

Spent Caustic Bioregeneration by using *Thiobacillus denitrificans* Bacteria

Sayed Reza Hashemi, Amir Heidarinasab

Abstract—Spent Sulfidic Caustic was biologically treated and regenerated for reusing by *Thiobacillus denitrificans* bacteria, sulfide content oxidized and RSNa reduced dramatically. PH in this test was 11.8 and no neutralization has been done on spent caustic, so spent caustic as the most difficult of industrial wastes to dispose could be regenerate and reuse instead of disposing to sea or deep wells

Keywords—Spent Caustic, *Thiobacillus denitrificans*, Bioregeneration

I. INTRODUCTION

SPENT Caustics are the most difficult of all industrial wastes to dispose properly, with the exception of radionuclide wastes. Since the dawn of petroleum refining, caustic solutions containing sodium hydroxide have been used to wash sulfur and other undesirable compounds out of petroleum. Its use has been in washing crude oils, intermediate fractions, and finished fuels throughout the refining processes. The result of this washing is the generation of Spent Caustics, also called Waste Caustics and Toxic Wastes.

In addition to the refining industry, other industries including chemical manufacturing, LPG (liquefied petroleum gas), Natural Gas (methane), and geothermal energy plants produce huge volumes of Spent Caustics. Chemical manufacturing produces spent caustics containing specific compounds compared to the wide variety from refining operations. LPG and Natural Gas plants predominately produce potassium hydroxide spent caustic, whereas, most other sources produce sodium hydroxide spent caustic.

Spent caustic produced in industries is handled in many traditional ways. Spent caustic may be of many types depending upon the industry producing it. Spent caustic is produced at refinery plants, chemical manufacturing plants, LPG plant, Natural gas plant and geothermal energy plants etc. The most common and most dangerous compound in all spent caustics is the hydrogen sulphide which is highly toxic and odorous. [1] There are many traditional and advanced methods used in the industry to get rid of the spent caustic.

Some of these are listed below,

- Deep well injections
- Dilution and then treatment at waste water treatment plant
- Incineration
- Oxidation methods like wet air oxidation, catalytic oxidation etc
- Export to pulp and paper mills

About the spent caustic produced at oil refineries it is also possible to reuse some kinds of spent caustic. Usually at oil refining plant there are three types of spent caustics produced i.e. sulphide, naphthenic and phenolic spent caustics. If sulphide and naphthenic spent caustics are produced at the refinery then their reuse is recommended by experts for crude oil neutralization. For using this spent caustic as crude oil neutralization there should be a wash water system present to avoid the accumulation of these compounds in the overhead system.

The benefit of using the spent caustic for neutralizing crude oil is that the amount of spent caustic produced at the plant will be decreased resulting in less spent caustic to get rid of. The negative effect of using this spent caustic is that the concentration of sodium is not constant and proper injection amount is difficult to control. So, some experts advice to never use spent caustic for neutralization purposes as it may cause higher concentration of sodium in the products and improper control of chloride content in the overhead

II. SPENT SULFIDIC CAUSTIC GENERATION

Sodium hydroxide (NaOH) solutions are used in petroleum refining to remove hydrogen sulfide (H₂S) or Mercaptans (R-SH) from various hydrocarbon streams. Once mercaptans reacts with the majority of NaOH, the solution becomes known as a spent caustic. Spent Sulfidic Caustic can be classified into Phenolic or sulfidic, depending on their Phenolic and free NaOH content .they can vary from 240 g of Phenolic/L, 2 to 25 g of sulfides/L, 5 to 30 g of mercaptans/L and 5 to 18% free NaOH, Ammonia, cyanide, together with mono and polyaromatic nitrogen and sulfur compounds can also be found Spent caustic characteristics can greatly vary from refinery to refinery. [3, 4]. It is possible to find trace of special catalysts as well. Spent caustics typically have a PH > 12 and sulfide concentrations exceeding 2-3 wt%. Depending on the source, Spent caustic may also contain phenols, mercaptans, amines, and other organic compounds that are soluble or emulsified in the caustic [4] Fig .1 shows the caustic regeneration cycle [5].

Extraction process is used to remove sulphur compound from the C3 cut and the C4 cut in propane and butane treatment units.

