoseva 12, 11000 Belgrade, Serbia and Montenegro, +381 11 636 061, olgacvet@chem.bg.ac.yu
[2]Faculty of Chemistry, University of Belgrade, Akademski trg 12-16, 11000 Belgrade, Serbia and Montenegro, +381 11 636 061
manojlo@ichem.bg.ac.yu; snezananm@chem.bg.ac.yu
[3]Center of New Technologies, M. Vidakovic 24, 11000 Belgrade Serbia and Montenegro
[4]NIS Oil Refinery Pancevo, Spoljnostarcevacka bb, 23 000 Pancevo, Serbia and Montenegro

Abstract

The aim of this paper is to point out to the possibility of the current cleaning treatment improvement of the refinery "spent" caustic. "Spent" caustic contains, besides various aromatic organic compounds, substantial quantities of sodium sulphide, sodium mercaptides and disulphides. In this case the existing "spent" caustic cleaning plant uses the hydrogen peroxide as an oxidizing agent. The shortfalls of this procedure are: excess hydrogen peroxide utilization, foam formation caused by surface active substances, as well as the temperature increase during oxidation. In order to minimize the procedure shortfalls using the same oxidizing agent, hydrogen peroxide, the sorbent SOMS (trivial expression) was applied, the function of which is the efficiency increase of the applied oxidizing agent. In all the samples, in pre- and post treatment, the same analytical method, UOP Method 209-00, was applied for different sulphur types determination (sulphides and mercaptides). The analyses results show that the increased reaction efficiency, by using the sorbent SOMS while cleaning the "spent"caustic, substantially decreasing hydrogen peroxide utilization, reduces the cost of waste water cleaning procedure.

Introduction

From the very beginning of oil exploitation, considerate attention has been paid to sulphur compounds, sulphides and mercaptides mentioned for the first time as long ago as in 1925 (1). The results of quantitative participation obtained during investigation of gasoline from Wasson (Texas), were shown in the American Petroleum Institute Research Project 48 (2). The existence of sulphur compounds in oil and its products causes numerous problems: odors are produced and released into the surrounding, which can be toxic as well, big quantities of sulphur oxides are released, being not only ecologically dangerous but strongly corrosive means.

In petroleum refining and petrochemical processing hydrocarbon conversion products are often scrubbed with caustic solution. Such «spent» caustic solutions are unsuitable for direct plant treatment because of such factors as high pH and incompatibly high levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). Because of that many refineries around the world are facing stricter controls on liquid and gas effluent discharge streams that can cause air or water pollution. In literature the various forms of chemical oxidation also have been proposed for treating «spent» caustic solutions, and many refineries have the experience in applying these plants.

However, there is no cleaning treatment so sophisticated that can not stand some improvements. The aim of this paper is to point out to the possibility of the current cleaning treatment improvement of the Refinery waste water so called «spent» caustic.

NIS Oil Refinery Pančevo releases «spent» caustic during crude oil processing, which must be purified before discharge into the Danube. «Spent» caustic contains, besides various aromatic organic

compounds, substantial quantities of sodium sulphide, sodium mercaptides, disulphides and polysulphides. Quality and quantity contents of the «spent» caustic depend on the process crude oil refining and its quality and it is necessary to determine its contents each time before the cleaning treatment.

Methods

The existing «spent» caustic cleaning plant uses the hydrogen peroxide as an oxidizing agent. The application of this agent flows according to well known reaction. In the alkaline solution of pH 8, namely pH 14, as in «spent» caustic in the Refinery, the dominant reaction is:

$$Na_2S + 4H_2O_2 \leftrightarrow Na_2SO_4 + 4H_2O$$

The disulphide reaction, since mercaptides in alkaline solutions exist mainly as di-, thre- and polysulphides, with the hydrogen peroxide is more complicated. The hydrogen peroxide consumption is substantially bigger and more difficult to determine exactly. Some of the possible reactions flow according to the following equation:

$$RSSR + 5H_2O_2 + 2OH^- \leftrightarrow 2RSO_3^- + 6H_2O$$

Due to the existence of many other inorganic and organic compounds in «spent» caustic, the oxidation reactions become more complicated, slower and never come to the end.

