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Spent Caustic Bioregeneration by using *Thiobacillus denitrificans* Bacteria

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***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.

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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 (H_2S) 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.

The process uses caustic soda solution as extractive medium, the low molecular weight mercaptans in the propane or butane cuts are very soluble in the caustic solution so when hydrocarbon and caustic phases are intimately contacted they are adsorbed in the caustic solution. COS, when it is present, hydrolyses to H2S and CO2 during this phase.

Caustic regeneration unit is dedicated to the rich caustic solution regeneration by means of a catalytic oxidation; the main reaction is:

$$2\ RSH + \tfrac{1}{2}\ O_2 \rightarrow RSSR + H_2O \quad (1)$$

Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) react with caustic with the following competing reactions:

$$H_2S + 2\ NaOH \rightarrow Na_2S + 2H_2O \quad (2)$$
$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H2O \quad (3)$$

These secondary reactions cause several problems:

- Caustic is irreversibly consumed and must be replaced
- The presence of sodium salts in caustic solution will reduce its property to adsorbed mercaptans
- Salt accumulation can cause precipitates.

A sufficient catalyst concentration is required in the circulating caustic. As the oxidation reaction is exothermic, the higher is the mercaptide concentration, the higher is the oxidizer effluent temperature; however the oxidation temperature shall be strictly maintained under 55°C to avoid disulfides decomposition to sulfonic acid and to prevent catalyst decomposition too. [2]

A three phases separator is provided to separate lean caustic, to be routed to the propane and butane treatment unit from spent air and disulfides oil. A caustic solution purge and a fresh caustic make-up are provided to avoid salt (Na_2S / Na_2CO_3) accumulation and to restore the right concentration of NaOH. Caustic purges as well as all caustic drains are collected to the spent caustic sump drum from where spent caustic is pumped to storage tank.

As the spent caustic alkalinity is reduced, so also is its capacity to extract mercaptans. When disulfides accumulate to a few milligrams per liter, the OH^- content drops below 5% so a fraction of the solution is regularly purged off and renewed. Other causes of spending are the accumulation of mercaptans, Na_2S, Phenolic compounds, emulsified naphthenates, thiosulfate, carbonate and Fe^{+2} precipitates. Spent Caustics are most difficult of all industrial waste to dispose properly. In this paper first we introduce common of spent caustic neutralization methods and then we discuss about biological treatment for spent caustic.[7]

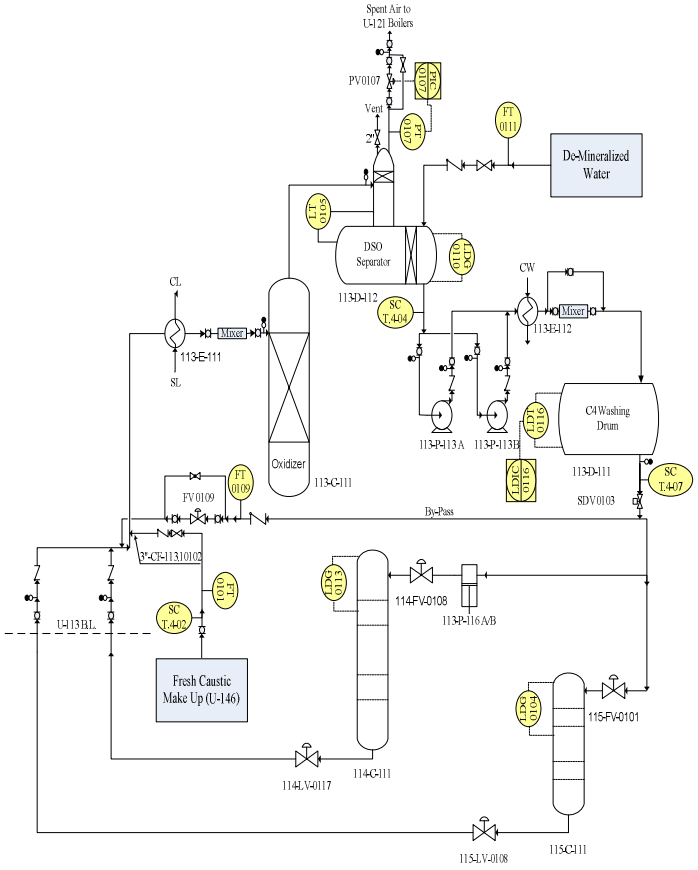

Fig. 1 Caustic Regeneration Cycle [5]

III. Method and Material

A. Organisms, Culture and Samples

A T. denitrificans (ATCC 23642) was originally obtained from the American Type .Culture Collection (Rockville, MD)[8].Thiobacillus sp. Cultures were maintained in liquid broth having composition Na_2HPO_4 ,1.2g/l ,KH_2PO_4 , 1.8/l , $MgSO_4$, 0.4 g/l , $MnSO_4$, 0.02 g/l , $FeCl_3$, 0.02 g/l, $NaHCO_3$, 1 g/l, KNO_3 , 5 g/l , $Na_2S_2O_3$ 10 g/l .[9]

Spent Sulfidic Caustic Samples were taken from South pars Gas complex 5th refinery .the trace element solution in distilled water with the final volume of 1 liter was composed of 50 gr Na2-EDTA, ZnSO4·7H2O, 7.34 g CaCl2, 2.5 g MnCl2·4H2O , 0.5gr CoCl2·6H2O, 0.5gr (NH4)6·Mo7O2·4H2O.

Samples centrifuged in 6000 rpm for 25 min to remove DSO. A suspension of bacteria with optical density of 1.33 was prepared. then different volume of suspension injected to five funnel with 50 cc of Spent Sulfidic caustic and 10 cc of Medium for each (see table I) and 0.5 cc of trace element added to all .then kept in shaker for 120 hrs , temperature 28 ºC and PH was in 11.8 and no neutralization implemented in this test .

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.

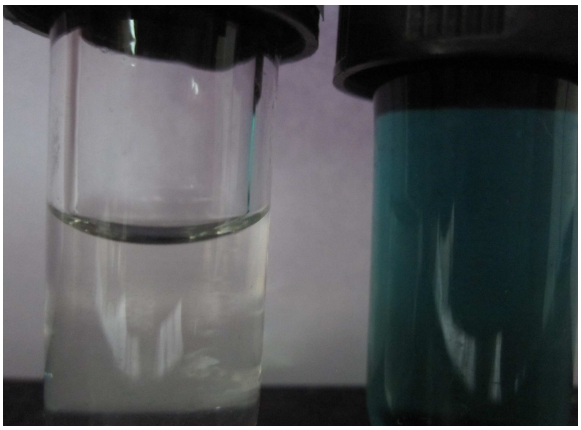

Fig. 2 Regenerated Spent caustic

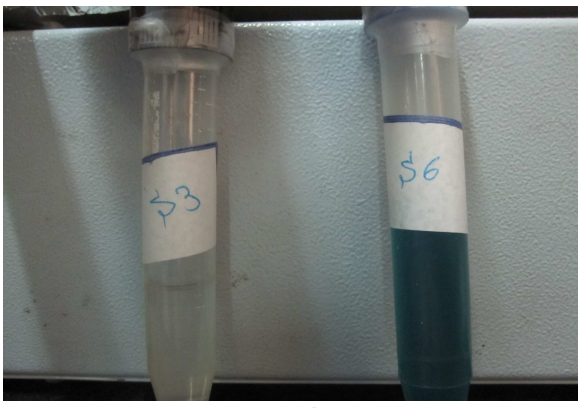

Fig. 3 Regenerated Spent Caustic

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.

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