Sayed Reza Hashemi is with Islamic Azad University Science and Research Branch of Tehran E-mail:Rezahashemi1973@gmail.com Tel: +989122096778

Dr. Amir Heidarinasab is with Islamic Azad University Science and Research Branch of Tehran, Engineering Department Faculty of Chemical Engineering

TABLE I
SPENT CAUSTIC PARAMETER BEFORE AND AFTER TREATMENT WITH
DIFFERENT DOSAGE OF BACTERIA INJECTION

Sample	Bacteria (CC)	RSNa mg/kg	% NaOH	Sulfide ppm
Spent caustic (S6)	0	119.4	11.06	330
S1	1	5.4	10.98	1.72
S2	1.5	4.4	10.9	0.67
S3	2	5.12	9.69	1.34
S4	2.5	17.3	9.05	3.4
S5	3	18.2	8.72	1.6

All Samples colure have been changed clearly and based on result of table I the optimum amount of bacteria to inject in the media is 1.5 cc with optical density of 1.33. Colure change have shown in Figure 2 and 3 for 2 samples, vial in left side is after 120 hr of injection and right vial is blank sample to compare.

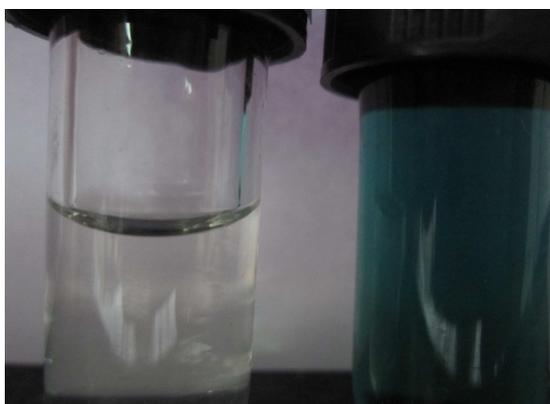


Fig. 2 Regenerated Spent caustic

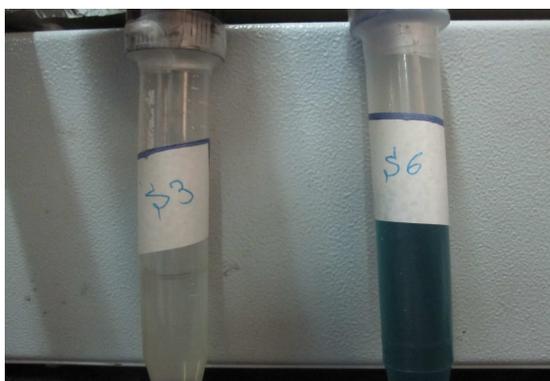


Fig. 3 Regenerated Spent Caustic

IV. CONCLUSION

According to result in table I and fig 2 and 3, Thiobacillus denitrificans bacteria could be used not only for treatment but also for regenerating, the proper PH in this test changed to 11.8 and the activity was acceptable, Neutralization of spent Sulfidic caustic is a costly operation and not so effective but operation in same PH of sample could be a benefit. This regenerated caustic could be reused again as its total sulfur is low enough and reactive soda parameter is also acceptable.

ACKNOWLEDGMENT

This research was supported by *South Pars Gas Complex* R&D. Also the authors thank phase 9&10 Manager Mr.H.Farhang and R&D Coordinator Mr.Samadi Afshar for their comments. Also, we thank to Phase 9 & 10 Laboratory Head Mr.Karaminejhad and his staff.

REFERENCES

- [1] Jelle Bouma, Preem GTB Spent Caustic and Desalter Review: Shell Global Solutions, June 23, 2010
- [2] Ali Samadi Afshar, Sayed Reza Hashemi ; Role and Effect of Temperature on LPG Sweetening Process; World Academy of Science, Engineering and Technology 79 2011 <http://www.waset.org/journals/waset/v79/v79-13.pdf>
- [3] A. Olmos, Physiochemical Characterization of Spent Caustic from the OXIMER Process and Sour Waters from Mexican Oil refineries
- [4] C. Maugans, M Howdshell, S. De Haan, A special report on Update: Spent Caustic Treatment: Hydrocarbon processing, April 2010
- [5] S. Mehmandoost, P. Hejaz, " Propane Treatment unit, Operating Manual, Basis of Design & Unit Operating Considerations, " Iran South Gas Field: Phases 9&10, 2005
- [6] Ali Samadi Afshar,; Sayed Reza Hashemi,; , Mohsen Miri ;Parviz SetayeshiHagh; Optimization of Effective Factors on Mercaptan Extraction by Alkaline Solution .Journal: Petroleum Science and Technology, Manuscript Type: Original Papers, Date Submitted by the Author: 25-Jan-2011
- [7] Amir Heidarinasab, Sayed Reza Hashemi; A study of biological treatment of spent sulfidic caustic,; International Conference on Chemical, Ecology and Environmental Sciences (ICCEES'2011),17 -18 Dec. Pattaya ,Thailand
- [8] American Public Health Association (1985), Standard Methods for the Examination of Water and Wastewater, 16th ed., APHA, New York
- [9] M/S , Aquatic Remedies Company Instruction , #2 /17 School Road , Kolathur , Chennai , India – 600 099. www.aquaremedies.com/efor