The shortfalls of this procedure are: excess hydrogen peroxide utilization, foam formation caused by surface active substances, as well as the temperature increase during oxidation.

In order to minimize the procedure shortfalls using the same oxidizing agent, «spent», the sorbent SOMS (trivial expression) was applied. The function of the mentioned sorbent is the efficiency increase of the applied oxidizing agent. SOMS is a salt with the catalytic effect put on the sorbent (Al_2O_3). It has been produced by technical specification of CNT (Center of New Technologies) and its application has been performed in the laboratories of IChTM – Center of Chemistry.

The experiments were carried out with samples taken from «spent» caustic reservoirs at the Refinery Pančevo. The «spent» caustic was diluted by deionizated water (1:6; v/v and 1:4;v/v), the procedure done at the Refinery before the hydrogen peroxide treatment.

The two types of experiments were carried out with the diluted samples.

One type with gradual 35% hydrogen peroxide, adding (condition simulation at the Refinery), intensive stirring and temperature increase monitoring. During these experiments, repeated a few times, the 2-11% (v/v) hydrogen peroxide was added to the diluted «spent» caustic solution of different volume (100 do 500 mL). The reaction temperature changed from 39ºC when 2% was added, to 65ºC at adding the 11% hydrogen peroxide.

Another type of experiment was carried out by shifting the total «spent» caustic volume (500 mL in each treatment with 4% v/v hydrogen peroxide), with a peristaltic pump (v = 55 mL/min), to the sorbent full column. The column temperature is maintained at 60±5ºC. The same sorbent, after some reaction time is regenerated by the peroxide treatment in the alkaline solution

In all the samples, in pre- and post-treatment, the same analytical method, UOP Method 209-00 (3), was applied for determination of different types of sulphur (sulphides and mercaptides).

Results

The results of the first series experiments in which «spent» caustic was treated only by the hydrogen peroxide, are shown in picture 1.

In the second series of experiments, by using the sorbent and the same oxidizing agent, substantially better results of sulphide and mercaptides degradation are obtained (picture 2).

Figure 1. The experiments in which «spent» caustic was treated only by hydrogen peroxide

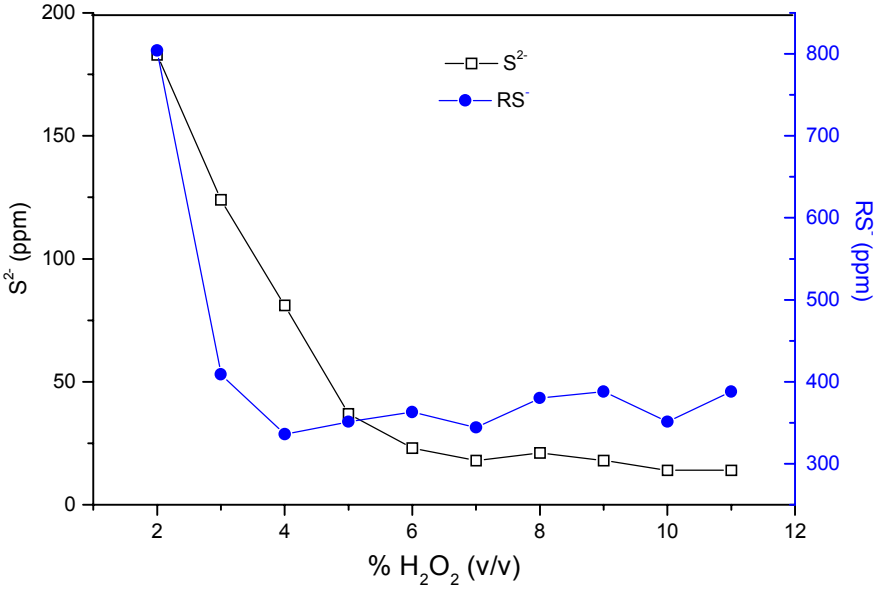
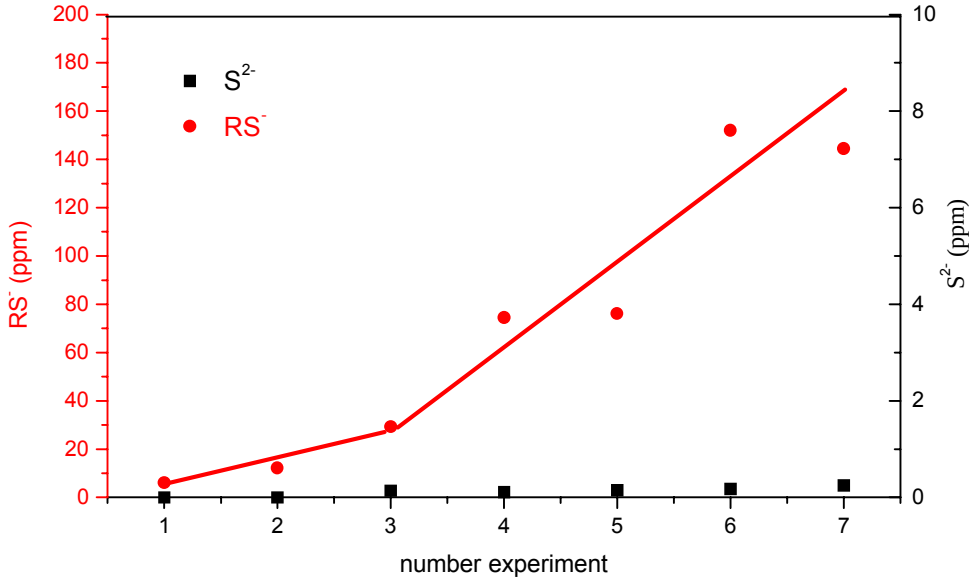


Figure 2. The experiments by using the sorbent and the hydrogen peroxide



.

Discussion

In picture 1, it could be noticed that only by adding more than 6% (v/v) hydrogen peroxide, the sulfide content in «spent» caustic decreases below 20 ppm. Further addition of the hydrogen peroxide does not result in considerable decrease of the sulphide as well as mercaptide sulphur concentration. The mercaptide content remains unchanged and very high (above 350 ppm), even when the 11 % (v/v) hydrogen peroxide is added.

By using the same principle in the pilot plant, in Refinery Pancevo, similar results are obtained (the results being within the experimental mistake). The sulphide and mercaptide content in the treated «spent» caustic is above allowed concentration in which case the mercaptide odor is felt. Because of that the treated caustic is additionally diluted and purified before discharge into the Danube.

The results of the second series of experiments show that by using a sorbent SOMS, efficiency of the oxidizing agent is greatly increased, with the lower hydrogen peroxide (4% v/v) consumption. The sulphide and mercaptide content in the treated caustic is substantially lower (5 ppm, namely 152 ppm maximum) after the seventh flow of a new quantity of «spent» caustic through the same sorbent.

Conclusions

Based on the results of two series of different experiments, one simulating the existing process of «spent» caustic of Refinery Pancevo by means of hydrogen peroxide, and another applying the same oxidizing agent, using a sorbent trivially called SOMS, the following could be inferred:

1. the use of a sorbent decreases hydrogen peroxide consumption for almost 25%
2. with decreased hydrogen peroxide quantity while using a sorbent, the efficiency of sulphide and mercaptide removal is substantially higher than while using the maximum quantity of 11% (v/v) hydrogen peroxide.
3. on the occasion of using the maximum hydrogen peroxide 11% (v/v) quantity, using a sorbent other accompanying organic substances existing in «spent» caustic of sulphide-mercaptide type would be removed.

Acknowledgements

We would like to express our gratitude to NIS Oil Refinery Pancevo for cooperation enabling us to take samples of «spent» caustic from its plants and obtain their results of sulphur and mercaptide determination in order to compare them with our results.

References

(1) H.E. Thierry, Sulphur compounds removed from Persian petroleum by means of sulphuric acid, Jour. Chem. Soc., **127**, 2756, (1925)

(2) J.C. Thompson, J.H. Coleman, T.H. Smith, M.H. Smith, Anal. Chem., **27**, 175, (1955)

(3) UOP Method 209-00, Alkalinity, sulfide and mercaptide analyses of used refinery caustic solutions, (2000)